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Anchoring of Polymers by Traps Randomly Placed on a Line

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We study the dynamics of a Rouse polymer chain which diffuses in a three-dimensional space under the constraint that one of its ends, referred to as the slip-link, may move only along a one-dimensional line containing randomly placed, immobile, perfect traps. Extensions of this model occur naturally in many fields, ranging from the spreading of polymer liquids on chemically active substrates to the binding of biomolecules by ligands. For our model we succeed in computing exactly the time evolution of the probability $P_{\mathrm{sl}}(t)$ that the chain slip-link will not encounter any of the traps until time t and, consequently, that until this time the chain will remain mobile.

KEY WORDS: Rouse model; anomalous diffusion; trapping.

I. INTRODUCTION

The time evolution of the survival probability $P(t)$ of particles diffusing in a d-dimensional space in the presence of immobile, randomly placed traps has been widely discussed in the physical and mathematical literature within the last two decades. An interest in this problem has been inspired by the evident physical significance of the subject (excitation and charge motion, photoconductivity, photosynthesis). Further on, such an interest has been stimulated by an important observation[1] that $P(t)$ exhibits a non-mean-field long-time behavior, which is intimately related to the so-called Lifschitz singularities near the edge of the band in the density of states of a particle in quantum Lorentz gas and is reflected in the moment

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generating function of the so-called Wiener sausage.[2,3] Later works (see, e.g., refs. 4 and 5) have also pointed out the relevance of the issue to percolation, self-avoiding random walks or self-attracting polymers, as well as to the anomalous behavior of the ground-state energy of a Witten's toy Hamiltonian in supersymmetric quantum mechanics.[6] Of extreme importance now is the correlated motion in the presence of traps, i.e., the motion of several particles bond together, such as occurs naturally in polymers and in biomolecules immersed in chemically active medium. A few pertinent examples are the formation of polymer brushes at interfaces and networks, i.e., kinetic grafting of carboxy-terminated polystyrene chains on epoxy networks or adsorption of polymer functional groups on colloidal particles or on the network strands of a gel,[7,8] the spreading of polymer liquids on substrates with chemically active sites[9] or, especially, the kinetics of binding of biomolecules by specific ligands.[10–12]

In the case of single particles various analytical techniques have been elaborated to calculate $P(t)$, including an extension of the "optimal fluctuation" method,[1] different methods of evaluating upper and lower bounds (see, e.g., refs. 2, 3, 13–15), Green functions approaches,[4] field-theoretic treatments,[5] as well as a variety of mean-field-type descriptions (see refs. 16–18 and references therein). These studies have revealed a two-stage decay pattern of the form

$$\ln P(t) \propto \begin{cases} -n_{\mathrm{tr}}\phi_d(t), & t_{\mathrm{m}} \ll t \ll t_{\mathrm{c}}, \quad \text{(A)} \\ -n_{\mathrm{tr}}^{2/(d+2)}\, t^{d/(d+2)}, & t \gg t_{\mathrm{c}}, \quad \text{(B)} \end{cases} \tag{1}$$

where n_{tr} denotes the mean density of traps, t_{m} is a microscopic time scale and t_{c} denotes the crossover time between the intermediate- (A) and long-time (B) kinetic stages. Further on, the function $\phi_d(t)$ appearing in Eq. (1.A) defines the mean volume of the so-called Wiener sausage (see, e.g., ref. 2)—i.e., the mean volume swept by a diffusive spherical particle during time t. Its discrete-space counterpart, i.e., an analog of $\phi_d(t)$ defined for lattice random walks, is referred to as the mean number of distinct sites visited by a particle up to the time t (see ref. 22 for more details). The functional form of $\phi_d(t)$ is different for different spatial dimensions d and obeys:

$$\phi_d(t) \propto \begin{cases} t^{1/2}, & d=1 \\ t/\ln(t), & d=2 \\ t, & d\geqslant 3 \end{cases} \tag{2}$$

The physical behavior underlying the kinetic regimes described by Eqs. (1.A) and (1.B) has also been elucidated. It has been understood that

Eqs. (1.A) and (1.B) are supported by completely different realizations of random walk trajectories: The intermediate-time behavior described by Eq. (1.A) is associated with typical realizations of random walk trajectories and is consistent with the predictions of the mean field, Smoluchowski-type approaches;[4, 16–18, 20–22] namely, $\phi_d(t) = \int^t dt'\, k_{\text{Smol}}(t')$,[4] where $k_{\text{Smol}}(t)$ is the so-called Smoluchowski constant, which equals the diffusive current through the surface of an immobile d-dimensional sphere. On the other hand, the long-time asymptotical form in Eq. (1.B) showing a slower time-dependence compared to the intermediate-time decay law, stems from the interplay between fluctuations in the spatial distribution of traps (namely, on the existence of rare but sufficiently large trap-free cavities), and atypical realizations of random walk trajectories which do not leave such cavities during the time of observation. Note also that Eq. (1.B) describes the anomalous long-time tail of the moment generating function for the Wiener sausage volume.[2]

Due to the general interest in fractal structures as useful approximate models of disordered media, and/or anomalous diffusion, Eq. (1) for single particles has been extended[18, 20–22] to describe trapping of random walkers on random or regular structures characterized, in the general case, by a non-integer spatial dimension d_f and anomalous diffusion exponent d_w, the latter being defined through the relation describing the time-dependence of the second moment of the particle's displacement, $\overline{r^2(t)} \sim t^{2/d_w}$, where d_ω may be different from the value $d_\omega = 2$, which holds for conventional diffusive motion in Euclidean d-dimensional space.[20–22] For such systems heuristic agruments[18–23] suggest that $P(t)$ follows an asymptotic behavior of the form

$$\ln P(t) \propto \begin{cases} -n_{\text{tr}}\tilde{\phi}_d(t), & t_{\text{m}} \ll t \ll t_{\text{c}}, \qquad (\text{A}) \\ -n_{\text{tr}}^{d_w/(d_f+d_\omega)}\, t^{d_f/(d_f+d_\omega)}, & t \gg t_{\text{c}}, \qquad (\text{B}) \end{cases} \tag{3}$$

with

$$\tilde{\phi}_d(t) \propto \begin{cases} t^{d_f/d_\omega}, & d_f < d_\omega \\ t/\ln(t), & d_f = d_\omega \\ t, & d_f > d_\omega \end{cases} \tag{4}$$

Note, that here d_f can attain integer values and d_ω may be set equal to 2, which leads to conventional diffusive motion in Euclidean space; then Eq. (3) reduces to Eq. (1).

The decay patterns as in Eqs. (3) and (4) have been verified numerically for different types of fractal systems, such as, e.g., Sierpinski gaskets or percolation clusters.[20–22] However, rigorous results describing the evolutional of $P(t)$ in systems showing anomalous diffusion are lacking at present.

In this paper we focus on the three-dimensional correlated motion of many particles, linked into a polymer chain by harmonic springs, in the presence of immobile traps distributed at random on a one-dimensional line—say, a fiber. The chain contains a chemically active end-group (referred to in what follows as a slip-link), which is constrained to move along the fiber only and may react irreversibly with any of the traps, thus anchoring the whole chain (Fig. 1). The chain's dynamics is described within the framework of the customary Rouse model.[24] We aim to compute here the time evolution of the probability $P_{sl}(t)$ that the slip-link will not encounter any of the traps until time t, or, in other words, the probability that an initially unanchored chain will remain mobile until time t. It appears that, despite the fact that the random motion of the slip-link is non-Markovian and, generally, non-diffusive, we are able to compute $P_{sl}(t)$ exactly starting from first principles. This allows us to show that Eqs. (3) and (4) can be strongly generalized to account for the motion of correlated particles; the decay form is then characteristic for the non-Markovian nature of the underlying dynamics.

The paper is structured as follows: In Section 2 we formulate the model. In Section 3 we discuss briefly the exact solution for the survival of a single particle which diffuses on a line in the presence of randomly distributed traps, and then rederive this solution in terms of a path-integral method. In Section 4 we describe, following[25] the path integral formalism for evaluating the measure of trajectories covered by a tagged bead of a Rouse chain. Next, we show how such a formalism can be applied for the exact computation of the probability that the slip-link is not trapped until time t. Finally, in Section 5 we conclude with a summary and discussion of the obtained results.

II. THE MODEL

Consider a polymer chain embedded in three-dimensional space and consisting of N beads (Fig. 1), which are connected sequentially by phantom harmonic springs of rigidity K. The rigidity can be also expressed as $K = 3T/b^2$, where T is the temperature (written in units of the Boltzmann constant k_B) and b is the mean equilibrium distance between beads. Further more, the positions of all beads are denoted by $\vec{r}_j = (x_j, y_j, z_j)$, where the subscript j enumerates the beads along the chain, $j = [0, N]$. All beads, except the slip-link ($j = 0$), may move freely in 3d. On contrary, we stipulate that the slip-link is constrained to move only along the X-axis, such that its position in space is given solely by the X-component of the

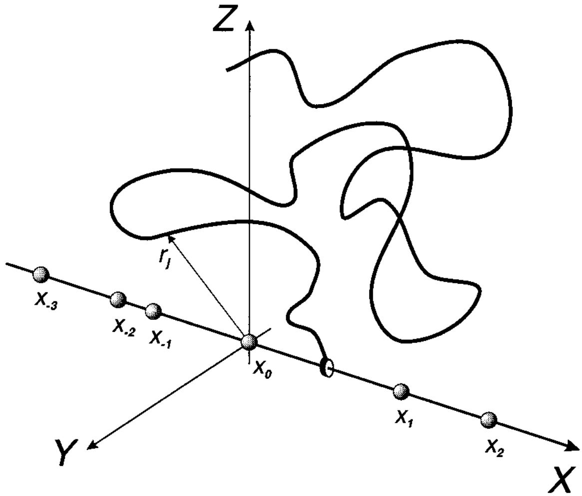


Fig. 1. Polymer chain with an active particle attached to one of its extremities (the slip-link).

vector $\vec{r}_0$, since y_0 and z_0 must always equal zero. Then the potential energy $U(\{\vec{r}_j\})$ of such a chain is given by

$$U(\{\vec{r}_j\}) = \frac{K}{2} \sum_{j=0}^{N-1} (\vec{r}_{j+1} - \vec{r}_j)^2$$
$$= \frac{K}{2} \left[\sum_{j=0}^{N-1} (x_{j+1} - x_j)^2 + \sum_{j=1}^{N-1} \{(y_{j+1} - y_j)^2 + (z_{j+1} - z_j)^2\} \right] \quad (5)$$

Next, apart from the holonomic constraints imposed by the springs, the beads experience the action of random forces $\vec{f}_j(t)$. These random forces are assumed to be Gaussian and uncorrelated in time and space; their Cartesian components $f_{j,\alpha}(t)$, where $\alpha = x, y, z$, obey:

$$\overline{f_{j,\alpha}(t)} = 0$$
$$\overline{f_{j,\alpha}(t)\, f_{j',\alpha'}(t')} = 2\zeta T \delta_{j,j'} \delta_{\alpha,\alpha'} \delta(t - t') \quad (6)$$

where the bar stands for averaging over thermal histories and ζ is the macroscopic friction coefficient.

In the absence of excluded-volume effects, the dynamics of the Rouse chain is guided by the corresponding Langevin–Rouse equations[24]

$$\zeta \dot{\vec{r}}_j = -\frac{\delta U(\{\vec{r}_j\})}{\delta \vec{r}_j} + \vec{f}_j(t) \quad (7)$$

where the dot denotes the time derivative. As one can verify readily, for the potential energy given by Eq. (5) the equations for the $\vec{r}_j$ decouple with respect to the Cartesian components. That is, the dynamics of, say, x_j, is independent of y_j and z_j and reads

$$\zeta \dot{x}_j = K(x_{j+1} + x_{j-1} - 2x_j) + f_{j,x}(t) \tag{8}$$

which equation holds for $j = 1,..., N-1$. On the other hand, the displacements of the chain's extremities along the X-axis, i.e., x_0 and x_N, obey

$$\zeta \dot{x}_0 = K(x_1 - x_0) + f_{0,x}(t) \tag{9}$$

and

$$\zeta \dot{x}_N = K(x_{N-1} - x_N) + f_{N,x}(t) \tag{10}$$

Hence, with regards to polymer dynamics, one faces an effectively one-dimensional model.

Lastly, we suppose that the N-axis contains perfect, immobile traps, which are placed at random positions with mean density n_{tr}. The positions of the traps are denoted by $\{X_n\}$, $-\infty < n < \infty$. According to our model, the traps influence the dynamics of the polymer only by trapping (immobilizing) the slip-link at the encounter. The influence of the trap on the other beads (i.e., such that $j \in [1, N]$) is indirect: as soon as the slip-link gets immobilized by any of the traps, the chain becomes anchored as a whole due to the links between the chain's monomers. Our aim is to compute exactly the time evolution of the probability, $P_{\text{sl}}(t)$, that a polymer chain with a slip-link sliding along the X-axis will not encounter any of the traps (and thus will remain mobile until time t).

III. MONOMER TRAPPING ON A LINE

It seems instructive to recall first the time evolution of the survival probability in the simplest case, for $N = 0$, i.e., for a single chemically active monomer diffusing on a one-dimensional line and reacting with randomly placed, immobile traps. It is intuitively clear that for a Rouse chain containing N beads, we should recover (apart from the renormalization of the diffusion coefficient) at sufficiently long times the behavior predicted for a single monomer, because for a finite chain the random motion of any of the chain's beads ultimately follows the conventional diffusion of the chain's center-of-mass.[24] On the other hand, at shorter times substantial deviations between the motion of the monomer and of the center-of-mass are to be found, due to the essentially non-diffusive characted of the slip-link motion, induced by the internal degrees of freedom of the polymer. This anomalous regime stemming from the internal relaxation modes of the chain will cause significant departures from the decay forms described by Eq. (1). The derivation of decay laws associated with this anomalous regime is the primary goal of the present paper and will be discussed in the next section.

As one may expect, in one-dimensional systems the situation simplifies considerably, since here the diffusive particle can react only with two neighboring traps and thus cannot leave the intertrap interval. This renders the problem exactly solvable, reducing it to the analysis of the particle survival inside a finite interval, followed by averaging over the distribution of the intertrap intervals. We outline such a calculation following the seminal method of ref. 1.

A. The One-Dimensional Exact Solution

We calculate first the probability $\Psi(x, x(0), t \mid L)$ that a diffusive particle (whose diffusion coefficient is $D = T/\zeta$), which starts at $x(0)$ will not encounter the traps at $X_0 = 0$ and at $X_1 = L$ until time t. This probability follows as the solution of the following one-dimensional boundary problem:

$$\begin{cases} \dfrac{\partial \Psi(x, x(0), t \mid L)}{\partial t} = D\,\dfrac{\partial^2 \Psi(x, x(0), t \mid L)}{\partial x^2} \\ \Psi(x, x(0), t \mid L)|_{x=0} = \Psi(x, x(0), t \mid L)|_{x=L} = 0 \\ \Psi(x, x(0), t=0 \mid L) = \delta(x - x(0)) \end{cases} \tag{11}$$

The solution of Eqs. (11) can be readily found by standard means and takes the form of a Fourier series:

$$\Psi(x, x(0), t \mid L) = \frac{2}{L} \sum_{n=1}^{\infty} \exp\left(-\frac{\pi^2 n^2 D t}{L^2}\right) \sin\left(\frac{\pi n x}{L}\right) \sin\left(\frac{\pi n x(0)}{L}\right) \tag{12}$$

Now, to compute the monomer survival probability we turn to the position-averaged function

$$\Psi(t \mid L) = \frac{1}{L} \int_0^L \int_0^L dx(0)\, dx\, \Psi(x, x(0), t \mid L) \tag{13}$$

which can be computed from Eq. (12) and reads

$$\Psi(t \mid L) = \frac{8}{\pi^2} \sum_{l=0}^{\infty} (2l+1)^{-2} \exp\left(-\frac{\pi^2 (2l+1)^2\, D t}{L^2}\right) \tag{14}$$

Next, the desired survival probability of the diffusive monomer $P(t)$ is determined as the convolution

$$P(t) = \int_0^\infty dL\, \Psi_{\rm mon}(t \mid L)\, \mathcal{P}(L) \tag{15}$$

where $\mathcal{P}(L)$ is the probability density of having a trap-free void of length L. For a completely random (Poisson) placement of traps $\mathcal{P}(L)$ reads:

$$\mathcal{P}(L) = n_{\rm tr} \exp(-n_{\rm tr} L) \tag{16}$$

Consequently, one finds the following general expression determining the monomer survival probability

$$P(t) = \frac{8 n_{\rm tr}}{\pi^2} \sum_{l=0}^{\infty} (2l+1)^{-2} \int_0^\infty dL \exp\left(-\frac{\pi^2 (2l+1)^2\, Dt}{L^2} - n_{\rm tr} L \right) \tag{17}$$

The asymptotical behavior of the expression in Eq. (17) has been discussed in detail in ref. 15; it has been shown that $P(t)$ follows a two-stage decay pattern as in Eq. (1). Explicitly on has

$$P(t) \approx \begin{cases} \exp(-4 n_{\rm tr} (Dt/\pi)^{1/2}), & t_m \ll t \ll t_{\rm c}, \quad \text{(A)} \\ \exp(-3(\pi^2 n_{\rm tr}^2 Dt/4)^{1/3}), & t \gg t_{\rm c}, \quad \text{(B)} \end{cases} \tag{18}$$

where the crossover time $t_{\rm c}$ separating two regimes obeys $t_{\rm c} \approx 1/D n_{\rm tr}^2$, and consequently, can be large if $n_{\rm tr}$ is small.

B. Path-Integral Formulation of the Monomer Trapping Problem in 1D

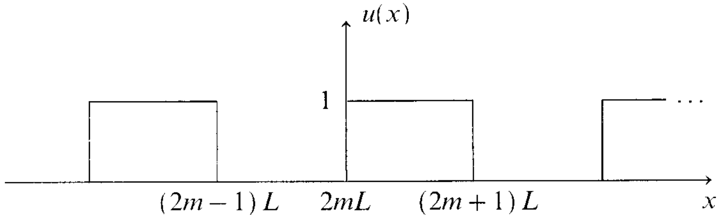
In this subsection we show how to recover the solution of the monomer trapping problem in terms of the path-integral formalism, which will be later used to determine the trapping kinetics of the slip-link. To do this, we will proceed as follows:

We first write thee solution of Eq. (11) as an integral over Brownian paths $x(\tau)$:

$$\Psi(x, x(0), t \mid L) = \frac{1}{2\sqrt{\pi D t}} \int_{x(0)}^{x} \mathcal{D}\{x(\tau)\} \times \exp\left\{ -\frac{1}{4D} \int_0^t d\tau \left(\frac{\partial x(\tau)}{\partial \tau} \right)^2 \right\} \Bigg|_{0 < x(\tau) < L,\ \tau \in [0;\, t]} \tag{19}$$

where $\mathscr{D}\{x(\tau)\}$ denotes integration over the monomer trajectories $x(\tau)$, the exponential is the standard Wiener measure, while the subscript $0 < x(\tau) < L$, $\tau \in [0, t]$ signifies that the integral has to be calculated under the constraint that none of the monomer's trajectories leaves the interval $[0, L]$ within the time period $[0, t]$.

Next, to recover the series involved in Eq. (12), we multiply the integrand by the periodic step function depicted in the figure below



Using the contour integral representation of such a step function[26]

$$u(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{d\lambda\, e^{-\lambda x}}{\lambda(1+e^{\lambda L})} = \begin{cases} 1 & \text{if } 2mL < x < (2m+1)\, L \\ 0 & \text{if } (2m+1)\, L < x < (2m+2)\, L \end{cases} \tag{20}$$

where $m = 0, 1, 2,...$, we can rewrite Eq. (19) as

$$\Psi(x, x(0), t \mid L) = \frac{1}{2\sqrt{\pi D t}} \sum_{m=-\infty}^{\infty} \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{d\lambda\, e^{\lambda x(0)}}{\lambda(1+e^{\lambda L})} \times \int_{x(0)}^{x} \mathscr{D}\{x(\tau)\} \exp[-S\{x(\tau)\}] \tag{21}$$

where the action $S\{x(\tau)\}$ is given by

$$S\{x(\tau)\} = \int_0^t d\tau \left\{ \frac{1}{4D} \left(\frac{\partial x(\tau)}{\partial \tau} \right)^2 + \lambda \left(\frac{\partial x(\tau)}{\partial \tau} \right) \right\} \tag{22}$$

Now, to compute the path integral in Eq. (21) with the quadratic action in Eq. (22) we have merely to define the action-minimizing trajectory $\tilde{x}(\tau)$ and calculate the action corresponding to such a trajectory. the action-minimizing trajectory is defined by the classical Euler equation of motion, which for the action in Eq. (22) is simply

$$\frac{d}{d\tau} \left(\frac{1}{2D} \frac{d\tilde{x}(\tau)}{d\tau} + \lambda \right) = 0$$

Integrating this equation subject to the conditions $\tilde{x}(\tau=0)=x(0)$ and $\tilde{x}(\tau=t)=x$, we find

$$\tilde{x}(\tau)=(x-x(0))\,\frac{\tau}{t}+x(0) \tag{23}$$

Consequently, the minimal action is given by

$$S\{\tilde{x}(t)\}=\frac{(x-x(0))^2}{4Dt}+\lambda(x-x(0))$$

and hence, the formal solution of the boundary problem in Eq. (11) can be written down as

$$\begin{aligned}\Psi(x,&\ x(0),\ t\mid L)\\ &=\frac{1}{2\sqrt{\pi D t}}\sum_{m=-\infty}^{\infty}\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{d\lambda}{\lambda(1+e^{\lambda L})}\exp\left\{-\frac{(x-x(0))^2}{4Dt}+\lambda x\right\}\\ &=\frac{1}{2\sqrt{\pi D t}}\sum_{m=-\infty}^{\infty}\exp\left\{-\frac{(x-x(0)-2mL)^2}{4Dt}\right\}\end{aligned} \tag{24}$$

Next, using the well-known representation of Jacobi theta-function[26]

$$\sum_{m=-\infty}^{\infty} q^{(m+a)^2}=\theta_3\left(\pi a,\ \exp\left(\frac{\pi^2}{\ln q}\right)\right)\ln^{-1/2}\frac{1}{q}$$

and setting

$$q=\exp\left(-\frac{L^2}{Dt}\right);\qquad a=\frac{x-x(0)}{2L} \tag{25}$$

we may rewrite Eq. (24) as

$$\begin{aligned}\Psi(x,\ x(0),\ t\mid L)&=\frac{2}{L}\sum_{m=-\infty}^{\infty}\exp\left(-\frac{\mathcal{D}\pi^2m^2t}{L^2}\right)\cos\left(\frac{\pi m(x-x(0))}{L}\right)\\ &=\frac{2}{L}\sum_{m=-\infty}^{\infty}\exp\left(-\frac{D\pi^2m^2t}{L^2}\right)\Bigg(\underbrace{\sin\left(\frac{\pi m x}{L}\right)\sin\left(\frac{\pi m x(0)}{L}\right)}_{\text{part A}}\\ &\qquad+\underbrace{\cos\left(\frac{\pi m x}{L}\right)\cos\left(\frac{\pi m x(0)}{L}\right)}_{\text{part B}}\Bigg)\end{aligned} \tag{26}$$

Note now that the contribution "A" (a product of two "odd" sine-functions —see Eq. (26)) vanishes at $x = 0$ and $x = L$. It thus mirrors the absorbing boundary conditions relevant to the trapping problem, while the second contribution "B" (a product of two "even" cosine-functions) corresponds to the totally reflecting boundary conditions. To understand this result note that the introduction of the step function does not force by itself the function $\Psi(x, x(0), t \mid L)$ to vanish at the boundaries of the interval $[0; L]$. Thus, the expression in Eq. (26) in which only the odd contribution "A" is taken into account coincides with the result presented in Eq. (12). It follows that the asymptotical behavior of the monomer survival probability can be evaluated in terms of the path-integral formalism by picking then the odd contribution. We would like to note also that the construction we have employed is nothing but the well known "mirror principle," widely used in electrostatics.

We conclude this subsection with the following prescription:

Prescription (the "mirror principle"). To find the solution of the diffusion problem with the Dirichlet boundary condition at the ends of the segment $[0, L]$, we have merely to: (a) obtain the Green's function solution $\Psi(x, x(0), t)$ on the full line $\{x, x(0)\} \in]-\infty, \infty[$; (b) restrict $x - x(0)$ to the segment $[0, L]$, perform the replacement $x - x(0) \to x - x(0) - 2mL$ and take the odd contribution to the sum $\sum_{m=-\infty}^{\infty} \Psi(x - x(0) - 2mL, t)$.

IV. TRAPPING OF THE SLIP-LINK OF A POLYMER

To calculate the evolution of $P_{sl}(t)$ in the case of a slip-link attached to a polymer chain, we will proceed essentially along the lines of the previous section. First, we present the derivation of $\Psi_{sl}(x_0, x_0(0), t)$—the probability distribution for the displacements of the slip-link on an infinite line without traps.[25] Then, using the above formulated prescription (the "mirror principle"), we determine $\Psi_{sl}(x_0, x_0(0), t \mid L)$—the probability that the slip-link of the chain, which is initially located at some point $x_0(0)$ inside the interval $[0, L]$, will not leave this interval until time t. Finally, the desired probability $P_{sl}(t)$ will be obtained from $\Psi_{sl}(x_0, x_0(0), t \mid L)$ by averaging over the Poisson distribution of the interval's lengths.

A. The Probability Distribution of the Slip-Link Displacement

In this subsection we outline, following the analysis of ref. 25, the steps involved in the derivation of the probability distribution $\Psi_{sl}(x_0, x_0(0), t)$ for the displacements of the slip-link on an infinite line.

This probability can be written as

$$\Psi_{\mathrm{sl}}(x_0, x_0(0), t) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dx_1 \cdots dx_N \, \Psi(x_0, x_1,..., x_N, t) \tag{27}$$

where $\{x_0, x_1,..., x_N\} \equiv \{x_1(t),..., x_N(t)\}$ here and henceforth denote the coordinates of all chain segments at time t, while $\Psi(x_0, x_1,..., x_N, t)$ is the joint distribution function of the N beads of the polymer chain. In other words, $\Psi(x_0, x_1,..., x_N, t)$ is the probability of having the x-coordinates of the N beads of the chain at the positions $\{x_j(t)\}$, provided that initially they where at $\{x_j(0)\}$.

For the Rouse chain whose potential energy obeys Eq. (5), the time evolution of the function $\Psi(x_0, x_1,..., x_N, t)$ is governed by the following Smoluchowski–Fokker–Planck equation:[24]

$$\frac{\partial}{\partial t} \Psi(x_0, x_1,..., x_N, t) = D \sum_{j=0}^{N} \frac{\partial}{\partial x_j} \left(\frac{\partial}{\partial x_j} + \beta \frac{\partial}{\partial x_j} U(x_0, x_1,..., x_N) \right) \Psi(x_0, x_1,..., x_N, t) \tag{28}$$

where $\beta = 1/T$ and $D = T/\zeta$ is the diffusion constant of an individual bead (monomer). Equation (28) has to be solved subject to the initial condition:

$$\Psi(x_0, x_1,..., x_N, t=0) = \prod_{j=0}^{N} \delta(x_j(t) - x_j(0)) \tag{29}$$

Eqs. (28)–(29) define completely the evolution function $\Psi(x_0, x_1,..., x_N, t)$.

The computation of the probability distribution $\Psi(x_0, x_0(0), t)$ using the path-integral formalism was first performed in ref. 25. Let us recall the main steps of this approach. First of all, it is expedient to cast Eq. (28) into the form of the $(N+1)$-dimensional Schrödinger-type equation. This can be readily performed by making use the following ansatz:

$$\Psi(x_0, x_1,..., x_N, t) = \exp\left\{ -\frac{K(N+1)}{2\zeta} t - \frac{\beta}{2} U(x_0, x_1,..., x_N) \right\} \times \Phi(x_0, x_1,..., x_N, t) \tag{30}$$

where the function $\Phi(x_0, x_1,..., x_N, t)$ satisfies

$$\frac{\partial}{\partial t} \Phi(x_0, x_1,..., x_N, t) = D \sum_{j=0}^{N} \left(\frac{\partial^2}{\partial x_j^2} - \beta^2 K^2 (x_{j-1} - 2x_j + x_{j+1})^2 \right) \Phi(x_0, x_1,..., x_N, t) \tag{31}$$

Now, by virtue of the Feynmann–Kac theorem, the formal solution of Eq. (31) can be written down explicitly as the following path-integral

$$\Phi(x_0, x_1,..., x_N, t) = \frac{1}{\mathcal{N}} \int_{x_0(0)}^{x_0} \cdots \int_{x_N(0)}^{x_N} \prod_{j=0}^{N} \mathcal{D}\{x_j(\tau)\} \times \exp[-S\{x_0(\tau), x_1(\tau),..., x_N(\tau)\}] \tag{32}$$

where $\mathcal{N}$ is the normalization constant and the action $S\{x_0(\tau), x_1(\tau),..., x_N(\tau)\}$ has the form:

$$S\{x_0(\tau), x_1(\tau),..., x_N(\tau)\} = \int_0^t d\tau \left\{ \frac{1}{4D} \sum_{j=0}^{N} \left(\frac{\partial x_j(\tau)}{\partial \tau} \right)^2 + D\beta^2 K^2 \sum_{j=1}^{N-1} (x_{j-1}(\tau) - 2x_j(\tau) + x_{j+1}(\tau))^2 \right\} \tag{33}$$

In the subsequent calculations we will not specify the normalization constant and preexponential factors; all our results will hold thus only to exponential accuracy.

Now, we suppose following ref. 25 that the slip-link moves along some prescribed trajectory $X_{sl}(\tau)$; as a matter of fact, such a constraint allows to symmetrize the boundary conditions for the action-minimizing trajectory, which are otherwise different at different chain's extremities. Such a constraint can be taken into account by multiplying the integrand in Eq. (32) by a functional delta-function of the form (see ref. 25 for details)

$$\delta(x_0(\tau) - X_{sl}(\tau)) = \int \mathcal{D}\{m(\tau)\} \exp\left\{ -i \int_0^t d\tau\, m(\tau)(x_0(\tau) - X_{sl}(\tau)) \right\}$$

which means that the action in Eq. (33) is replaced by an effective action of the following form:

$$S'\{x_0(\tau), x_1(\tau),..., x_N(\tau)\} = \int_0^t d\tau \left\{ \frac{1}{4D} \sum_{j=0}^{N} \left(\frac{\partial x_j(\tau)}{\partial \tau} \right)^2 + D\beta^2 K^2 \sum_{j=1}^{N-1} (x_{j-1}(\tau) - 2x_j(\tau) + x_{j+1}(\tau))^2 + im(\tau)(x_0(\tau) - X_{sl}(\tau)) \right\} \tag{34}$$

and one has to perform afterwards an additional integration over the measure $\mathcal{D}\{m(\tau)\}$.

Now, the action in (32) is minimal for classical trajectories satisfying the Euler equation:

$$\left\{\frac{d}{d\tau}\left(\frac{\partial}{\partial \dot{x}_j}\right)-\frac{\partial}{\partial x_j}\right\} \mathscr{L}(\dot{x}_0, \dot{x}_1,..., \dot{x}_N, x_0, x_1,..., x_N)=0; \qquad j\in[0, N]$$

where $\mathscr{L}$ is the Lagrangian function:

$$\mathscr{L}=\frac{1}{4D}\sum_{j=0}^{N}\left(\frac{\partial x_j(\tau)}{\partial \tau}\right)^2+D\beta^2K^2\sum_{j=1}^{N-1}(x_{j-1}(\tau)-2x_j(\tau)+x_{j+1}(\tau))^2$$
$$+im(\tau)((x_0(\tau)-X_{\text{sl}}(\tau)) \qquad (35)$$

Turning to the continuous j-limit, one obtains the following Euler equation, determining the optimal trajectories of the chain's monomers:[25]

$$\left(\frac{\partial}{\partial\tau}-2K\beta D\,\frac{\partial^2}{\partial j^2}\right)\left(\frac{\partial}{\partial\tau}+2K\beta D\,\frac{\partial^2}{\partial j^2}\right)\tilde{x}_j(\tau)=4Di\delta(j)\,m(\tau) \qquad (36)$$

which has to be solved subject to the boundary conditions (see ref. 25)

$$\begin{cases}\left.\dfrac{\partial\tilde{x}_j(\tau)}{\partial j}\right|_{j=0,\,N}=0, & \left.\dfrac{\partial^3\tilde{x}_j(\tau)}{\partial j^3}\right|_{j=0,\,N}=0\\[2ex] \dfrac{\partial\tilde{x}_j(\tau)}{\partial\tau}=-2K\beta D\left.\dfrac{\partial^2\tilde{x}_j(\tau)}{\partial j^2}\right|_{\tau=0}, & \dfrac{\partial\tilde{x}_j(\tau)}{\partial\tau}=+2K\beta D\left.\dfrac{\partial^2\tilde{x}_j(\tau)}{\partial j^2}\right|_{\tau=t}\end{cases} \qquad (37)$$

The action-minimizing trajectories $\tilde{x}_j(\tau)$, defined by the boundary problem (36)–(37), are obtained explicitly[25] in form of a series expansion over the normal Rouse modes:[24]

$$\tilde{x}_j(\tau)=-\frac{2iN}{\pi^2K\beta}\sum_{p=1}^{\infty}p^{-2}\cos\left(\frac{\pi pj}{N}\right)\int_0^t d\tau'\,m(\tau')\exp\left\{-\frac{|\tau-\tau'|}{\tau_R}\,p^2\right\} \qquad (38)$$

where $\tau_R=\zeta N^2/2\pi^2K$ is the largest fundamental relaxation time of the harmonic chain, i.e., the so-called Rouse time. This time may be interpreted as being the time needed for some local defect, e.g., kink, to spread out diffusively along the arclength of the chain.

Next, substituting the expression for the optimal trajectory in Eq. (38) into Eq. (35) and performing the integration over $\mathscr{D}\{m(\tau)\}$, one arrives at the following general result:[25]

$$\Psi_{\mathrm{sl}}(x_0, x_0(0), t) = \frac{1}{\mathcal{N}} \int_{x_0(0)}^{x_0} \mathscr{D}\{X_{\mathrm{sl}}(\tau)\} \exp\left[-\int_0^t \left(\frac{dX_{\mathrm{sl}}(\tau)}{d\tau}\right) d\tau \int_0^\tau \left(\frac{dX_{\mathrm{sl}}(\tau')}{d\tau'}\right) d\tau' \, \phi(\tau-\tau')\right] \tag{39}$$

where $\phi(\tau-\tau')$ is given by

$$\phi(\tau-\tau') \approx \begin{cases} \dfrac{N}{4D}\,\delta(\tau-\tau'), & |\tau-\tau'| > \tau_R, \quad \text{(A)} \\ \left(\dfrac{\beta K}{D}\right)^{1/2} |\tau-\tau'|^{-1/2}, & |\tau-\tau'| < \tau_R, \quad \text{(B)} \end{cases} \tag{40}$$

Equations (39) and (40) represent the desired generalization of the classical Wiener result for the measure of Brownian particle trajectories to the more complicated case of a particle attached to a diffusive Rouse chain.

Finally, in order to compute the probability $\Psi_{\mathrm{sl}}(x_0, x_0(0), t \mid L)$ that the slip-link of the Rouse chain will remain until time t within the interval $[0, L]$, we make use of the "mirror principle" prescription of the previous section. Multiplying the integrand in Eq. (39) by a step-function, we get

$$\Psi_{\mathrm{sl}}(x_0, x_0(0), t \mid L) = \frac{1}{\mathcal{N}} \sum_{m=-\infty}^{\infty} \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{d\lambda \, e^{\lambda x_0(0)}}{\lambda(1+e^{\lambda L})} \int_{x_0}^{x_0(0)} \mathscr{D}\{X_{\mathrm{sl}}(\tau)\} \exp[-S\{X_{\mathrm{sl}}(\tau)\}] \tag{41}$$

where

$$S\{X_{\mathrm{sl}}(\tau)\} = \int_0^t \left(\frac{dX_{\mathrm{sl}}(\tau)}{d\tau}\right) d\tau \int_0^\tau \left(\frac{dX_{\mathrm{sl}}(\tau')}{d\tau'}\right) d\tau' \, \phi(\tau-\tau') + \lambda \int_0^t d\tau \left(\frac{dX_{\mathrm{sl}}(\tau)}{d\tau}\right) \tag{42}$$

Below we discuss the asymptotical forms of $\Psi_{\mathrm{sl}}(x_0, x_0(0), t \mid L)$ using Eqs. (41) and (42) in the limits $|\tau-\tau'| < \tau_R$ and $|\tau-\tau'| > \tau_R$.

B. Asymptotic Behavior of $\Psi_{\mathrm{sl}}(x_0, x_0(0), t \mid L)$

We focus first on the behavior in the intermediate-time limit, $t < \tau_R$. Note, however, that since $\tau_R \sim N^2$, for sufficiently long chains this intermediate-time regime may last over quite an extended time interval.

It follows from Eqs. (41) and (42) that for $t < \tau_R$ the internal relaxations of the chain are most important and lead to the following form of the action

$$S\{X_{\rm sl}(\tau)\} = \left(\frac{\beta K}{D}\right)^{1/2} \int_0^t \left(\frac{\partial X_{\rm sl}(\tau)}{\partial \tau}\right) d\tau \int_0^\tau \left(\frac{\partial X_{\rm sl}(\tau')}{\partial \tau'}\right) \frac{d\tau'}{\sqrt{|\tau - \tau'|}} + \lambda \int_0^t d\tau \left(\frac{dX_{\rm sl}(\tau)}{d\tau}\right) \tag{43}$$

Now S in Eq. (43) is non-local and possesses non-Wiener scaling properties. In particular, it yields for the mean-square displacement of any chain's bead, including the slip-link the following law[19, 24, 25]

$$\overline{x_j^2(t)} \sim t^{1/2} \tag{44}$$

i.e., a subdiffusive behavior, which signifies that (for the time scales considered here) the trajectories of the chain's beads are spatially more confined that there of simple Brownian particle.

Now, one can readily find that the optimal trajectory $\tilde{X}_{\rm sl}(\tau)$ which minimizes the action in Eq. (43) obeys the following Euler equation

$$\frac{d}{d\tau}\left(\left(\frac{\beta K}{D}\right)^{1/2} \int_0^\tau \dot{\tilde{X}}_{\rm sl}(\tau') \frac{d\tau'}{\sqrt{\tau - \tau'}} + \lambda\right) = 0 \tag{45}$$

We seek the solution of Eq. (45) in the form

$$\dot{\tilde{X}}_{\rm sl}(\tau') = A(\tau')^{\alpha}$$

where $\tau' = \tau u$ and $0 \leqslant u \leqslant 1$. Substituting this form into Eq. (45), we get the functional equation

$$\left(\frac{\beta K}{D}\right)^{1/2} A\tau^{\alpha+1/2} \int_0^1 \frac{u^{\alpha}\, du}{\sqrt{1-u}} + \lambda = C \tag{46}$$

where C is some constant. Note now, that the left-hand side of Eq. (46) is independent of τ for $\alpha = -1/2$ only, which thus fixes the value of α to $\alpha = -1/2$. Hence, we obtain

$$\dot{\tilde{X}}_{\rm sl}(\tau) = \frac{C - \lambda}{\pi} \left(\frac{D}{\beta K \tau}\right)^{1/2} \tag{47}$$

which leads to the following expression for the minimal action

$$S\{\tilde{X}_{sl}(\tau)\} = \frac{2}{\pi}\left(\frac{Dt}{\beta K}\right)^{1/2}(C-\lambda)^2 + \lambda(x_0 - x_0(0)) \tag{48}$$

In turn, the value of the constant C can be found by integrating Eq. (47), which gives:

$$C = \lambda + \frac{\pi}{2}\left(\frac{\beta K}{Dt}\right)^{1/2}(x_0 - x_0(0))$$

Substituting this expression into Eq. (48), we arrive at the final equation for the minimal action

$$S\{\tilde{X}_{sl}(\tau)\} = \frac{\pi}{2}\left(\frac{\beta K}{Dt}\right)^{1/2}(x_0 - x_0(0))^2 + \lambda(x_0 - x_0(0)) \tag{49}$$

Next, taking advantage of Eqs. (49) and (41), we find that the probability that the slip-link which is at point x_0 at $t=0$ will stay inside the interval $[0, L]$ until time t is given to exponential accuracy by

$$\Psi_{sl}(x_0, x_0(0), t \mid L) \approx \sum_{m=-\infty}^{\infty} \exp\left\{-\frac{2}{\pi}\left(\frac{\beta K}{Dt}\right)^{1/2}(x_0 - x_0(0) - 2mL)^2\right\} \tag{50}$$

which yields, by virtue of the "mirror principle," the following result

$$\Psi_{sl}(x_0, x_0(0), t \mid L) \approx \sum_{m=-\infty}^{\infty} \exp\left\{-\frac{\pi m^2}{2L^2}\left(\frac{Dt}{\beta K}\right)^{1/2} \sin\left(\frac{\pi m x_0}{L}\right)\sin\left(\frac{\pi m x_0(0)}{L}\right)\right\} \tag{51}$$

Further on, integrating Eq. (43) over x_0 and $x_0(0)$, we get for the position-averaged function $\Psi_{sl}(t \mid L)$ (see Eq. (13))

$$\Psi_{sl}(t \mid L) \approx \sum_{l=0}^{\infty} (2l+1)^{-2} \exp\left\{-\frac{\pi(2l+1)^2}{2L^2}\left(\frac{Dt}{\beta K}\right)^{1/2}\right\} \tag{52}$$

and consequently, the desired probability $P_{sl}(t)$ that the slip-link will not encounter any of the traps until time t is given by the following integral

$$P_{sl}(t) \approx \sum_{l=0}^{\infty} (2l+1)^{-2} \int_0^{\infty} dL \exp\left(-\frac{\pi^2(2l+1)^2}{L^2} D\theta - n_{tr} L\right) \tag{53}$$

where for notational convenience we have introduced the "effective" time θ, where $\theta = (t/\beta KD)^{1/2}/2\pi$. Note that Eq. (53) becomes identical to Eq. (17) upon the mere replacement $t \to \theta$, which readily enables us to get the corresponding decay forms from Eqs. (18). We recall, however, that Eq. (53) is valid only for $t < \tau_R$, which will result in a slightly more complicated overall decay pattern than the one described by Eqs. (18).

Consider next the evolution of $\Psi_{sl}(x_0, x_0(0), t \mid L)$ and, respectively, of $P_{sl}(t)$ in the limit $t > \tau_R$. Note that here the action in Eq. (42) reduces to the standard result

$$S\{\tilde{X}_{sl}(\tau)\} = \frac{N}{4D} \int_0^t d\tau \left(\frac{d\tilde{X}_{sl}(\tau)}{d\tau}\right)^2 + \lambda \int_0^t d\tau \left(\frac{d\tilde{X}_{sl}(\tau)}{d\tau}\right) \tag{54}$$

which is simply the action of an isolated Brownian particle which moves with the diffusion coefficient D/N (compare to Eq. (22)). Consequently, in this time limit we have that the mean-square displacement of the slip-link obeys

$$\overline{x_0^2(t)} \sim \frac{D}{N} t \tag{55}$$

and the probability $P_{sl}(t)$ follows

$$P_{sl}(t) \approx \sum_{l=0}^{\infty} (2l+1)^{-2} \int_0^{\infty} dL \exp\left(-\frac{\pi^2 (2l+1)^2 Dt}{NL^2} - n_{tr} L\right) \tag{56}$$

Note that this result could be expected on intuitive grounds, since, as we have already mentioned, in the limit $t > \tau_R$ the motion of every bead of the chain follows mainly that of chain's center-of-mass.

C. Trapping Pattern $P_{sl}(t)$ for the Slip-Link of a Rouse Chain

Consider first the case of an infinitely long chain, then $\tau_R = \infty$ and the dynamics of the slip-link is described by Eqs. (39), (40.B) and (44) over the entire time domain. Comparing the decay forms in Eqs. (17), (18) and (53), we readily find that the probability that the slip-link will not encounter any of the traps until time t shows the following two stage decay pattern:

$$P(t) \approx \begin{cases} \exp\left(-\frac{2}{\pi} n_{tr} (4Dt/\beta K)^{1/4}\right), & \text{for} \quad t_m \ll t \ll \tilde{t}_{c,1}, \quad \text{(A)} \\ \exp\left(-\frac{3}{2} n_{tr}^{2/3} (\pi^2 Dt/\beta K)^{1/6}\right), & \text{for} \quad t \gg \tilde{t}_{c,1}, \quad \text{(B)} \end{cases} \tag{57}$$

In Eq. (57) the crossover time $\tilde{t}_{c,1}$ separating the regimes A and B obeys $\tilde{t}_{c,1} \approx \beta K/Dn_{tr}^4$. Note that $\tilde{t}_{c,1} \approx (bn_{tr})^{-2}\, t_c$, where b is the mean distance between the chain's beads in equilibrium and t_c is the corresponding crossover time in Eq. (18). Hence, for systems with a small density of traps $\tilde{t}_{c,1}$ can be significantly larger than the monomer crossover time t_c in Eq. (18). Note also that the Eq. (57.A) is the mean-field, Smoluchowski-type result corresponding to the sub-diffusive motion of the slip link, described by Eq. (44), in presence of uniformly distributed traps; the exponent in Eq. (57.A) is just the product of the trap mean density and the mean maximal range (span) of the slip link displacement. On the other hand, Eq. (57.B) stems from the interplay between exponentially rare, large trap-free voids, (the large-L tail of Eq. (16)), and anomalously confined trajectories of the slip-link. Equation (57.B) also describes the long-time tail of the moment generating function of the Wiener sausage volume for the the slip-link trajectories of an infinitely long chain.

We turn next to the case of finite chains, and hence to finite τ_R, which sets the upper bound on the time of applicability of the decay pattern in Eq. (57). Here, at times greater than τ_R the conventional diffusive motion of the slip-link is restored, Eqs. (39), (40.A) and (55), and the decay has a form similar to that in Eqs. (1),

$$P(t) \approx \begin{cases} \exp(-4n_{tr}(Dt/\pi N)^{1/2}), & \tau_R \ll t \ll \tilde{t}_{c,2}, \quad (A) \\ \exp(-3(\pi^2 n_{tr}^2\, Dt/4N)^{1/3}), & t \gg \tilde{t}_{c,2} \quad (B) \end{cases} \tag{58}$$

Here the crossover time $\tilde{t}_{c,2}$ between the A and B regimes is given by $\tilde{t}_{c,2} \approx N/Dn_{tr}^2 = Nt_c$.

Note, however, that the overall decay pattern of $P_{sl}(t)$ is not the does not necessarily follow sequentially after Eq. (57), i.e., the sequence given by Eqs. (57.A), (57.B), (58.A) and finally, (58.B) may be realized only if the crossover times would obey the following multiple inequality $t_m \ll \tilde{t}_{c,1} \ll \tau_R \ll \tilde{t}_{c,2}$ which practically is never the case. To show this explicitly and to construct the actual overall decay pattern, it is expedient to rewrite the crossover times $\tilde{t}_{c,1}$ and $\tilde{t}_{c,2}$ in terms of the Rouse time τ_R. We have then $\tilde{t}_{c,1} \approx Q^{-4}\tau_R$ and $\tilde{t}_{c,2} \approx Q^{-2}\tau_R$, where $Q = n_{tr}(bN^{1/2})$, i.e., is equal to the mean number of traps in the area covered by a Rouse chain of arclength bN in its typical equilibrium configuration.

Below we analyse different possible situations with respect to the values of the parameters Q and $q = n_{tr}b$ and discuss the corresponding decay patterns.

Case I. High Density of Traps, $q \sim 1$, and Long Chains, $Q \ll 1$. Note first that in this case the crossover time $\tilde{t}_{c,1}$ is comparable to the microscopic diffusion time, i.e., $\tilde{t}_{c,1} \sim t_m \sim b^2/D$, which implies that the Smoluchowski-type regime corresponding to the sub-diffusive slip-link motion, Eq. (57.A), is unobservable. Hence, the law in Eq. (57.B) will describe the decay of $P_{sl}(t)$ until $t \approx \tau_R$. Further on, the condition $Q \gg 1$ implies that $\tilde{t}_{c,2} \ll \tau_R$ and the regime described by Eq. (58.A) does not exist. Consequently, the overall decay pattern in the Case I reads

$$P_{sl}(t) \approx \begin{cases} \exp(-\frac{3}{2} n_{tr}^{2/3} (\pi^2 Dt/\beta K)^{1/6}), & t_m \ll t \ll \tau_R, \quad \text{(A)} \\ \exp(-3 n_{tr}^{2/3} (\pi^2 Dt/4N)^{1/3}), & t \gg \tau_R, \quad \text{(B)} \end{cases} \tag{59}$$

Note that both A and B regimes are essentially non-mean-field and stem from the presence of fluctuation trap-free voids. We also remark that in Eqs. (59) the most representative regime is the one in, Eq. (59.A), which is associated with the sub-diffusive behavior of the slip-link, Eq. (44). Note that the value of $P_{sl}(t)$ at the crossover time separating the A and B regimes, i.e., $P_{sl}(t = \tau_R)$, is of order of $\exp(-Q^{2/3}) \ll 1$, which means that the probability that the slip-link will be trapped during the stage described by Eq. (59.A) is considerably higher than the probability that it will be trapped according to the law in Eq. (59.B).

We note finally that the behavior in Eqs. (59.A) and (59.B) appears to be compatible, in regard to the time-dependence, with the heuristic generalization of the results for a single particle trapping in case when the latter possesses anomalous diffusive properties, Eq. (3.B). Thus Eq. (3.B) with $d_f = 4$, Eq. (44), (which corresponds to anomalous sub-diffusive motion of the slip-link at times less than the Rouse time), reproduces the time dependence in Eq. (59.A), while setting $d_f = 2$ in Eq. (3.B), (which applies to the conventional diffusive motion with renormalized diffusion coefficient in Eq. (55)), we arrive at Eq. (59.B).

Case II. Low Density of Traps, $q \ll 1$, and Very Long Chains, $Q \gg 1$. In this case $\tilde{t}_{c,1} \gg t_m$, which implies that the regime in Eq. (57.A) describes the initial kinetic stage. Next, since here $\tilde{t}_{c,1} \ll \tau_R$, the regime in Eq. (57.B) will also exist and will describe the intermediate-time kinetic behavior of $P_{sl}(t)$. Lastly, the final stage will follow the decay in Eq. (58.B), because $\tilde{t}_{c,2}$ appears to be much less than the Rouse time τ_R and thus the regime in Eq. (58.A) will be absent. Consequently, in Case II one has the following overall decay pattern:

$$P_{sl}(t) \approx \begin{cases} \exp(-\frac{2}{\pi} n_{tr} (4Dt/\beta K)^{1/4}), & t_m \ll t \ll \tilde{t}_{c,1}, \quad \text{(A)} \\ \exp(-\frac{3}{2} n_{tr}^{2/3} (\pi^2 Dt/\beta K)^{1/6}), & \tilde{t}_{c,1} \ll t \ll \tau_R, \quad \text{(B)} \\ \exp(-3(\pi^2 n_{tr}^2 Dt/4N)^{1/3}), & t \gg \tau_R, \quad \text{(C)} \end{cases} \tag{60}$$

In Eqs. (60) the decay laws in the first two lines are associated with the sub-diffusive motion of the slip-link and describe the mean-field, Smoluchowski-type (A) and fluctuation-induced (B) kinetic stages, respectively, while the law in the third line describes the survival of a Brownian particle (with diffusion coefficient D/N) in the fluctuation trap-free voids. Note that here the most representative regime is the one associated with the sub-diffusive motion in the slip-link and fluctuation trap-free voids, namely, regime (B). As in Case I, we have here $P_{\rm sl}(t=\tau_R) \approx \exp(-Q^{2/3})$, which is very small. This implies that the most probable decay is given by Eq. (60.B). The first stage, i.e., the decay described by Eq. (60.A), appears to be relatively unimportant, since during this stage $P_{\rm sl}(t)$ does not drop appreciably, $P_{\rm sl}(t=\tilde{t}_{{\rm c},1}) \approx 1/3$.

Note that again, as in the Case I, Eqs. (60.A) to (60.C) agree with the heuristic prediction of Eqs. (3.A) and (3.B). Namely, Eq. (60.A) corresponds to the result in Eq. (3.A) with $d_f=4$, Eq. (44), Eq. (60.C) yields the same time-dependence as Eq. (3.B) with $d_f=4$, Eq. (44), while the long-time decay in Eq. (60.C) coincides with that given by Eq. (3.B) when $d_f=2$, i.e., when conventional diffusive motion is restored.

Case III. Low Density of Traps, $q \ll 1$, and Short Chains, $Q \ll 1$. In this particular situation we have that $\tilde{t}_{{\rm c},1} \gg t_m$ and consequently, the initial decay obeys Eq. (57.A). Further on, since here $\tilde{t}_{{\rm c},1}$ also exceeds the Rouse time, i.e., $\tilde{t}_{{\rm c},1} \gg \tau_R$, the regime predicted by Eq. (57.B) is absent, which means that the decay in Eq. (57.A) crosses over at $t=\tau_R$ to the decay predicted by Eq. (58.A). Lastly, the stretched exponential dependence in Eq. (58.A) is followed at $t > \tilde{t}_{{\rm c},2}$, $\tilde{t}_{{\rm c},2} \gg \tau_R$ by the form Eq. (58.B). Hence, in Case III one has that $P_{\rm sl}(t)$ follows

$$P_{\rm sl}(t) \approx \begin{cases} \exp(-\frac{2}{\pi} n_{\rm tr}(4Dt/\beta K)^{1/4}), & t_m \ll t \ll \tau_R, \quad \text{(A)} \\ \exp(-4n_{\rm tr}(Dt/\pi N)^{1/2}), & \tau_R \ll t \ll \tilde{t}_{{\rm c},2}, \quad \text{(B)} \\ \exp(-3n_{\rm tr}^{2/3}(\pi^2 Dt/4N)^{1/3}), & t \gg \tilde{t}_{{\rm c},2}, \quad \text{(C)} \end{cases} \tag{61}$$

In this case, however, only the last, fluctuation-induced regime C appears to be significant; one can readily verify that $P_{\rm sl}(t)$ practically does not change during the regimes A and B, $P_{\rm sl}(t=\tilde{t}_{{\rm c},2}) \approx \exp(-4/\pi) \sim 1$.

We note finally that also in the Case III the decay pattern agrees with the prediction in Eqs. (3). Here, the regimes described by Eqs. (61.A) and (61.B) correspond to the mean-field decay law in Eq. (3.A) with $d_f=4$ and $d_f=2$, respectively, while the long-time decay in Eq. (61.C) is compatible with the time dependence predicted by Eq. (3.B) with $d_f=2$.

V. CONCLUSIONS

To summarize, we have studied the dynamics of an isolated Rouse chain, which diffuses in a three-dimensional space under the constraint that one of its extremities, the slip-link, may move only along a line containing randomly placed immobile traps. For such a model we have computed exactly the time evolution of the probability $P_{sl}(t)$ that the slip-link will not encounter any of the traps until time t, i.e., that the chain will remain completely mobile until this moment of time. We have shown that in the most general case this probability is a succession of several stretched-exponential functions of time, where the dynamical exponents depend on the time of observation and on characteristic crossover times. We have specified these crossover times and have determined explicitly the forms of $P_{sl}(t)$ in several particular situations. We expect our results to serve as benchmarks in more complex situations, which are not amenable to a fully analytical treatment. Thus programs involving realistic computer simulations can be tested by comparing the results to our exact expressions.

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