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Electronic energy transfer between molecules diffusing on spherical particles: approximate expressions for the decay law of the donor

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Abstract

The problem of dipole–dipole energy transfer with diffusion on spherical particles is studied theoretically. Simple approximate expressions that can be used to predict or evaluate the effect of diffusion are obtained from a detailed numerical analysis of the diffusion equation. The results cover a wide range of situations, from the static limit to the rapid diffusion limit, and should apply to most energy transfer processes in spherical particles. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Electronic excitation energy transfer (ET) by the dipole–dipole or Förster mechanism is a well-established tool for the study of nanometer-sized systems such as supermolecules [1–3], macromolecules [4], colloids [5,6], biological systems [7] and interfaces [8]. The probability of ET depends strongly on the intermolecular distance, relative orientation and relative motion of donor and acceptor chromophores. In this way, the kinetics of molecular luminescence in the presence of ET reflects both structural and dynamical aspects and information on these can be obtained from fluorescence or phosphorescence intensity and anisotropy decays.

In most cases of interest, the fluorescence decay and accompanying transfer processes occur on a time scale much shorter than that of translational diffusion and the system can be treated as diffusionless. There are, however, systems where the chromophores, whether free to move or bound to a mobile structure, may have fast relative motion. In these cases, diffusion can be significant during the chromophore's excited state lifetime. One such situation refers to solute molecules located in the superficial region of micelles. A semi-quantitative discussion of the problem, based on experimental diffusion coefficients, showed that for typical lifetimes and moderate to large critical radii for transfer, diffusion effects on ET are negligible [9]. This corresponds to most experimental cases [9–12]. However, in the opposite situation, i.e. long lifetimes and short critical radii, the situation approaches that of collisional quenching [5,6,13–15] and the role played by diffusion becomes essential.

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Recently, Matzinger et al. [16] considered this problem in detail from a theoretical point of view. They have written the diffusion equation for the relative motion of two particles on the surface of a sphere. A distance of closest approach was also incorporated in the model. The ensemble decay laws, for both reversible (donor–donor) and irreversible (donor–acceptor) transfers, based on the independent-pair approximation, were then obtained. The diffusion equation was numerically solved and the corresponding decay laws compared with the results of a Monte Carlo simulation of the same problem. Good agreement between the two methods was found. The general conclusion reached in Ref. [9], namely that for typical lifetimes and moderate to large critical radii for transfer diffusion effects on ET are negligible, was confirmed.

Although quantitative results were obtained, both numerically and by simulation, no approximate expressions that can be used to predict or evaluate the effect of diffusion were given in the paper mentioned [16].

It is the purpose of the present work to obtain such relations for the irreversible ET case, from a detailed numerical analysis of the previously derived diffusion equation [16]. The results obtained should apply to other types of spherical particles, provided the assumptions made are valid.

2. Model

We assume that excitation transfer occurs among non-interacting chromophores lying on the surface of monodisperse spherical particles of radius R (see Fig. 1). There are two types of chromophores (donors and acceptors) which have a smaller size than that of the particle. At the initial time $t=0$ only donors are excited. ET occurs irreversibly from the excited donor to one of the acceptors. ET and other interactions between donors are neglected. Donor–acceptor coupling mediated by the particle is also not considered. The spherical particle concentration is chosen to be low, so that excitation transfer between different spherical particles can be excluded. Chromophores are allowed to diffuse on the surface of the spherical particle, their relative diffusion constant being $D = D_D + D_A$, where D_D and D_A are the lateral diffusion constants of the donor and the acceptor, respectively. Without loss of generality, the initially excited donor can be considered to be immobile and the acceptor to move with diffusion constant D. This allows the characterisation of the donor–acceptor distance r by one polar angle θ only (see Fig. 1)

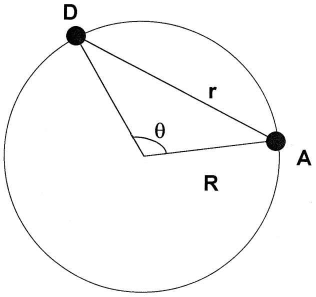

Fig. 1. Geometry and variables for a donor–acceptor pair located on the surface of a spherical particle.

$$r = \sqrt{2R^2(1-\cos\theta)}\ . \tag{1}$$

The equations describing the relative diffusion of a pair on a spherical surface, with a long-range interaction term, which is a particular case of the more general problem of diffusion with reaction [17], were obtained in Ref. [16]. The donor decay is determined by the two-particle survival probability $S(\theta,t)$ which satisfies the equation

$$\frac{\partial}{\partial t}S(\theta,t) = \left[D\nabla_\theta^2 - w(\theta)\right]S(\theta,t)\,. \tag{2}$$

$S(\theta,t)$ is the probability density that the excited donor and the acceptor are at the distance r at time t and,

$$D\nabla_\theta^2 = \frac{D}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right]. \tag{3}$$

This probability is time-dependent owing to both molecular diffusion and donor–acceptor ET with rate $w(\theta)$. For the dipole–dipole mechanism of ET one has

$$w(\theta) = w(r) = \frac{1}{\tau_0}\left(\frac{R_0}{r}\right)^6 = \frac{1}{\tau_0}\frac{R_0^6}{\left[2R^2(1-\cos\theta)\right]^3}\,, \tag{4}$$

where τ_0 is the lifetime of the excited donor and R_0 is the critical (or Förster) radius [18], computed with an orientational factor of $2/3$ (fast and isotropic rotational motion is assumed).

Eq. (2) is solved with the reflecting boundary condition

$$2\pi R^2 \sin\theta_c D \frac{\partial}{\partial\theta} S(\theta,t)|_{\theta=\theta_c} = 0 . \qquad (5)$$

The physical meaning of this condition being that the donor and acceptor cannot be nearer than the distance of closest approach

$$r_c = \sqrt{2R^2(1-\cos\theta_c)} , \qquad (6)$$

which depends on the effective radii of the donor and acceptor.

At initial time $(t=0)$ the relative distribution of excited donors and acceptors is random and homogeneous, hence

$$S(\theta,0) = 1/(1+\cos\theta_c) . \qquad (7)$$

The denominator of Eq. (7) ensures the fulfilment of the normalisation condition

$$\int_{\theta_c}^{\pi} S(\theta,0) \sin\theta \, d\theta = 1 .$$

In the general case in which one donor is surrounded by several acceptors positioned at the angular positions $\theta_1 \ldots \theta_N$, the excited donor survival probability density, $P(\theta_1 \ldots \theta_N, t)$, is expressed as a product of independent two-particle probability densities because ET from the donor to one acceptor does not depend, to a good approximation, on the presence of other acceptors

$$P(\theta_1 \ldots \theta_N, t) = \prod_{i=1}^{N} S(\theta_i, t) . \qquad (8)$$

This approach is valid if the size of the spherical particle is much larger than the size of chromophores. Usually this condition is fulfilled.

To obtain the macroscopic decay one needs to average the survival probability over all positions of θ, as follows:

$$P_N(t) = \int_{\theta_c}^{\pi} \cdots \int_{\theta_c}^{\pi} P(\theta_1 \ldots \theta_N, t) \times \sin\theta_1 \, d\theta_1 \cdots \sin\theta_N \, d\theta_N . \qquad (9)$$

As all the acceptors are equivalent one has

$$P_N(t) = \left[\int_{\theta_c}^{\pi} S(\theta,t) \sin\theta \, d\theta \right]^N = [P_1(t)]^N , \qquad (10)$$

with

$$P_1(t) = \int_{\theta_c}^{\pi} S(\theta,t) \sin\theta \, d\theta .$$

Taking into account the Poisson distribution of acceptors over spherical particles one finally obtains the donor fluorescence decay

$$I(t) = e^{-t/\tau_0} \sum_{N=0}^{\infty} \frac{\bar{N}}{N!} e^{-\bar{N}} [P_1(t)]^N = \exp\{-t/\tau_0 - \bar{N}[1-P_1(t)]\} , \qquad (11)$$

where $\bar{N}$ is the average number of acceptors per spherical particle. For long times and because $P_1(t) \to 0$ when $t \to \infty$,

$$I(t) = \exp\left\{ -\frac{t}{\tau_0} - \bar{N} \right\} , \qquad (12)$$

which is simply the intrinsic decay multiplied by the fraction of spheres without acceptors.

Note that the use of the Poisson distribution is valid if the size of spherical particles is much larger the size of chromophores and if $\bar{N}$ is much smaller than the maximum allowed number of chromophores T that can be placed on the spherical particle surface. Otherwise one should use the binomial distribution [6,19]

$$B_N(\bar{N},T) = \frac{T!}{N!(T-N)!} \left(\frac{\bar{N}}{T} \right)^N \left(1 - \frac{\bar{N}}{T} \right)^{T-N} . \qquad (13)$$

For small $\bar{N}$ and $T > 20$, the Poisson and the binomial (12) distributions give similar results for small N. Thus, in the usual experimental conditions the Poisson distribution is valid.

For $\bar{N} \approx T$ the binomial distribution must be used, and qualitatively different results are obtained. Indeed, in this case all allowed sites are occupied, all spherical particles are equivalent and the luminescence kinetics become exponential:

$$I(t) = \exp\left\{ -\frac{t}{\tau_0} - t\sum_i^T w(\theta_i) \right\}, \tag{14}$$

the summation in Eq. (14) being carried over all allowed positions of the acceptors.

3. Approximate results

For the conditions corresponding to the usual experimental conditions, one can use Eqs. (2), (10) and (11) to calculate the donor decay. Thus, the problem reduces to the calculation of the two-particle probability $S(\theta, t)$. As above mentioned, this was previously done both numerically and by Monte Carlo simulation in Ref. [16].

We tried to solve Eq. (2) with the stated initial and boundary conditions, Eqs. (7) and (5), respectively. For this, the use of the following dimensionless parameters and variables is convenient:

$$t^* = \left(\frac{R_0}{2R}\right)^6 \frac{t}{\tau_0}, \tag{15a}$$

$$D^* = \frac{D\tau_0}{R^2}\left(\frac{2R}{R_0}\right)^6, \tag{15b}$$

$$y = 1 - \cos\theta, \tag{15c}$$

where t^* is the reduced time and D^* is the reduced mutual diffusion coefficient.

With these changes, Eqs. (2), (5) and (7) respectively become

$$\frac{\partial}{\partial t^*} S(y, t^*) = \left\{ D^* \frac{\partial}{\partial y}\left[y(2-y)\frac{\partial}{\partial y} \right] - \frac{8}{y^3} \right\} S, \tag{16a}$$

$$\left.\frac{\partial}{\partial y} S\right|_{y=y_c} = 0, \tag{16b}$$

$$S(y, 0) = 1/(2 - y_c), \tag{16c}$$

with

$$P_1(t^*) = \int_{y_c}^2 S(y, t^*)\, dy \tag{16'}$$

From published experimental data, it can be estimated that the dimensionless diffusion coefficient D^* can take values up to 5000, whereas the parameter y_c characterising the distance of closest approach is typically smaller than 0.03.

3.1. Slow diffusion

To obtain approximate analytical results when diffusion is slow (small D^*) Eq. (16a) is rewritten as follows:

$$\frac{\partial}{\partial t^*} S = (\hat{A} + \hat{B}) S, \tag{17}$$

where $\hat{A}$ and $\hat{B}$ are operators ($\hat{B} = D(\partial/\partial y)[y(2-y)\partial/\partial y]$ and $\hat{A} = -8/y^3$). The formal solution of Eq. (17) is

$$S(y, t^*) = e^{\hat{A}t^*} S(y, 0) + \int_0^{t^*} e^{\hat{A}(t^* - u)} \hat{B} e^{\hat{A}u} S(y, 0)\, du, \tag{18}$$

where $S(y, 0)$ is the initial distribution. Considering that the operator $\hat{B}$ is small in comparison with $\hat{A}$, and using Eq. (18), one can obtain the solution, $S(y, t^*)$, in iterative form

$$S(y, t^*) = S^{(0)}(y, t^*) + S^{(1)}(y, t^*) + S^{(2)}(y, t^*) + \cdots. \tag{19}$$

The zeroth-order approximation is

$$S^{(0)}(y, t^*) = e^{\hat{A}t^*} S(y, 0). \tag{20}$$

The first-order correction is

$$S^{(1)}(y, t^*) = \int_0^{t^*} e^{\hat{A}(t^* - u)} \hat{B} S^{(0)}(y, u)\, du. \tag{21}$$

The second-order correction is

$$S^{(2)}(y, t^*) = \int_0^{t^*} e^{\hat{A}(t^* - u)} \hat{B} S^{(1)}(y, u)\, du, \tag{22}$$

and so on. In accordance with Eqs. (16′) and (19) we obtain the iteration row for two-particle luminescence kinetics

$$P_1(t^*) = P_1^{(0)}(t^*) + P_1^{(1)}(t^*) + P_1^{(2)}(t^*) + \cdots. \tag{23}$$

If the diffusion coefficient is equal to zero (static limit) then $S^{(0)}(y,t^*)=\exp(-8t^*/y^3)$ and the zero-order kinetics are [6,9,16]

$$P_1^{(0)}(t^*)=\exp(-t^*)-(t^*)^{1/3}\Gamma\left(\tfrac{2}{3},t^*\right), \qquad (24)$$

where $\Gamma(a,t^*)$ is the incomplete gamma function

$$\Gamma(a,t^*)=\int_{t^*}^{\infty}\mathrm{e}^{-z}z^{a-1}\,\mathrm{d}z, \qquad (25)$$

Eq. (24) is valid when $y_c=0$ (or $r_c=0$). In real situations, although nonzero, $y_c \ll 1$ and one can check that if $y_c=0.02$ Eq. (24) differs from the exact solution by less than 1%. Similar conclusions were reached by Pilling and Rice [20] for the infinite three-dimensional case. Using the zero approximations $S^{(0)}(y,t^*)$, the first two corrections to the two-particle kinetics were calculated. The first one is

$$P_1^{(1)}(t^*)=\frac{D^*}{2}\Big\{-t^*[3\Gamma(1,t^*)-2\Gamma(2,t^*)] +2(t^*)^{4/3}\left[\Gamma\left(\tfrac{2}{3},t^*\right)-\Gamma\left(\tfrac{5}{3},t^*\right)\right]\Big\}. \qquad (26)$$

The second one has the order $P_1^{(2)}(t^*)\approx \mathrm{O}[(D^*)^2(t^*)^{5/3}]$. Comparing the first and the second approximations one can see that the small parameter is $D^*(t^*)^{2/3}$.

Using Eqs. (24) and (26), we tried to construct the approximate kinetics which would be valid up to a dimensionless diffusion coefficient $D^*\cong 1$.

Firstly, we obtained a simple function describing the zero-order result, Eq. (24), with high accuracy, in the domain $t^*\in[0,2]$. This empirical function is

$$P_{1,\mathrm{ap}}^{(0)}(t^*)=\exp\left[-1.2541(t^*)^{1/3} -1.13(t^*)^{2/3}-0.37t^*\right]. \qquad (27)$$

The coefficient of $(t^*)^{1/3}$ is obtained by expanding Eq. (24) into a power series in t^*. The other two coefficients were obtained using a least-squares criterion. In the interval $t^*\in[0,2]$, functions (27) and (24) are practically indistinguishable.

Secondly, Eqs. (16a), (16b) and (16c) were solved numerically for $D^*\in[0,20]$. Note that chromophore diffusion begins to affect the luminescence kinetics noticeably when $D^*\geq 0.2$. Using Eqs. (26) and (27) and the numerical solution of Eqs. (16a), (16b) and (16c) we constructed the approximate function

$$P_{1,\mathrm{ap}}(t^*)=\exp\Big\{-1.2541(t^*)^{1/3}-1.13(t^*)^{2/3} -0.37t^*(1+1.35D^*) -0.61(t^*)^{4/3}D^*(1-0.05D^*)\Big\}. \qquad (28)$$

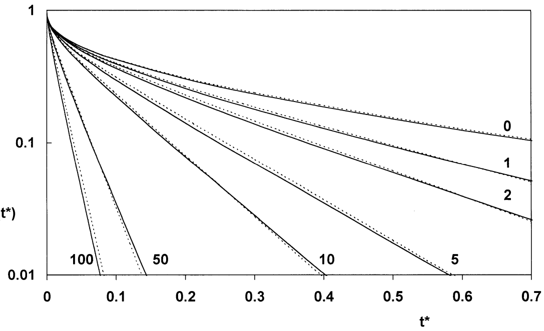

Fig. 2. Function $P_1(t^*)$ in the slow and intermediate diffusion cases. Comparison of the approximate solution (solid line), Eq. (28), with the exact solution obtained by numerical resolution of the diffusion equation (dashed line), for reduced diffusion coefficients D^* varying from 0 (static limit) to 100. The value of D^* is shown next to each pair of curves.

The coefficients 0.61 and 0.05 in Eq. (28) were obtained using a least-squares criterion. If $D^*\leq 20$ then Eq. (28) coincides (with a precision better than 5%) with the exact result obtained by the numerical resolution of Eq. (16a) in the time domain, for $P_{1,\mathrm{ap}}(t^*)\geq 0.05$ (see Fig. 2).

Our calculations show that one can also use Eq. (28) for values $20\leq D^*\leq 100$ (see Fig. 2) if one equates the last term in Eq. (28) to zero.

3.2. Fast diffusion

As noted above, the dimensionless diffusion coefficient D^* can reach values of the order of 10^3. It is therefore interesting to investigate the case of a high diffusion coefficient also.

From a physical point of view, if $D^*\to\infty$ (the so-called rapid-diffusion limit [21]), then the survival probability $S(y,t^*)$ cannot depend on variable y (the position of the acceptor on the spherical particle) because diffusion is so fast that the decrease of the function $S(y,t^*)$ at small y (see Eq. (16a)) is immediately compensated by the acceptor diffusion from large distances ($y \le 2$). Only for finite diffusion coefficients is the survival probability S a function of y. This function, although time-dependent for short times, rapidly attains a stationary distribution, $S_{\rm st}(y)$. Therefore it is natural to look for the solution of Eq. (16a) as a product of two functions (one dependent only on the space coordinate, the other dependent on the time coordinate).

$$S(y,t^*) = S_{\rm st}(y)F(t^*) . \tag{29}$$

Insertion of Eq. (29) into Eq. (16a) and integrating over y, one obtains (taking into account the boundary condition)

$$\frac{\mathrm{d}}{\mathrm{d}t^*}F(t^*)\int_{y_{\rm c}}^{2}S_{\rm st}(y)\,\mathrm{d}y = -F(t^*)\int_{y_{\rm c}}^{2}\frac{8}{y^3}S_{\rm st}(y)\,\mathrm{d}y . \tag{30}$$

Introducing the quantity

$$B = \int_{y_{\rm c}}^{2}\frac{8}{y^3}S_{\rm st}(y)\,\mathrm{d}y \Bigg/ \int_{y_{\rm c}}^{2}S_{\rm st}(y)\,\mathrm{d}y , \tag{31}$$

we obtain the solution

$$F(t^*) = \exp(-Bt^*) . \tag{32}$$

Note that, according to Eq. (31), the parameter B depends only on the shape of the function $S_{\rm st}(y)$ but not on $S_{\rm st}(0)$.

Introducing the solutions (32) and (29) into Eq. (16a) we get

$$\left[\frac{\mathrm{d}}{\mathrm{d}y}y(2-y)\frac{\mathrm{d}}{\mathrm{d}y}\right]S_{\rm st}(y) + \frac{1}{D^*}\left(B-\frac{8}{y^3}\right)S_{\rm st}(y) = 0 . \tag{33}$$

We will look for the solution of this equation in the form of a power series in $1/D^*$,

$$S_{\rm st}(y) = S_{\rm st}^{(0)}(y) + S_{\rm st}^{(1)}(y) + S_{\rm st}^{(2)}(y) + \cdots , \tag{34}$$

where $S_{\rm st}^{(1)}(t^*) = O(1/D^*)$, $S_{\rm st}^{(2)}(t^*) = O(1/D^{*2})$, and so on. As it was noted, for a very large diffusion coefficient ($D^* \to \infty$) the function is not dependent on y and therefore, in the zeroth-order approximation, it follows from Eq. (33) that

$$S_{\rm st}^{(0)}(y) = 1/(2-y_{\rm c}) . \tag{35}$$

Introducing this value into Eq. (31) we have

$$B^{(0)} = (2+y_{\rm c})/y_{\rm c}^2 . \tag{36}$$

Inserting the power series, Eq. (34), into Eq. (33) we obtain the equation for the first-order approximation

$$\left[\frac{\mathrm{d}}{\mathrm{d}y}y(2-y)\frac{\mathrm{d}}{\mathrm{d}y}\right]S_{\rm st}^{(1)}(y) + \frac{1}{D^*}\left(B^{(0)}-\frac{8}{y^3}\right)S_{\rm st}^{(0)}(y) = 0 \tag{37}$$

with

$$\frac{\mathrm{d}}{\mathrm{d}y}S_{\rm st}^{(1)}(y)\bigg|_{y=y_{\rm c}} = 0 .$$

The solution of this equation is

$$S_{\rm st}^{(1)}(y) = \frac{1}{D^*(2-y_{\rm c})}\left[\frac{1}{y^2}+\frac{1}{y} + \frac{C_1-1}{2}\ln y - C_2\right], \tag{38}$$

with

$$C_1 = B^{(0)}y_{\rm c} + \frac{4}{y_{\rm c}^2} ,$$

and

$$C_2 = \frac{3}{4} + \frac{C_1-1}{2}\ln 2 .$$

Inserting the function $S_{\rm st}(y)$, Eq. (38), obtained with precision up to the first order, into Eq. (31), and taking into account the condition $y_{\rm c} \ll 1$, a more exact value of B is obtained:

$$B = \frac{2}{y_{\rm c}^2}\left(1-\frac{2\ln(1/y_{\rm c})}{D^* y_{\rm c}^2}\right) . \tag{39}$$

So, as the minimum distance r_c between donors and acceptors is connected with the parameter y_c by the equation $r_c^2 = 2R^2 y_c$,

$$B = 8\left(\frac{R}{r_c}\right)^4\left(1 - \frac{R_0^6 \ln(2R^2/r_c^2)}{8D\tau_0 r_c^4}\right). \tag{40}$$

We see from Eq. (40) that the small parameter in the case of fast diffusion is $R_0^6 \ln(2R^2/r_c^2)/(D\tau_0 r_c^2)$. The rapid-diffusion limit (results independent of D^*) is attained when the second term is negligible.

Knowing parameter B, we can calculate the two-particle function from Eq. (16′)

$$P_1(t^*) = \exp(-A - Bt^*), \tag{41}$$

where

$$\exp(-A) = \int_{y_c}^{2} S_{st}(y)\,\mathrm{d}y = 1 - \frac{2}{D^* y_c^2} \tag{42}$$

and

$$A \approx \frac{2}{D^* y_c^2} \ll 1. \tag{43}$$

Using the Poisson distribution of acceptors, one obtains for the decay

$$I(t) = \exp(-t/\tau_0)\exp\{-\bar{N}(1 - \mathrm{e}^{Bt^*})\}. \tag{44}$$

Thus, the average decay takes a form identical to that of a quenching process with a time-independent rate constant [5,6]. The rate constant is in this case,

$$k = B\frac{t^*}{t} = \frac{R_0^6}{8\tau_0 r_c^4 R^2}. \tag{45}$$

Eqs. (16a), (16b) and (16c) were solved numerically for $D^* \geq 100$. Indeed, if $D^* \geq 100$ the two-particle decay can be written with good accuracy as

$$P_1(t^*) = \exp(-A - Bt^*), \tag{46}$$

where A and B are numerical parameters, see Fig. 3. These parameters depend on D^* and y_c (see Figs. 4 and 5). If y_c increases (r_c increases) then the parameter A decreases and the parameter B increases. Parameter B was obtained with a numerical precision ±1, and the precision of parameter A was ±0.01. The dependence of parameters A and B on

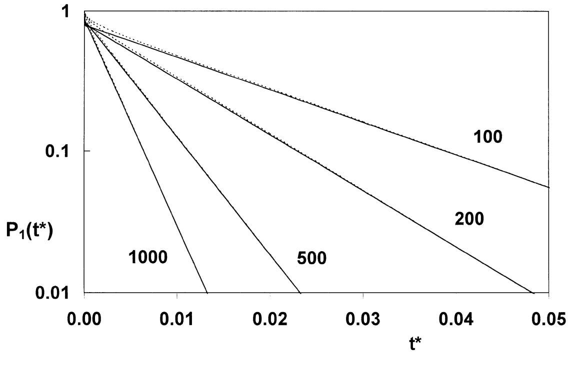

Fig. 3. Function $P_1(t^*)$ in the fast diffusion case. Comparison of the approximate solution (solid line), Eq. (46), with the exact solution obtained by numerical solution of the diffusion equation (dashed line), for reduced diffusion coefficients D^* varying from 100 to 1000. The value of D^* is shown next to each pair of curves.

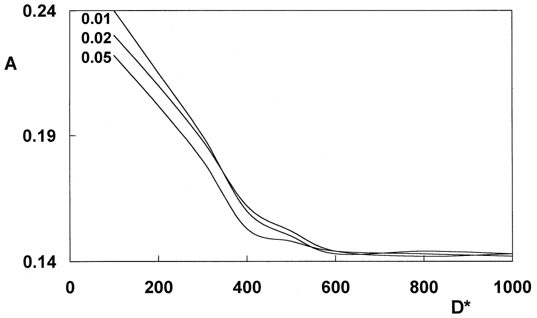

Fig. 4. Fast diffusion case. Dependence of parameter A appearing in Eq. (46) on D^* and on y_c. The value of y_c is shown next to each curve.

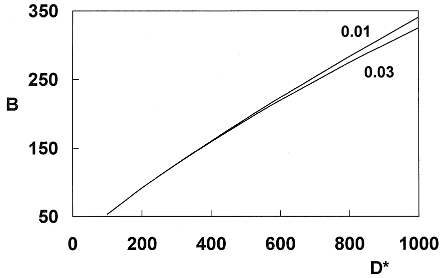

Fig. 5. Fast diffusion case. Dependence of parameter B appearing in Eq. (46) on D^* and on y_c. The value of y_c is shown next to each curve.

Table 1
Numerical parameters b_0, b_1, b_2, and a

y_c	b_0	b_1	b_2	a
0.01	192	0.322	5.9×10^{-5}	9.7
0.02	191.5	0.320	6.1×10^{-5}	8.7
0.03	190	0.310	8.0×10^{-5}	7.8

the dimensionless diffusion coefficient D^* were approximated by the functions $(100 \le D^* \le 1000)$

$$B = b_0 + b_1(D^* - 500) - b_2(D^* - 500)^2, \qquad (47a)$$

$$A = 0.143 + \frac{a}{100(D^*/100)^{0.45} + 10^{-3}(D^*/100)^9}. \qquad (47b)$$

The parameter A (in the limit of the attained numerical precision, ± 0.01) does not practically depend on D^*. Obviously, the value of parameter A depends on the time needed to reach the stationary distribution $S_{st}(y)$. The greater the diffusion coefficient, the smaller this time and the parameter A (see Fig. 3). Numerical parameters a, b_0, b_1, and b_2 depend on y_c and are given in Table 1.

4. Large particle limit: contact with two-dimensional ET

If the radius of the spherical particles is increased, while keeping the surface concentration $\overline{N}/(4\pi R^2) = n$ constant, one can use in Eq. (11) the two-particle function $P_1(t^*)$ calculated only for the short-time domain. Using Eqs. (24) and (26) we obtain, in the slow diffusion limit and leaving only the leading terms in the power series,

$$P_1(t^*)1 - \Gamma\left(\frac{2}{3}\right)(t^*)^{1/3} + \frac{1}{2}t^*(1 - D^*) \qquad (48)$$

and finally obtain

$$I(t) = \exp\left\{-c\left[1.2541\left(\frac{t}{\tau_0}\right)^{1/3} - \frac{1}{32}\left(\frac{R_0}{R}\right)^4\frac{t}{\tau_0} + 2\frac{D\tau_0}{R_0^2}\frac{t}{\tau_0}\right]\right\}, \qquad (49)$$

where $c = \pi R_0^2 n$ is the average number of acceptors in a circle of radius R_0.

In Eq. (49), the first term in the square brackets ($\propto t^{1/3}$) is recognised as the static ET on a plane. The second one is a correction to the first ($R_0 \ll R$) due to the fact that ET takes place on a sphere and not in a plane. Naturally, this term disappears when $R \to \infty$. The third term is the correction due to molecular diffusion on the plane. Note that the second and third terms have the same time dependence ($\propto t$) but opposite sign. Thus, these terms can compensate each other in certain conditions. Eq. (49) can be used, for example, in ET kinetics in vesicles.

Concerning the rapid-diffusion limit ($D \to \infty$), we note that Eqs. (40) and (44) are valid if the second term in Eq. (40) is smaller than unity (or $R_0^6 \ln(2R^2/r_c^2) \ll 8D\tau_0 r_c^4$). If R increases, this condition becomes more and more stringent. In the limit $R \to \infty$, it cannot be satisfied for any reasonable diffusion constant. This stems from the fact that the solution of the stationary diffusion equation in two-dimensional space is proportional to ln R and tends to infinity when $R \to \infty$. Thus, the rapid-diffusion limit cannot exist for an infinite plane, as opposed to the situation in an infinite volume [21]. However, as discussed above (Eq. (45)), the rapid-diffusion limit can be realised in a *finite* two-dimensional system.

5. Conclusions

In most nanometer-sized systems, the fluorescence decay and accompanying transfer processes occur on a time scale much shorter than that of translational diffusion and a static picture is appropriate. There are, however, systems where diffusion can be significant during the chromophore's excited state lifetime. One such situation refers to solute molecules located in the superficial region of micelles, for which diffusion coefficients of 1–10 Å^2/ns apply. With long lifetimes (tens of nanoseconds) and short critical radii (≤ 20 Å), the role played by diffusion becomes essential.

Recently, Matzinger et al. [16] considered in detail the problem of dipole–dipole energy transfer in micelles with diffusion. Although quantitative results were obtained, both by the numerical resolution of the diffusion equation and by Monte Carlo simulation, no simple approximate expressions that can be used to easily predict or evaluate the effect of diffusion were given. It was the purpose of the present work to obtain such relations for the irreversible ET case. From a detailed numerical analysis of the diffusion equation, an approximate form of the donor decay law (Eqs. (11), (28) and (46)) was obtained. These results cover a wide range of reduced diffusion coefficients ($D^* \in [0, 1000]$), and should apply to most ET processes in spherical particles.

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