Barrier crossing by a star polymer

Ananya Debnath and K. L. Sebastian
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India
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We analyze the dynamics of a star polymer of F arms trapped in a double well potential. Initially the molecule is confined to one of the minima and can cross over the barrier to the other side. We use the continuum version of the Rouse-Ham model and calculate the rate of crossing using the multidimensional approach due to Langer [Ann. Phys. (N.Y.) **54**, 258 (1969)]. Finding the transition state for the process is shown to be equivalent to the solution of Newton's equations for F independent particles, moving in an inverted potential. For each star polymer, there is a critical barrier top curvature, below which the star crosses over in coiled conformation. The value of the critical curvature is determined by the first Rouse mode of the star. If the curvature is greater than this critical value, the saddle point for the crossing is a stretched conformation of the star. For the coiled transition state, the activation energy is proportional to the total arm length of the star. For the stretched transition state, as one increases the length of an arm of the star, the activation energy at first increases and then decreases. This results from the fact that in the stretched state, only one arm of the polymer is stretched across the top of the barrier, while others need not be. We calculate the rate by expanding the energy around the saddle up to second order in the fluctuations. As we use the continuum model, there are infinite modes for the polymer and, consequently, the prefactor has infinite products. We show that these infinite products can be reduced to a simple expression, and evaluated easily. However, the rate diverges near N_{Tc} due to the multifurcation, which results in more than one unstable mode. The cure for this divergence is to keep terms up to fourth order in the expansion of energy for these modes. Performing this, we have calculated the rate as a function of the length of the star. It is found that the rate has a nonmonotonic dependence on the length, suggesting that longer stars may actually cross over the barrier faster.

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I. INTRODUCTION

The study of star polymers is of great interest as they have applications in micellar and other polymeric surfactant systems [1], electrophoresis, and gel permeation chromatography [2]. These procedures are extensively used for the separation of polymers of various sizes. They are very important in molecular biology as DNA with lengths from a few bases to many millions of bases, with and without branching, can be accurately fractionated by electrophoresis. Passage of DNA through microfabricated channels have been studied by Han *et al.* [3–5]. In a recent experiment along such lines by Volkmuth *et al.* [6], successful fractionation of 12 branched molecules (most of which are Y shaped) out of thousands of linear polymers was performed. They observed electrostatic trapping of tribranched DNA molecules undergoing electrophoresis in a microfabricated pseudo-two-dimensional array of posts. This methodology could in principle be used as an analytical device and preparative tool to examine and purify branched molecules that are known to arise during DNA replication, recombination, and repair. In another experiment Heuer *et al.* [7] have developed a procedure for synthesizing large stable branched DNA structures that are visible in a fluorescence microscope and studied their electrophoretic behavior in polymer solutions and gels. In another experiment, done at a given gel concentration, they found that relatively small branch lengths are enough to cause a detectable reduction in the electrophoretic mobility [8]. The reason for this change in mobility when branching is introduced is not known. They explore two possibilities: (i) the branched DNA could have a greater interaction with the gel than linear DNA, causing it to move slower or (ii) the linear DNA could have modes of motion or access to pores that are unavailable to the branched DNA. The electrophoretic behavior is different for different concentrations of polymer solutions and gels. In dilute polyacrylamide solutions, DNA moves as a random coil, while in semidilute solution [9] it moves in a squidlike profile with the star arms outstretched in the direction opposite to electric field and dragging the branch point through the sieving medium. In concentrated polymer solutions, the arms of the star extend and form V-shaped structures with the core as the apex. In polyacrylamide and agarose gels, where matrix entanglements are fixed, DNA stars become trapped.

For all the above procedures, the polymer has to pass through nanosized pores where it cannot attain all the conformations. So essentially the passage of a star polymer through pores is akin to the passage of a star polymer over a barrier in space. In an interesting experiment Han *et al.* [10] investigated the motion of double stranded DNA through nanochannels of different depths in different regions. In the narrower region of the channel, the DNA cannot sit comfortably and hence it feels an entropic barrier. Hence, the molecule has to stretch out in that region. A large number of papers have looked into the barrier crossing of a long chain molecule [11–13]. Park and Sung [14,15] were the first to investigate the passage of long chain molecules through nanopores where the barrier was purely entropic. In this case the barrier is broad and the motion of the chain is taken to be diffusive. They argued that the time of crossing is proportional to N^3 if there is no free energy bias between the two sides, but it is proportional to N^2 if there is a free energy difference. Experimentally it was found that the time of

crossing is proportional to N [16]. Lubensky and Nelson [17] proposed a model in which only the friction acting on the part of the chain inside the pore is important. Hence, the crossing time is proportional to N if there is a free energy difference between the two sides. Following this, many studies were done where diffusion of only the part which is inside the pore is important. A more detailed model was considered by Sebastian and Paul [18,19]. They considered long chains whose total length is greater than the width of the barrier and used a continuum version of the Rouse model. They suggested a kink mechanism and showed that the time of crossing is proportional to N. On the other hand, in an interesting paper, Park and Sung [20] considered a short chain with chain length shorter than the width of the barrier and used the discrete version of the Rouse model. They showed that as one increases the length, the transition state configuration of the chain can undergo a coil to stretch transition above a critical length. Below that length the chain crosses the barrier as a coil and above the length it crosses with a stretched conformation. The stretching lowers the activation energy, thus helping the crossing process. They have found a minimum in the rate, suggesting that a longer chain can move over the barrier faster. The case of a semiflexible polymer crossing over a barrier has been studied by Lee and Sung [21] and also by Kierfeld *et al.* [22]. In another study by Sebastian and Debnath [23], barrier crossing of short to intermediate length molecules was investigated using the continuum version of the Rouse model. As found by Park and Sung [20], the chain takes a coiled form while crossing if the length of the chain is below the critical length. Above this length, the chain adopts a stretched conformation while crossing. Using Langer's [24] approach to the multidimensional nucleation problem, one can calculate the rate as a product of a prefactor (an attempt frequency) and an exponential factor. The prefactor involves infinite products of frequencies of normal modes of the initial and transition states. But Sebastian and Debnath [23] showed that this infinite product can be rewritten as a single term following an earlier derivation, due to Coleman [25]. This leads to a compact expression for the rate and an easy way to calculate it. However, the rate calculated using this expression diverges at that length where the transition state changes from the coil to the stretched conformation. The reason for this divergence is pointed out to be due to the bifurcation of the saddle point leading to two new saddles. Paul [26] has studied the activated barrier crossing of a star polymer at a submicron-size entropic trap. The barrier crossing rate was calculated using Langer's approach and the Rouse-Ham model. He considered only a short armed star polymer, which crosses over the barrier as a coil. Consequently the activation energy depends only on the total contour length of the star and not on the lengths of individual arms.

In this paper we examine the crossing of a star chain with short to intermediate lengths. We find that the transition state while crossing has different conformations depending on the lengths of the arms of the star. To get the conformation of the transition state, we show that one has to analyze a Newton-like equation of motion for fictitious particles moving in an inverted potential. We find that for sufficiently small arm lengths, the saddle is a coil conformation, and otherwise the saddle is a stretched conformation. The stretched conformation can be found by solving Newton-like equations. Using Langer's multidimensional approach one can calculate the rate and just as previously, it is possible to write an infinite product as a single term using Coleman's approach [25]. This way of calculation avoids the complexity of infinite product calculation. Using this we calculate the rate for a star of equal arm lengths. We find that the activation energy first increases linearly with arm length, then after a critical length it starts decreasing as the arms are extended on both sides of the barrier. This leads to a nonmonotonic behavior in the rate of crossing.

II. OUR MODEL

We consider a star of F arms and use the simplest possible model for the dynamics of a star polymer: the Rouse-Ham model [27] in one dimension. Each arm of the star is a flexible linear string of length N_γ ($\gamma=1,2,\ldots,F$). The nth segment in the γth arm is labeled as n_γ. The center (branch point) of the star is taken to correspond to $n_\gamma=0$ and the end of the γth arm has $n_\gamma=N_\gamma$. Thus the total number of segments in the star is $\Sigma_\gamma N_\gamma=N_T$. Using the discrete Rouse-Ham model for a star, in a double well potential would lead to nonlinear difference equations, which are difficult to handle. Hence we use the continuum version of the model and it is analytically tractable. Use of the continuum approach leads to differential equations, which are easy to analyze. Also, we do not lose any generality by this, as even the discrete version itself only represents the real chain, by a phantom chain of beads. Further, the results of the discrete and continuum versions would be close if $N \gtrsim 10$. If the position of the n_γth segment at the time t is $R_\gamma(n_\gamma,t)$, then the continuum version of the Rouse-Ham equation is

$$\zeta\frac{\partial R_\gamma(n_\gamma,t)}{\partial t} = m\frac{\partial^2 R_\gamma(n_\gamma,t)}{\partial n_\gamma^2} - V'(R_\gamma(n_\gamma,t)) + f_\gamma(n_\gamma,t), \quad \gamma=1,\ldots,F, \tag{1}$$

where ζ is the segmental frictional coefficient and $m\left(=\frac{3k_BT}{l^2}\right)$ is the spring constant for the arms. It takes into account the fact that the free energy of the chain increases on stretching the chain. $V(R)$ is the potential experienced by a segment of the polymer located at R and $V'(R)=\frac{dV(R)}{dR}$. f_γ is a Gaussian random force, having moments $\langle f(n_\gamma,t)\rangle=0$ and $\langle f(n_\gamma,t)\times f(n'_\gamma,t')\rangle=2\zeta k_BT\delta(n_\gamma-n'_\gamma)\delta(t-t')$. The boundary conditions are

$$\left(\frac{\partial R_\gamma(n_\gamma,t)}{\partial n_\gamma}\right)_{n_\gamma=N_\gamma}=0, \quad \gamma=1,\ldots,F \tag{2}$$

at the free ends of the star. At the branch point

$$\sum_{\gamma=1}^{F}\left(\frac{\partial R_\gamma(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma=0}=0 \tag{3}$$

and

$$R_\alpha(0)=R_\beta(0) \quad \text{for all } \alpha \text{ and } \beta. \tag{4}$$

Note that Eq. (4) has only $(F-1)$ independent conditions.

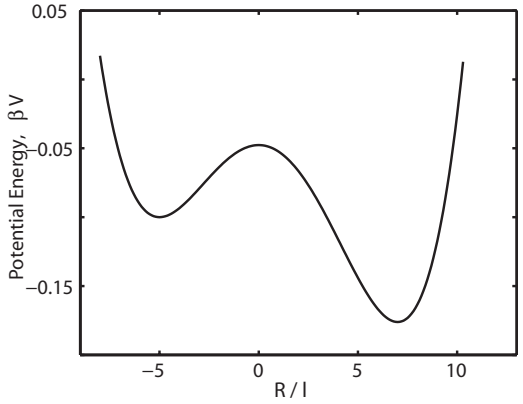

FIG. 1. Plot of $\beta V(R)$ against R/l—the potential is an asymmetric double well. The values of the parameters used are $k=2.6436\times10^{-4}$, $a_0=5$, $a_1=7$, $V_b=0.1046$ in dimensionless units. [See Eq. (7) and the discussion in Sec. V.]

One can write Eq. (1) in the form

$$\zeta\frac{\partial R_\gamma(n_\gamma,t)}{\partial t}=-\frac{\delta E[R_\gamma(n_\gamma,t)]}{\delta R_\gamma(n_\gamma,t)}+f_\gamma(n_\gamma,t), \tag{5}$$

where $E[R_\gamma(n_\gamma,t)]$ is the free energy functional defined by

$$E[R_\gamma]=\sum_{\gamma=1}^{F}\int_0^{N_\gamma}\left[\frac{m}{2}\left(\frac{\partial R_\gamma}{\partial n_\gamma}\right)^2+V(R_\gamma)\right]dn_\gamma. \tag{6}$$

III. ACTIVATION ENERGY FOR BARRIER CROSSING

We assume that the potential $V(R)$ is of the form of an asymmetric double well, given by

$$V(R)=k(R+a_0)^2(3R^2-2Ra_0-4Ra_1+a_0^2+2a_0a_1)/6 \tag{7}$$

(see Fig. 1). This potential has two minima at $R=-a_0$ and at $R=a_1$ separated by a barrier located at $R=0$. Note that $V(-a_0)=0$ and that the barrier has a height of $V_b=V(0)=\frac{1}{6}a_0^2(a_0^2+2a_0a_1)k$. We denote the frequency of the potential at the top of the barrier by ω_b, while the frequency at the initial state ($R=-a_0$) is denoted as ω_0. Initially, the star is in the metastable well located at $-a_0$, and then has to overcome the barrier. To escape from the well the star has to go over a saddle on the free energy hypersurface. Thus, to calculate the extrema on the free energy hypersurface, we have to extremize E in Eq. (6) with respect to the conformation of the star. We get

$$\frac{\delta E[R_\gamma(n_\gamma,t)]}{\delta R_\gamma(n_\gamma,t)}=-m\frac{\partial^2 R_\gamma(n_\gamma,t)}{\partial n_\gamma^2}+V'(R_\gamma(n_\gamma,t))=0. \tag{8}$$

For each γ, if n_γ is thought of as analogous to time, this equation is just Newton's equation for a fictitious particle of mass m. The potential that the particle moves in is the upside down potential [19] $-V(R)$ and it moves for a total " time" N_γ. Equations (3) and (4) imply that all the F particles start

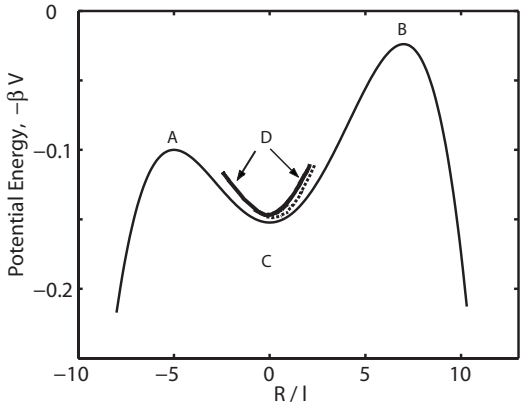

FIG. 2. Plot of $-\beta V(R)$ against R/l—the potential is an inverted asymmetric double well. A denotes the metastable, initial state, while B is the more stable, final state. C denotes the transition state when the crossing occurs as a coil. The thick full and dotted lines marked as D show the arms of the star appropriate for the stretched transition state for a star of three arms, obtained by solving Newton-like equations. Two of the arms are on the right side of C. The two arms have to be represented as one exactly behind the other, but for the sake of clarity one of the arms on the right-hand side has been slightly shifted upwards.

at the same point with a total initial momentum zero and Eq. (2) means that the γth particle has to come to rest after a "time" N_γ. Looked this way, it is obvious that there are some very simple solutions to Eqs. (2)–(4) and (8). These are the solutions in which the F particles are all just sitting at exactly the same point. This means that they do not feel any force at any time, which implies that the point has to be an extremum of the potential $V(R)$. Thus, the solutions are (a) $R_\gamma(n_\gamma)=-a_0$ (labeled as A in Fig. 2), (b) $R_\gamma(n_\gamma)=a_1$ (labeled as B in Fig. 2), and (c) $R_\gamma(n_\gamma)=0$ (labeled as C in Fig. 2). The first solution corresponds to the star sitting in the metastable minimum of the potential, and is the initial state for the crossing process. The second gives the final state, while the third could be the transition state for the crossing process. In fact for sufficiently short star polymers, it is the transition state. However, if the arms are long, the solution (c) is no longer a saddle as we find below. This means that there must be additional solutions to the four equations (2)–(4) and (8). Such a solution too is illustrated in Fig. 2. A similar situation occurs in the case of barrier crossing of a linear chain [23].

The initial state has an energy, which may be found by substituting $R_\gamma(n_\gamma)=-a_0$ into Eq. (7). This gives $E_{\text{initial}}=0$. The second solution $R_\gamma(n_\gamma)=0$ gives $E^\ddagger=N_TV_b$. We use the symbol ‡ to indicate quantities that are associated with a saddle (transition state). If the arms are long, then there will be nontrivial solutions to Eqs. (2)–(4) and (8). These are the solutions in which all the particles start out with some initial momenta, such that the total initial momentum is zero, and each particle moves in the upside down potential. The initial momentum and position will confer the γth particle an energy E_γ; consequently it will travel outwards from the initial point and will come to a stop after a "time" N_γ at which point its potential energy $-V(R_\gamma(N_\gamma))=E_\gamma$. We shall denote the solution by $R_\gamma^\ddagger(n_\gamma)$. Energy conservation for the γth particle implies that

$$\frac{m}{2}\left(\frac{\partial R_\gamma^\ddagger(n_\gamma)}{\partial n_\gamma}\right)^2 - V(R_\gamma^\ddagger) = E_\gamma. \tag{9}$$

The energy of the chain corresponding to this solution is

$$E^\ddagger = \sum_{\gamma=1}^{F} \int_0^{N_\gamma} \left[\frac{m}{2}\left(\frac{\partial R_\gamma^\ddagger}{\partial n_\gamma}\right)^2 + V(R_\gamma^\ddagger)\right] dn_\gamma. \tag{10}$$

On using Eq. (9) this becomes

$$E^\ddagger = \sum_{\gamma=1}^{F} \left(E_\gamma N_\gamma + 2\int_0^{N_\gamma} V(R_\gamma^\ddagger(n_\gamma))dn_\gamma\right).$$

Plots of $E^\ddagger$ are given in Figs. 4 and 5.

IV. THE RATE CALCULATION

After finding the saddle and the corresponding activation energy we are interested in calculating the rate of thermally activated crossing of the star from one well to the other. We use the multidimensional Kramer's theory due to Langer [24]. The Rouse-Ham equation leads to the functional Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \frac{1}{\zeta}\sum_\gamma \int_0^{N_\gamma} dn_\gamma \frac{\delta}{\delta R_\gamma(n_\gamma)}\left[k_B T \frac{\delta P}{\delta R_\gamma(n_\gamma)} + \frac{\delta E[R_\gamma(n_\gamma)]}{\delta R_\gamma(n_\gamma)} P\right], \tag{11}$$

for the probability distribution functional P. This equation means that associated with the coordinate $R_\gamma(n_\gamma)$ there is a flux $j_\gamma[R_\gamma(n_\gamma)]$ given by

$$j_\gamma[R_\gamma(n_\gamma)] = -\frac{1}{\zeta}\left[k_B T \frac{\delta P}{\delta R_\gamma(n_\gamma)} + \frac{\delta E[R_\gamma(n_\gamma)]}{\delta R_\gamma(n_\gamma)} P\right]. \tag{12}$$

Let us now consider the initial state, which is metastable. We assume the barrier height for the crossing process ($E^\ddagger$) to be large. As a result, the rate of crossing is small and one can assume that the probability distribution in the well is given by the equilibrium one. Hence it is

$$P = \frac{1}{Z_0}\exp\{-E[R_\gamma(n_\gamma)]/k_B T\}. \tag{13}$$

Z_0 is defined by

$$Z_0 = \prod_\gamma \int D[R_\gamma(n_\gamma)] \exp\{-E[R_\gamma(n_\gamma)]/k_B T\}. \tag{14}$$

For small amplitude motion around the minimum, one would have $R_\gamma(n_\gamma) = -a_0 + \delta R_\gamma(n_\gamma)$. Using this, the energy functional correct up to second order in $\delta R_\gamma(n_\gamma)$ is

$$E[R_\gamma(n_\gamma)] = \sum_{\gamma=1}^{F} \frac{m}{2}\int_0^{N_\gamma} dn_\gamma \delta R_\gamma(n_\gamma)\left[-\frac{\partial^2}{\partial n_\gamma^2} + \omega_0^2\right]\delta R_\gamma(n_\gamma), \tag{15}$$

where we have defined ω_0 by putting $V''(-a_0) = m\omega_0^2$ and used the fact that $V(-a_0) = 0$. Now we introduce ψ_k and ε_k, as the normal modes of the star, at the transition state by

$$\left(-\frac{\partial^2}{\partial n_\gamma^2} + \omega_0^2\right)\psi_{\gamma k}(n_\gamma) = \varepsilon_k \psi_{\gamma k}(n_\gamma) \tag{16}$$

and satisfying boundary conditions of Eqs. (2)–(4). It is also useful to introduce the normal Rouse modes of the free star. These are just $\psi_{\gamma k}(n_\gamma)$ themselves and obey the equation

$$-\frac{\partial^2}{\partial n_\gamma^2}\psi_{\gamma k}(n_\gamma) = \lambda_k^2 \psi_{\gamma k}(n_\gamma), \tag{17}$$

where λ_k^2 are the frequencies of the Rouse-Ham modes of the free star. Note that the lowest eigenvalue $\lambda_0^2 = 0$ and $\psi_{\gamma 0}(n_\gamma) = 1/\sqrt{N_T}$ and corresponds to translation of the star as a whole. The mode $\psi_{\gamma 1}(n_\gamma)$ is a vibrational mode. As ω_0^2 is just a constant, one gets $\varepsilon_k = \lambda_k^2 + \omega_0^2$. Now we expand $\delta R_\gamma(n_\gamma)$ in terms of $\psi_{\gamma k}$ as $\delta R_\gamma(n_\gamma) = \Sigma_k c_k \psi_{\gamma k}(n_\gamma)$, where c_k is the coefficient of the expansion, and get

$$E[R_\gamma(n_\gamma)] = \frac{m}{2}\sum_k \varepsilon_k c_k^2. \tag{18}$$

This expression for the energy may be used in Eq. (14) and the functional integration performed by integrating over all the c_k's. The result is

$$Z_0 = \prod_k (2\pi/m\beta\varepsilon_k)^{1/2}. \tag{19}$$

Now we calculate the flux over the saddle point. As before, we expand $R_\gamma(n_\gamma)$ around the saddle as $R_\gamma(n_\gamma) = R_\gamma^\ddagger(n_\gamma) + \delta R_\gamma^\ddagger(n_\gamma)$ and get

$$E_{\text{saddle}} = E^\ddagger + \sum_{\gamma=1}^{F} \frac{m}{2}\int_0^{N_\gamma} dn_\gamma \delta R_\gamma(n_\gamma) \times\left[-\frac{\partial^2}{\partial n_\gamma^2} + V''(R_\gamma^\ddagger(n_\gamma))/m\right]\delta R_\gamma(n_\gamma). \tag{20}$$

$E^\ddagger = E[R^\ddagger(n)]$ is the activation energy. We introduce the "normal modes" at the saddle by $\left(-\frac{\partial^2}{\partial n_\gamma^2} + \frac{V''(R_\gamma^\ddagger)}{m}\right)\psi_{\gamma k}^\ddagger(n_\gamma) = \varepsilon_k^\ddagger \psi_{\gamma k}^\ddagger(n_\gamma)$ with $\psi_{\gamma k}^\ddagger(n_\gamma)$ obeying the boundary conditions similar to Eqs. (2)–(4). As we are at a saddle, there would be one unstable mode which we take to be the zeroth mode. Now we expand the displacement of the star away from the transition state as

$$\delta R_\gamma^\ddagger(n_\gamma, t) = \sum_k c_k^\ddagger \psi_{\gamma k}^\ddagger(n_\gamma) \tag{21}$$

to get

$$E_{\text{saddle}} = E^\ddagger + \frac{m}{2}\sum_k (c_k^\ddagger)^2 \varepsilon_k^\ddagger. \tag{22}$$

Following Refs. [23,24], we get the rate

$$\Gamma = \frac{m}{2\pi\zeta}(-\varepsilon_0^\ddagger)^{1/2}\left(\frac{\prod_k \varepsilon_k}{\prod_k{}' \varepsilon_k^\ddagger}\right)^{1/2} \exp(-\beta E^\ddagger)$$

$$= \frac{m}{2\pi\zeta}(-\varepsilon_0^\ddagger)\left(\frac{\prod_k \varepsilon_k}{(-1)\prod_k \varepsilon_k^\ddagger}\right)^{1/2} \exp(-\beta E^\ddagger). \quad (23)$$

The infinite product in this equation can be rewritten (see the Appendix) to get

$$\Gamma = \frac{m}{2\pi\zeta}(-\epsilon_0^\ddagger)\left(\frac{\left[\prod_\gamma \Psi_\gamma(0)\right]\sum_\gamma \left(\frac{\partial \ln \Psi_\gamma(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma=0}}{(-1)\left[\prod_\gamma \Psi_\gamma^\ddagger(0)\right]\sum_\gamma \left(\frac{\partial \ln \Psi_\gamma^\ddagger(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma=0}}\right)^{1/2} \times \exp(-\beta E^\ddagger), \quad (24)$$

where the $\Psi_\gamma(n_\gamma)$ and $\Psi_\gamma^\ddagger(n_\gamma)$ obey the following equations:

$$\left(-\frac{\partial^2}{\partial n_\gamma^2} + \omega_0^2\right)\Psi_\gamma(n_\gamma) = 0 \quad \text{and} \quad \Psi_\gamma(N_\gamma) = 1;\ \Psi_\gamma'(N_\gamma) = 0 \quad (25)$$

and

$$\left(-\frac{\partial^2}{\partial n_\gamma^2} + V''(R_\gamma^\ddagger(n_\gamma))/m\right)\Psi_\gamma^\ddagger(n_\gamma) = 0 \quad \text{and}$$

$$\Psi_\gamma^\ddagger(N_\gamma) = 1; \quad \Psi_\gamma^{\ddagger\prime}(N_\gamma) = 0. \quad (26)$$

Equation (25) is easily solved to get $\Psi_\gamma(0)=\cosh(\omega_0 N_\gamma)$, so that

$$\Gamma = \frac{m(-\epsilon_0^\ddagger)}{2\pi\zeta}\left(\frac{\omega_0\left[\prod_{\gamma=1}^F \cosh(N_\gamma\omega_0)\right]\sum_{\gamma=1}^F \tanh(N_\gamma\omega_0)}{\left[\prod_{\gamma=1}^F \Psi_\gamma^\ddagger(0)\right]\sum_{\gamma=1}^F \left(\frac{\partial \ln \Psi_\gamma^\ddagger}{\partial n_\gamma}\right)_{n_\gamma=0}}\right)^{1/2} e^{-\beta E^\ddagger}. \quad (27)$$

This expression can be used to calculate the rate for any kind of saddle (coiled or stretched).

A. When coiled conformation is the saddle

We consider a star having F arms of arbitrary lengths. For sufficiently small arm lengths (to be quantified below), the saddle point is given by $R_\gamma^\ddagger(n_\gamma)=0$. In this case $V''(R_\gamma^\ddagger) = -m\omega_b^2$. As this is a constant, independent of n_γ, $\psi_{\gamma k}^\ddagger(n_\gamma)$ are just the same as the eigenfunctions of a free star and the eigenvalues are given by $\varepsilon_k^\ddagger=\lambda_k^2-\omega_b^2$. The unstable mode has the eigenfunction $\psi_{\gamma k}^\ddagger(n_\gamma)=1/\sqrt{N_T}$ and the corresponding eigenvalue $\varepsilon_0^\ddagger=\lambda_0^2-\omega_b^2=-\omega_b^2$. We solve Eq. (26) to get $\Psi_\gamma^\ddagger(0)$ and use it in Eq. (27) to get the rate. The result is

$$\Gamma_< = \frac{m\omega_b^2}{2\pi\zeta}\left(\frac{\omega_0\left[\prod_{\gamma=1}^F \cosh(N_\gamma\omega_0)\right]\sum_{\gamma=1}^F \tanh(N_\gamma\omega_0)}{\omega_b\left[\prod_{\gamma=1}^F \cos(N_\gamma\omega_b)\right]\sum_{\gamma=1}^F \tan(N_\gamma\omega_b)}\right)^{1/2} \times e^{-\beta N_T V_b}. \quad (28)$$

If one imagines that the barrier top curvature as measured by $m\omega_b^2$ is small, then this extremum in the potential energy surface ($R=0$) has only one unstable mode, with an eigenvalue $\varepsilon_0^\ddagger=\lambda_0^2-\omega_b^2=-\omega_b^2$. As the curvature is increased, the value of $\varepsilon_1^\ddagger=\lambda_1^2-\omega_b^2$ decreases and at values of $\omega_b>\lambda_1$, the extremum develops one more unstable direction, and is no longer a saddle. Instead of changing the curvature, one can think of increasing the length of the γth arm of the star, keeping the lengths of the other arms fixed. Then, the value of λ_1 would decrease and the extremum will cease to be a saddle at a critical length $N_{\gamma c}$ of the chain (this value will depend on the lengths of the other arms). This is manifested as a divergence of the rate, as seen above and occurs because $R=0$ is not a saddle anymore, due to the fact that $\varepsilon_1^\ddagger$ vanishes. $\Gamma_<$ is the rate constant in the region where the coil is the transition state. In the special case where all the arms are equal ($N_\gamma=N$), Eq. (28) becomes

$$\Gamma_< = \frac{m\omega_b^2}{2\pi\zeta}\left(\frac{\omega_0}{\omega_b}\right)^{1/2}\left(\frac{\sinh(N\omega_0)}{\sin(N\omega_b)}\right)^{1/2}\left(\frac{\cosh(N\omega_0)}{\cos(N\omega_b)}\right)^{(F-1)/2} \times e^{-\beta N F V_b} \quad (29)$$

and the rate diverges when $\cos(N\omega_b)=0$, i.e., when $\omega_b=\pi/2N$. In the case where N_γ is small (i.e., $N_\gamma\omega_0 \ll 1$ and $N_\gamma\omega_b \ll 1$), Eq. (29)

$$\Gamma_< = \frac{m\omega_b\omega_0}{2\pi\zeta} e^{-\beta V_b N_T}, \quad (30)$$

which is what one would expect for the crossing of a single particle which has to climb over a barrier of height $V_b N_T$.

It is of interest to consider the eigenfunctions and eigenvalues associated with the coiled saddle, as they are used later in the paper. For an equal armed star, when the saddle point is the coil conformation, the normal modes are determined by

$$\left(-\frac{\partial^2}{\partial n_\gamma^2} - \omega_b^2\right)\psi_{\gamma k}^\ddagger = \epsilon_k^\ddagger \psi_{\gamma k}^\ddagger \quad (31)$$

with the boundary conditions

$$\left(\frac{\partial \psi_{\gamma k}^\ddagger}{\partial n_\gamma}\right)_{n_\gamma=N} = 0 \quad (32)$$

and

$$\sum_{\gamma=1}^F \left(\frac{\partial \psi_{\gamma k}^\ddagger}{\partial n_\gamma}\right)_{n_\gamma=0} = 0, \quad (33)$$

and

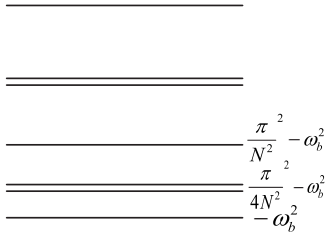

FIG. 3. Energy levels for the modes of the star polymer having three arms of equal lengths. This figure shows that the 0th mode is nondegenerate while the first mode is twofold degenerate.

$$\psi_{k\alpha}^{\ddagger} = \psi_{k\beta}^{\ddagger} \text{ at } n_\alpha = n_\beta = 0 \quad \text{for } \alpha \neq \beta \quad \text{for any } \alpha = 1 \text{ to } F. \tag{34}$$

The solution for the γth arm, satisfying Eqs. (31) and (32), is

$$\psi_{\gamma k}^{\ddagger} = a_{\gamma k}^{\ddagger} \cos[(n_\gamma - N)\lambda_k] \tag{35}$$

with $\lambda_k = \sqrt{\omega_b^2 + \varepsilon_k^{\ddagger}}$. Equation (34) leads to

$$a_{k1}^{\ddagger} \cos[N\lambda_k] = a_{k2}^{\ddagger} \cos[N\lambda_k] = \cdots = a_{kf}^{\ddagger} \cos[N\lambda_k]. \tag{36}$$

Two cases can now be distinguished.

1. Case I

If $\cos[N\lambda_k] \neq 0$, then there is only one way of satisfying these equations and that is to have $a_{k1}^{\ddagger} = a_{k2}^{\ddagger} = \cdots = a_{kF}^{\ddagger}$. Then use of Eq. (33) gives

$$\sin[N\lambda_k] = 0 \tag{37}$$

so that $\lambda_k = \frac{\pi k}{2N}$ for $k = 0, 2, 4, \ldots$. Therefore, $\varepsilon_k^{\ddagger} = (\frac{\pi k}{2N})^2 - \omega_b^2$.

2. Case II

On the other hand, if

$$\cos[N\lambda_k] = 0,$$

then Eq. (36) is satisfied identically. In this case Eq. (33) gives

$$\sum_\gamma a_{\gamma k}^{\ddagger} = 0. \tag{38}$$

This means that even though we have F unknowns, there is only one condition to determine them. Thus there are $(F-1)$ linearly independent solutions (normal modes). For all of them $\lambda_k = k\pi/2$ with $k = 1, 3, \ldots$. Thus $\varepsilon_k^{\ddagger} = (\frac{\pi k}{2N})^2 - \omega_b^2$, and the mode is $(F-1)$-fold degenerate.

The two cases that we have found may together be written as $\varepsilon_k^{\ddagger} = \frac{k^2\pi^2}{4N^2} - \omega_b^2$ with $k = 0, 1, 2, 3, 4, \ldots$. The k=even solutions are nondegenerate while k=odd solutions are $(F-1)$—fold degenerate. (We have shown the energy levels for the modes of a star polymer having three equal arms in Fig. 3). As we will be using the eigenfunctions for the $k=1$ modes, we give their explicit expression for the case where the star has three equal arms:

$$\psi_{11}^{\ddagger}(n_1) = \sqrt{\frac{2}{3N}} \cos[(n_1 - N)\lambda_1],$$

$$\psi_{21}^{\ddagger}(n_2) = \sqrt{\frac{2}{3N}} e^{\frac{2\pi i}{3}} \cos[(n_2 - N)\lambda_1],$$

$$\psi_{31}^{\ddagger}(n_3) = \sqrt{\frac{2}{3N}} e^{\frac{-2\pi i}{3}} \cos[(n_3 - N)\lambda_1]. \tag{39}$$

The other degenerate mode is simply the complex conjugate of the above and is given by

$$\psi_{\gamma 2}^{\ddagger}(n_\gamma) = \psi_{\gamma 1}^{\ddagger}(n_\gamma)^*.$$

B. When the saddle is a stretched conformation

We now calculate the rate of crossing for a star of three equal arms, as a function of the length of one arm N. For small values of N one can use the expression of Eq. (29). However, this rate would diverge as N approaches the value $N_c = \pi/2\omega_b$. For $N > N_c$, the expression is not valid at all, as the coil is no longer the saddle. The fact that it is not a saddle any longer may be realized from the eigenvalue $\varepsilon_1^{\ddagger} = (\frac{\pi}{2N})^2 - \omega_b^2$ which becomes negative for $N > N_c$. As this mode is degenerate, one can conclude that the coil, which was the saddle for $N < N_c$, has developed two more unstable directions, meaning that it is now a third order extremum. What is happening is that the saddle point undergoes a multifurcation, leading to new saddles. Simple counting shows that there are twelve new saddles. The reasoning goes as follows. Suppose we have a stretched transition state. Then one of the arms has to be on one side (say the left side) of the barrier and the remaining two on the other. There are 3! permutations of the arms with this arrangement. Then one arm can be on the right side and the other two on the left, and then again, there are 3! ways in which this may happen giving one $2 \times 3!$ transition states. The energies of the first six are identical and so are the energies of the other six. For a symmetrical double well, all these energies are the same. For an unsymmetrical double well, the energies would be slightly different but we shall ignore that in the following and calculate the rate assuming that they are the same. These twelve saddles can be accounted for by multiplying the rate in Eq. (27) with a factor of 12 to get

$$\Gamma_> = \frac{6m(-\epsilon_0)}{\pi\zeta} \left(\frac{3\omega_0 \cosh^3(N\omega_0)\tanh(N\omega_0)}{\prod_{\gamma=1}^{3} \Psi_\gamma^{\ddagger}(0) \sum_{\gamma=1}^{3} \left(\frac{\partial \ln \Psi_\gamma^{\ddagger}}{\partial n_\gamma} \right)_{n_\gamma = 0}} \right)^{1/2} e^{-\beta E^{\ddagger}}. \tag{40}$$

$\Gamma_>$ denotes the rate constant, for $N > N_c$.

C. Rate in the vicinity of N_c

The rate obtained using equations (29) and (40) are shown in Fig. 6. It is seen that both the equations suffer from divergences near $N = N_c$. An expression for the rate that is valid for $N \simeq N_c$ (but not much above it) can be obtained as follows. The divergence occurs due to the vanishing of the eigenvalue $\varepsilon_1^{\ddagger}$. The cure for the divergence is obviously to go beyond the second order in the expansion for energy for just the $k=1$

modes. Up to $N=N_c$, the saddle point is given by the coiled conformation. As N is increased further, the eigenvalue $\varepsilon_1^\ddagger$ becomes negative so that there are now three unstable modes ($k=0$ and the two $k=1$ modes). To remove the consequent divergence, the expression for energy in Eq. (22) may be modified to include terms up to fourth order $\delta R_\gamma^\ddagger$ so that it becomes

$$E = E^\ddagger + \frac{m}{2}\sum_{k\neq 1} c_k^\ddagger c_k^{\ddagger *}\varepsilon_k^\ddagger + \frac{m}{2}(c_{11}^\ddagger c_{11}^{\ddagger\ *} + c_{12}^\ddagger c_{12}^{\ddagger\ *})^2\varepsilon_1^\ddagger + \frac{V^{(3)}(R=0)}{6}\int_0^N (\delta R_\gamma^\ddagger)^3 dn_\gamma + \frac{V^{(4)}(R=0)}{24}\int_0^N (\delta R_\gamma^\ddagger)^4 dn_\gamma. \tag{41}$$

[Note that in order that δR is real, one has to have $c_{11}^\ddagger = (c_{22}^\ddagger)^*$.] In the above $V^{(n)}(R=0)$ is the nth order derivative of the potential $V(R)$ evaluated at $R=0$. On using the expansion of Eq. (21) and retaining only terms involving $c_{11}^\ddagger$ and $c_{12}^\ddagger$, we get

$$E = E^\ddagger + \frac{m}{2}\sum_{k\neq 1} c_k^\ddagger c_k^{*\ddagger}\varepsilon_k^\ddagger + \frac{m}{2}c_{11}^\ddagger c_{12}^\ddagger \varepsilon_1^\ddagger + \frac{V^{(4)}(R=0)}{3N}(c_{11}^\ddagger)^2(c_{12}^\ddagger)^2. \tag{42}$$

Using this in the expression for the flux and proceeding as earlier, we get the corrected rate Γ_c to be

$$\Gamma_c = \sigma\Gamma_<. \tag{43}$$

σ is the correction factor given by

$$\sigma = \frac{|a|}{2}\sqrt{\frac{\pi}{b}}e^{a^2/4b}\left[1 - \mathrm{erf}\left(\frac{|a|}{2\sqrt{b}}\right)\right],$$

where $a = m\beta\epsilon_1^\ddagger = m\beta\left(\frac{\pi^2}{4N^2} - \omega_b^2\right)$ and $b = \frac{V^{(4)}(R=0)\beta}{3N}$. These expressions are valid for N above or below N_c, but because of the approximate nature of our calculations, if $N > N_c$ then N has to be close to N_c.

V. NUMERICAL CALCULATIONS

Using the above expressions, it is easy to calculate the rate using MATHEMATICA. For the calculations, it is convenient to use dimensionless variables $\tilde{V}=V/k_BT$, $\tilde{R}=R/l$, $\tilde{k}=kl^4/k_BT$, and $\tilde{\Gamma}=\Gamma l^2\zeta/k_BT$. We shall do this, and for the sake of convenience, drop the tildes above these variables. Thus in this section all the variables are dimensionless. In these dimensionless variables the parameters chosen were $k=2.6436\times 10^{-4}$, $a_0=5$, $a_1=7$.

First we have considered the case of a star with unequal arm lengths. A plot of activation energy as a function of the length of one of the arms, with the lengths of the other two fixed, is given in Fig. 4. It is seen that for the coiled saddle, the activation energy increases linearly with the chain length, but then from the critical length onward, the transition state has the stretched conformation. As a result, the activation energy does not increase linearly. In fact, it increases and then starts decreasing. A similar plot for a barrier with the same set of parameters for a star with equal arms is shown in Fig. 5. Here too, the activation energy at first increases, reaches a maximum value and then decreases. The reason for this is simple. Until N_c the transition state is coiled. Beyond N_c , the transition state is a stretched conformation. For a star of three arms, in the stretched state, two arms would have to be on one side of the barrier while the third has to be on the other side. The branch point will not in general be at the top of the barrier. Therefore, it gives the possibility of having only one arm stretched over the barrier, while the remaining two arms are not. They are sitting away from the top of the barrier, thus lowering the energy.

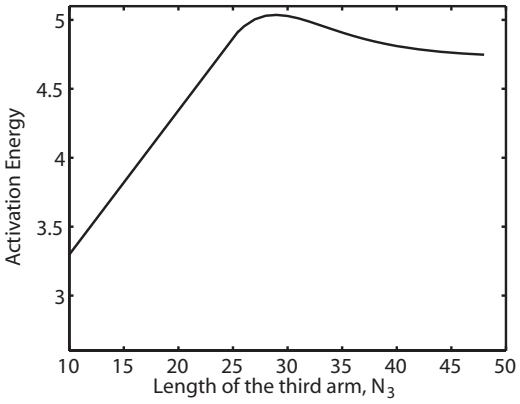

FIG. 4. Plot of dimensionless activation energy ($\beta E^\ddagger$) against the length of the third arm of the star (N_3), for the potential in Eq. (7) (in dimensionless units). The parameters chosen here are $a_0=5$, $a_1=7$, $k=2.6436\times 10^{-4}$. We keep the lengths of two arms fixed with $N_1=10$ and $N_2=11.5$, and vary the length of the third arm. $E^\ddagger$ increases linearly at first, reaches a maximum, and then slowly decreases. When the arms of the star are short, it crosses the barrier in the coiled up conformation, for which the activation energy is proportional to the total number of segments in the star. When we increase the length beyond the critical value, the star crosses with extended conformation. In this extended conformation all the segments do not sit at top of the barrier and activation energy no longer increases linearly. Of the three arms, two arms are on one side of the barrier and the other arm is on the other side. The branch point is not necessarily at the top of the barrier. One arm is stretched over the top of the barrier while the other two are not. The two arms, which are not stretched over the barrier top, occupy the relatively lower energy region and thus lower the activation energy, resulting in the observed decrease in activation energy as one increases the lengths of the arms.

We have calculated the rate of barrier crossing of a star polymer having three equal arms confined to an asymmetric double well potential. The results are plotted in Fig. 6. The full line is the rate given by Eq. (29) where the transition state is a coiled one. This equation is for $N<N_c$, and gives a rate that diverges at $N=N_c$. From N_c onward the transition state is the stretched one, so that the rate has to be calculated using Eq. (40). This is shown as the dashed line in the figure. This also diverges as one approaches N_c. The rate near N_c is calculated using Eq. (43), which takes higher order terms in $c_1^{\ddagger,1}$and $c_1^{\ddagger,2}$ into account. The result is shown by the dotted line in Fig. 6. It is seen that this result is able to bridge across the singularity at N_c. For short arm lengths the rate decreases

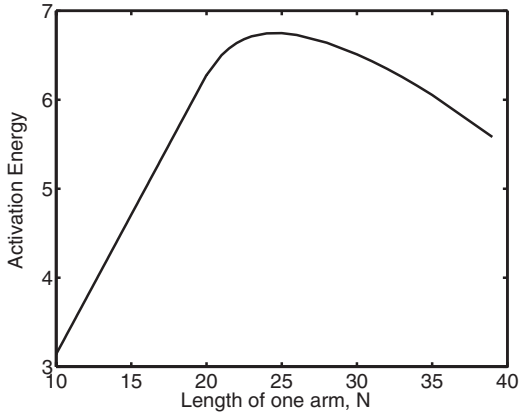

FIG. 5. Plot of activation energy ($\beta E^{\ddagger}$) for a star having three equal arms. The parameters used are $a_0=5.0$, $a_1=7.0$, $k=2.6436\times10^{-4}$. This leads to $V_b=0.1046$. For small N, the star crosses the barrier as a globule. So the activation energy is linearly proportional to the total length of the chain. As the star gets extended it stretches on both sides of the barrier, thus lowering the energy. As a result the activation energy at first increases linearly with length, reaches a maximum, and then decreases.

with length, but as the length increases further the rate starts to increase slowly due to a decrease in activation energy, that was discussed earlier. Thus the rate has a nonmonotonic dependence on the length of the arms.

VI. CONCLUSION

We have considered the dynamics of a star polymer of F arms, confined to an asymmetric double well potential $V(R)$ in space, which is of relevance to several areas of science. To make the problem analytically tractable, we use the continuum version of the one-dimensional Rouse-Ham model. Initially, the molecule is confined to the less stable minimum and would eventually escape over the barrier to the more stable minimum. To calculate the rate of crossing, we use the multidimensional barrier crossing formula, due to Langer [24]. Within the Rouse-Ham model, finding an extremum on the potential reduces to analyzing the Newtonian dynamics of F fictitious particles each of mass m $(=3k_BT/l^2)$ in the upside down potential $-V$. The particles all have to start at the same point in space with a total momentum zero and come to an end at "times" equal to the arm lengths. We have derived a simple closed form expression for the rate, using the methods of Coleman [25]. We found that for sufficiently short arm lengths the transition state (saddle point) is a coiled state just as in the case of linear polymers [21,23]. For longer chains, the saddle point is not a coiled state, but is an extended (stretched) state. For the coiled transition state, the activation energy is proportional to the total arm length of the star, but for longer chains this is no longer true. In fact the activation energy is a linear function of the chain length until a critical total arm length (N_{Tc}) and beyond that it is not. Beyond N_{Tc}, the activation energy increases at first, but then, in general, it decreases. This happens due to the fact that at the saddle the star adopts a conformation in which only one of its arms is stretched over the top of the barrier, while the other arms are not, while for the coiled state, all the arms are sitting over the barrier top. Due to this decrease in activation energy, one has the very interesting situation that a star with longer arms can escape over the barrier faster than a smaller one.

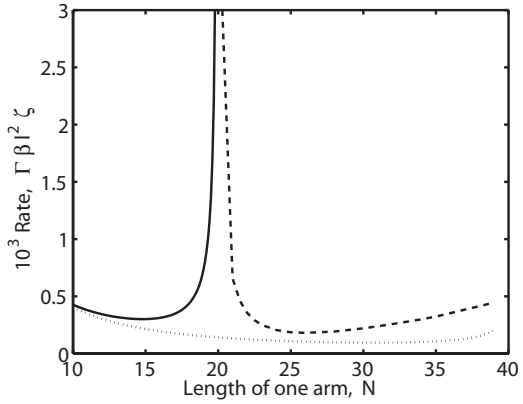

FIG. 6. Plot of rate vs length of one arm (N) of the star having three equal arms, for the potential in Eq. (7) for $a_0=5.0$, $a_1=7.0$, $k=2.6436\times10^{-4}$, $V_b=0.1046$. The full line is the rate calculated with Eq. (29). Here $N_c=20$ as is clear from the divergence of the rate. The dotted line represents the rate calculated for the extended transition state using Eq. (43) while the dashed line is a result of using Eq. (40). When the star crosses the barrier with an extended conformation, its activation energy starts decreasing as it gets stretched over both sides of the top of the barrier. So the rate slowly increases with the length of the arm.

We used the approach of Langer to calculate the rate of crossing the barrier in illustrative cases. The analysis identifies the extrema on the potential energy surface and uses harmonic expansion around it to calculate the rate of crossing. As we used the continuum version of the Rouse-Ham model, we have an infinite number of normal modes of motion around each extremum and hence our formula involved infinite products over these modes. Using the method of Coleman and others, we showed that the infinite products can be written in a simple closed form. This expression was used to calculate the rate for the coiled and stretched transition states. However, the rate so obtained was found to diverge at the crossover point between the two. This is due to the fact that at the point of divergence, the frequency of a mode other than the unstable mode becomes zero, indicating a multifurcation of the saddle point to give many saddle points. Thus for a three armed star of equal arm lengths, it gives rise to twelve new transition states. In order to calculate the rate in the vicinity of this point, it is necessary to go beyond the harmonic expansion, for the modes that become unstable. On performing this, we found the resultant rate to extrapolate well between the ones obtained using coiled and stretched transition states. As expected, the rate has a nonmonotonic dependence on the total arm length of the star, suggesting the very interesting possibility that a bigger star may cross over the barrier faster than a smaller one.

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APPENDIX: CALCULATION OF DETERMINANTS

We prove the formula for the infinite product used to get Eq. (24) from Eq. (23). We follow the analysis of Coleman [25]. We consider the function

$$D(\varepsilon) = \frac{\prod_k (\varepsilon_k - \varepsilon)}{\prod_k (\varepsilon_k^{\ddagger} - \varepsilon)} \tag{A1}$$

of the complex variable ε. In the above ε_k are eigenvalues that satisfy

$$\left(-\frac{\partial^2}{\partial n_\gamma^2} + \frac{V''(-a_0)}{m}\right)\psi_{k,\gamma}(n_\gamma) = \varepsilon_k \psi_{k,\gamma}(n_\gamma) \tag{A2}$$

obeying

$$\left(\frac{\partial \psi_\gamma(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma = N_\gamma} = 0, \tag{A3}$$

$$\sum_\gamma \left(\frac{\partial \psi_\gamma(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma = 0} = 0, \tag{A4}$$

and

$$\psi_1(0) = \psi_2(0) = \cdots = \psi_f(0). \tag{A5}$$

$\varepsilon_k^{\ddagger}$ obeys the same set of conditions exactly but with $V''(-a_0)$ replaced with $V''(R_\gamma^{\ddagger}(n_\gamma))$. We define $\Psi(n_\gamma, \varepsilon)$ such that

$$\left(-\partial_{n_\gamma}^2 + \frac{V''(-a_0)}{m}\right)\Psi_\gamma(n_\gamma, \varepsilon) = \varepsilon \Psi_\gamma(n_\gamma, \varepsilon) \tag{A6}$$

satisfying the boundary conditions $\Psi_\gamma(N_\gamma, \varepsilon) = 1$ and $\Psi'_\gamma(N_\gamma, \varepsilon) = 0$. Similarly, we also define $\Psi_\gamma^{\ddagger}(n_\gamma, \varepsilon)$, which obeys exactly the same set of conditions but with $V''(-a_0)$ replaced with $V''(R^{\ddagger}(n_\gamma))$. Now let

$$R(\varepsilon) = \frac{\prod_{\gamma'} \Psi_{\gamma'}(0, \varepsilon) \sum_\gamma \left(\frac{\partial \ln \Psi_\gamma(n_\gamma, \varepsilon)}{\partial n_\gamma}\right)_{n_\gamma = 0}}{\prod_{\gamma'} \Psi_{\gamma'}^{(\ddagger)}(0, \varepsilon) \sum_\gamma \left(\frac{\partial \ln \Psi_\gamma^{\ddagger}(n_\gamma, \varepsilon)}{\partial n_\gamma}\right)_{n_\gamma = 0}}. \tag{A7}$$

As ε goes to infinity in any direction except along the real, positive ε direction, both $D(\varepsilon)$ and $R(\varepsilon)$ go to unity. Both $D(\varepsilon)$ and $R(\varepsilon)$ are meromorphic function of ε. Further, any zero or pole of $R(\varepsilon)$ is a zero or pole of $D(\varepsilon)$ and vice versa. Therefore, $R(\varepsilon) = D(\varepsilon)$. In particular, when $\varepsilon = 0$, Eq. (A7) reduces to Eq. (25) and we get

$$\frac{\prod_k \varepsilon_k}{\prod_k \varepsilon_k^{\ddagger}} = R(0) = \frac{\prod_\gamma \Psi_\gamma(0) \sum_\gamma \left(\frac{\partial \ln \Psi_\gamma(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma = 0}}{\prod_\gamma \Psi_\gamma^{(\ddagger)}(0) \sum_\gamma \left(\frac{\partial \ln \Psi_\gamma^{\ddagger}(n_\gamma)}{\partial n_\gamma}\right)_{n_\gamma = 0}}, \tag{A8}$$

where we have adopted the notation $\psi_\gamma(n_\gamma) = \Psi_\gamma(n_\gamma, 0)$ and $\psi_\gamma^{\ddagger}(n_\gamma) = \Psi_\gamma^{\ddagger}(n_\gamma, 0)$.

[1] G. S. Grest, L. J. Fetters, J. S. Huang, and D. Richter, Adv. Chem. Phys. **94**, 67 (1996).
[2] J. L. Viovy, Rev. Mod. Phys. **72**, 813 (2000).
[3] J. Han, S. W. Turner, and H. G. Craighead, Phys. Rev. Lett. **83**, 1688 (1999).
[4] J. Han and H. Craighead, Science **288**, 1026 (2000).
[5] J. Han and H. Craighead, Anal. Chem. **74**, 394 (2002).
[6] W. D. Volkmuth, T. Duke, R. H. Austin, and E. Cox, Proc. Natl. Acad. Sci. U.S.A. **92**, 6887 (1995).
[7] D. M. Heuer, S. Saha, and L. A. Archer, Electrophoresis **24**, 3314 (2003).
[8] D. M. Heuer, S. Saha, A. T. Kusumo, and L. A. Archer, Electrophoresis **25**, 1772 (2004).
[9] S. Saha, D. M. Heuer, and L. A. Archer, Electrophoresis **27**, 3181 (2006).
[10] J. Han, S. W. Turner, and H. G. Craighead, Phys. Rev. Lett. **83**, 1688 (1999).
[11] J. Mathe, A. Aksimentiev, D. R. Nelson, K. Schulten, and A. Meller, Proc. Natl. Acad. Sci. U.S.A. **102**, 12377 (2005).
[12] R. Fan, R. Karnik, M. Yue, A. Majumdar, and Yang, Nano Lett. **5**, 1633 (2005).
[13] J. Heng, A. Aksimentiev, C. Ho, P. Marks, Y. Grinkova, S. Sligar, K. Schulten, and G. Timp, Nano Lett. **5**, 1883 (2005).
[14] W. Sung and P. J. Park, Phys. Rev. Lett. **77**, 783 (1996).
[15] P. J. Park and Sung, J. Chem. Phys. **108**, 3013 (1998).
[16] J. J. Kasianowicz, E. Brandin, D. Branton, and D. W. Deamer, Proc. Natl. Acad. Sci. U.S.A. **93**, 13770 (1996).
[17] D. K. Lubensky and D. R. Nelson, Biophys. J. **77**, 1824 (1999).
[18] K. L. Sebastian, Phys. Rev. E **61**, 3245 (2000).
[19] K. L. Sebastian and A. K. R. Paul, Phys. Rev. E **62**, 927 (2000).
[20] P. J. Park and Sung, J. Chem. Phys. **111**, 5259 (1999).
[21] S. K. Lee and W. Sung, Phys. Rev. E **63**, 021115 (2001).
[22] P. Kraikivski, R. Lipowsky, and J. Kierfeld, Europhys. Lett. **66**, 763 (2004).
[23] K. L. Sebastian and A. Debnath, J. Phys.: Condens. Matter **18**, 1 (2006).
[24] J. Langer, Ann. Phys. (N.Y.) **54**, 258 (1969).
[25] S. Coleman, *The Whys of Subnuclear Physics, Erice Lectures*, edited by A. Zichichi (Plenum, New York, 1977).
[26] A. K. R. Paul, Phys. Rev. E **72**, 061801 (2005).
[27] J. S. Ham, J. Chem. Phys. **26**, 625 (1957).