Kinetics of anchoring of polymer chains on substrates with chemically active sites

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We consider dynamics of an isolated polymer chain with a chemically active end-bead on a two-dimensional (2D) solid substrate containing immobile, randomly placed chemically active sites (traps). For a particular situation when the end-bead can be irreversibly trapped by any of these sites, which results in a complete anchoring of the whole chain, we calculate the time evolution of the probability $P_{ch}(t)$ that the initially nonanchored chain remains mobile until time t. We find that for relatively short chains $P_{ch}(t)$ follows at intermediate times a standard-form 2D Smoluchowski-type decay law $\ln P_{ch}(t) \sim -t/\ln(t)$, which crosses over at very large times to the fluctuation-induced dependence $\ln P_{ch}(t) \sim -t^{1/2}$, associated with fluctuations in the spatial distribution of traps. We show next that for long chains the kinetic behavior is quite different; here the intermediate-time decay is of the form $\ln P_{ch}(t) \sim -t^{1/2}$, which is the Smoluchowski-type law associated with subdiffusive motion of the end-bead, while the long-time fluctuation-induced decay is described by the dependence $\ln P_{ch}(t) \sim -t^{1/4}$, stemming out of the interplay between fluctuations in traps distribution and internal relaxations of the chain. [S1063-651X(98)01611-0]

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I. INTRODUCTION

The understanding of polymer dynamics on solid substrates impacts many areas of modern technology, including coating, gluing, painting, or lubrication. Most of the liquids used in these material processing operations are either polymer liquids or contain polymeric additives.

Meanwhile, polymer dynamics on bare substrates or in adsorbed polymer films has been studied theoretically and numerically only for model substrates with an ideal, crystalline-type order [1–3]. However, recent experimental studies [4–9] of polymer monolayers spreading on solid substrates have given ample evidence that in realistic situations chain dynamics is strongly influenced by different types of disorder, associated with the presence of contaminants, chemically active ''hot'' sites, or surface roughness. Such a disorder is unavoidable for real surfaces and induces significant departures from the behavior predicted for model systems.

In particular, studies of light polydimethylsiloxane (usually abbreviated as PDMS) molecules spreading on oxidized silicon wafers have demonstrated that the form of the PDMS diffusivity D is very sensitive to the chemical composition of the surface, or more specifically, to the presence of the silanol sites, which can form a hydrogen bond with any chain's monomer and thus temporarily anchor the chain. Experiments reveal [6] an ideal, Rouse-type behavior of the form $D \sim N^{-1}$, where N is the number of monomeric units in a polymer, at low density of such sites. On the other hand, a stronger dependence of the form $D \sim N^{-2}$ is observed [6] at higher density of the silanol sites, which behavior resembles the reptative motion and stems apparently from some collective effects, associated with trapping of some portion of chains serving then as obstacles for the rest.

An even more striking effect of chemical disorder has been observed in the case of the so-called PDMS-OH polymers, i.e., the PDMS molecules bearing an OH group at one or at both of the chain's extremities. The OH group can form a strong chemical bond with any of the silanol sites, resulting in a complete anchoring of the whole chain by one of its ends. In consequence, despite the fact that the macroscopic spreading power of such a liquid/solid system is positive and thus favors complete wetting, spreading of a sufficiently thin film of the PDMS-OH molecules terminates at a certain moment of time due to the presence of chemically active trapping sites (see [8] and [9]).

Surprisingly enough, dynamics of polymers in the presence of randomly placed traps has not been addressed so far, in contrast to the theoretically well-studied problems of chain dynamics on the surface with randomly placed barriers or obstacles (see, e.g., [10,11] and references therein) or diffusion of monomers in a medium with traps (for a review see [12–14]). In the present paper we discuss this practically important problem focusing first on a simple model appropriate to the just-described situation with the PDMS-OH molecules deposited on a bare silicon wafer with silanol sites. More specifically, we study here dynamics of a single polymer, modeled as an ideal Rouse chain with a chemically active end-bead (see Fig. 1) on a two-dimensional ideal substrate with randomly placed perfect immobile traps. The end-bead can be irreversibly trapped upon the first encounter with any of the traps, which results in anchoring of the whole chain. The dynamics of all the other beads is completely unaffected by traps. For this model we find explicit results for the probability $P_{ch}(t)$ that the chemically active end-bead of the chain does not meet any of the trap until time t, or, in other words, that the polymer chain, which is unanchored at $t=0$, remains completely mobile until time t. Other possible

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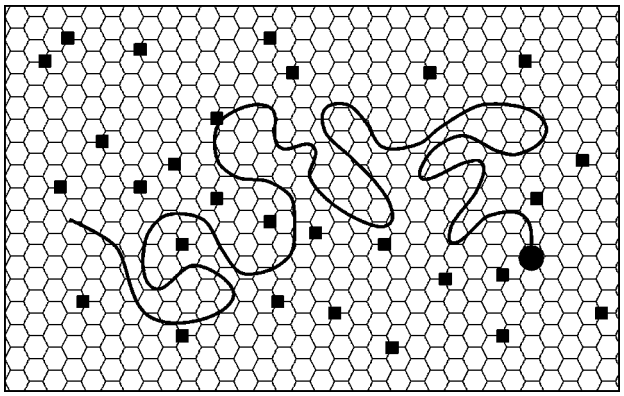

FIG. 1. Polymer chain diffusing on a solid surface. The squares denote immobile, randomly placed chemically active sites—the traps. The filled circle is a chemically active group attached to the polymer.

situations involving, in particular, reversible traps or many active groups per chain, as well as the effects of the excluded volume interactions, will be discussed in a forthcoming publication.

The paper is structured as follows. In Sec. II we describe in more detail the model to be studied and introduce notations. In Sec. III we present a reminder on trapping kinetics of a monomer particle, which allows us to explain some basic ideas concerning the effect of fluctuations in traps' spatial distribution on trapping kinetics. Next, in Sec. IV we show how these results can be extended to describe the anchoring kinetics of a Rouse polymer chain and analyze different kinetic regimes. Finally, we conclude in Sec. V with a summary and discussion of our results.

II. THE MODEL

Consider a polymer chain deposited on a two-dimensional solid surface, Fig. 1, and forming no loops in the direction perpendicular to the surface. The chain consists of $N+1$ identical beads, connected into the chain by harmonic springs with rigidity χ, $\chi=2T/b^2$, T being the temperature of the solid substrate and b being the average distance between the beads. The radii of the beads are denoted by two-dimensional (time-dependent) vectors $\mathbf{r}_n$, n being the number of the bead in the chain, $n=0,\ldots,N$, $N\gg 1$. We suppose that one of the end-beads of the chain, namely the bead with $n=0$, differs from all others in that it contains a chemically active group, while all other beads are chemically inert. Assuming that the springs are phantom, which means that we discard excluded volume interactions, we have for the potential energy $U(\{\mathbf{r}_n\})$ of the chain

$$U(\{\mathbf{r}_n\})=\sum_{n=0}^{N-1} U(\mathbf{r}_{n+1}-\mathbf{r}_n)=\frac{T}{b^2}\sum_{n=0}^{N-1}(\mathbf{r}_{n+1}-\mathbf{r}_n)^2. \quad (1)$$

The effect of the excluded volume interactions on the anchoring kinetics, which can be rather important for two-dimensional systems, will be discussed in detail elsewhere. Here we will present only some brief comments on this point at the very end of the paper.

Further on, we suppose that the beads experience an action of random forces, which originate from chaotic, thermal vibrations of solid atoms around their lattice positions; the beads may thus perform random motion along the surface under the constraints imposed by the springs. Simplifying the actual situation to some extent [15], we model these random forces as Gaussian white noise $\zeta_{n,\alpha}(t)$, uncorrelated in time and space, such that

$$\overline{\zeta_{n,\alpha}(t)}=0,$$
$$\overline{\zeta_{n,\alpha}(t)\zeta_{n',\alpha'}(t')}=2\eta T\delta_{n,n'}\delta_{\alpha,\alpha'}\delta(t-t'). \quad (2)$$

In Eqs. (2) the overline stands for the averaging over thermal noise, $\delta_{\alpha,\alpha'}$ and $\delta_{n,n'}$ are the Kronecker symbols, $\alpha=x,y$ denote the Cartesian components of random forces, while η is the friction coefficient, which is dependent on the height of the barrier against the lateral motion and the temperature (see [15] for more details).

We suppose next that the surface (of the surface area S) contains M perfect, immobile traps, which are placed at random positions, which are denoted by vectors $\{\mathbf{R}_j\}$, $j=1,\ldots,M$. In what follows we will always assume the limit $S,M\to\infty$ with the fixed mean density $n_{\mathrm{tr}}=M/S$, $n_{\mathrm{tr}}\ll 1$. Next, we stipulate that the action of the traps on the chain's beads is selective: the traps have absolutely no effect on all the beads of the chain (except for the end-bead $n=0$), which means that the traps do not react with the beads with $n=1,\ldots,N$ and do not influence their dynamics. On the contrary, the end-bead is trapped at the first encounter with any trap and gets immobilized anchoring the whole chain. As we have already mentioned, from the physical point of view such a model mimics the situation with PDMS-OH molecules diffusing on silicon wafers with the silanol sites; here, the silanol sites, i.e., the traps, may form strong chemical bonds with the OH groups (end-bead) immobilizing them. On the other hand, these sites form only weak hydrogen bonds with any other monomer of the PDMS molecule. These weak bonds create an additional (small) barrier against the lateral motion; we suppose that the influence of the silanol sites on the dynamics of the PDMS monomers can be accounted for by introducing some effective friction coefficient η. A nontrivial question, as a matter of fact, of the form of this friction coefficient and its dependence on the polymer length will be discussed elsewhere.

The property which will be studied here is the probability $P_{\mathrm{ch}}(t)$ that the end-bead of the chain, which is not trapped at $t=0$, remains not trapped until time t. Evidently, $P_{\mathrm{ch}}(t)$ determines also the probability that an initially unanchored chain remains completely mobile until time t. To calculate the time evolution of this property we will proceed as follows: we will first present a formally exact expression for $P_{\mathrm{ch}}(t)$ and show how its time dependence can be evaluated in the simplest case of a trivial chain with $N=0$, i.e., a single chemically active monomer. This will allow us to explain some basic methods and highlight the representative realizations of disorder and of the monomer trajectories which support the intermediate and the long-time evolution of $P_{\mathrm{ch}}(t)$. Next, we will discuss the characteristic features of dynamics of the polymer chain end-bead, which will allow then for a rather straightforward generalization of the monomer trapping problem to a more complicated case with the end-bead of a long polymer chain.

III. A REMINDER ON THE MONOMER TRAPPING PROBLEM IN *D*-DIMENSIONAL SYSTEMS

To fix the ideas, it seems instructive to recall first the kinetic behavior of $P_{\rm ch}(t)$ in the simplified case $N=0$, i.e., the case of a chemically active monomer diffusing in d dimensions and reacting with randomly placed, immobile perfect traps. It is intuitively clear that in our case with a chemically active monomer attached to a chain, we should retrieve at sufficiently large times (and up to some renormalization of the diffusion coefficient) the behavior predicted for a single monomer, since for a finite chain random motion of any bead of the chain ultimately converges to conventional diffusion with a renormalized diffusion coefficient [16]. At shorter times, however, substantial deviations should be observed because of essentially nondiffusive behavior of the end-bead, induced by internal relaxations of the chain.

The problem of a kinetic description of chemical reactions between diffusive particles and immobile, randomly distributed traps has been widely discussed in the literature within the past two decades. Different analytical techniques have been elaborated, including an extension of the ''optimal fluctuation'' method [17], different methods of bounds (see, e.g., [18–22]), Green functions approach [22], field-theoretic treatments [23], as well as a variety of mean-field-type descriptions (see [14,24,25] and references therein). The interest in this problem was inspired by the physical significance of the subject and, last but not least, by an early observation [17] that the long-time survival probability of diffusive particles exhibits highly nontrivial, fluctuation-induced behavior, which is relevant to the so-called Lifschitz singularities near the edge of the band in the density of states of a particle in quantum Lorentz gas. Later works (see, e.g., [22,23]) have also pointed out the relevance of the issue to the problems of percolation, self-avoiding random walks, or self-attracting polymers, as well as the anomalous behavior of the ground-state energy of the Witten's toy Hamiltonian of supersymmetric quantum mechanics [26].

Consider a single monomer, which diffuses (with diffusion coefficient D_0) in a d-dimensional volume V with randomly placed M traps, modeled as d-dimensional spheres of radius a. Positions of the traps are denoted by $\{\mathbf{R}_j\}$, where the subscript j numerates the traps, $j=1,\ldots,M$. The probability $\Psi_{\rm mon}(t;\{\mathbf{R}_j\})$ that, for a given realization $\{\mathbf{R}_j\}$ of traps' distribution, a diffusive monomer will not encounter any of M traps until time t is given by (see, e.g., [19,22])

$$\Psi_{\rm mon}(t;\{\mathbf{R}_j\})=E_\Omega\left\{\exp\left[-\int_0^t dt'\sum_{j=1}^{M} W(\mathbf{r}_0(t')-\mathbf{R}_j)\right]\right\}, \tag{3}$$

where the potential $W(\mathbf{r}_0(t)-\mathbf{R}_j)$ is the step function, centered around the position of the jth trap, such that

$$W(\mathbf{r})=\begin{cases}\infty & |\mathbf{r}|\leqslant a\\ 0 & |\mathbf{r}|>a,\end{cases} \tag{4}$$

while the symbol $E_\Omega\{\,\}$ denotes expectation on the complete set Ω of trajectories $\{\mathbf{r}_0(t)\}$ of a diffusive monomer. We note parenthetically that Eq. (3), which determines the monomer survival probability for a fixed configuration of traps, is not, of course, only limited to the case when $\{\mathbf{r}_0(t)\}$ describes conventional diffusion; Eq. (3) is formally exact for *any* type of random or regular motion, including the motion of the end-bead of a polymer chain, provided that the operator E_Ω is properly defined.

In what follows we will be interested, however, not in the behavior of the realization-dependent probability $\Psi_{\rm mon}(t;\{\mathbf{R}_j\})$, but rather of its realization-averaged value $P_{\rm mon}(t)$, defined as

$$P_{\rm mon}(t)=\langle\Psi_{\rm mon}(t;\{\mathbf{R}_j\})\rangle_{\{\mathbf{R}_j\}}, \tag{5}$$

where the angular brackets denote here and henceforth the averaging with respect to the distribution of traps positions $\{\mathbf{R}_j\}$. For random uncorrelated (Poisson) distribution of the traps, such an averaging can be carried out straightforwardly [19,22]. Turning to the limit $V,M\to\infty$ and keeping the ratio $M/V=n_{\rm tr}$ fixed, one finds

$$P_{\rm mon}(t)=E_\Omega\left\{\prod_{j=1}^{M}\left\langle\exp\left[-\int_0^t dt'\,W(\mathbf{r}_0(t')-\mathbf{R}_j)\right]\right\rangle_{\mathbf{R}_j}\right\}=E_\Omega\left(\exp\left\{-n_{\rm tr}\int_{R^d}d\mathbf{R}\left(1-\exp\left[-\int_0^t dt'\,W(\mathbf{r}_0(t')-\mathbf{R})\right]\right)\right\}\right), \tag{6}$$

where the integral with the subscript R^d in the last line of Eq. (6) signifies that the integration extends over the entire d-dimensional space. It may be worthwhile to note that the function

$$1-\exp\left[-\int_0^t dt'\,W(\mathbf{r}_0(t')-\mathbf{R})\right]=\begin{cases}1, & |\mathbf{r}_0(t')-\mathbf{R}|\leqslant a,\quad t'\in[0;t]\\ 0, & |\mathbf{r}_0(t')-\mathbf{R}|>a,\quad t'\in[0;t]\end{cases} \tag{7}$$

is just the indicator function of the so-called Wiener sausage (see [18,27] for more details) of size a, since it equals zero everywhere except for the a vicinity of any point of the particle trajectory $\mathbf{r}_0(t)$. Consequently, the integral

$$\mathcal{V}_{\rm ws}[\mathbf{r}_0(t)]=\int_{R^d}d\mathbf{R}\left(1-\exp\left[-\int_0^t dt'\,W(\mathbf{r}_0(t')-\mathbf{R})\right]\right) \tag{8}$$

measures the volume swept out by a diffusive spherical particle of radius a during time t for a particular realization $\mathbf{r}_0(t)$ of its trajectory. In this regard, the realization-averaged

probability $P_{\rm mon}(t)$ can be thought off as the moment generating function of the volume of the Wiener sausage (see [28] for more details). We also hasten to remark that Eq. (6) is quite general and can also be applied to describe the time evolution of the probability that the end-bead of the chain does not encounter any of the traps until time t; to do this, we have to define the operator E_Ω as an expectation on the set of the end-bead trajectories, whose properties, in general, will be different from those of a single monomer.

The expression in the last line of Eq. (6) determines an exact solution of the monomer trapping problem, which is valid at all times. Calculation of $P_{\rm mon}(t)$ amounts now to performing averaging over the monomer trajectories. Such an averaging procedure has been extensively discussed in [17–19,22] using different types of analytical approaches. Here we intentionally choose a method of bounds among other theoretical considerations, because it gives us a possibility not only to display in the most simple fashion the evolution of $P_{\rm mon}(t)$ at intermediate and large times, but also to highlight the representative monomer trajectories, which support the corresponding decay pattern. This method allows also for a rather straightforward computation of the analogous probability not to encounter any of the traps until time t in a more complicated situation with an active particle attached to a polymer chain.

A. Intermediate-time behavior of $P_{\rm mon}(t)$

Following Ref. [22], a lower bound on $P_{\rm mon}(t)$ in Eq. (6) which describes properly the intermediate-time decay pattern can be readily found by making use of the Jensen-type inequality; this states that the averaged value of an exponential of some random function f is greater than or equal to the exponential of the averaged value of this function; i.e.,

$$E\{\exp(-f)\}\geqslant\exp(-E\{f\}). \tag{9}$$

Hence, by setting

$$f=\exp\left\{-n_{\rm tr}\int_{R^d}d\mathbf{R}\left(1-\exp\left[-\int_0^t dt'\,W[\mathbf{r}_0(t')-\mathbf{R}]\right]\right)\right\}, \tag{10}$$

and applying the inequality in Eq. (9), one finds that $P_{\rm mon}(t)$ can be bounded from below by

$$P_{\rm mon}(t)\geqslant\exp(-n_{\rm tr}E_\Omega\{\mathcal{V}_{\rm ws}[\mathbf{r}_0(t)]\}). \tag{11}$$

The time evolution of the function $E_\Omega\{\mathcal{V}_{\rm ws}[\mathbf{r}_0(t)]\}$ has been discussed, in particular, in Refs. [22] and [28]. It has been shown that expectation of the Wiener sausage volume obeys

$$E_\Omega\{\mathcal{V}_{\rm ws}[\mathbf{r}_0(t)]\}=S_d\int_a^\infty r^{d-1}dr\,\mathcal{L}_\lambda^{-1}\left[\frac{G(r;\lambda)}{\lambda G(a;\lambda)}\right]$$

$$=\int_0^t dt'\,K_d(t'), \tag{12}$$

where S_d is the surface area of a d-dimensional sphere of radius a, $S_d=2\pi^{d/2}/\Gamma(d/2)$, $\Gamma(x)$ being the gamma function, $\mathcal{L}_\lambda^{-1}[\ ]$ denotes the inverse Laplace-transform operator, $K_d(t)$ is equal to the diffusive current through the surface of a d-dimensional immobile, adsorbing sphere of radius a [i.e., $K_d(t)$ is the d-dimensional analog of the so-called Smoluchowski constant [29,30]], while

$$G(r;\lambda)=\int_0^\infty dt\exp(-\lambda t)G(r;t), \tag{13}$$

where (the propagator) $G(r;t)$ is the probability of finding a diffusive particle at distance r from the starting point at time t. Explicitly, one has that in the limit $t\gg a^2/D_0$ the expectation of the Wiener sausage volume or the time integral of the Smoluchowski-type constant shows the following asymptotical behavior:

$$E_\Omega\{\mathcal{V}_{\rm ws}[\mathbf{r}_0(t)]\}=\int_0^t dt'\,K_d(t')$$

$$\approx\begin{cases}4\pi aD_0t, & d=3\\ 4\pi D_0t/\ln(4D_0t/a^2), & d=2\\ 4(D_0t/\pi)^{1/2}, & d=1,\end{cases} \tag{14}$$

which thus depends on the spatial dimension d. This implies that in systems of different dimensionality the typical number of intersections of the Wiener sausage behaves quite differently. Discussion of this point in terms of compact and noncompact exploration of space by random walk trajectories, as well as the relation between the mean volume of the Wiener sausage and the Smoluchowski-type rate constant, was presented first in [31]. We note also that Eq. (12) allows for computation of the mean Wiener sausage volume for the trajectories of the end-bead, provided that its propagator $G_{\rm ch}(r;t)$ is known (see Sec. IV A).

Consequently, the bound based on the Jensen-type inequality leads to the result

$$P_{\rm mon}(t)\geqslant P_{\rm Smol}(t)=\exp\left[-n_{\rm tr}\int_0^t dt'\,K_d(t')\right], \tag{15}$$

where the expression on the right-hand side of Eq. (15), as first noted in [22], is tantamount to the solution of the monomer trapping problem in terms of the celebrated Smoluchowski approach [29,30]. It is well known from numerical studies of the monomer trapping problem (see, e.g., [32]) that an approximation $P_{\rm mon}(t)\approx P_{\rm Smol}(t)$ describes fairly well the intermediate time behavior of the survival probability and fails to describe the decay properly only at very large times, when certain fluctuation effects come into play. The crossover times from the intermediate-time to the fluctuation-induced behavior will be discussed in the next subsection.

B. Long-time behavior of $P_{\rm mon}(t)$

Note now that the just outlined derivation [22] of the Smoluchowski-type result in Eq. (15) demonstrates that an approximation $P_{\rm mon}(t)\approx P_{\rm Smol}(t)$ is equivalent to a certain assumption concerning the representative class of the monomer's trajectories $\mathbf{r}_0(t)$, which is embodied in the Jensen inequality. This can be most easily seen if we set $F=\exp(-f)$ and rewrite formally the inequality in Eq. (9) as

$$E\{F\} \geqslant \exp[E\{\ln(F)\}]. \tag{16}$$

One notices now that the Jensen inequality Eq. (9) bounds the averaged value of the functional F by an exponential of the averaged logarithm of this functional; since a logarithm is a very slowly varying function, it is generally believed that the behavior of the averaged logarithm of some functional is supported by typical realizations of disorder. Consequently, one may claim that the Smoluchowski-type decay law $P_{\rm mon}(t) \approx P_{\rm Smol}(t)$, which describes properly the intermediate-time behavior, is supported by *typical* realizations of random walk trajectories $\mathbf{r}_0(t)$, i.e., such that $\mathbf{r}_0(t) \sim t^{1/2}$. In what follows we will thus refer to the behavior supported by typical realizations of random walk trajectories as the *mean-field type* behavior.

On the other hand, at completely random placement of traps their local density will deviate throughout the volume from the volume-average value $n_{\rm tr}$; there will be spatial regions in which the density of traps is higher than $n_{\rm tr}$, as well as regions containing no traps at all. One may thus expect that at large t only those monomers will survive that appear initially in sufficiently large trap-free regions and do not leave these regions until time t. Such restricted, atypical trajectories $\mathbf{r}_0(t)$, which also belong to the set Ω and which are not taken into account in the Smoluchowski solution, will contribute additively to the value of the probability $P_{\rm mon}(t)$. Consequently, one may expect that the overall probability $P_{\rm mon}(t)$ will be of the form (see [22] for more details)

$$P_{\rm mon}(t) \approx P_{\rm Smol}(t) + P_{\rm fl}(t), \tag{17}$$

where the first term determines the behavior stemming out of typical realizations of random walk trajectories, while the second one represents the contribution of constrained trajectories entirely remaining within the trap-free regions.

Let us discuss now in more detail the contribution to the overall survival probability stemming out of the constrained, atypical trajectories. As in the preceding subsection, we will determine their contribution evaluating a lower bound on $P_{\rm mon}(t)$; for this purpose we adapt to the path-integral formulation of the problem the approach developed originally for three-dimensional systems in Ref. [27] and, independently, for arbitrary d in Ref. [20].

We start again with the expression for the survival probability of a monomer diffusing in the presence of traps fixed at positions $\{\mathbf{R}_j\}$, which is given by Eq. (3). The basic idea for evaluating the lower bound on the right-hand side of Eq. (3) and, subsequently, on $P_{\rm mon}(t)$, is now as follows.

(i) Suppose that in calculating an expectation of a positive definite functional on a set of random walk trajectories we extend the integration not over the entire set of all possible trajectories Ω, but only over some subset ω of it, $\omega \in \Omega$. In doing so, we evidently diminish the actual averaged value; consequently, one has

$$E_\Omega\left\{\prod_{j=1}^{M} \exp\left[-\int_0^t dt'\, W(\mathbf{r}_0(t') - \mathbf{R}_j)\right]\right\} \geqslant E_\omega\left\{\prod_{j=1}^{M} \exp\left[-\int_0^t dt'\, W(\mathbf{r}_0(t') - \mathbf{R}_j)\right]\right\}. \tag{18}$$

(ii) Let us define the subset ω. To do this, we first assume, without lack of generality, that a diffusive monomer is at the origin at $t=0$ and that the trap nearest to the origin, say, the trap with $j=1$, is at distance R. Now, we stipulate that ω is formed by such trajectories $\mathbf{r}_0(t)$ which start at the origin at $t=0$ and during time interval t do not cross the surface of a d-dimensional sphere of radius R. (Actually, it means that the number of traps is effectively increased by introducing additional traps which cover completely the surface of a d-dimensional sphere of radius R centered around the origin. This certainly can only diminish the bound.) For the trajectories $\mathbf{r}_0(t) \in \omega$, we evidently have that

$$\prod_{j=1}^{M} \exp\left[-\int_0^t dt'\, W(\mathbf{r}_0(t') - \mathbf{R}_j)\right] = 1, \tag{19}$$

since neither of such trajectories reaches any of the traps. Consequently, we find from Eq. (18) that

$$E_\Omega\left\{\prod_{j=1}^{M} \exp\left[-\int_0^t dt'\, W(\mathbf{r}_0(t') - \mathbf{R}_j)\right]\right\} \geqslant \mathcal{P}(R;t) = E_\omega\{1\}, \tag{20}$$

in which $\mathcal{P}(R;t)$ denotes the measure of the trajectories comprising the subset ω. Eventually, one finds that the monomer survival probability is bounded by [20,27]

$$P_{\rm mon}(t) \geqslant \mathcal{P}(R;t)\mathcal{P}(R), \tag{21}$$

where $\mathcal{P}(R)$ is the probability of having a trap-free spherical void of radius R.

For random uncorrelated (Poisson) distribution of traps the probability of finding a spherical cavity of radius R completely devoid of traps is given by

$$\mathcal{P}(R) \sim \exp(-n_{\rm tr} v_d R^d), \tag{22}$$

where $v_d = [2\pi^{d/2}/d\Gamma(d/2)]$ is the volume of a d-dimensional sphere of unit radius. The measure $\mathcal{P}(R;t)$ of trajectories comprising the subset ω equals the probability that a diffusive particle, which starts at the origin at $t=0$, does not hit the sphere at $|\mathbf{r}| = R$ until time t. This probability is given asymptotically by

$$\mathcal{P}(R;t) \sim \exp\left(-\gamma_d \frac{D_0 t}{R^2}\right), \tag{23}$$

γ_d being a dimensionless d-dependent number, $\gamma_{1,3} = \pi^2$, and $\gamma_2 \approx 2.41$. Combining Eqs. (23), (22), and (21) one finds [20,27]

$$P_{\rm mon}(t) \geqslant \exp\left(-\gamma_d \frac{D_0 t}{R^2} - n_{\rm tr} v_d R^d\right), \tag{24}$$

which bound is valid for *any* value of R. Hence, one has to choose such R which provides the maximal value to the right-hand side of Eq. (24). The maximal lower bound obtains for

$$R=R^*(t)=\left(\frac{2\gamma_d}{dv_d}\frac{D_0 t}{n_{\rm tr}}\right)^{1/(d+2)}. \quad (25)$$

Note now that $R^*(t)$ shows a slow growth with time. This implies that as time progresses larger and larger trap-free voids contribute most importantly. Equation (25) allows us to determine the representative atypical realizations more precisely: these are such realizations of random walk trajectories $\mathbf{r}_0(t)$ which grow with time not faster than $R^*(t) \sim t^{1/(d+2)}$, i.e., they are essentially more spatially confined than the typical ones, for which one has $\mathbf{r}_0(t)\sim t^{1/2}$. That this should be the case is intuitively clear since only those random walks survive at large times which do not make too large excursions from their starting point.

The bound corresponding to $R=R^*(t)$ now reads [20]

$$P_{\rm mon}(t)\geqslant P_{\rm fl}(t)=\exp(-\nu_d n_{\rm tr}^{2/(d+2)}(D_0 t)^{d/(d+2)}), \quad (26)$$

where ν_d are d-dependent numerical factors; in particular, for two- and three-dimensional systems ν_d is given, respectively, by $\nu_2=2z_0\sqrt{\pi}$, where $z_0\approx 2.405$ is the first zero of Bessel function $J_0(x)$, and $\nu_3=5\times 4^{1/5}\pi^{8/5}/3$ [20]. In what follows we will refer to the decay laws in Eq. (26) as *fluctuation-induced*, since such a behavior results from the presence of fluctuations in the spatial distribution of traps and, respectively, from atypical realizations of random walk trajectories.

Gathering Eqs. (15) and (26), we have now the following result for the time evolution of $P_{\rm mon}(t)$ in two-dimensional systems, which will serve us in what follows as a point of reference,

$$P_{\rm mon}(t)\approx\begin{cases}\exp[-4\pi n_{\rm tr}D_0 t/\ln(4D_0 t/a^2)], & a^2/D_0<t<t_c\\ \exp[-\nu_2(n_{\rm tr}D_0 t)^{1/2}], & t>t_c.\end{cases} \quad (27)$$

In Eqs. (27), the time t_c denotes the crossover time, separating the Smoluchowski-type and the fluctuation-induced kinetic regimes; this characteristic time is given by

$$t_c=\frac{z_0^2 a^2}{4D_0\sigma_{\rm tr}}\ln^2\left(\frac{z_0^2}{\sigma_{\rm tr}}\right), \quad (28)$$

in which equation the parameter $\sigma=\pi a^2 n_{\rm tr}$ determines the area of the surface covered by traps.

Lastly, several comments on the magnitude of the crossover time and the relative importance of two regimes displayed in Eq. (27) are in order. On comparing the terms in the exponentials of Eqs. (15) and (26), we infer that atypical realizations become progressively more important at such times when $D_0 t_c$ becomes greater than $\sigma_{\rm tr}^{-2}$, $\sigma_{\rm tr}^{-1}\ln^2(\sigma_{\rm tr})$, and $\sigma_{\rm tr}^{-3/2}$ for one-, two-, and three-dimensional systems, respectively. Thus the crossover time may be quite large for systems in which the area covered by traps is low. Moreover, there is another subtle circumstance which makes the fluctuation-induced tail, generally speaking, not pertinent for real experimental systems. Namely, the point is that the amount of particles reacting at the intermediate-time Smoluchowski-type kinetic stage is usually comparable to the total amount of particles in the system such that up to the time t_c only a few particles are left. Numerical simulations of the monomer trapping kinetics (see [32]), which observe the Smoluchowski-type regime and enter into the fluctuation-induced one, suggest that, in particular, in three dimensions the fluctuation-induced regime shows up when $P_{\rm mon}(t)$ drops below 10^{-16}, 10^{-25}, 10^{-36}, and 10^{-80} for $\sigma_{\rm tr}$ equal to 0.25, 0.10, 0.05, and 0.01, respectively. In two dimensions this should not be so dramatic as in 3D, but still the value of $P_{\rm mon}(t_c)$, which is defined as

$$P_{\rm mon}(t_c)\approx\exp[-z_0^2\ln(z_0^2/\sigma_{\rm tr})], \quad (29)$$

can be very small due to the appearance of the factor $-\ln(\sigma_{\rm tr})$ in the exponent. Equation (29) suggests that in two dimensions the values of $P_{\rm mon}(t)$ at the crossover will equal 10^{-8}, 10^{-10}, 10^{-12}, and 10^{-16} for $\sigma_{\rm tr}$ equal to 0.25, 0.10, 0.05, and 0.01, respectively. We set out to show, however, that for a chemically active monomer attached to a *long* polymer chain the situation may change considerably such that the value of $P_{\rm mon}(t)$ at the crossover time t_c will not be that small. This resembles, in a way, behavior predicted for the reverse counterpart of the problem to be considered here—the trapping of diffusive monomers on traps arranged in polymer chains. For this problem it has also been shown that the fluctuation-induced behavior starts at much earlier times and most of particles are trapped via the fluctuation-induced mechanism [14]. We also note that a similar effect of strong reinforcement of the magnitude of the fluctuation-induced kinetics has been predicted for reactions involving active particles attached to movable polymer chains in solution [33].

IV. ANCHORING KINETICS OF A ROUSE POLYMER CHAIN WITH A CHEMICALLY ACTIVE END-BEAD

In this section we will make use of the bounds, displayed in Eqs. (15) and (26), for computation of the probability $P_{\rm ch}(t)$ that an active monomer attached to one of the extremities of a Rouse polymer chain still remains untrapped until time t. Consequently, as in the case with a single diffusive monomer, we have to determine the form of two essential parameters: the Smoluchowski-type constant describing reactions between the active end-bead and traps, and the probability $\mathcal{P}(R;t)$ that the end-bead of a long polymer chain remains within a trap-free cavity of radius R until time t. While behavior of $K_d(t)$ has been already discussed in the literature within the context of reactions between particles attached to polymers (see Refs. [14,31,33]), the form of the

probability $\mathcal{P}(R;t)$ has not been considered so far. Clearly, computation of both $K_d(t)$ and $\mathcal{P}(R;t)$ requires the knowledge of the end-bead dynamics.

A. Langevin dynamics of the end-bead of a Rouse polymer chain

Let us briefly outline the Langevin equation description of the Rouse polymer chain dynamics on a two-dimensional surface. In neglect of the excluded volume interactions and regarding the number n of the bead in the chain as a continuous variable, $n \in [0,N]$, one has that dynamics of the vector of the nth bead is governed by the following Rouse-Langevin equation (for more details see [16]):

$$\eta \frac{\partial \mathbf{r}_n}{\partial t} = \frac{2T}{b^2} \frac{\partial^2 \mathbf{r}_n}{\partial n^2} + \zeta_n(t), \tag{30}$$

where $\zeta_n(t)$ are random forces, whose properties are described by Eq. (2). Solution of Eq. (30), which corresponds to the free boundary conditions at the chain extremities [16], i.e.,

$$\frac{\partial \mathbf{r}_{n=0}(t)}{\partial n} = 0; \quad \frac{\partial \mathbf{r}_{n=N}(t)}{\partial n} = 0, \tag{31}$$

can be written down as the Fourier series of the form

$$\mathbf{r}_n(t) = \sum_{p=-\infty}^{\infty} \mathbf{X}_p \cos\left(\frac{p\pi n}{N}\right), \tag{32}$$

where the two-dimensional vectors $\mathbf{X}_p$ are the normal coordinates of Eq. (30) (see [16]). For further analysis it suffices to know only their time correlation functions:

$$\overline{X_{p,\alpha}(t) X_{q,\alpha'}(0)} = \delta_{p,q}\delta_{\alpha,\alpha'} \frac{D_0 \tau_R}{Np^2} \exp\left(-\frac{p^2 t}{\tau_R}\right) \tag{33}$$

for $p > 0$, and

$$\overline{[X_{0,\alpha}(t) - X_{0,\alpha}(0)][X_{0,\alpha'}(t) - X_{0,\alpha'}(0)]} = \delta_{\alpha,\alpha'} \frac{2D_0 t}{N} \tag{34}$$

for $p = 0$. In Eqs. (33) and (34), the symbols $\alpha, \alpha' = x, y$ denote, as before, the Cartesian components of the normal coordinates and τ_R is the largest relaxation time of the chain, $\tau_R = b^2 N^2 / 2\pi^2 D_0$. Physically, τ_R can be interpreted as being the time needed for some local defect, e.g., kink, to spread out diffusively with diffusion constant D_0 along the arclength bN of the chain.

Now, the property of interest for us is the moment generating function for displacements of the chain's end-bead, which determines its propagator $G_{\mathrm{ch}}(r;t)$ and thus contains the information we need for calculation of $K_d(t)$ and $\mathcal{P}(R;t)$. The moment generation function is defined as

$$\Phi(\mathbf{k}) = \overline{\exp[i\mathbf{k} \cdot \mathbf{r}_{n=0}(t)]}. \tag{35}$$

The averaging in Eq. (35) over Gaussian white noise can be performed straightforwardly, using Eq. (32) and the expressions for the time correlation functions of the normal coordinates. One finds after some simple calculations

$$\Phi(\mathbf{k}) = \exp\left(-\frac{\mathbf{k}^2}{4}\overline{\mathbf{r}^2_{n=0}(t)}\right) = \exp(-\mathbf{k}^2 D_0 \tau), \tag{36}$$

where the effective ''time'' τ is a single-valued complicated function of real time t:

$$\tau = \tau(t) = \frac{t}{N} + \frac{2\tau_R}{N} \sum_{p=1} p^{-2} \left[1 - \exp\left(-\frac{p^2 t}{\tau_R}\right)\right]. \tag{37}$$

Equation (36) implies that the probability of finding the end-bead at distance r from the starting point at time t is a standard Gaussian function

$$G_{\mathrm{ch}}(r;t) = \frac{1}{4\pi D_0 \tau(t)} \exp\left(-\frac{r^2}{4D_0 \tau(t)}\right). \tag{38}$$

Consequently, dynamics of the end-bead of a polymer can be considered as that of a single monomer evolving in time τ.

Asymptotical dependence of τ on t can be readily calculated from Eq. (37), which gives

$$\tau(t) \approx \begin{cases} t/N, & t > \tau_R \\ b(t/\pi D_0)^{1/2}, & t < \tau_R . \end{cases} \tag{39}$$

Equation (39) signifies that τ scales with time differently depending on whether t is less than or greater than the fundamental relaxation time τ_R. We note also that the end-bead mean-square displacement (MSD) displays different time-behavior for $t \ll \tau_R$ and $t \gg \tau_R$; for $t \ll \tau_R$ the motion of the end-bead is due mainly to the internal relaxation of the chain. At such time scales

$$\overline{\mathbf{r}^2_{n=0}(t)} \approx 4b\left(\frac{D_0 t}{\pi}\right)^{1/2}, \tag{40}$$

which differs from conventional diffusion law in that the trajectory of the end-bead is spatially more confined. In the opposite time limit, $t \gg \tau_R$, the chain diffuses as one entity and the end-bead trajectories follow the motion of the chain's center of mass. In this regime the end-bead MSD obeys

$$\overline{\mathbf{r}^2_{n=0}(t)} \approx \frac{4D_0 t}{N}, \tag{41}$$

i.e., conventional diffusion law with reduced diffusion coefficient $D = D_0/N$.

We close this subsection with the following conclusion. Dynamics of the end-bead of a Rouse polymer is strongly influenced by the presence of the polymeric ''tail;'' at times less than the fundamental time τ_R the end-bead trajectories are spatially more confined compared to conventional diffusion and its MSD shows a sublinear growth with time, Eq. (40). At greater times, the MSD grows linearly with time but the diffusion coefficient is a factor of $1/N$ less than that for a monomer, Eq. (41). Nonetheless, in view of the form of Eqs. (36) and (38), the dynamics of the chain's end-bead can be

considered as that of an individual diffusive monomer, which evolves in effective ''time'' τ. We will use this observation in what follows to estimate the time evolution of $K_d(t)$ and $\mathcal{P}(R;t)$.

B. Time evolution of $P_{\rm ch}(t)$

Consider first the contribution to $P_{\rm ch}(t)$ stemming out of typical realizations of the end-bead trajectories, which problem amounts to calculation of the Smoluchowski-type constant $K_d(t)$ for an active group attached to a polymer chain. This question was first addressed in [31] and [33] within the context of chemical reactions involving particles attached to movable polymer chains in solution (for a general discussion see [14]). It has been shown that the form of the time dependence of $K_d(t)$ depends on the time of observation t: for times t less than the largest relaxation time of the chain, the Smoluchowski-type constant for a chemically active monomer attached to a polymer chain should follow [31]

$$K_d(t) \sim \frac{[\overline{\mathbf{r}^2_{n=0}(t)}]^{d/2}}{t}. \tag{42}$$

For a Rouse chain on a two-dimensional substrate, it gives, in particular,

$$K_2(t) \sim b\left(\frac{D_0}{t}\right)^{1/2}. \tag{43}$$

On the other hand, within the opposite limit, i.e., for $t \gg \tau_R$, when conventional diffusive motion with a renormalized diffusion coefficient is restored, one has (up to the replacement $D_0 \to D_0/N$) conventional behavior as in Eq. (14).

Let us now compute the time evolution of the Smoluchowski constant making use of Eq. (12), which will allow us to determine also the prefactors. Substituting the propagator in Eq. (38) into Eq. (12), we have that for the end-bead of a Rouse polymer chain the expectation of the Wiener sausage volume obeys

$$E\{\mathcal{V}_{\rm ws}[\mathbf{r}_{n=0}(t)]\} = 4\pi D_0 \mathcal{L}_\lambda^{-1}\left(\frac{\int_0^\infty dt \exp[-\lambda t - a^2/4D_0\tau(t)]}{\lambda\int_0^\infty dt\,\tau^{-1}(t)\exp[-\lambda t - a^2/4D_0\tau(t)]}\right). \tag{44}$$

Consider the asymptotical behavior of $E\{\mathcal{V}_{\rm ws}[\mathbf{r}_{n=0}(t)]\}$ in the limits $t<\tau_R$ and $t>\tau_R$. Supposing that τ_R is large and setting $\tau(t)=b(t/\pi D_0)^{1/2}$, we find that the integrals in the nominator and the denominator in Eq. (44) behave as $1/\lambda$ and $\pi(D_0/\lambda)^{1/2}/b$, respectively. One finds then

$$E\{\mathcal{V}_{\rm ws}[\mathbf{r}_{n=0}(t)]\} = \int_0^t dt' K_2(t') \approx 8b(D_0 t/\pi)^{1/2}, \tag{45}$$

which holds for the time interval $a^2/D_0 < t < \tau_R$. Next, we have that in the limit $t>\tau_R$ the effective time $\tau(t)\approx t/N$. For such a time dependence both integrals in Eq. (44) can be performed explicitly. This yields, upon some straightforward calculations, the following result:

$$E\{\mathcal{V}_{\rm ws}[\mathbf{r}_{n=0}(t)]\} = \int_0^t dt' K_2(t') \approx 4\pi D_0 t/N \ln(4D_0 t/a^2 N), \tag{46}$$

which is valid for times $t>\tau_R$. Consequently, we find that the time evolution of $P_{\rm ch}(t)$ due to *typical* trajectories of the end-bead is defined by

$$P_{\rm Smol}(t) \approx \begin{cases} \exp[-8bn_{\rm tr}(D_0 t/\pi)^{1/2}], & a^2/D_0 < t < \tau_R \\ \exp[-4\pi n_{\rm tr} D_0 t/N \ln(4D_0 t/a^2 N)], & t>\tau_R, \end{cases} \tag{47}$$

where the first line in Eq. (47) corresponds to the subdiffusive motion of the chemically active end-bead, while the second one describes the Smoluchowski-type decay pattern in the regime when the trajectories of the end-bead start to follow the motion of the chain's center of mass.

To consider now the contribution to the decay of the atypical realizations of the end-bead trajectories, constrained not to leave the fluctuation trap-free voids until time t, we suppose that the probability that the end-bead remains with a circular trap-free void of radius R until time t equals the probability that an individual diffusive particle remains within such a cavity until time $\tau(t)$. Such an assumption gives

$$P(R;t) \approx \exp\left(-\gamma_2 \frac{D_0\tau(t)}{R^2}\right). \tag{48}$$

Hence, the contribution to $P_{\rm ch}(t)$ due to atypical realizations of the polymer end-bead trajectories can be found by maximizing (with respect to R) the following expression:

$$P_{\rm fl}(t)\approx\max_{R}\left[\exp\left(-n_{\rm tr}v_2R^2-\gamma_2\frac{D_0\tau(t)}{R^2}\right)\right], \qquad (49)$$

where the first term determines the probability of having a trap-free circle of radius R, while the second one gives the probability that the end-bead remains within such a circle until time t.

Maximizing the right-hand side of Eq. (49), one readily finds that the value of R which yields the maximal value of the lower bound is given by

$$R=R^*(t)=\left(\frac{2\gamma_2}{2v_2}\frac{D_0\tau(t)}{n_{\rm tr}}\right)^{1/4}\sim\begin{cases}(D_0t/n_{\rm tr}^2)^{1/8}, & t<\tau_R\\ (D_0t/Nn_{\rm tr})^{1/4}, & t>\tau_R,\end{cases} \qquad (50)$$

which implies that the representative atypical realizations of the end-bead trajectories behave differently depending on the scale of observation; for times t less than τ_R, atypical trajectories of $\mathbf{r}_0(t)$ do not grow faster than $t^{1/8}$, while within the opposite limit they are constrained by $\mathbf{r}_0(t)<R^*(t)\sim t^{1/4}$. Consequently, the contribution due to atypical realizations can be written down explicitly as

$$P_{\rm fl}(t)\approx\begin{cases}\exp[-\nu_2(bn_{\rm tr})^{1/2}(D_0t/\pi)^{1/4}], & a^2/D_0<t<\tau_R\\ \exp[-\nu_2(n_{\rm tr}D_0t/N)^{1/2}], & t>\tau_R.\end{cases} \qquad (51)$$

Now, to construct an actual decay pattern describing the anchoring kinetics in the case of an active monomer attached to a polymer chain, we have to compare four different decay laws displayed in Eqs. (47) and (51) and calculate the corresponding crossover times. From Eq. (17), which states that the mean-field and the fluctuation-induced decay laws complement each other, we infer that different possible sequences of kinetic regimes may be observed, depending on the magnitude of the parameters $n_{\rm tr}$ and N, or, more precisely, depending on the relation between $n_{\rm tr}$ and R_g, where $R_g=bN^{1/2}$ is the chain's gyration radius.

Let us start with the case of sufficiently short chains and low trap concentration, which limit is described by two inequalities: $abn_{\rm tr}\ll 1$ and $n_{\rm tr}R_g^2\ll 1$. In this case we predict for the time evolution of $P_{\rm ch}(t)$ the following sequence of regimes:

$$P_{\rm ch}(t)\approx\begin{cases}\exp[-8bn_{\rm tr}(D_0t/\pi)^{1/2}], & a^2/D_0<t<\tau_R\\ \exp[-4\pi n_{\rm tr}D_0t/N\ln(4D_0t/a^2N)], & \tau_R<t<t_c\\ \exp[-\nu_2(n_{\rm tr}D_0t/)^{1/2}], & t>t_c,\end{cases} \qquad (52)$$

where the crossover time from the Smoluchowski-type behavior to the long-time fluctuation-induced tail is given by

$$t_c=\frac{z_0^2a^2N}{4D_0\sigma_{\rm tr}}\ln^2\left(\frac{z_0^2}{\sigma_{\rm tr}}\right), \qquad (53)$$

i.e., it is greater by a factor of N than the corresponding crossover time for the monomer trapping problem.

Compare now the relative importance of the kinetic regimes displayed in Eq. (52). First of all, we note that the Smoluchowski-type regime associated with the subdiffusive behavior of the end-bead [first line in Eq. (52)] is not representative: although it can persist over a wide time range if τ_R is large, the number of active groups trapped via this decay law is low, since $P_{\rm mon}(t=\tau_R)\approx\exp(-8(n_{\rm tr}R_g^2)/(2\pi)^{1/2})\approx 1$. Consequently, here we encounter essentially the same behavior as in the monomer trapping problem [see Eq. (27)]; we note that even $P_{\rm mon}(t=t_c)$ appears to be the same as that in Eq. (29). Hence, in this limit the only effect of the polymer tail is that the crossover time between the Smoluchowski-type and the fluctuation-induced behavior gets increased.

Next we turn to the opposite limit of long chains, such that $n_{\rm tr}R_g^2\gg 1$, but still assume that the trap concentration is sufficiently small and $abn_{\rm tr}\ll 1$. Here the comparison of the decay laws in Eqs. (47) and (51) suggests that the overall decay pattern is a succession of three different regimes:

$$P_{\rm ch}(t)\approx\begin{cases}\exp[-8bn_{\rm tr}(D_0t/\pi)^{1/2}], & a^2/D_0<t<t_c=z_0^4\pi^2/4^4D_0(bn_{\rm tr})^2\\ \exp[-\nu_2(bn_{\rm tr})^{1/2}(D_0t/\pi)^{1/4}], & t_c<t<\tau_R,\\ \exp[-\nu_2(n_{\rm tr}D_0t/N)^{1/2}], & t>\tau_R,\end{cases} \qquad (54)$$

i.e., the Smoluchowski-type decay law associated with the subdiffusive motion of the end-bead, the fluctuation-induced regime corresponding to the same anomalous motion of the end-bead, and lastly, the fluctuation-induced regime corresponding to conventional diffusive motion (with renormalized diffusion coefficient) of the end-bead.

We note now that in the limit $n_{\rm tr}R_g^2 \gg 1$, the crossover time t_c from the Smoluchowski-type to the fluctuation-induced behavior is given by

$$t_c \approx (D_0 b^2 \sigma_{\rm tr}^2)^{-1}, \tag{55}$$

i.e., it is proportional to the second inverse power of $\sigma_{\rm tr}$ and can be large if $\sigma_{\rm tr} \ll 1$ (but still less than τ_R). Taking the value of $P_{\rm ch}(t)$ at the crossover time t_c, we find that $P_{\rm ch}(t_c) \approx \exp(-\pi z_0^2/2)$, i.e., it is independent of both the concentration of traps and the chain length. Since here $P_{\rm ch}(t_c) \approx 10^{-4.5}$, we infer that such a mean-field-type regime will be rather representative; however, the amount of active end-beads of polymers trapped via this law will be substantially less as that for individual monomers. Consequently, contrary to the previously considered situation with short chains, here the amount of polymers anchored via the fluctuation-induced decay law in the second line in Eq. (54) will be much higher. Lastly, we note that the value of $P_{\rm ch}(t)$ at the end of this kinetic stage is

$$P_{\rm ch}(t=\tau_R) \approx \exp[-(n_{\rm tr}R_g^2)^{1/2}], \tag{56}$$

i.e., it is very small in the limit under consideration. Hence, the regime described by the third line in Eq. (54) will not be observed.

We close our analysis with some remarks concerning the excluded-volume effects, which are discarded here but may be certainly very important, especially for two-dimensional systems. We note that excluded-volume interactions impose additional constraints on the end-bead dynamics which will result apparently in a slower growth, compared to Eq. (40), of the end-bead MSD at the intermediate times (less than characteristic relaxation time of the 2D chain with excluded-volume interactions), and a stronger N dependence, compared to Eq. (41), of the end-bead diffusion coefficient in the long-time limit. Consequently, one expects that the behavior in Eqs. (47a) and (51a), [and accordingly, the intermediate kinetic stages in Eqs. (52a), (54a), and (54b)], which are associated with internal relaxations of the chain and anomalous end-bead dynamics, would be described by stretched-exponential dependences with different (compared to 1/2 and 1/4) values of the dynamical exponents. On the other hand, the long-time behavior as in Eqs. (47b) and (51b) [as well as that in Eqs. (52b), (52c), and (54c)] will remain essentially unchanged except that N will enter in a somewhat different power. Lastly, we would like to mention that our qualitative conclusions concerning different realizations of disorder which support the intermediate-time and long-time behaviors will hold even in the presence of the excluded-volume interactions; in other words, we expect that also in this case the intermediate-time behavior of $P_{\rm ch}(t)$ will be supported by typical realizations of the end-bead trajectories, while the long-time behavior will stem out from the interplay between the internal relaxations of the chain and fluctuations in the spatial distribution of traps.

V. CONCLUSIONS

To summarize, we have studied Rouse-Langevin dynamics of an isolated polymer chain bearing a chemically active functional group, attached to one of the chain's extremities, on a 2D solid substrate with immobile, randomly placed chemically active sites (traps). For a particular situation when the end-bead of a chain consisting of N segments can be irreversibly trapped by any of these sites, which results in a complete anchoring of the whole chain, we calculate the time evolution of the probability $P_{\rm ch}(t)$ that the initially unanchored chain remains mobile until time t. We show that in the case of relatively short chains the time evolution of $P_{\rm ch}(t)$ proceeds essentially in the same way as that for the monomer trapping problem; at intermediate times $P_{\rm ch}(t)$ follows a standard-form 2D Smoluchowski-type decay law $\ln P_{\rm ch}(t) \sim -t/N \ln(t)$, which crosses over at very large times to the fluctuation-induced stretched-exponential dependence $\ln P_{\rm ch}(t) \sim -(t/N)^{1/2}$, stemming out of fluctuations in the spatial distribution of traps. We find next that for long chains the kinetic behavior is quite different; here two representative kinetic stages are the intermediate-time decay of the form $\ln P_{\rm ch}(t) \sim -t^{1/2}$, while the long-time stage is described by the dependence $\ln P_{\rm ch}(t) \sim -t^{1/4}$. The intermediate-time decay is the Smoluchowski-type law associated with subdiffusive motion of the end-bead, while the long-time fluctuation-induced decay stems out of the interplay between fluctuations in traps distribution and internal relaxations of the chain.

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