

## Direct Energy Transfer in Polymer Systems

S. F. Burlatsky, G. S. Oshanin, and A. V. Mogutov

*Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Kosygin St. 4, 117334 Moscow V-334, U.S.S.R.*

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We study the direct incoherent energy transfer from a single excited donor molecule to acceptors, which all are attached to chainlike polymers, randomly distributed in viscous solvent. We present both analytical and simulation results that document the essential departure from Forster-type decay laws due to correlations in acceptor placement.

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Following the seminal work of Forster,<sup>1</sup> the direct energy transfer from an energetically excited donor molecule to acceptor molecules embedded in condensed media has been of considerable interest and has been extensively studied in various ramifications.<sup>2-7</sup> Much emphasis has been put on studying energy relaxation in systems where acceptors are mutually independent and occupy random positions in  $d$ -dimensional Euclidean space or occur on regular infinite sublattices. However, the recent increase in interest in investigations of disordered media, e.g., clays, micelles, polymer solutions, and porous solids, has encouraged the examination of how the relaxation of excited molecules is modified in systems that impose spatial restrictions on acceptor or donor distributions. For instance, the decay forms were found for fractal lattices<sup>8</sup> and for porous media with various pore geometries.<sup>9</sup> One should also mention the remarkable results concerning donor decay in systems where one donor and one acceptor are placed at the ends of an isolated immobile polymer chain, or when the chain contains a small concentration of randomly placed acceptors.<sup>10</sup> The outcome of these works<sup>8-10</sup> is that the restrictions in space cause essential deviations from the Forster decay laws.

In this paper we focus on some other aspects of geometrical restrictions on the acceptor distribution. We consider polymer solutions (with mean concentration of polymer chains  $C_{ch}$ ) where all segments of the polymer chains ( $N$  segments per each chain,  $N \gg 1$ ) are the acceptors for a single immobile donor molecule. We assume that the polymer chains are immobile and mutually independent, i.e., the acceptors on one chain are correlated by the fixed covalent bonds that join them, and independent of the acceptors placed on the other chains. Here we consider the case of isotropic multipolar interactions. For these, the rate of energy transfer from the donor to an acceptor is  $W(r) = C_A r^{-n}$ .

This paper is organized as follows: First, we study the ensemble-averaged decay function for  $d$ -dimensional Gaussian coils and evaluate the exact decay forms in three dimensions. Next, we present the results of numerical simulations and compare them with 2D decay forms obtained analytically. Last, we reproduce the results obtained for Gaussian coils by means of simple scaling arguments and extend this scaling approach to non-Gaussian chain conformations.

The relaxation of an excited donor located at the origin due to the direct energy transfer to acceptors that act independently and occupy positions  $R_{ij}$  of a given structure is governed by

$$F(t, R_{ij}) = \exp \left[ -t \sum_i \sum_j W(R_{ij}) \right], \quad (1)$$

where index  $i$  extends over all chains ( $K$  chains in volume  $V$ ,  $K/V = C_{ch}$  for  $K, V \rightarrow \infty$ ), and index  $j$  extends over all acceptors occupying each Gaussian chain. Averaging over all configurations of the acceptor structure one obtains

$$\Phi(t) = \left\langle \prod_{i=1}^K E_{R_{0i}}^i \left[ \exp \left( -t \sum_j W(R_{ij}) \right) \right] \right\rangle_{R_{0i}}. \quad (2)$$

The angular brackets refer to averaging by  $\{R_{0i}\}$ , uniformly distributed with mean concentration  $C_e = 2C_{ch}$ . The symbol  $E_R[\dots]$  denotes the Wiener integration along the trajectory of  $i$ th chain with starting point at  $R_{0i}$ . Replacing all  $R_{0i}$  in Eq. (2) by the origin, one gets

$$\Phi(t) = \left\langle \prod_{i=1}^K E_0^i \left[ \exp \left( -t \sum_j W(R_{ij} - R_{0i}) \right) \right] \right\rangle_{R_{0i}}.$$

Since all chains are mutually independent, we can omit the subscript  $i$  in Eq. (2),

$$\Phi(t) = \left\langle \left\{ E_0 \left[ \exp \left( -t \sum_j W(R_j - R_0) \right) \right] \right\}^K \right\rangle_{R_0}.$$

Consequently, an exact averaging can be carried out:

$$\begin{aligned} \Phi(t) &= \left\langle \left[ 1 - \left\{ 1 - E_0 \left[ \exp \left( -t \sum_j W(R_j - R_0) \right) \right] \right\} \right]^K \right\rangle_{R_0} = \left[ 1 - \int dV V^{-1} \left\{ 1 - E_0 \left[ \exp \left( -t \sum_j W(R_j - R_0) \right) \right] \right\} \right]^K \\ &= \exp \left[ -C_e \int dR_0 \left\{ 1 - E \left[ \exp \left( -t \sum_j W(R_j - R_0) \right) \right] \right\} \right]. \end{aligned} \quad (3)$$

According to the Feynman-Kac theorem the Wiener integration in Eq. (3) is associated with the following Schrödinger equation:

$$\partial G(r, R_0, N) / \partial N = D^* \Delta G(r, R_0, N) - t W(r) G(r, R_0, N), \quad (4a)$$

$$G(r, R_0, N=0) = \delta(r - R_0), \quad D^* = a^2 / 2d,$$

where  $a$  is the segment mean length,  $\Delta$  and  $\delta(r - R_0)$  are the  $d$ -dimensional Laplacian and delta function, and

$$E \left[ \exp \left[ -t \sum W(R_j - R_0) \right] \right] = \int dr G(r, R_0, N). \quad (4b)$$

Next, we introduce the location-averaged function

$$g(r, N) = \int dR_0 G(r, R_0, N).$$

In the rescaled variables  $\tau = Nt^{-2/n-2}$  and  $x = rt^{-1/n-2}$  (i.e., small "time"  $\tau$  corresponds to large  $t$ ) we rewrite Eqs. (4) as follows:

$$\partial g / \partial \tau = D^* \Delta_x g - C_A x^{-n} g, \quad g|_{\tau=0} = 1, \quad (5a)$$

$$\Phi(t) = \exp[-t^{d/n-2} Q(\tau)], \quad (5b)$$

$$Q(\tau) = C_e \int dx [1 - g(x, \tau)].$$

Equation (5a) cannot be solved exactly for physically interesting transfer rates  $W(r)$ . However, we can avoid the cumbersome calculations by resorting to a visual analogy: Evidently, one can deduce that the function  $\exp[-Q(\tau)]$  is tantamount to the mean-field representation of the probability that an excited state, which diffuses (with diffusion coefficient  $D^*$ ) in the presence of randomly distributed uncorrelated acceptors, survives until "time"  $\tau$ . For an extensive review on this subject see, e.g., Refs. 4-6. We emphasize, however, that Eqs. (4) or (5) entail the exact (not mean-field) many-particle solution to the initial problem of donor decay in systems with polymeric acceptors.

We begin with the three-dimensional case. At the initial stages, small  $\tau$ , the continuous diffusion of an excited state is not essential and the energy is transferred only to the nearest acceptor environment. This leads to the Forster-type decay

$$Q(\tau) = \frac{4}{3} \pi \Gamma(1 - 3/n) C_e (C_A \tau)^{3/n},$$

where  $\Gamma(z)$  is the gamma function. As  $\tau$  grows the diffusion becomes decisive and one has for  $Q(\tau)$  the "migration-accelerated" dependence<sup>6,11,12</sup>

$$Q(\tau) = 4\pi D^* R_S C_e \tau [1 + 2R_S / (\pi D^* \tau)^{1/2}], \quad (6)$$

where the "effective" radius  $R_S$  equals<sup>6,11,12</sup>

$$R_S = v^{2\nu} \frac{\Gamma(1-\nu)}{\Gamma(1+\nu)} \left( \frac{C_A}{D^*} \right)^\nu,$$

with  $\nu = 1/n - 2$ . Inserting  $Q(\tau)$  from Eq. (6) into Eqs.

(5) we obtain the large- $t$  decay,

$$\Phi(t) = \exp[-2\Gamma(1 - 3/n) \varepsilon_p N^{(3-n)/n} (C_A t)^{3/n}], \quad (7)$$

i.e., Forster-type dependence; and for intermediate times  $t$ , the novel stretched exponential law,

$$\Phi(t) = \exp\{-\gamma \varepsilon_p N^{1/2} (t/T)^{1/n-2} \times [1 + 2\gamma(6/\pi)^{1/2} (t/T)^{1/n-2}]\}, \quad (8)$$

where  $\varepsilon_p$  is the volume fraction of polymer,  $\varepsilon_p = 4\pi C_{ch} \times Na^3/3$ , and the numerical factor  $\gamma \approx 1$  depends on spatial dimensionality, index  $n$ , and characteristic time  $T = (aN^{1/2})^n / C_A N$ . One should remark that  $T$  is the "crossover" time from (8) to (7) and the Forster-type dependence (7) can hardly be observed since  $\Phi(T) \approx \exp(-N^{1/2})$  is exponentially small for large  $N$ . Last, we mention that for  $t \leq T$  the second term in square brackets in (8) is small compared to unity and the temporal behavior of  $\Phi(t)$  is governed by the leading first term.

Next, we consider the donor decay in two dimensions. For this, let us notice that  $Q(\tau)$  in Eq. (6) is simply

$$Q(\tau) = C_e \int^\tau K_S(\tau) d\tau, \quad (9)$$

where  $K_S(\tau)$  is the three-dimensional Smoluchowsky "diffusive" constant.<sup>13</sup> It is easy to show that for large "times"  $\tau$ , Eq. (9) still holds in two dimensions, where in approximate form<sup>14</sup>

$$K_S(\tau) = 4\pi D^* \exp(z) / E_1(z), \quad z = -R_S^2 / 4D^* \tau, \quad (10)$$

where  $E_1(z)$  is Euler function. Combining Eqs. (9), (10), and (5) one gets the intermediate asymptotic decay,

$$\Phi(t) = \exp\left\{-\frac{2\varepsilon_p \exp[-(t/T)^{2/n-2}]}{E_1((t/T)^{2/n-2})}\right\}, \quad (11)$$

where  $\varepsilon_p = \pi C_{ch} Na^2$ . Turning now to the large- $t$  limit we find that the Forster-type decay is restored.

Now, we present the results of illustrative computer simulations of donor decay in systems with polymeric acceptors. For this computation we employed the following simple lattice model. We consider a two-dimensional lattice containing  $300 \times 300$  sites, in which some are occupied by segments of freely jointed chains. The realizations of polymer chains on the lattice are constructed as follows. We randomly choose  $X=30$  "seed" sites and grow from them (with periodic boundaries) freely jointed chains containing  $N=3000$  segments each. Naturally, the value of  $XN$  differs from the "real" concentration of lattice sites occupied by the polymer chain segments, since each chain can intersect its own trajectory and the trajectories of the other chains. We take into account this discrepancy by substituting the real concentration of occupied sites into the analytical dependence (11) instead of the value  $C_{ch}N$ . Next, on the lattice with a

given chain realization we randomly chose  $j = 100$  donor positions and calculate the averaged-over- $j$  donor decay function corresponding to this chain realization. The donor decay function averaged over ten chain realizations is plotted in Fig. 1 along with the novel analytical result (11). The numerical data are quite consistent with our analytical results.

Next, we make an effort to reproduce (7) and (8) by means of the other approach, having in mind the further extension to the case of non-Gaussian chain conformations, e.g., swollen coils, rodlike molecules, and branched polymers. The energy relaxation is, in general, governed by the probability distribution for the existence of acceptor-free volumes  $V_d R^d$ , where  $V_d$  is the volume of the  $d$ -dimensional unit sphere. If one assumes a Poissonian distribution of uncorrelated acceptors, the probability  $P_{\text{cav}}(R)$  to have an acceptor-free volume  $V$  of radius  $R$  is  $\exp(-V_d R^d C_{\text{acc}})$ , where  $C_{\text{acc}}$  is the mean concentration of acceptors. One can show that for a Poissonian distribution of acceptors the ensemble-averaged decay is

$$\Phi(t) = \exp \left\{ -dV_d C_{\text{acc}} \times \int R^{d-1} dR \{1 - \exp[-tW(R)]\} \right\}.$$

Evaluating the integral exactly, one arrives at Forster decay. On the other hand, the saddle-point method reproduces this decay and shows that  $\Phi(t)$  is governed by  $\Phi(t) \approx P_{\text{cav}}(R(t))$ , where  $R(t)$  is defined via the "black sphere" relation  $tW(R(t)) = 1$ . We will base our further considerations on the latter expression. The analogous distribution for the existence of chain-free (acceptor-free) volumes was recently derived<sup>15</sup> for polymer solutions containing mutually independent polymer coils. For Gaussian 3D coils such a distribution was

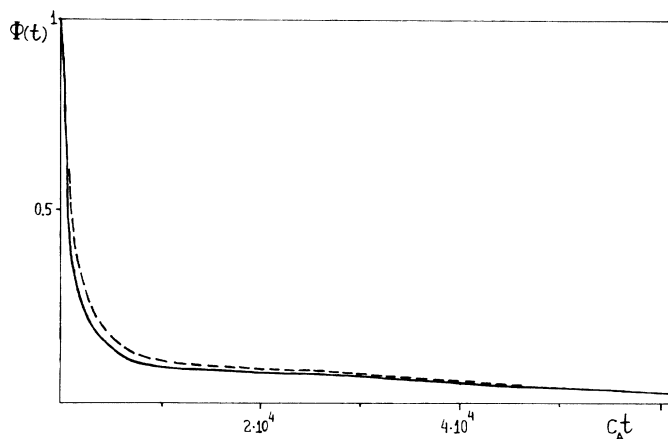


FIG. 1. Comparison of analytical predictions for  $\Phi(t)$  [Eq. (11) with  $n=6$  and  $a=1$ , solid line] with simulation results (dashed line). The total concentration of acceptors (sites occupied by polymers) is  $C_{\text{acc}} = 0.4$ ; 3000 acceptors per chain.

evaluated exactly,<sup>15</sup>

$$P_{\text{cav}}(R) = \exp \left\{ -2V_3 C_{\text{ch}} R^3 - \varepsilon_p \frac{R}{a} \left[ 1 + 2 \left( \frac{6}{\pi} \right)^{1/2} \frac{R}{R_{\text{ch}}} \right] \right\}. \quad (12)$$

Equation (12) shows that on large scales, above the correlation length  $R_{\text{ch}} = aN^{1/2}$ , the acceptor distribution has Poissonian properties, while for  $R < R_{\text{ch}}$  it is inhomogeneous. Correspondingly, we can expect quite different temporal behavior of energy relaxation at intermediate and large [ $R(t) > R_{\text{ch}}$ ] times. In the large- $t$  limit [small "times"  $\tau$  in Eqs. (5)],  $R(t)$  is defined via  $tNW(R(t)) = 1$  and, therefore, we reproduce the Forster-type result (7). For  $R(t)$  less than the correlation length (large  $\tau$ ), the situation is more complicated since both reaction and "diffusion" terms in Eq. (5a) are essential. It means that one must account for two distinct reaction channels, and the energy relaxation is governed by the effective rate constant<sup>6</sup>  $K_{\text{eff}} = KK_S / (K + K_S)$ , where  $K_S$  is Smoluchowsky-type "diffusive" constant,  $K_S = 4\pi D^* R$ , and  $K$  is the "chemical" constant,  $K \approx t \int R^{d-1} W(R) dR$ . Some variational-principle-like arguments entail the following definition of  $R(t)$  for  $R(t) < R_{\text{ch}}$ : It must depend on  $t$  in such a way that  $K_{\text{eff}}$  is maximal. For Gaussian coils it leads to the relation  $R(t) \approx (C_{\text{At}}/D^*)^{1/n-2}$ . Substituting this scaling law into the second term in curly brackets in (12), we recover the decay of Eq. (8).

Now, we turn to the case of non-Gaussian chains. The corresponding cavity-size distribution  $P_{\text{cav}}(R)$  has the following form:<sup>15</sup>

$$P_{\text{cav}}(R) = \exp[-2V_d C_{\text{ch}} R^d - C_{\text{ch}} N a^d (R/a)^{d-d_f}], \quad (13)$$

where  $d_f$  is the fractal dimension of polymer chain which relates the "mass"  $N \approx (R/a)^{d_f}$  to the radius of coil. For instance, for swollen coils  $d_f$  is inverse to the Flory index  $\nu_F = 3/d + 2$ , i.e.,  $d_f = 1/\nu_F$ . For rodlike molecules  $d_f$  equals unity in all dimensions. For branched polymers in dilute solution  $d_f = 2$  in 3D and near the gelation threshold  $d_f \approx 2.5$  (see, e.g., Refs. 16-18).

Equation (13) has Poissonian and fractal terms, where the first one dominates above the correlation length. It means that the long-time decay (7) is universal and independent of the conformations of the polymers. In contrast, at intermediate times the temporal behavior is essentially influenced by the chain conformations. Maximizing  $K_{\text{eff}}$ , where  $K_S \approx a^{d_f} R^{d-d_f}$  and  $K$  is not changed, one gets that  $R(t)$  scales as  $(C_{\text{At}}/a^{d_f})^{1/n-d_f}$ . Substituting this scaling law into the second term in Eq. (13), we find the intermediate-time decay,

$$\Phi(t) \approx \exp[-C_{\text{ch}} N a^\gamma (C_{\text{At}})^\beta], \quad (14)$$

$$\gamma = d_f(n-d)/(n-d_f), \quad \beta = (d-d_f)/(n-d_f).$$

To summarize, we have studied the direct incoherent donor decay in a system with correlations in the acceptor distribution, i.e., in a system where acceptors are not randomly placed but are attached to the segments of immobile polymer chains. We have shown that correlations in the 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 novel decay laws [(8) and (14)] which are dependent on chain conformations. These decay laws define the deactivation of the bulk of excited donors. On the other hand, in the large-time limit the universal Forster-type time dependence is restored. However, the dependence on the concentration of acceptors,  $C_{\text{ch}}N$ , in Eq. (7) is suppressed due to the correlation-induced screening parameter  $N^{(3-n)/n}$ .

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