PHYSICAL REVIEW E VOLUME 61, NUMBER 3 MARCH 2000

Kink motion in the barrier crossing of a chain molecule

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(Received 15 March 1999; revised manuscript received 4 November 1999)

We consider the activated escape of chain molecule of N segments over a barrier, a generalization of the classic Kramers problem. Using the Rouse model, we show that the free energy of activation has a square root dependence on the temperature T, leading to a non-Arrhenius form for the rate. We further show that there is a special time dependent solution of the model, which corresponds to a kink in the chain, confined to the region of the barrier. The polymer goes from one side to the other by the motion of the kink in the reverse direction. If there is no free energy difference between the two sides of the barrier, then the kink moves by diffusion and the time of crossing $t_{cross} \sim N^2/T^{3/2}$. If there is a free energy difference, then the kink moves with a nonzero velocity from the lower free energy side to the other, leading to $t_{cross} \sim N/\sqrt{T}$.

PACS number(s): 83.10.Nn

The problem of thermally activated escape of a particle over a barrier (the Kramers problem) is very well studied (see the review [1]). We investigate the generalization of this to the crossing of a free energy barrier by a long chain molecule. An example can be a polymer moving across the interface of two immiscible liquids. Recent simulations on this problem [2] found that a peptide, when placed in the aqueous phase near a water-hexane interface, rapidly translocates toward the hexane phase. A more interesting example is polymer molecule forced to move through a pore [3]. We ask: given the shape of the barrier, (i) what is the free energy of activation for polymer entry into the barrier, and (ii) once an end of the polymer has crossed the barrier, what is the time t_{cross} taken by the entire polymer to move across it? Muthukumar and Baumgartner [4] studied the effect of entropic barriers on dynamics of polymers. They found the total passage time to depend exponentially on the number of segments in the polymer N. Park and Sung [5] have considered the translocation of a long chain molecule through a pore in a membrane. For a flexible molecule they argue that t_{cross} scales as N^3, but this can go over to $\sim N^2$ if there is a free energy difference between the two sides. We consider the case where the width of the barrier, w is larger than the Kuhn length l of the polymer, but small in comparison with the length of the polymer. That is, $l \ll w \ll Nl$. In comparison, the entropic barrier of Ref. [5] is wide and has a width $\sim Nl$. The opposite limit $w >> Nl$ has been considered recently [6].

We consider a one dimensional model for both the barrier and the chain molecule and use continuum version of the Rouse model [7] to describe the dynamics:

$$\zeta \partial_t R(n,t) = m \partial_{nn} R(n,t) - V'[R(n,t)] + f(n,t). \tag{1}$$

$R(n,t)$ denotes the position of the nth unit of the polymer at the time t. The boundary conditions are $\{\partial_n R(n,t)\}_{n=0} = \{\partial_n R(n,t)\}_{n=N} = 0$. $V(R)$ is the free energy of a segment of the polymer located at the position R. The barrier is assumed to extend in space from $-a_0$ to a_1, with $a_0 < a_1$. We take $V(R)$ to be a smooth continuous function, with $V'(R) = 2kR(R+a_0)(R-a_1)$ for $-a_0 < R < a_1$ and $V'(R) = 0$ outside these limits. Taking the potential to be zero for $R < -a_0$, we get

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

for $-a_0 < R < a_1$ and $V(R) = \frac{1}{6}k(a_0 - a_1)(a_0 + a_1)^3$ for $R > a_1$. The form of the potential is shown in Fig. 1 [we refer to this potential as the pure repulsive barrier (PRB)]. The maximum of the barrier occurs at $R_{\max} = 0$. The barrier height in the forward direction is $V_f = \frac{1}{6}ka_0{}^3(a_0 + 2a_1)$ while in the reverse direction it is $V_b = \frac{1}{6}ka_1^3(2a_0 + a_1)$. On crossing the barrier, a unit of the polymer lowers its free energy by $\Delta V = \frac{1}{6}k(a_0 - a_1)(a_0 + a_1)^3$. We also discuss the case where the functional form of Eq. (2) is applicable over the entire range of R so that the dynamics occurs in a biased double well (BDW). Our conclusions are general and independent of the form of the actual functional forms of the potentials that we use.

$f(n,t)$ in Eq. (1) is the random force acting on the n^{th} segment. It has the correlation function $\langle f(n,t) f(n_1,t_1) \rangle = 2\zeta k_B T \delta(n - n_1)\delta(t - t_1)$. When the system is at equilibrium, the probability distribution functional is $\exp(-(1/k_BT)\int dn\{\frac{1}{2}m(\partial_n R)^2 + V[R(n)]\})$. The activation free energy for the crossing can be found by extremising this functional, subject to the condition that one end of the polymer has crossed $R_{\max}$. The extremum configuration obeys the equations $m\partial_{nn}R = V'(R)$ and $\{\partial_n R(n,t)\}_{n=0} = \{\partial_n R(n,t)\}_{n=N} = 0$. This is just Newton's equations for a (fictitious particle) of mass m, moving under a potential $-V(R)$. If the polymer is very long, we can find the extremum configuration by taking $R(-\infty) = -a_0$ and the other end of the polymer to be at a point with $R > R_{\max}$. The total energy of the particle $E_c = \frac{1}{2}m(\partial_n R)^2 - V[R(n)]$ is conserved. For the extremum configuration one finds $E_c = 0$. This means that the fictitious particle starts at $R(-\infty) = -a_0$ and ends up at R_f, where $R_f (> R_{\max})$ is such that $V(R_f) = 0$. The free energy of activation is $E_{act} = \int_{-a_0}^{R_f} \sqrt{2mV(R)}\,dR$. For the PRB potential, there are large

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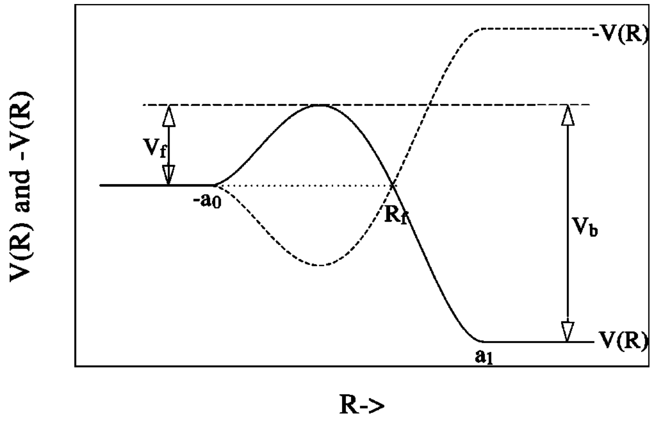

FIG. 1. The barrier and its inverted form. The barrier heights in the forward and backward directions are shown. The dotted line represents the path that determines the activation energy.

fluctuations of the portion of the chain in the region $R < -a_0$. Neglecting the length of the portion of the chain that is over the barrier, one can estimate the effect of forcing the chain to the vicinity of the barrier as an entropic contribution to the activation free energy equal to $(k_BT/2)\ln[N]$ [5]. Thus, for the PRB, the net rate is proportional to proportional to $e^{-E_{act}/k_BT}/\sqrt{N}$. If, however, the potential is not flat, but binding (as in a BDW potential), then the chain segments cannot undergo such large amplitude fluctuations. Then, this contribution would not be there to the activation free energy and the Boltzmann factor would simply be proportional to e^{-E_{act}/k_BT} (a detailed calculation of this can be done with instanton methods [9]). This scenario would be valid, if one were forcing the polymer to cross the barrier, by application of external field, or even if there is at least a weak attractive tail portion to the barrier, resulting from van der Waals interactions.

The parameter m in the Rouse model is proportional to the temperature [7]. So if $V(R)$ is temperature independent, $E_{act}\alpha\sqrt{T}$. This leads to a Boltzmann factor $\sim e^{-constant/\sqrt{T}}$. For the potential of Eq. (2), we find $R_f = a_0(\gamma - \sqrt{\gamma^2-\gamma})$ with $\gamma = [1+2(a_1/a_0)]^{\frac{1}{3}}$ and $E_{act} = (\sqrt{mk}a_0^3/6)\{(3\gamma^2+1)\sqrt{1+3\gamma} - 3\gamma(\gamma^2-1)\ln[\sqrt{\gamma(\gamma-1)}/(1+\gamma-\sqrt{1+3\gamma})]\}$.

Now, to calculate t_{cross}, we first look at the mathematical solutions of the deterministic equation, in which we replace random noise term $f(n,t)$ by its average. The result is

$$\zeta\partial_t R(n,t) - m\partial_{nn}R(n,t) + V'(R) = 0 \tag{3}$$

with $\{\partial_n R(n,t)\}_{n=0} = \{\partial_n R(n,t)\}_{n=N} = 0$. The simplest solutions of this equation are: $R(n,t) = R_0$ (R_0 is a constant), with $R_0 < -a_0$, or with $R_0 > a_1$. These correspond to the polymer being on either side of the barrier. Thermal noise makes $R(n,t)$ fluctuate about the mean position R_0. These may be analyzed using the normal coordinates for fluctuations about this mean position [7]. In addition to these two time independent solutions, the above equation has a time dependent solution (a kink) too, which corresponds to the polymer crossing the barrier. We analyze the dynamics of the chain, with the kink (distortion) in it, using the normal modes for fluctuations about the kink configuration [8].

The kink solution may be found using the ansatz $R(n,t) = R_s(\tau)$ where $\tau = n - vt$ [8], when Eq. (3) reduces to $m(d^2R_s/d\tau^2) + v\zeta(dR_s/d\tau) = V'(R_s)$. If one imagines τ as time, then this is a simple Newtonian equation for the motion of particle of mass m, moving in the upside down potential $-V(R)$, and $v\zeta/m$ is the coefficient of friction. We can easily find a solution of this equation, obeying the conditions $R_s(\tau) = -a_0$ for $\tau \to -\infty$ and $R_s(\tau) = a_1$ for $\tau \to \infty$. It is $R_s(\tau) = (-a_0 + e^{\tau\omega(a_0+a_1)}a_1)(1+e^{\tau\omega(a_0+a_1)})^{-1}$, where $\omega = \sqrt{k/m}$ and the velocity $v = (\sqrt{mk}/\zeta)(a_0 - a_1)$. The solution is a kink, occurring in the portion of the chain inside the barrier. The point with $\tau = 0$ shall be referred to as the center of the kink. [Actually one has a one-parameter family of solutions of the form $R_s(\tau+\tau_0)$, where τ_0 is any arbitrary constant.] As $\tau = n - vt$, the center of the kink moves with the constant velocity v, which depends on the barrier heights V_f and V_b. Note that if $a_0 < a_1$, then $V_f < V_b$, and this velocity is negative. This implies that the kink is moving in the negative direction, which corresponds to the chain moving in the positive direction. That is, the chain moves to the lower free energy region, with this velocity. If the barrier is symmetric $a_0 = a_1$ ($V_f = V_b$) then the velocity of the kink is zero.

The center of the kink would also execute Brownian motion, due to thermal fluctuations of the medium. To analyze this, following ''instanton methods'' of field theory [9], we write

$$R(n,t) = R_s[n - a(t)] + \sum_{p=1}^{\infty} X_p(t)\phi_p(n - a(t), t). \tag{4}$$

Movement of the kink occurs by change of the location of its center $a(t)$. $a(t)$ is a random function of time which is to be determined. ϕ_p are a set of functions defined below and $X_p(t)$ are expansion coefficients. ϕ_p eventually will turn out to describe motion along the pth normal mode in presence of the kink in the chain. Using Eq. (4) in Eq. (1) and expanding around the kink, retaining first order terms in $X_p(t)$, and changing over to the new variables $(\bar{n}, t)$ with $\bar{n} = n - a(t)$, ($\bar{n}$ is segment position along the chain with respect to the center of the kink) we get

$$\zeta[v - \dot{a}(t)]\partial_{\bar{n}}R_s(\bar{n}) + \zeta\sum_{p=1}^{\infty}\dot{X}_p(t)\phi_p(\bar{n},t) + \sum_{p=1}^{\infty} X_p(t)\hat{\mathcal{L}}\phi_p(\bar{n},t) = f(\bar{n}+a(t),t), \tag{5}$$

where $\hat{\mathcal{L}} = \zeta\partial_t - m\partial_{\bar{n}\bar{n}} - \zeta\dot{a}(t)\partial_{\bar{n}} + V''[R_s(\bar{n})]$. We take ϕ_p to obey the equation $\{\zeta\partial_t - m\partial_{\bar{n}\bar{n}} - \zeta v\partial_{\bar{n}} + V''[R_s(\bar{n})]\}\phi_p(\bar{n},t) = 0$, subject to the condition $\partial_{\bar{n}}\phi_p(\bar{n},t) = 0$ at both ends of the chain [i.e., at $\bar{n} = -a(t)$ and at $\bar{n} = N - a(t)$]. For a very long chain, with the kink located well inside it, the ends cannot influence the dynamics of barrier crossing. Therefore we would make only a minor error by imposing these boundary conditions at $\bar{n} = \pm N/2$. Then, putting $\phi_p(\bar{n},t) = \psi_p(\bar{n})e^{-\lambda_p t/\zeta - v\zeta\bar{n}/(2m)}$, we find that $\psi_p(\bar{n})$ has to obey $\hat{H}\psi_p(\bar{n}) = \lambda_p\psi_p(\bar{n})$ with $\hat{H} = \{-m\partial_{\bar{n}\bar{n}} + V''[R_s(\bar{n})] + (v\zeta)^2/(4m)\}$. The translation mode of the kink leads to a solution

$\psi_0(\bar{n})$ of the above equation with $\lambda_0=0$ [9]. Its functional form may be found by putting $e^{v\zeta\bar{n}/(2m)}\partial_{\bar{n}}R_s(\bar{n})=\omega(a_0+a_1)^2e^{(1/2)\bar{n}\omega(3a_0+a_1)}(1+e^{\bar{n}\omega(a_0+a_1)})^{-2}=C\psi_0(\bar{n})$, where is C the is the normalization factor, chosen such that $\langle\psi_0|\psi_0\rangle=1$. On evaluation, we find $C^2=\langle\partial_{\bar{n}}R_s(\bar{n})|e^{v\zeta\bar{n}/m}|\partial_{\bar{n}}R_s(\bar{n})\rangle=\frac{2}{3}\pi\omega\csc[2\pi(a_1-a_0)/(a_0+a_1)](a_1-a_0)a_0a_1$. The eigenfunctions $\psi_p(\bar{n}),p=0\cdots\infty$ form an orthonormal set.

Equation (5) thus becomes

$$\sum_{p=1}^{\infty}\dot{X}_p(t)\psi_p(\bar{n})e^{-\lambda_p t/\zeta}+[v-\dot{a}(t)]Y(t)=\frac{1}{\zeta}e^{v\zeta\bar{n}/(2m)}f(\bar{n}+a(t),t) \tag{6}$$

where $Y(t)=\psi_0(\bar{n})C+\Sigma_{p=1}^{\infty}X_p(t)e^{-\lambda_p t/\zeta}\tilde{\partial}_{\bar{n}}\psi_p(\bar{n})$, with $\tilde{\partial}_{\bar{n}}=e^{v\zeta\bar{n}/(2m)}\partial_{\bar{n}}e^{-v\zeta\bar{n}/(2m)}$. On taking the inner product of this with $\psi_0(\bar{n})$, we get

$$[v-\dot{a}(t)]\left(C+\sum_{p=1}^{\infty}X_p(t)e^{-\lambda_p t/\zeta}\langle\psi_0|\tilde{\partial}_{\bar{n}}\psi_p(\bar{n})\rangle\right)=\xi_0(t) \tag{7}$$

with $\xi_0(t)=(1/\zeta)\int_{-N/2}^{N/2}d\bar{n}\,\psi_0(\bar{n})e^{v\zeta\bar{n}/(2m)}f(\bar{n}+a(t),t)$. Obviously, $\langle\xi_0(t)\rangle=0$ and

$$\begin{aligned}\langle\xi_0(t)\xi_0(t_1)\rangle&\\ &=\delta(t-t_1)(2k_BT/\zeta)\int_{\text{over the kink}}d\bar{n}e^{v\bar{n}\zeta/m}[\psi_0(\bar{n})]^2\\ &=\delta(t-t_1)k_BT/(2\zeta a_0a_1)\sec[2\pi(a_1-a_0)/(a_0+a_1)]\\ &\quad\times(3a_1-a_0)(3a_0-a_1).\end{aligned}$$

On taking the inner product of Eq. (6) with $\psi_l(\bar{n})$, we get

$$\dot{X}_le^{-\lambda_l t/\zeta}+[v-\dot{a}(t)]\sum_{p=1}^{\infty}X_p(t)e^{-\lambda_p t/\zeta}\langle\psi_l|\tilde{\partial}_{\bar{n}}|\psi_p\rangle=\xi_l(t), \tag{8}$$

where $\xi_p(t)=(1/\zeta)\int_{-N/2}^{N/2}d\bar{n}\,\psi_l^*(\bar{n})e^{v\zeta\bar{n}/(2m)}f(\bar{n}+a(t),t)$. Equation (8) may be solved, and using the kets $|X(t)\rangle=\Sigma_{p=1}^{\infty}X_p(t)|\psi_p\rangle$ and $|\xi(t)\rangle=\Sigma_{p=1}^{\infty}\xi_p(t)|\psi_p\rangle$, the solution is

$$|X(t)\rangle=|X_d(t)\rangle+|X_r(t)\rangle \tag{9}$$

with $|X_d(t)\rangle=\hat{T}(\exp\{\int_0^t dt_1[\dot{a}(t_1)-v]\hat{A}(t_1)\})|X(0)\rangle$, $|X_r(t)\rangle=\int_0^t dt_1\hat{T}[\exp\{\int_{t_1}^t dt_2(\dot{a}(t_2)-v)\hat{A}(t_2)\}]e^{\hat{H}t_1}|\xi(t_1)\rangle$, where $\hat{A}(t)$ is the operator $\hat{A}(t)=e^{\hat{H}t/\zeta}\tilde{\partial}_{\bar{n}}e^{-\hat{H}t/\zeta}$. $\hat{T}$ is the time ordering operator. Equation (7) gives

$$\dot{a}(t)=v+\xi_0(t)/[C+\langle\psi_0|\tilde{\partial}_{\bar{n}}e^{-\hat{H}t/\zeta}|X(t)\rangle]. \tag{10}$$

Now taking the average of the above, and using Eq. (9) and the fact that $\xi_0(t)$ is independent of everything that occurred at previous instants, we get $\langle\dot{a}(t)\rangle=v$, so that on an average, the kink moves with a velocity v. For the polymer to cross the barrier, the kink has to go in the reverse direction, by a distance equal to the length of the chain. Hence $t_{cross}\sim N/v$. As v is proportional $\sqrt{mk}$, assuming $V(R)$ to be temperature independent we find $t_{cross}\sim N/\sqrt{T}$. If one neglects the kink-phonon scattering term in Eq. (10) [i.e., the term $\langle\psi_0|\tilde{\partial}_{\bar{n}}e^{-Ht/\zeta}|X(t)\rangle$], then the diffusion coefficient of the kink is $D=(3k_BT/8\pi\zeta)\sqrt{m/k}[(3a_{1-}a_0)(3a_0-a_1)/a_0{}^2a_1{}^2(a_1-a_0)]\tan[2\pi(a_1-a_0)/(a_0+a_1)]$.

The above analysis of kink dynamics is valid for the BDW, while for the PRB, one has to include the effect of the entropy contribution to the free energy [5]. The kink represents the local distortion of the chain caused by the barrier potential $V(x)$. It would exist as a stable object on the chain provided the barrier height originating from the potential $V(x)$ is large in comparison with k_BT. Further, it is localized within the width w of the potential. The entropic effects leads to an additional contribution to the barrier, of height $\sim k_BT(\ln N)$, which is spread over a large length scale, of the order of N. Hence its effect on the structure of the kink is negligible. The driving force for kink motion is the free energy change $\Delta V(<0)$ per segment, on crossing the barrier. In comparison, the free energy change per segment, from the entropy part is only $\sim k_BT(\ln N)/N$, which can be neglected if $|\Delta V|>>k_BT(\ln N)/N$, a condition which is easily satisfied for large N. Thus $t_{cross}\sim N/\sqrt{T}$ for the PRB too, if $\Delta V<0$.

Now we consider the case where the driving force $\Delta V=0$. Then, in double well case, the kink has no preferred direction to move, and its average velocity $v=0$. One can find $D=(3k_BT/4\zeta a_0^3)\sqrt{m/k}$. In this case, the kink just executes random walk without any bias and the time required for the polymer to cross the barrier is $t_{cross}\sim N^2/D\sim N^2/T^{3/2}$. For the PRB, if $\Delta V=0$, the condition $\Delta V>>k_BT(\ln N)/N$ is not obeyed and hence the entropic effects have to be included in the description of dynamics. The presence of the barrier $V(x)$ assures the existence of the kink, and as the kink is localized, its diffusion coefficient has no dependence on N. The kink just diffuses under the influence of the entropic part of the potential. Now using the first passage approach of Ref. [5], one finds again that $t_{cross}\sim N^2/D\sim N^2/T^{3/2}$. Thus, if $\Delta V=0$, $t_{cross}\sim N^2/D\sim N^2/T^{3/2}$ in general.

One may finally ask: under what conditions does one expect the kink mechanism to be operative? We have already given the condition $w\ll Nl$, so that the polymer extends from one side to the other during most of the time that is spent on crossing. The kink would exist as a coherent entity, only if thermal fluctuations do not destroy it. This means that the barrier height originating from $V(x)$ be much larger than k_BT. It is also to be noted that our analysis implies that as long as these conditions are satisfied, the kink is always there, and its motion is the mechanism for the barrier crossing. This is true, even for very long chains which have an appreciable contribution to the total barrier from the entropy effect, which may even be greater than the barrier due to $V(x)$, simply due to the fact that the entropic contribution is spread over a length of order N, and hence does not affect the structure of the kink.

In Ref. [5] the motion is assumed to be equivalent to that of the center of mass and hence the effective diffusion coefficient taken to be $\sim 1/N$. So, to cover a distance N, it needs a time $\sim N^3$. A free energy difference between the two sides makes the time $\sim N^2$. In our analysis, the crossing occurs by the motion of the kink. The diffusion coefficient of the kink is N independent and hence our results are different from those of Ref. [5]. In the case where there is no free energy difference, our crossing time is proportional to N^2(in contrast to N^3 of Ref. [5]), while if there is a free energy difference, our crossing time is proportional to N (in contrast to N^2 of Ref. [5]). The $t_{cross} \sim N$ behavior discussed here has been observed in the experiments by Kasianowicz *et al.* [3], in which single stranded DNA molecules were forced to move through a nanopore.

I am deeply indebted to Professor S. K. Rangarajan, for the encouragement that he has given me over the years. I thank Professor S. Vasudevan and Professor B. Cherayil for their comments.

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