Energy Migration and Transfer Between Chromophores Embedded in Gaussian Space

S. Blonski[1] and K. Sienicki[2]

We have used a Monte Carlo method to investigate energy migration and transfer between chromophores embedded in Gaussian space. In using this method we have obtained fluorescence quantum yields, fluorescence depolarization, and the respective decay profiles of donor fluorescence. It was shown that all photophysical observables are dependent upon the number of donor and acceptor chromophores and upon the Förster radii ratio. The latter feature is particularly interesting, and it indicates the existence of correlations between donor and acceptor chromophores. It was shown that the excitation of the donor chromophore at the origin leads to different values of observables, in comparison with an excitation of a randomly selected donor chromophore. The results presented show the importance of the averaging procedures needed to be developed while dealing with specific distribution functions, as, for example, in the case of energy migration and trapping in aromatic polymers and copolymers.

INTRODUCTION

In the past decade there has been a rapid development of experimental and theoretical contributions studying the physical and chemical properties of molecules embedded in media with specific distribution functions [1–6]. The approach to analyze properties and molecular processes by using more realistic distribution functions than uniform and random ones is a natural continuation of the previous studies. An abundance of molecular systems is governed by specific spatial relations which, in the final effect, reflect their mechanical, electrical, etc., properties [1–3]. Among many others, organic and inorganic polymers have specific distribution functions of distances between monomer units [4–6].

Many experimental methods have been used to ob-

tain insight into the specific structure of molecular systems. It is difficult to judge which particular method is the most universal. However, laser techniques and laser fluorescence spectroscopy appear to have several advantages: among others, a sensitivity and pico to steady-state resolution. In a typical fluorescence experiment, one can observe fluorescence from a molecule embedded in a specific geometry and/or medium without a uniform dependence of distances. By measuring transient photophysical observables as donor fluorescence decay profiles, it is possible to estimate by a fitting procedure the fractal dimension of the system under investigation [7]. Although a number of physical systems have a fractal structure, there is perhaps an even larger number of molecular systems which do not have fractal properties and their dimensionality is not integer [7]. The dimensionality of the system is only one parameter which determines its properties. The second parameter is, as we mentioned above, the nature of the distribution functions of the molecules forming the system. Those two parameters are crucial for photophysical studies.

[1] Center for Materials Characterization, University of North Texas, Denton, Texas 76203-5308.
[2] Institute of Technical Physics and Applied Mathematics, Technical University of Gdansk, 80-952 Gdansk, Poland.

The problem of energy transfer and energy migration in molecular systems has been addressed in many theoretical and experimental papers [8]. Although progress in this subject is impressive, several important problems remain. We discuss only two problems associated with energy migration and transfer in molecular systems. Those problems are dimensionality and the distribution functions.

Only in the case of three-dimensional systems with a uniform and random distribution of molecules were satisfactory solutions obtained when using self-consistent diagrammatic solutions of the Pauli Master equation [9]. In spite of many other features, the results obtained have shown that photophysical observables are dependent upon the concentrations of donor and acceptor molecules as well as upon the ratio of Förster radii of acceptor and donor molecules [9]. The mathematical difficulties encountered for two- and one-dimensional systems did not give the expected Förster radii dependence of photophysical observables for those dimensionalities [10]. However, using Monte Carlo simulations we have shown [11] that in two-dimensional Langmuir-Blodgett films, the expected Förster radii dependence of the experimental observables exists in those systems.

In the works mentioned, the common assumption of a uniform and random distribution of molecules in the medium was taken into consideration. Only recently have several authors investigated the process of energy transfer and migration in the systems with specific distribution functions [12–14]. In this case the well-known problems of averaging for uniform and random distributions are even more complicated by the fact that the spatial distribution of molecules is different for each molecule. Only in the case of one-step energy transfer on fractal structures and in restricted geometries were satisfactory solutions obtained and experimentally verified [15]. In a similar way a number of photophysical observables were calculated for chromophores attached to a polymer chain under the assumption of a Gaussian distribution of distances between each of them [13]. This assumption holds for an end-to-end distance of the polymer chain in Θ conditions. However, the intrachain distribution functions have a complicated and not fully known form [16]. The theoretical approach in a description of energy migration and transfer for nonuniform spatial distribution functions, as, for example, in polymeric systems, remains an open and difficult question.

In this paper we present Monte Carlo simulations of energy migration and energy transfer in a polymer-like system of which chromophores are embedded in a Gaussian space. We show that photophysical observables such as fluorescence quantum yield, fluorescence depolarization, and respective fluorescence decay profiles depend on the concentration of chromophores and the Förster radii ratio. The importance of the averaging procedures in the case of specific distributions of chromophores is also shown.

SPECIFICS OF THE SIMULATION

Suppose that we have N chromophores distributed in a Gaussian fashion around the origin. Let $p_i(t)$ be the probability that the ith chromophore is excited at time t. Then the dynamics of the excitations among the chromophores are described by the Pauli Master equation,

$$dp_i(t)/dt = -\tau^{-1}p_i(t) - \sum_{\substack{j=1 \\ j \neq i}}^{N} k_{ji}^{DD}p_i(t)$$
$$- \sum_{j=1}^{M} k_{ji}^{DA}p_i(t) + \sum_{\substack{j=1 \\ j \neq i}}^{N} k_{ij}^{DD}p_j(t) \quad (1)$$

for $i = 1, ..., N$. In Eq. (1) τ is the lifetime of the donor fluorescence, and k^{DD} and k^{DA} are the rate constants for energy migration between donor chromophores and energy transfer from the donor to the acceptor chromophore, respectively. The macroscopic observables, such as the donor chromophore fluorescence decay $G^D(t)$, the decay profile of the originally excited donor chromophore $G^S(t)$, the donor chromophore fluorescence quantum yield η, and the donor chromophore fluorescence depolarization r/r_o, can be calculated for Eq. (1). The respective analysis of a numerical solution of the Pauli Master equation was recently discussed [17].

To perform a Monte Carlo simulation of energy migration and transfer, one has to specify the respective rate constants for those processes. Because we are preliminarily interested in resonance interactions between chromophores, the rate constants are in the form given by Förster [18]:

$$k_{ij}^{DD} = \tau^{-1} (R_{ODD}/r_{ij})^6 \quad (2)$$
$$k_{ik}^{DA} = \tau^{-1} (R_{ODA}/r_{ik})^6 \quad (3)$$

where $r_{ij(k)}$ is the distance between the ith and the jth (kth) chromophore. R_{ODD} and R_{ODA} are the Förster radii for donor–donor and donor–acceptor excitation transfer, respectively. One should note that the orientational factor is omitted in Eqs. (2) and (3). One general method to simulate an arbitrary nonuniform probability distribution was proposed by Metropolis et al. [19]. This method is a special case of an acceptance-rejection method due to von Neumann, which we used in a simulation of a Gaussian distribution of molecules [19]. The distri-

bution of donor and acceptor chromophores was simulated in spherical coordinates (φ, Θ, r). The angles were generated using the inverse transform method to obtain a uniform spherical distribution of chromophores. The distances between the origin and the chromophore were simulated using the acceptance-rejection method according to the Gaussian distribution

$$u(r) = 4\pi(3/(2\pi\sigma^2))r^2 \exp(-3r^2/2\sigma^2) \quad (4)$$

where σ is the mean-square end-to-end distance. We have chosen the unit of length $\sigma = (3/2)^{1/2}$. Within that unit a comparison function was chosen to be

$$w(r) = 1/[1 + 4(r - 1)^2] \quad (5)$$

We generated a uniform random number in the interval $[0, A]$ [where A is the total area under the curve $w(r)$], which was used to obtain a corresponding value of r distributed according to $w(r)$. For the value of r, we obtained a uniform random number ρ in the interval $[0, w(r)]$. If $\rho \leq u(r)$, then we accepted r as a random number distributed according to the Gaussian distribution. Otherwise, we repeated the procedure.

The presented simulations were performed for $R_{ODD} = 0.2$, which means that R_{ODD} was equal to $0.2 \ (3/2)^{1/2} \sigma$. The results of the simulations were averaged over 1000 configurations of chromophores for each number of donor and acceptor chromophores.

RESULTS AND DISCUSSION

We mentioned in the Introduction that there is no satisfactory theoretical description of transport processes in nonuniform molecular systems. Before performing Monte Carlo simulations for donor–acceptor chromophores embedded in Gaussian space, it was appropriate to check our computer programs with more reliable theory and experimental data. Therefore, we have simulated energy migration and transfer in a three-dimensional two-component donor–acceptor system with a random and uniform distribution of chromophores [17]. The results obtained for quantum yields, fluorescence depolarization, and fluorescence decay profiles were in excellent agreement with the theoretical models, experimental results, and our and other simulations. The simulations performed revealed two important features. The first feature shows that the isotopic rate constants (no orientational factor) give an excellent description of an excitation transport phenomena. The second feature shows that all photophysical observables are dependent not only on the concentration of molecules, but also on the Förster radii ratio R_{ODA}/R_{ODD} [9]. This particular dependence is the

indicator that not only is excitation transport influenced by successive donor configurations but also it is dependent on successive acceptor configurations. This Förster radii ratio dependence was observed for three-dimensional systems [9,17] and recently communicated for two-dimensional Langmuir-Blodgett films [11]. The following question arises: Does the transport behavior in nonuniform systems, as, for example, in an aromatic polymer, have the same characteristics? We show that indeed this is the case.

Quantum Yields

Figure 1 depicts the dependence of the relative quantum yield η/η_0 as a function of the number of donor chromophores for three Förster radii ratio and a constant number of acceptor chromophores. The respective quantum yields were simulated by assuming that every donor chromophore can be excited by an external light pulse. One can easily see two characteristics. The first is that the relative quantum yield of donor fluorescence strongly depends upon the Förster radii ratio. This Förster radii ratio dependence for donor and acceptor chromophores embedded in a Gaussian chain is much more profound than a similar dependence for a uniform distribution of chromophores. The second characteristic is that the relative quantum yield is almost independent of the concentration of donor chromophores which participate in the energy migration process. This behavior is even more unusual in comparison to a uniform distribution of donor
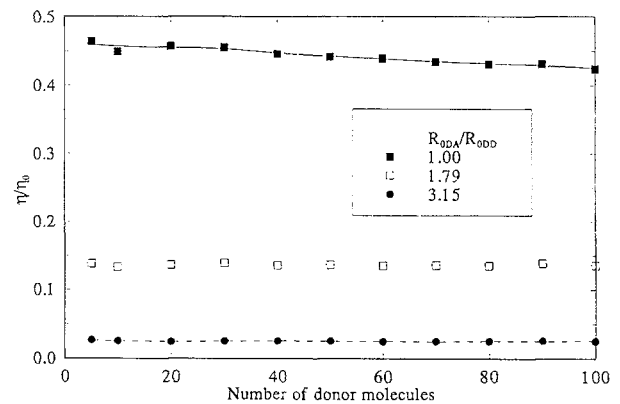

Fig. 1. The relative quantum yield η/η_0 of donor fluorescence as a function of the number of donor chromophores and a constant number (100) of acceptor chromophores for three ratios of Förster radii. The values of the relative quantum yield were obtained under the assumption that every donor chromophore can be excited by an external light pulse.

and acceptor chromophores, where a strong concentrational dependence of donor quantum yields is observed.[3]

It is obvious that in the case of a nonuniform distribution, one has to deal with the problem of different configurations of chromophores. To illustrate this particular problem, we have performed Monte Carlo simulations of relative quantum yields of donor fluorescence under the assumption that the donor chromophore which is closest to the origin is excited by an external light pulse. The results obtained are depicted in Fig. 2. One can see that, in comparison with the results presented in Fig. 1, the donor fluorescence quantum yield is much lower than in the case of random excitation. However, as in the case of random excitation, the donor fluorescence quantum yield does not depend upon the concentration of donor chromophores. Figure 2 has important theoretical implications. It gives insight into the necessity of an individual averaging over every donor and acceptor configuration.

Fluorescence Depolarization

While relative quantum yields of donor fluorescence are almost uninfluenced by the concentration of donor chromophores, the changes of donor fluorescence
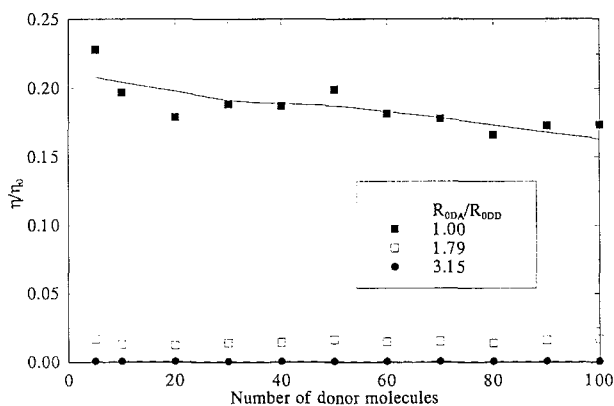

Fig. 2. The relative quantum yield η/η_0 of donor fluorescence as a function of the number of donor chromophores and a constant number (100) of acceptor chromophores for three ratios of Förster radii. The values of the relative quantum yield were obtained under the assumption that the donor chromophore closest to the origin is excited by an external light pulse.

[3] A direct comparison of Monte Carlo simulations for chromophores embedded in a Gaussian chain and uniform space is difficult. This difficulty arises from the fact that simulated chromophores are distributed in a Gaussian volume, contrary to a uniform distribution, where chromophores are distributed in whole space.

depolarization are more visible, as shown in Figs. 3 and 4. Similarly to observations made from changes of donor fluorescence quantum yields, donor fluorescence depolarization is dependent upon the concentration of chromophores as well as the Förster radii ratio. One should also note that fluorescence depolarization is sensitive to the selection of a chromophore which was originally excited. In Fig. 3 all donor chromophores were originally excited with the same probability, and in Fig. 4 the do-
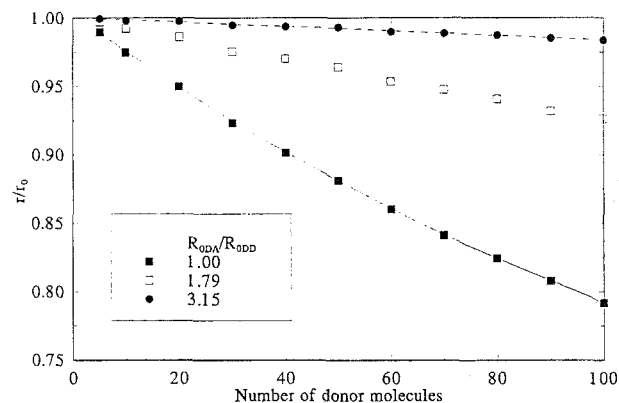

Fig. 3. The donor fluorescence depolization r/r_0 as a function of the number of donor chromophores and a constant number (100) of acceptor chromophores for three ratios of Förster radii. The values of donor fluorescence depolarization were obtained under the assumption that every donor chromophore can be excited by an external light pulse.
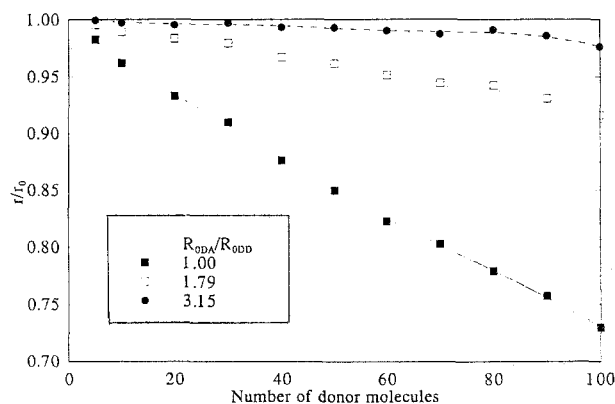

Fig. 4. The donor fluorescence depolarization r/r_0 as a function of the number of donor chromophores and a constant number (100) of acceptor chromophores for three ratios of Förster radii. The values of donor fluorescence depolarization were obtained under the assumption that the donor chromophore closest to the origin is excited by an external light pulse.

nor chromophore which is closest to the origin was originally excited.

The decrease in fluorescence depolarization as a function of the concentration of donor and acceptor chromophores depicted in Figs. 3 and 4 is rather slow, and much slower than the similar changes observed in a three-dimensional random and uniform distribution of chromophores. A much more profound change of fluorescence depolarization was observed for the one-component system (only donor chromophores), as shown in Fig. 5. However, as in the case of the two-component system (donor and acceptor chromophores), the decrease in fluorescence depolarization is much slower than for the one-component donor system with a uniform distribution of chromophores.

In the Introduction, we mentioned that a polymer chain can be modeled as a random walk, self-avoiding walk, or random walk in disordered lattice [16]. However, regardless of the situation, the probability density for finding the end-to-end distance of the walk in a polymer consisting of N monomer units is given by the Gaussian-like equation. In the case of aromatic polymers, the role of the acceptor is assumed by the excimer, which acts as a trap for the migrating excitation energy along chromophores [20]. For the sake of simplicity, we assume in the following considerations that the excimer is not dissociating, as, for example, in the case of polystyrene at room temperature [20]. Because the excimer does not exist in the ground state, we assume that the Förster critical radii for the transferring of excitation energy from a monomer to a monomer forming excimer
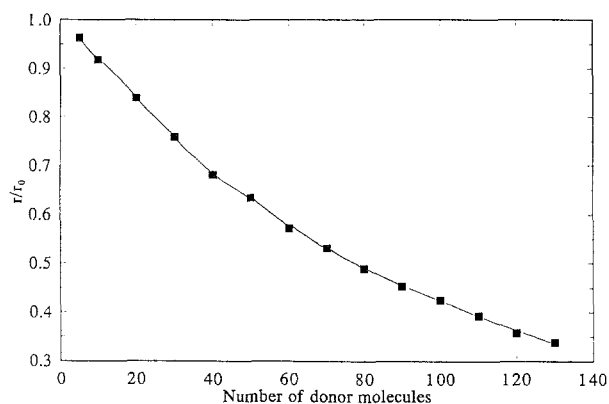
site is the same as for energy migration between monomers, $R_{ODA}/R_{ODD} \equiv 1$. In Fig. 6 we have shown changes of the relative quantum yield and of fluorescence depolarization for a constant number of monomers and a different number of excimers (traps). Obviously, there is no Förster radii dependence, and the general changes of the relative quantum yield and fluorescence depolarization are in accordance with the above-discussed results. At this point we are concerned mostly with energy migration and trapping in aromatic polymers. It was shown, on the basis of quantum mechanical considerations [21], that in the case of polystyrene, excimers are formed in meso-tt dyads of which the concentration at Θ conditions is very low, about 4%. If we assume that the polystyrene chain contains 100 mers, then the concentration of excimers is approximately 4. The concentration of excimers can be increased by casting the polystyrene film where one can observe a significant increase in excimer fluorescence [22]. There is no unified agreement, however, and most of the authors suggest that the increase in excimer fluorescence observed in the polystyrene film is due to an additional intermolecular excimer formation. Although the concentration of intermolecular sites is not precisely known, it cannot be too high because a low intensity of monomer fluorescence is observed even in the film. Returning to the results depicted in Fig. 6, one can note that for the simulated Gaussian distribution of molecules, the changes of the relative quantum yield of monomer fluorescence are not comparable to those observed experimentally. One should also note that an increase in excimer con-
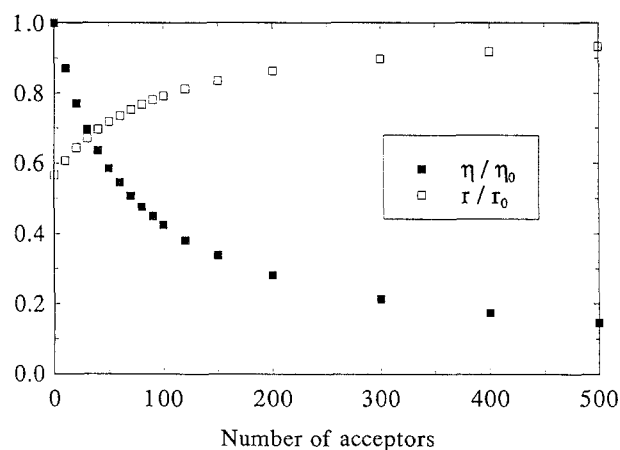
Fig. 5. The donor fluorescence depolarization r/r_0 as a function of the number of donor chromophores for a one-component system. The values of donor fluorescence depolarization were obtained under the assumption that every donor chromophore can be excited by an external light pulse.

Fig. 6. The relative donor fluorescence quantum field (■) and donor fluorescence depolarization (□) as a function of the number of acceptor chromophores for a constant number of donor chromophores, 100.

centration leads to an increase in donor fluorescence anisotropy, as shown in Fig. 6.

Fluorescence Decays

We have discussed above the steady-state photophysical observables, such as the fluorescence quantum yield and fluorescence depolarization. However, one can use transient measurements to investigate these interesting systems. Under Quantum Yields, we have shown that transient and steady-state observables are interrelated. In the case of transient studies two observables can be investigated: the decay profile of the originally excited donor chromophores $[G^S(t)]$ and the decay of the donor chromophores $[G^D(t)]$. $G^S(t)$ gives us insight into energy migration, while $G^D(t)$ is related to the total transport properties of the system. Figure 7 depicts the decay of the originally excited donor chromophores for a constant concentration of donor chromophores and a variable concentration of acceptor chromophores. Similarly to the case of steady-state observables, one can notice two features. First, the decay of $G^S(t)$ is very slow, and second, the influence of the acceptor concentration is rather small in comparison to the respective system with a uniform and random distribution of chromophores. A similar behavior is observed for $G^D(t)$ decay as shown in Fig. 8.
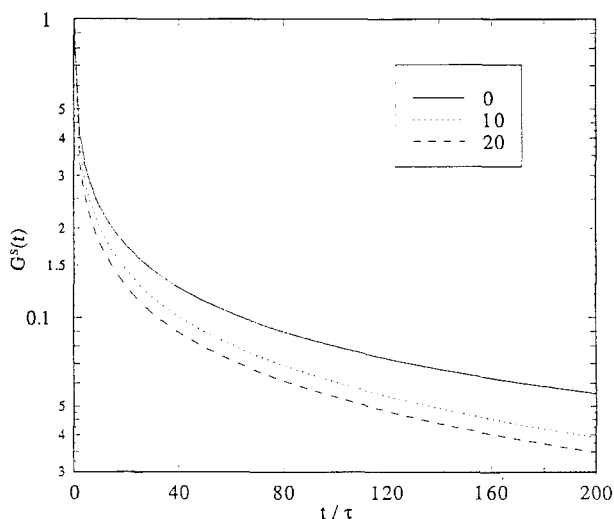
Fig. 8. The decay profiles of donor fluorescence $[G^D(t)]$ for a constant number of donor chromophores (100) and two numbers of acceptor chromophores: 10 and 20, respectively.

SUMMARY AND CONCLUSIONS

In this paper we have investigated energy transfer and migration between chromophores of polymer-like molecules embedded in a Gaussian space. It was shown that all photophysical steady-state and transient observables are very strongly influenced by the distribution function in comparison to the uniform and random distribution. However, contrary to the uniform and random distribution, photophysical observables are very weakly dependent on donor and acceptor concentrations. It was also shown that all observables are strongly dependent upon the Förster radii ratio. A similar dependence is observed for uniform and random distributions. However, embedding chromophores in a Gaussian space leads to a more significant influence of the Förster radii ratio on photophysical observables.

ACKNOWLEDGMENT

Fig. 7. The decay profile of originally excited donor chromophores $[G^S(t)]$ for a constant number of donor chromophores (100) and three numbers of acceptor chromophores: 0, 10, and 20, respectively.
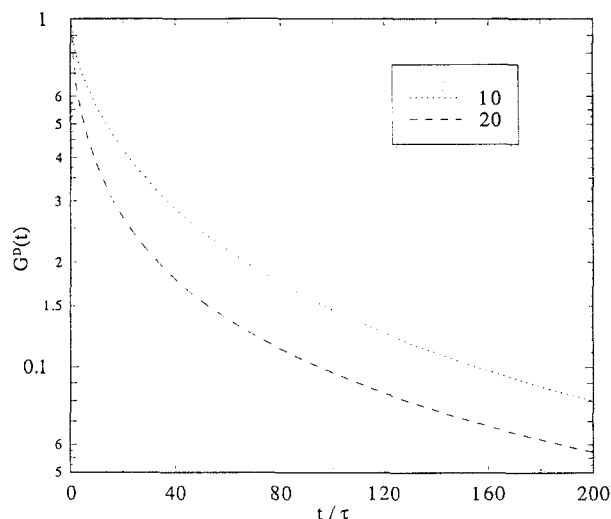
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