DIRECT ENERGY TRANSFER IN SYSTEMS OF POLYMERIZED ACCEPTORS

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We study the direct incoherent energy transfer from an immobile excited donor molecule to acceptor molecules, which are all attached to polymer chains, randomly arranged in a viscous solvent. The decay forms are found explicitly, in terms of an optimal-fluctuation method, for arbitrary conformations of polymers.

Long-range transfer of excitation energy from excited donor to acceptor molecules, i.e. the direct energy transfer (DET), has attracted a great deal of interest since the pioneering work by Förster on the subject. A considerable effort has been invested to the analysis of decay patterns in liquid or solid systems with random or regular distributions of molecules and with different types of transfer channels.

Motivated by an extensive technological, experimental and theoretical interest in the physics and chemistry of heterogeneous systems, more recent research focused on the question how the internal morphology of the material may influence the relaxation laws, or inversely, on the question whether DET measurements may serve for probing both the local and the global (large scale) structural details of heterogeneous media. In this regard, considerable progress has been achieved in the understanding of the relaxation dynamics in certain types of heterogeneous systems; the decay forms were found out for porous solids and micellar solutions, as well as for systems with fractal distributions of donor and acceptor molecules.

In the present paper we address the problem of the donor decay in model systems, in which acceptor molecules are all located on immobile, randomly arranged polymer chains (see Fig. 1). The theoretical understanding of the relaxation laws in such systems is practically important for the analysis of experimental data on the DET processes in polymer solutions and, besides, may provide a deep insight on the relaxation dynamics in fractal media, since polymer solutions exhibit fractal properties on scales less than polymers’ gyration radii. Exact solutions of this and several related models have been obtained in the particular case of Gaussian chains. Here we focus on the general case of chains having arbitrary conforma-
Fig. 1. Direct energy transfer in polymer systems. An open circle denotes an excited donor molecule, closed circles denote acceptors. The parameter $\xi$ is the radius of the acceptor-free void.

...tions and derive explicit forms for the decay laws, employing the optimal-fluctuation method. We show that actually the exponents characterizing the donor decay depend on the polymer’s conformations, and thus the DET measurements may be a source of useful information on the intrinsic properties of polymer solutions.

We start with the formulation of the problem and notations. Consider a single immobile donor molecule, located at the origin, and an array of immobile acceptor molecules placed at positions $\{r_j\}$, $r_j$ being the radius-vector of the $j$-th acceptor. For the moment we do not specify the geometrical restrictions imposed on $\{r_j\}$. The rate of energy transfer to the $j$-th acceptor molecule is denoted by $W(r_j)$. We consider here only the case of isotropic multipolar interactions, for which

$$W(r) = \frac{W}{r^s},$$

with, e.g. $s = 6$ for dipolar and $s = 10$ for quadrupolar interactions. Disregarding the possibility of the back transfer to the donor and assuming that all acceptors act independently, one has that the decay of a donor for a given realization $\{r_j\}$ of the spatial distribution of acceptors is described by the function

$$F(t; \{r_j\}) = \exp(-t \sum_j W(r_j)).$$

The property which is measured in experiments of direct energy transfer is not, however, the realization-dependent function in (2), but rather the global decay function

$$\Phi(t) = \langle \exp(-t \sum_j W(r_j)) \rangle,$$

where the brackets denote the average over all configurations of $\{r_j\}$.

Let us adapt now the optimal-fluctuation method to the system under study. Consider some given realization $\{r_j\}$ and, as depicted in Fig. 1, denote as $\xi$ the distance between the donor and the nearest acceptor. Neglecting next the fluctuations...
in the spatial distribution of acceptors outside the acceptor-free void (Fig. 1), we have
\[
F(t; \{r_j\}) \approx \exp(-n_A t \int_\xi^\infty r^{d-1}drW(r)),
\]
where \(n_A\) denotes the average acceptors’ density. The radius \(\xi\) is a random variable, and knowing its distribution function \(P(\xi)\) we may estimate the function in (3) as
\[
\Phi(t) \approx \int d\xi P(\xi) \exp(-n_A t \int_\xi^\infty r^{d-1}drW(r)).
\]
(5)

The form of the distribution function \(P(\xi)\) depends on the details of the acceptors’ placement. Particularly, in the situation when all acceptors are placed at random and independently of each other, \(P(\xi) \approx \exp(-n_A \xi^d)\). Substituting such a form of \(P(\xi)\) into (5) and evaluating the integral using the steepest-descent method, we arrive at the conventional Förster-type decay law
\[
\Phi(t) \approx \exp(-n_A (Wt)^{d/s}).
\]

Next, we briefly discuss how the form of \(P(\xi)\) can be derived for the situation depicted in Fig. 1, when all acceptors are attached to polymers (\(N\) acceptors per polymer, the length of each polymer is \(L\) and the mean concentration of polymer chains is \(n_p, n_A = n_p N\)). A more complete analysis of this problem can be found in [9, 10]. In this case, the probability of having an acceptor-free (or, in other words, polymer-free) void of radius \(\xi\), can be represented as a product
\[
P(\xi) = P_{end}(\xi) P_{surf}(\xi),
\]
(6)
where the first multiplier defines the probability that a given void of radius \(\xi\) contains no polymer ends, while the second one defines the conditional probability that no polymer chain, whose end is placed outside the void, crosses the surface of the void. Since the polymers’ ends are uniformly distributed in space, \(P_{end}(\xi) \approx \exp(-n_p \xi^d)\). The second multiplier can be also found explicitly if one invokes the analogy between the conformational statistics of polymers and the statistics of random walks. It appears then that \(P_{surf}(\xi)\) equals the probability that an immobile particle of radius \(\xi\) survives until time \(N\) in the presence of a concentration \(n_p\) of traps performing random motion, i.e. equals the survival probability in the so-called ”target” problem [11, 12]. This gives
\[
P(\xi) \approx \exp(-n_p \xi^d - n_p l^{d_f} N\xi^{d-d_f}),
\]
(7)
where \(l\) denotes the mean distance between the acceptors occupying a given polymer chain (\(l = L/N\)) and \(d_f\) is the fractal dimension of polymers, which relates the polymers’ radius of gyration, \(R_g\), to its contour length \(L\), \(R_g \sim L^{1/d_f}\). For Gaussian coils \(d_f = 2\), while for the swollen coils (self-avoiding walks) \(d_f\) is inverse to the Flory exponent, \(d_f = (d + 2)/3\).

Now, inserting (7) into (5) and taking advantage of the steepest-descent method, we have that in systems with polymerized acceptors the decay of \(\Phi(t)\) displays two
different regimes. At intermediate times, such that $t < \tau_g/N$, $\tau_g = R_g^s/W$, the donor decay is described by

$$\Phi(t) \approx \exp(-n_A t^{d_f(1-z)}(W t)^z), \quad \text{with } z = \frac{d - d_f}{s - d_f},$$

which thus depends explicitly on the polymer conformations. For 3D solutions of Gaussian polymers we get from (8) $z = 1/(s - 2)$, ($z = 1/4$ for $s = 6$), while for rod-like or swollen polymers (8) yields $z = 2/(s - 1)$, ($z = 2/5$ for $s = 6$) and $z = 4/(3s - 5)$, ($z = 4/13$ for $s = 6$) respectively. At large times, $t \gg \tau_g/N$, the global decay function attains the Förster-type time dependence

$$\Phi(t) \approx \exp(-n_p(W N t)^{d/s}),$$

which is universal, i.e. independent of the conformational properties of polymer chains. A dependence such as in (9) can be expected on physical grounds, since the long-time behavior of $\Phi(t)$ mirrors the large scale properties of polymer solutions, when, due to the fact that all polymers are of a finite extent, each chain can be viewed as being an ”effective” point acceptor of strength $W N$. We note, however, that the decay in (9) will be accessible experimentally only for very diluted polymer solutions, when $n_p R_g^d \ll 1$. In the opposite case, the bulk of excited donors will be deactivated at the intermediate time regime, described by (8).

**Acknowledgements**

A.B. acknowledges financial support by the Deutsche Forschungsgemeinschaft (SFB 60) and by the Fonds der Chemischen Industrie; G.O. acknowledges support from the FNRS, Belgium; J.D.C. and M.M. are partially supported by the COST Project D5/0003/95. The research of S.F.B. is supported by the ONR Grant N 00014-94-1-0647 and by the PAST Programme of the French Ministry of Education.

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