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Reaction Kinetics in Polymer Systems

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We present both mean-field and many-particle descriptions of trapping reaction kinetics in systems in which traps are not randomly distributed in space, but are attached to the segments of polymer coils.

KEY WORDS: Trapping reaction; fluctuation phenomena; diffusion.

1. INTRODUCTION

Within the last two decades there has been considerable progress in the theoretical analysis of diffusion-controlled chemical reactions. While earlier work (see, e.g., refs. 1 and 2) focused on refinements of the classical Smoluchowski concentration gradient method, more recent developments have tended to emphasize the consequences of spatial fluctuations and fluctuation-induced kinetics.(3-11) One of the most fascinating examples of nontrivial fluctuation-induced behavior is provided by the trapping reaction $A + B \rightarrow B$, where diffusing particles A react with immobile randomly scattered traps B. Theoretical investigations of the problem have shown that at long times the mean-field descriptions of the reaction kinetics are invalid and the survival probability of particle A, which we denote $P_A(t)$, in the large-time regime follows an anomalous stretched-exponential dependence(3,4)

$$\ln P_A(t) \propto -C_B^{2/d+2} t^{d/d+2}, \qquad t \rightarrow \infty \tag{1}$$

where d is the spatial dimension and C_B is the mean concentration of traps.

Since the earliest investigations of this subject,(3,4) the problem of trapping reaction kinetics has attracted a growing interest, and a number

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of variations of the problem have been studied. For example, an analysis of trapping kinetics in systems with multiplication of diffusive particles$^{(5)}$ has appeared, in addition to the exactly solvable one-dimensional case,$^{(6)}$ and the mobile trap model.$^{(7)}$ These problems have also been tackled for diffusion on fractal structures (see, e.g., refs. 12–14). Aside from the investigations of the kinetic problems, there have been a number of works dealing with the nonanalytic dependence of the diffusion constant$^{(15)}$ and mean trapping time$^{(16)}$ on the concentration of traps, and the dependence of the steady-state survival probability upon the intensity of an external source of particles in Euclidean dimension $d=3$ (see ref. 17) as well as in low-dimensional and fractal spaces.$^{(18,19)}$

One can remark that the remarkable asymptotic form of Eq. (1) is a mathematical abstraction and is irrelevant to real physical systems, since it can only be observed at astronomically large times when the survival probability is extremely small. There is some disagreement among different authors concerning the question of how large t and how small $P_A(t)$ must be to ensure the utility of the asymptotic form. Klafter *et al.*$^{(20)}$ suggested from their simulations that Eq. (1) is valid for values of t such that $P_A(t) < 10^{-21}$ in $d=2$ dimensions. Using a combination of exact enumeration and simulations, Weiss *et al.*$^{(8)}$ have found that Eq. (1) is valid for $P_A(t) < 10^{-13}$. However, some recent studies of trapping reactions proceeding in restricted geometries—in dense percolation-like systems,$^{(21,22)}$ in crystals with topological defects,$^{(23)}$ and on fractals$^{(12-14)}$—suggest that a fluctuation-induced behavior, similar to that given in Eq. (1), can be observed beginning at more reasonable times.

In this contribution we summarize several results concerning trapping reaction kinetics in systems with some other types of geometrical restrictions—in systems where traps B are not randomly arranged, but rather are attached to segments of polymer chains, randomly distributed in a solvent. We show that the kinetics of trapping in such systems is mainly determined by correlations in trap placement and spatial fluctuations are decisive from very early times.

An outline of this paper is an follows: In Section 2 we discuss the mean-field solution, based on Smoluchowski-type arguments. In Section 3 we study the probability distribution for the existence of trap-free volumes in polymer solution and present rigorous results for the case of Gaussian chains. The case of non-Gaussian chain conformations is also analyzed. In Section 4 we discuss the explicit dependences that characterize fluctuation-induced trapping kinetics in polymer systems. Finally, in Section 5 we consider the case of distant reactions, i.e., direct energy transfer from an excited immobile donor molecule A to acceptors B placed on polymer chains.

2. MEAN-FIELD TREATMENT OF TRAPPING REACTIONS WITH POLYMERS

Let us present the mean-field description(24) of the trapping kinetics in terms of Smoluchowski-type arguments. Consider a system of mutually-independent polymer chains, containing N absorbing particles each, placed in a sea of diffusing (with diffusion constant D) particles, initially scattered uniformly throughout space with concentration 1. Following Smoluchowski, we write down the survival probability $P_{\mathrm{A}}(t)$ of particles A as follows:

$$P_{\mathrm{A}}(t)=\exp\left[-n_{\mathrm{ch}}\int^{t} d\tau\, K_s(\tau)\right] \tag{2}$$

where n_{ch} is the mean concentration of polymer chains and $H_s(\tau)$ is the rate at which particles A react with a single polymer chain containing N absorbing particles. To calculate this rate constant, one has to solve a diffusion equation

$$\partial C(r,t)/\partial t=D\,\Delta C(r,t) \tag{3a}$$

subject to absorbing boundary conditions on the surfaces of N traps arranged in a polymer chain,

$$C\left(r\subseteq\sum S_B\cdot t\right)=0 \tag{3b}$$

in addition to the initial and boundary conditions

$$C(r,t=0)=1, \qquad C(r\to\infty,t)=1 \tag{3c}$$

The rate is defined as the sum of fluxes

$$K_s(\tau)=D\sum_{j=1}^{N}\left[\int_{|r-R_j|=R}\nabla C(r,\tau)\,dS\right] \tag{4}$$

where R_j is the radius vector of jth trap and R is the reaction radius.

The Laplace-transformed solultion to Eq. (3) can be written down as follows:

$$C(r,\lambda)=1/\lambda+\sum_{1}^{N}B(i,\lambda)\,G(|r-R_i|) \tag{5}$$

where $G(r)$ is the Cauchy function of Eq. (3). In $d=3$,

$$G(|r-R_j|)\propto\exp(-\kappa|r-R_i|)/|r-R_i|, \qquad \kappa=(\lambda/D)^{1/2}$$

The coefficients $B(i, \lambda)$, $i = 1, 2, \ldots, N$, are arbitrary independent functions. In general, the function (5) is insufficient to satisfy the boundary conditions of Eq. (3b) for every reaction surface $|r - R_j| = R$, $j = 1, 2, \ldots, N$. The exact solution of Eqs. (3) contains an infinite set of multipole-type corrections $[\nabla^m G(r)]$, $m = 1, 2, \ldots, \infty$. However, for the typical trap configurations $|R_i - R_j| \gg R$, for $i \neq j$, and, consequently, $G(|R_i - R_j| - R) \approx G(|R_i - R_j|)$. Within this approximation N boundary conditions (3b) can be satisfied by the function (5) with an appropriate set of $B(i, \lambda)$. One can show that at low concentration of traps ($\varepsilon = NR^3/a^3N^{3/2} \ll 1$, a is the mean distance between neighboring traps, which equals the chain segment length) such an approximation is quite acceptable and gives the leading term in expansion on the powers of the gas parameter ε.

Combining Eqs. (5) and (3a), we obtain the following system of equations, which governs the behavior of unknown coefficients $B(i, \lambda)$:

$$B(j, \lambda) + R \cdot \exp(\kappa R) \sum_{i=1}^{N} B(i, \lambda) \cdot G(|R_j - R_i|) = -R \cdot \exp(\kappa R)/\lambda \qquad (6)$$

Equation (6) holds for any chain conformation. Let us first consider the case of the Gaussian chain. Averaging the last equation with respect to the Wiener measure and passing to the continuum limit, we find the following integral equation (for infinitesimally small λ)

$$\gamma \int_{-1}^{1} B(x, \lambda) \cdot |x - y|^{1/2} \, dx = 1, \qquad \gamma = -\lambda(N/\pi a^2)^{1/2}, \qquad x = (2i - N)/N \qquad (7)$$

This is the well-known Kirkwood–Riseman equation$^{(25)}$ and one can solve it explicitly by expanding the function $B(x, \lambda)$ and the kernel in a series of Gegenbauer polynomials. The solution is (aside from numerical multipliers)

$$B(x, \lambda) \propto aN^{-1/2}(1 - x^2)^{-1/4}\lambda^{-1}$$

Consequently, the quasistationary rate constant can be obtained as$^{(24)}$

$$K_s(\tau \to \infty) \propto DaN^{1/2} \qquad (8)$$

i.e., it grows at a rate that is sublinear in N. This is a rather curious result inasmuch it contradicts apparently quite reasonable intuitive arguments. To be more specific, the mean radius of a coil grows as $N^{1/2}$, and correspondingly, the mean concentration of monomers (traps) drops as $N^{1-d/2}$, i.e., as $N^{-1/2}$ in 3D. It seems quite natural to expect that screening of the chosen trap, caused by the many-trap effects, is negligibly small for large N. However, the correlations in the trap placement lead to strong screening effects which have the effect of drastically decreasing the rate constant, i.e., the survival probability of the A particles is enhanced.

We remark that the analogous problem of a diffusion in the presence of an absorbing fractal (Gaussian chain) has recently been studied by renormalization group methods in ref. 26. The result of Cates and Witten(26) is quite similar to the result in Eq. (8), which was obtained by means of a simple Smoluchowski-like approach.

It is easy to extend the result of Eq. (8) to the case of non-Gaussian chain conformations. It has been shown(26) that if the radius of the coil R_{ch} scales with N as $R_{\mathrm{ch}} \propto aN^{1/d_f}$, then the rate constant K_s grows with N as aN^{1/d_f}. In order words, the Smoluchowski-type rate constant depends linearly on the mean coil radius.

We close this section with some remarks concerning the time-dependent correction terms to Eq. (8), which represent the effect of the depletion of particles in the immediate neighborhood of the chain. By taking into account the leading long-time (small-λ) terms in Eq. (6), we obtain the asymptotic expansion of the rate constant

$$K_s(t) = 4\pi D\alpha N^{1/2}[1 + aN^{1/2}/(\pi Dt)^{1/2}] \qquad (9)$$

i.e., the usual form of the Smoluchowski(27) rate constant. The only difference is that the correction term in Eq. (9) is proportional to the radius of the coil, $aN^{1/d}f$, but not to the much smaller reaction radius R. Therefore, at sufficiently long times (times of diffusion on distance R_{ch}, $\tau_R \propto a^2N/D$) the correction term dominates and the decrease of $P_{\mathrm{A}}(t)$ is governed by

$$\ln P_{\mathrm{A}}(t) \propto -F(Dt/a^2)^{1/2}, \qquad F = n_{\mathrm{ch}}Na^3 \qquad (10)$$

3. DISTRIBUTION OF TRAP-FREE VOLUMES IN POLYMER SOLUTION

In this section we present the explicit form of the probability distribution of chain-free (trap-free) volumes in polymer solution containing randomly distributed, mutually-independent chains.

We mention that the problem of calculating this distribution has also been discussed in papers by Ohtsuki(29) and Kerstein.(30) Ohtsuki has shown that the distribution drastically differs from that for uncorrelated traps and implies a particular form for the kinetic behavior of the reaction kinetics for trapping. He was also able to find the forms of such a distribution for Gaussian coils, swollen chains, and branched polymers by means of scaling arguments. Kerstein(30) found such distribution for a system of infinite rigid rods randomly placed in space.

The probability $P_{\text{cav}}(R)$ for the existence of a chain-free cavity of radius R can be found by multiplying two components

$$P_{\text{cav}}(R) = P_{\text{end}}(R)\, P_{\text{sur}}(R) \tag{11}$$

The term $P_{\text{end}}(R)$ is the probability that there are no chains ends in this cavity. The second term in this equation, $P_{\text{sur}}(R)$, is the conditional probability that neither chain beginning outside the cavity crosses its surface. For mutually-independent coils the distribution of their ends is a negative exponential of the form

$$P_{\text{end}}(R) = \exp(-2V_d n_{\text{ch}} R^d)$$

where V_d is the volume of a d-dimensional unit sphere.

The form of $P_{\text{sur}}(R)$ for Gaussian coils can be understood if we rewrite its definition:

The distribution $P_{\text{sur}}(R)$ exactly equals the probability that neither of the random walk trajectories will cross the surface of a static sphere of radius R until the effective "time" $t = N$, if all the starting points of these trajectories are uniformly distributed outside the sphere, the mean concentration being $2n_{\text{ch}}$. Therefore, the distribution $P_{\text{sur}}(R)$ is nothing but the survival probability of a static particle of radius R in the presence of diffusing point traps (i.e., a scavenger reaction) and

$$P_{\text{sur}}(R) = \exp\left[-2n_{\text{ch}} \int_0^N K_S(N')\, dN'\right] \tag{12}$$

where $K_S(N)$ is the d-dimensional Smoluchowski constant,

$$K_S(N) = V_{d-1} D^* (\partial C/\partial r)|_{r=R} \tag{13}$$

and $C(r, t)$ is governed by Eqs. (3) (with the replacement $t \to N$) and $D^* = a^2/2d$.

It is important to note that the scavenger reaction is one of a few cases when the Smoluchowski approach yields an exact result, or, more correctly, the rigorous lower bound (see, e.g., refs. 5, 7, and 11). Hence, Eqs. (11) and (12) define a rigorous lower bound to the probability distribution $P_{\text{cav}}(R)$ in the case of mutually-independent Gaussian chains.

In 3D the form of the Smoluchowski constant is well known and we can easily write an explicit representation of $P_{\text{cav}}(R)$ as(28)

$$P_{\text{cav}}(R) = \exp\{-8\pi n_{\text{ch}} R^3/3 - 4/3\pi n_{\text{ch}} a^2 RN[1 + 2(R/\alpha)(6/\pi N)^{1/2}]\} \tag{14}$$

This equation actually exhibits a much slower functional dependence on R for $R < R_{\mathrm{ch}}$ than the comparable expression for uncorrelated trap placement.

Later we present another approach(28) which can fruitfully be applied to describe more general polymer structures. The value of $\int K_s(l)\, dl$ exactly equals the volume of the "reaction tube," i.e., a tube of cross section πR^{d-1} that surrounds the random walk trajectory. This volume, up to a numerical multiplier, equals the total volume of blobs(32) $V_b = MR^d$, where the number of blobs is equal to $M = N/L$, and L is the number of segments in each blob, which can be approximated by $L \propto (R/a)^{d_f}$. For a Gaussian chain, $L \propto (R/a)^2$ and we reproduce Eq. (14) for $P_{\mathrm{sur}}(R)$. For swollen coils where the number of segments in blob scales as $L \propto (R/a)^{1/\nu}$, where $\nu = 3/d + 2$, we get

$$\ln P_{\mathrm{sur}}(R) = -n_{\mathrm{ch}} N a^{(d+2)/3} R^{2(d-1)/3} \tag{15}$$

We mention that a derivation of the mean size of a cavity (or correlation length ξ) from Eq. (15) leads to the well-known dependence $\langle R \rangle \propto \alpha (n_{\mathrm{ch}} N)^{-3/4}$ for $d = 3$ (see, e.g., ref. 32).

Next we consider the system of orientationally-disordered, long, rodlike molecules. Neglecting excluded-volume effects (we assume that rods can cross each other), we get that $L \propto R/a$ and

$$\ln P_{\mathrm{sur}}(R) = -n_{\mathrm{ch}} N a R^{d-1} \tag{16}$$

This expression coincides with a result of Kerstein.(30)

When R is less than $R_{\mathrm{ch}} = aN^{1/d_f}$ we find

$$nP_{\mathrm{cav}}(R) = -F(R/\alpha)^{\gamma}, \qquad \gamma = d - d_f, \qquad F = n_{\mathrm{ch}} N a^d \tag{17}$$

i.e., the probability for the existence of chain-free cavities for all the cases under consideration vanishes with R at a much slower rate than in systems of randomly distributed monomers having the same mean density. This fundamental difference is caused by the connectivity properties of these structures—for each model the probability that there are no chain segments in some region is entirely defined by the probability that a chain does not cross the surface surrounding this region. The exponent γ is connected with the specific properties of chains.

4. TRAPPING REACTIONS WITH POLYMERS

The ensemble average of the survival probability of A particles is dominated by

$$P_{\mathrm{A}}(t) = v_{d-1} \int_0^{\infty} R^{d-1}\, dR\, P_{\mathrm{cav}}(R)\, P(R, t) \tag{18}$$

where $P(R, t)$ is the probability that a given diffusing particle A survives for a time t in the trap-free cavity of radius R enclosed by a trapping boundary. The form of $P(R, t)$ depends, however, on the type of reaction. If the reaction occurs at the first encounter of A with any trap B, i.e., we assume perfect trapping, $P(R, t)$ is given by

$$P(R, t) \propto 4\mu^{-2} \exp(-\mu^2 Dt/R^2) \tag{19}$$

where the eigenvalue μ is an easily determined dimensionless constant. If not all encounters of A with B lead to absorption, i.e., trapping occurs with some finite probability that determines the reaction rate K, particles tend to be confined in the cavities between the segments due to steric entanglements. In such system the probability $P(R, t)$ for R less than Da^{d-1}/K is given by$^{(21,22)}$

$$P(R, t) \propto \exp(-Kt/a^{d-1}R) \tag{20}$$

Naturally, the distribution in Eq. (20) implies a different kinetic behavior of the trapping reaction compared to that given in Eq. (1). In dense systems of randomly distributed monomeric traps it leads to the replacement of Smoluchowski-type intermediate asymptotics by the dependence $P_A(t) \propto \exp(-\text{const} \cdot t^{d/d+1})$.$^{(21,22)}$ Further on we will terms the regime associated with Eq. (20) the kinetic-controlled trapping (KCT) regime, and the regime associated with Eq. (19) the diffusion-controlled trapping (DCT) regime.

We notice that the probability for the existence of large cavities ($R \gg R_{\text{ch}}$) is limited by the negative exponential distribution of chain ends $P_{\text{end}}(R)$. Hence, at $t \to \infty$ we recover the universal result of Eq. (1) for arbitrary chain conformation. However, the coefficient in the exponent is proportional to the power of n_{ch} for all the cases under consideration (but not to the power of a "real" concentration of traps $n_{\text{ch}} N$).

We discuss below the kinetic behavior found in the intermediate stage of trapping reactions of diffusive particles A with traps on polymer chains. For the generalized distribution, Eq. (17), in the case of perfect traps we obtain (omitting the special case of 2D Gaussian coils, when the spatial dimension and d_f coincide$^{(31)}$)

$$P_A(t) = -2F^{2/\gamma+2}(Dt/\alpha^2)^{\gamma/\gamma+2}, \qquad t < t^{**} \tag{21a}$$

where $t^{**} = t_D F N^{\beta}$, $t_D = a^2/D$. For 3D gaussian coils, swollen coils, and rodlike molecules, $\gamma/(\gamma+2)$ is equal to 1/3, 2/5, and 1/2, respectively. The corresponding values of the exponent β are 3/2, 2, and 4. For 2D rodlike molecules $\beta = 3$ and $\gamma/(\gamma+2)$ is equal to 1/3. Let us note that β is always larger than 1, i.e., the crossover time t^{**} is large. In the case of imperfect traps for times less than $t^* = t_{\mathrm{ch}} F(t_{\mathrm{ch}}/t_D)^{1+\gamma}$, $t_{\mathrm{ch}} \approx 1/Kn_{\mathrm{ch}}$,

$$\ln P_{\mathrm{A}}(t) = -2F^{1/\gamma+1}(Kt/a^d)^{\gamma/\gamma+1} \tag{21b}$$

and for $t^* < t < t^{**}$ the formula for decay given in Eq. (21a) is valid. The reaction depth, which characterizes the fraction of particles A trapped until time t^{**}, is given by

$$\begin{aligned} \delta &= -\ln P_{\mathrm{A}}(t^{**}) \\ &= 2F[(Da^{d-2}/K)^\gamma + N^{\gamma/d_f}] \gg 1 \qquad \text{when} \quad N \gg 1 \quad \text{or} \quad K \to 0 \end{aligned}$$

i.e., the bulk of particles are trapped during the intermediate stage.

We complete this section with estimations of the crossover times from the mean-field equations (2), (9), and (10) to the fluctuation-induced behavior of Eq. (21a) in the case of Gaussian coils. For this purpose we first compare the exponents in Eq. (2) [with the steady-state rate constant of Eq. (9)] and Eq. (21a). These exponents are equal to each other when $t \propto \tau_D N^{3/4}/F^{1/2}$. Since the case of Gaussian coils is realized in concentrated polymer solutions, i.e., $F \propto 1$, this time is less than τ_R, the time to diffuse a distance $aN^{1/2}$. This implies that the steady-state mean-field regime associated with Eq. (9) does not exist. Next, on comparing Eqs. (21a) and (10), we find that they are equal to each other when $t \propto \tau_D/F^2$. Therefore, we infer that the fluctuation-induced behavior of Eq. (21a) will be observed from the earliest times. This is strongly supported by numerical simulations in systems of Gaussian coils(31) in two dimensions. However, in the case of swollen coils (i.e., dilute solutions, in which $F \ll 1$) the mean-field behavior can be observed.

5. DIRECT ENERGY TRANSFER IN POLYMER SYSTEMS

In this section we study the direct energy transfer in polymer solutions in which all segments of polymer chains are accedptors for single immobile donor molecules.(33) Here we restrict ourselves to the case of isotropic multipolar initeractions only. For these, the rate of energy transfer from the donor to an acceptor is $W(r) = C_{\mathrm{A}} r^{-n}$.

The relaxation of an excited donot located at the origin due to direct energy transfer to acceptors at positions R_{ij} that act independently is governed by

$$F(t, \{R_{ij}\}) = \exp\left[-t \sum_i \sum_j W(\{R_{ij}\})\right] \tag{22}$$

where the index i extends over all chains (the K chains are embedded in a volume V, so that $K/V = n_{\mathrm{ch}}$ for $K, V \to \infty$); and the index j extends over all acceptors occupying each Gaussian chain. Averaging over all configurations, we find

$$\Phi(t) = \langle F(t, \{R_{ij}\}) \rangle = \left\langle \prod_{j=1}^{K} E^{i}_{R_{0i}} \left\{ \exp\left[-t \sum_{j} W(R_{ij}) \right] \right\} \right\rangle_{R_{0i}}$$

The angular brackets represent an average with respect to the $\{R_{0i}\}$, which are uniformly distributed with mean concentration $n_e = 2n_{\mathrm{ch}}$. The symbol $E_R\{\cdots\}$ denotes Wiener integration along the trajectory of the ith chain with a starting point at R_{0i}. Consequently, an exact average can be carried out,[33] which yields

$$\Phi(t) = \exp\left[-n_e \int dR_0 \left(1 - E\left\{ \exp\left[-t \sum_{j} W(R_j - R_0) \right] \right\} \right) \right] \tag{23}$$

According to the Feynman–Kac theorem, the Wiener integration in Eq. (23) is associated with the following Schrödinger equation:

$$\begin{aligned} &\partial G(r, R_0, N)/\partial N = D^* \Delta G(r, R_0, N) - t \cdot W(r) \cdot G(r, R_0, N) \\ &G(r, R_0, N = 0) = \delta(r - R_0); \qquad D^* = a^2/2d \end{aligned} \tag{24a}$$

where Δ and $\delta(r - R_0)$ are the d-dimensional Laplacian and delta function, respectively; and

$$E\left\{ \exp\left[-t \sum W(R_j - R_0) \right] \right\} = \int dr\, G(r, R_0, N) \tag{24b}$$

Equation (24a) cannot be solved exactly for physically interesting forms of $W(r)$. However, we can avoid cumbersome calculations by working in terms of rescaled variables $\tau = N \cdot t^{-2/n-2}$ and $x = r \cdot t^{-1/n-2}$. When written in terms of these variables, Eq. (24a) defines the mean-field description of the well-known problem of the survival of an excited state, which diffuses (with diffusion coefficient D^*) in the presence of randomly distributed uncorrelated acceptors. For an extensive review of this subject see, for example, refs. 34–36. We emphasize, however, that Eqs. (24) contain the exact (not mean-field) many-particle solution to the initial problem of donor decay in systems with polymeric acceptors.

We consider next the three-dimensional case. At long times the diffusive term in Eqs. (24) is negligible and the function $\Phi(t)$ is as follows[33]:

$$\Phi(t) = \exp[-2\Gamma(1 - 3/n)(4\pi/3)\, F N^{(3-n)/n} (C_{\mathrm{A}} t)^{3/n}] \tag{25}$$

i.e., a Forster-type dependence on time(37); while at intermediate times t the novel stretched-exponential law is valid,(33)

$$\Phi(t) = \exp\{-\omega(4\pi/3)\, FN^{1/2}(t/T)^{1/n-2}[1 + 2\omega(6/\pi)^{1/2}(t/T)^{1/n-2}]\} \quad (26)$$

where the numerical factor $\omega \propto 1$ depends on the dimension and n; and the characteristic time is $T = (aN^{1/2})^n/C_A N$. We remark that T is the "cross-over" time from Eq. (26) to Eq. (25). The Forster-type dependence in Eq. (25) can hardly be observed, since $\Phi(T) \propto \exp(-N^{1/2})$ drops off exponentially for large N. Last, we mention that for $t < T$ the second term in brackets in Eq. (26) is small as compared to unity and the temporal behavior of $\Phi(t)$ is governed by the behavior of the first term. The forms of donor decay in $d = 2$ were analyzed in ref. 33.

Next we make an effort to reproduce (25), (26) by means of another approach, having in mind a further extension to the case of non-Gaussian chain conformations.

The energy relaxation is, in general, governed by the probability distribution for the existence of acceptor-free volumes. If one assumes a Poisson distribution of uncorrelated acceptors, the probability $P_{\mathrm{cav}}(R)$ of having an acceptor-free volume V of radius R is $P_{\mathrm{end}}(R)$. One can show that for a Poisson distribution of acceptors the ensemble-averaged decay is

$$\Phi(t) = \exp\left(-dV_d C_B \int R^{d-1}\, dR\, \{1 - \exp[-tW(R)]\}\right)$$

Evaluating the integral exactly, one finds Forster decay. On the other hand, the saddlepoint method reproduces this decay and shows that $\Phi(t)$ is governed by the relation $\Phi(t) \propto P_{\mathrm{cav}}(R(t))$, where $R(t)$ is defined by the "black sphere" relation $tW(R(t)) = 1$. We base our further analysis on this expression.

Let us now turn to the cavity-size dcistribution derived in Section 3. Equation (14) shows that on large scales, i.e., those above the correlation length $R_{\mathrm{ch}} = aN^{1/2}$, the acceptor distribution is Poisson, while for $R < R_{\mathrm{ch}}$ it is inhomogeneous. Correspondingly, we can expect quite different temporal behavior of energy relaxation at the intermediate and large [defined by $R(t) > E_{\mathrm{ch}}$] times. In the large-t limit $R(t)$ is defined by the relation $tNW(R(t)) = 1$ and, therefore, we reproduce the Forster-type result in Eq. (25). For $R(t)$ less than the correlation length the situation is more complicated, since both the reaction and "diffusion" terms in Eq. (24a) are important. In this regime one must take into account two distinct reaction channels and the energy relaxation is governed by the effective rate constant(1) $K_{\mathrm{eff}} = K \cdot K_{\mathrm{S}}/(K + K_{\mathrm{S}})$, where $K_{\mathrm{S}} = 4\pi D^* R$, and the "chemical" constant $K \propto t \int R^{d-1} W(R)\, dR$. A variational argument can be invoked to provide the following definition of $R(t)$ for $R(t) < R_{\text{ch}}$: it must depend on t in such a way that K_{eff} is maximal. For Gaussian coils this requirement leads to the relation $R(t) \propto (C_{\text{A}} t/D^*)^{1/n-2}$. Substituting this scaling law into the second term in curly brackets in Eq. (14), we recover the decay of Eq. (26).

Next we consider the case of non-Gaussian chains. The corresponding cavity-size dcistribution $P_{\text{cav}}(R)$ is given by Eqs. (11) and (17). The former includes both a negative exponential and a fractal term, where the first term is the dominant one above the correlation length. This means that the long-time decay in Eq. (25) is universal and independent of the polymer conformations. In contrast, at intermediate times the temporal behavior is essentially influenced only by the chain conformations. Maximizing K_{eff}, where $K_{\text{S}} \propto a^{d_f} R^{d-d_f}$ and K is unchanged, one finds that $R(t)$ scales as $(C_{\text{A}} t/a^{d_f})^{1/n-d_f}$. Substituting this scaling law into the second term in Eq. (17), we find the following form on the decay at intermediate times

$$\Phi(t) \propto \exp\{-n_{\text{ch}} N a^z (C_{\text{A}} t)^\beta\} \tag{27}$$

$$z = d_f(n-d)/(n-d_f), \qquad \beta = (d-d_f)/(n-d_f)$$

6. CONCLUSIONS

To summarize, we have studied the trapping kinetics in systems in which traps are not mutually independent, but are attached to randomly placed polymers having arbitrary conformations. We have presented both a mean-field and a many-particle treatment of the reaction kinetics.

We have shown that within the framework of a mean-field description, based on the Smoluchowski-type approach, the diffusive constant (which defines the rate at which particles react with a single chain) depends linearly on the mean radius of the polymer, i.e., grows sublinearly with a number of traps arranged in the polymer chain. Therefore, the correlations in trap placement lead to the strong screening effects and suppress the rate constant.

Next, we have examined the probability for the existence of chain-free voids in a polymer solution containing mutually independent chains. For Gaussian chains we have presented the rigorous forms of such distributions. In the case of swollen coils or rodlike molecules explicit expressions for these distributions have been derived. We have shown that in polymer systems the probability for the existence of a cavity whose radius is equal to R is much greater than in systems of mutually independent monomers at the same concentration.

On the basis of these distributions we have studied the trapping kinetics in polymer systems. We have shown that at long times the trapping kinetics is characterized by the universal dependence given in Eq. (1) for any conformations of chains. At intermediate times, which define the annihilation of the bulk of particles, the trapping kinetics is governed by the new conformation-dependent laws in Eq. (21).

Lastly, we have studied direct incoherent donor decay in a system in which acceptors are not randomly placed, but are all attached to the segments of immobile polymer chains. We have shown that correlations in acceptor placement drastically influence the relaxation of probe molecules over the entire time domain. On the one hand, at intermediate times the temporal behavior is governed by the novel decay laws in Eqs. (26) and (27) that depend on chain conformations. These decay laws define the deactivation of the bulk of excited donors. On the other hand, at the long-time limit the universal Forster-type time dependences are restored. However, the dependence upon the concentration of acceptors $n_{\mathrm{ch}} N$ in Eq. (25) is suppressed by the correlation-induced screening parameter $N^{(3-n)/n}$

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