

## DIFFUSION-MEDIATED ANNIHILATION REACTIONS VIA SHORT- AND LONG-RANGE INTERACTIONS: DETERMINATION OF THE CORRECT BOUNDARY CONDITION

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The influence of short- and long-range (multipole-multipole) interactions on diffusion-mediated annihilation reactions is studied. The precise form of the boundary condition is obtained from the microscopic description of the incoherent exciton annihilation. The dependence of the rate coefficient in the radiation boundary condition on the excitonic parameters is determined. As a result the apparent rate coefficient of the annihilation reaction is obtained using only those parameters which appear in the microscopic equations describing the annihilation process. This enables us to find the general dependence of this coefficient on the parameters of motion and both short- and long-range interactions of excitons.

### 1. Introduction and theory

The main subject of interest in the theory of diffusion-mediated reactions is the apparent rate coefficient (ARC)  $\gamma(t)$  which determines the time dependence of the concentration  $c(t)$  of reacting species, when bimolecular reactions, such as donor-acceptor energy transfer or exciton annihilation (considered here), take place. The standard procedure of calculating  $\gamma$ , recognized to be valid at small  $c$ , is based on the solution of the diffusion equation

$$\partial g(r, t) / \partial t = 2D \nabla^2 g(r, t) - \lambda(r) g(r, t) \quad (1)$$

subject to the so-called radiation boundary condition (RBC)

$$\partial g(r, t) / \partial r |_{r=R} = kg(R, t). \quad (2)$$

The ARC  $\gamma(t)$  is defined by the relation (see, for example, refs. [1,2] and references therein)

$$\begin{aligned} \gamma(t) = & 8\pi DR^2 \partial g(r, t) / \partial r |_{r=R} \\ & + 4\pi \int_{r=R}^{\infty} \lambda(r) g(r, t) r^2 dr. \end{aligned} \quad (3)$$

In eqs. (1)–(3)  $g(r, t)$  is the two-particle correlation function normalized with respect to  $c^2(t)$ . This

means that for three-dimensional diffusion  $g(r, t) \rightarrow 1$  when the distance between reactants  $r$  goes to infinity.  $D$  is the diffusion coefficient of the reactants assumed here to be identical,  $\lambda(r)$  is the distance-dependent probability per second which will be specified below,  $R$  is the contact (minimal) distance between any two reactants;  $k$  is usually considered as a phenomenological quantity characterizing the efficiency of the collision reactions:  $k \rightarrow \infty$  corresponds to the case of the collision reactions which occur instantly,  $k = 0$  represents the opposite case when no reaction occurs at  $r = R$ .

To complete the description of the diffusion-mediated reaction kinetics, one must link the reaction coefficient (RC)  $k$  to physically significant quantities depending on the specific microscopic picture of the reaction process. In this work the annihilation reaction of incoherent excitons in a crystalline lattice is considered starting from the master equation

$$\begin{aligned} \partial g(n, t) / \partial t |_{n \neq 0} \\ = & 2 \sum_{n', n'' \neq 0} W_{|n-n'|} (g(n', t) - g(n, t)) \\ & - \lambda(n) g(n, t), \end{aligned} \quad (4)$$

where  $n$  is a discrete index denoting the relative posi-

tion of two excitons in a crystal with lattice constant  $a$ ;  $W_{|n-n'|}$  is the probability per second of an exciton jump from the lattice site  $n$  to  $n'$ , supposed to be dependent on  $|n - n'|$  only;  $\lambda(n)$  is the probability per second of the annihilation of two excitons localized on lattice sites separated by the distance  $n$

Eq. (4) comes from the coupled chain of equations for the exciton density matrix first introduced to exciton annihilation theory by Suna [3]. In obtaining (4) we have followed the recipe for the chain truncation procedure proposed in ref. [4] which, in the absence of sources of reacting species, is equivalent to Waite's method [5]. In the framework of such an approach the many-particle problem is reduced to a two-particle one and the solution of (4) makes it possible to calculate the ARC defined as [3]

$$\gamma(t) = a^3 \sum_n \lambda(n) g(n, t) . \quad (5)$$

The theory of ref. [3] and subsequent papers [4, 6] concerns the annihilation reaction due to the short-range type of exciton-exciton interaction appropriate to the case of triplet-triplet annihilation. For singlet exciton annihilation in molecular crystals, the long-range dipole-dipole interaction is known to be important experimentally [7]. Since, in this case, an analytical solution of (4) is not available, the theoretical treatment of the process is usually performed with the help of eqs. (1)–(3) where the reaction coefficient  $k$  is interpreted on intuitive physical grounds. As a result the actual dependence of the ARC on microscopic parameters of excitons is left unclear. To clarify this dependence in the particular case of the diffusion-mediated annihilation of incoherent excitons, eqs. (4) and (5) are used here to obtain the correct form of the boundary condition (BC) on the "reacting surface" free of adjustable parameters and to give an estimate of the accuracy of the integral formula (3) used instead of (5) for the calculation of the ARC of annihilation reactions. The definition of  $k$  used so far in the theory of diffusion-mediated reactions [1,2,7–13] cannot be used in our case, since the particular form of the BC as well as the range of validity of the diffusion equation approach used in the cited papers are rather sensitive to the parent transport equation, the character of interaction of the reaction species, the dimensionality of the system, etc. — see, for example, refs. [14–18].

In what follows, we obtain the correct form of the BC accompanying the reduction of (4) to the diffusion equation, and then we demonstrate how the definition of the reaction coefficient  $k$  relevant to the case of incoherent exciton annihilation via short- and long-range interaction can be understood from the dependence of the ARC on the exciton diffusion rate. This dependence turns out to be qualitatively different from that obtained for the same kind of the reaction process [1,2] but with another definition of  $k$ .

At first let us specify the annihilation probability in the form

$$\lambda(n) = \omega(a/n)^{2M} + \delta_{n,a} \Omega , \quad (6)$$

where the first term corresponds to the probability of exciton-exciton annihilation via multipole-multipole interaction:  $M = 3, 4, \dots$  for dipole-dipole, dipole-quadrupole, ... interactions. This probability is analogous to the one obtained by Förster [19] and Dexter [20] for donor-acceptor energy transfer. It differs only in the interpretation of the corresponding Förster radius which, in our case, is proportional to the overlap of fluorescence and lower excited singlet state absorption spectra.

The second term contributes to the annihilation probability when excitons are located on nearest-neighbour molecules. Note that the Förster type of annihilation probability results from the expansion of the electrostatic interactions between excited states (responsible for the non-radiative disappearance of excitons) in a multipole series. The utilization of the dominant term of the expansion represented by the first term in (6) is justified for all distances between excitons, except the minimal one  $n = a$  at which the annihilation probability can differ considerably from that predicted by a monotonic dependence of the type  $n^{-2M}$ . To account for this difference we introduce the second term in the annihilation probability.

The reduction of the master equation (4) to the diffusion equation (1) is justified at  $t \gg W$ . At long times the change in the two-particle correlation function at a distance of the order of the lattice constant is small, and one can expand  $g(n', t)$  in (4) as a Taylor series in the vicinity of the point  $n$  retaining only linear and quadratic terms. Then, eq. (1) follows from eq. (4) for  $n = a$ . In this case the discrete index  $n$  is changed to the continuous coordinate  $r$ , and  $D = Wa^2$

on the assumption that the exciton can jump between nearest neighbours only. The zeroth and first terms of the expansion in the summation in (4) vanish for all  $n$  except  $n = a$ . It is easy to see that for  $n = a$  the first term resulting from the expansion of  $g(n', t)$  in powers of  $|n' - n|$  and from the summation over  $n'$  in (4) is proportional to  $\partial g(n, t)/\partial n|_{n=a}$ . To pass from discrete coordinates to the continuous case, we use the relation

$$\sum_{n, n=a} \partial g(n, t)/\partial n = 4\pi \partial g(r, t)/\partial r|_{r=a}. \quad (7)$$

Under this condition the equation for  $g(r, t)$  at  $r = a$ , i.e. the BC, takes the form

$$\partial g(1, t)/\partial t = \frac{4}{3}\pi W \partial g(r, t)/\partial r - \lambda(1)g(1, t). \quad (8)$$

In (8) and below the coordinates are expressed in units of the lattice constant  $a$ . The BC obtained coincides with the form proposed in ref. [12].

It can be shown that at long times  $t \gg W$  the solution of (1) approaches a steady state. At this stage of the annihilation process the time derivatives in (1) and (8) can be ignored. Under this condition (8) reduces to the RBC with  $R = a$  and the reaction coefficient defined as

$$k = (3/4\pi)(\Omega + \omega)/W. \quad (9)$$

Thus,  $\Omega + \omega$  is associated with the collisional (short-range) mechanism of the annihilation and can be interpreted as the probability of reaction taking place inside the reaction volume  $6a^3$ .

Using in (5) the steady-state solution of (1) subject to the RBC with  $k$  defined by (9) one can calculate  $\gamma$  at long times. Examples of such a calculation are presented in fig. 1a (dotted lines) where the dependence of the effective annihilation radius (in units of  $a$ ) defined by

$$\gamma = 8\pi D a^3 R_{\text{eff}} \quad (10)$$

is shown. Substituting the same solution into (3) we obtain the analytic expression for  $R_{\text{eff}}$  as a function of the microscopic parameters  $\omega/W$  and  $\Omega/W$ ,

$$R_{\text{eff}} = q_\nu \left( \frac{\omega}{2W} \right)^\nu \frac{z I_{1-\nu}(z) + 2\nu k I_{-\nu}(z)}{z I_{\nu-1}(z) + 2\nu k I_\nu(z)}, \quad (11)$$

where  $\nu = 1/2(M - 1)$ ,  $Z = 2\nu(\omega/2W)^{1/2}$ ,  $I_\nu$  is a modified

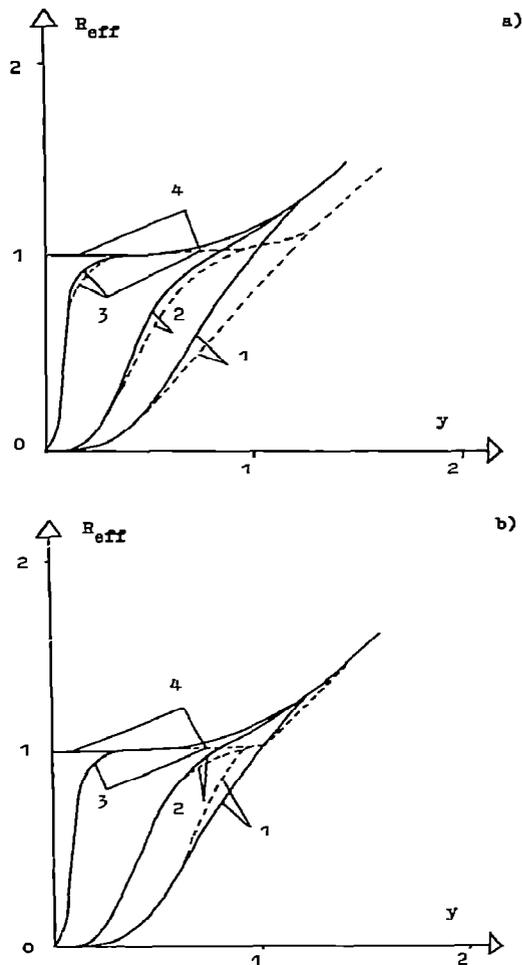


Fig. 1. The effective annihilation radius  $R_{\text{eff}} = (8\pi W a^3)^{-1} \gamma$  as a function of the parameter  $y = 0.676(\omega/2W)^{1/4}$  for different values of the ratio  $\tilde{\Omega} = \Omega/\omega$ : (1)  $-\tilde{\Omega} = 0$ , (2)  $-\tilde{\Omega} = 10$ , (3)  $-\tilde{\Omega} = 10^4$ , (4)  $-\tilde{\Omega} = \infty$ . On both graphs the solid lines correspond to the values of  $R_{\text{eff}}$  obtained from eq. (11). Dashed lines represent the function  $R_{\text{eff}}(y)$  calculated in accordance: (a) with eq. (5) in the diffusion equation approximation; (b) with the interpolation formula (18).

ified Bessel function,  $q_\nu = \nu^{2\nu} \Gamma(1 - \nu)/\Gamma(1 + \nu) = 0.676$ ,  $0.67$ ,  $0.68$  for  $M = 3, 4, 5$  respectively.

Note that (3) is equivalent to

$$a^{-3} \gamma = 6(\Omega + \omega)g(1) + 4\pi\omega \int_{r=1}^{\infty} [g(r)/r^{2M-2}] dr. \quad (12)$$

which corresponds to the simplest estimate of the lat-

tice sum (5) [21]. The curves in fig. 1a show the accuracy of this estimate. It is seen that (11) is adequate for both qualitative and quantitative analysis of the dependence  $R_{\text{eff}} = R_{\text{eff}}(\omega/W, \Omega/W)$ . The quantitative differences between the values of  $R_{\text{eff}}$  predicted by (11) and those obtained from (5) in the diffusion equation approximation do not exceed 20% for the dipole-dipole type of interaction. In most cases it is less than the uncertainty in experimental data for  $\gamma$ .

## 2. Discussion

Formula (11) for the effective radius of the reaction which takes place via long-range (multipole-multipole) and short-range (upon direct contact) interactions has been derived previously (see, for example, refs. [1,7]). Nevertheless, since the dependence of  $R_{\text{eff}}$  on the parameters of motion and interaction of the reactants is tightly linked with the interpretation of the reaction coefficient in the RBC and since many choices of this coefficient have been used [1, 2,7-13,22-27], it is worth discussing the qualitative behaviour of  $R_{\text{eff}}$  for different exciton parameters. This behaviour is fixed by eqs. (9) and (11) which contain no free parameters.

For  $z \gg 1$  (slow diffusion) eq. (11) gives

$$R_{\text{eff}} = q_\nu(\omega/2W)^\nu, \quad 2\nu(\omega/2W)^{1/2} \gg 1. \quad (13)$$

Eq. (13) was obtained by Yokota and Tanimoto [23] for dipole-dipole excitation energy transfer and has been redervied in many subsequent papers [1,2,7,13, 24-27].

For small values of  $z$ ,

$$R_{\text{eff}} = \frac{k + 0.25[\nu(1-\nu)]^{-1}z^2}{1+k} = \frac{(\omega/W)[\nu/(1-\nu) + (3/2\pi)(1 + \Omega/\omega)]}{1 + (3/2\pi)(\omega/2W)(1 + \Omega/\omega)}. \quad (14)$$

In this case one can expect a quite different dependence of  $R_{\text{eff}}$  on the diffusion rate, namely

$$R_{\text{eff}} = 1; \quad 2\nu(\omega/2W)^{1/2} \ll 1, \quad W \ll \Omega \quad (15)$$

and

$$R_{\text{eff}} = [\nu/(1-\nu) + 3/2\pi] \omega/2W + (3/4\pi) \Omega/W$$

$$2\nu(\omega/2W)^{1/2} \ll 1, \quad W \gg \Omega. \quad (16)$$

Thus, in general, there exist three regions of the diffusion rate: slow, intermediate and fast, where the dependence of  $R_{\text{eff}}$  on  $W$  is qualitatively different.

Eq. (13) corresponds to the reaction via multipole-multipole interaction only. In this case the reaction takes place at most at distances larger than  $r = a$  and therefore the result (13) is not sensitive to a particular choice of the rate coefficient in the RBC.

Eq. (15) is the same as in the case of the collisional type of diffusion-controlled reactions. This regime of the reaction is more or less pronounced depending on the magnitude of  $\Omega$ . Numerical calculation shows that, for example, for  $M = 6$  a noticeable region of  $W$  where  $R_{\text{eff}} = 1$  does not exist when  $\Omega/\omega < 10^3$  (see fig. 1).

Finally, eq. (16) represents the so-called kinetic regime of the reaction when the ARC is independent of diffusion.

Note that the kinetic regime of annihilation does not exist only for  $\Omega = \infty$ , i.e.  $k = \infty$ . Such a BC was used [2,24,25] for the description of long-range excitation energy transfer with diffusion. For an estimate of  $R_{\text{eff}}$  a useful interpolation formula was proposed:

$$R_{\text{eff}} = 1, \quad r_f = q_\nu(\omega/2W)^\nu < 1; \\ = r_f, \quad r_f > 1. \quad (17)$$

When the rate of the reaction upon direct contact is finite ( $k \neq \infty$ ) it follows from our derivation that the interpolation formula for  $R_{\text{eff}}$  in the annihilation reaction, valid for any  $\Omega$ , reads

$$R_{\text{eff}} = \frac{(\omega/2W)[\nu/(1-\nu) + (3/2\pi)(1 + \Omega/\omega)]}{1 + (3/2\pi)(\omega/2W)(1 + \Omega/\omega)}, \\ r_f < 1; \\ = r_f, \quad r_f > 1. \quad (18)$$

The deviation of the values of  $R_{\text{eff}}$  obtained from (18) from those calculated from (9) and (11) do not exceed 15%. Results of the corresponding calculations are shown in fig. 1b.

It is instructive to compare the present treatment with the treatment of the donor-acceptor excitation energy transfer given by Heisel and Mische [1]. They also used in their analysis the expression for the ARC

defined by (10) and (11) but the reaction coefficient in the RBC was treated differently. In particular, the absence of the collisional channel of the reaction in ref. [1] (and in refs. [2,13,26]) associated with the condition  $k = 0$ . For a reaction taking place purely via multipole-multipole interaction they obtained

$$R_{\text{eff}} = q_\nu (\omega/2W)^\nu I_{1-\nu}(z)/I_{\nu-1}(z), \quad (19)$$

whereas in our case this condition cannot be used in the sense mentioned above except for the situation when the long-range interaction is absent. Then

$$\gamma = 8\pi Dap, \quad p = k/(1+k), \quad k = 3\Omega/4\pi W. \quad (20)$$

Therefore a dependence of  $R_{\text{eff}}$  on the exciton parameters such as (19) cannot be realised for incoherent exciton annihilation in crystals.

It is also to be noted that according to our analysis the reaction (annihilation) regime is kinetic when the diffusion of the reactants is sufficiently fast (see eq. (16)), excluding the case of immediate collisional reaction ( $\Omega = \infty$ ). In contrast, Heisel and Miehe arrived at the conclusion that for fast diffusion the reaction regime is diffusion-controlled:  $R_{\text{eff}} \propto p$ . This discrepancy arises from the fact that  $p$  is treated in ref. [1] as a fixed parameter.

Thus, despite the fact that the expression obtained for ARC (11) coincides with the corresponding result of ref. [1], we arrive at quite different conclusions as to the dependence of  $\gamma$  on the diffusion rate. To the best of our knowledge, the possibility of three regimes of incoherent exciton annihilation differing in the qualitative dependence of  $\gamma$  on  $D$  has not been predicted before.

In conclusion, we summarize the results of this work.

(i) The correct form of the BC for diffusion-mediated annihilation of incoherent excitons is obtained from the microscopic equation describing the process. At long times the BC found here reduces to the usual form of the RBC with the reaction coefficient defined in terms of microscopic parameters of the exciton system. These parameters  $\Omega$ ,  $\omega$ ,  $W$  can be defined from a quantum-mechanical description of the spatial motion and the non-conserved part of the exciton interaction with non-excitonic degrees of freedom (see for example, refs. [3,28]). Therefore all the quantities appearing in the expression for ARC are well defined microscopically.

(ii) The reaction coefficient  $k$  in the RBC (see eqs.

(2) and (9)), just as the ARC of annihilation  $\gamma$ , turn out to be a function of three independent parameters, two of which represent short- and long-range interactions responsible for annihilation. It is shown that the absence of the collision channel of the reaction cannot be described by the BC  $\partial g(r, t)/\partial r|_{r=a} = 0$  in the presence of an annihilation channel via long-range interaction. The appropriate form of the RBC in this case is  $a\partial g(r)/\partial r|_{r=a} = 3\omega g(a)/4\pi W$ .

(iii) The dependence of the reaction coefficient in the RBC on the interaction parameters gives rise to a peculiar behavior of the annihilation rate as a function of the diffusion rate. Specifically, under the influence of combined short- and long-range interactions on the annihilation process, in general three regimes of annihilation can emerge that differ by the qualitative dependence of the ARC (the effective annihilation radius  $R_{\text{eff}}$  on  $D$ ). They are (1)  $\gamma \propto D^{1-\nu}$  for slow diffusion, (2)  $\gamma \propto D$  for intermediate rate of diffusion and (3)  $\gamma$  is independent of  $D$  for fast diffusion.

(iv) For the description of this dependence an interpolation formula (18) is proposed which extends the applicability of an equation given in refs [2,25], which was valid in the case of instant reaction upon direct contact of reactants only.

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