

The effect of the particle generation function on the rate of the diffusion-controlled $A+B\rightarrow B$ reaction with a permanent particle source

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Abstract

The results of calculations of the quasi-steady state reaction rate dependence on B-sink concentration, describing the diffusion-controlled luminescence quenching, $A+B\rightarrow B$, are presented. The effects of different particle generation functions and interaction potentials are studied analytically using the Kirkwood superposition approximation. © 1997 Elsevier Science B.V.

1. Introduction

The effect of the energy sink, B, concentration on the kinetics of the diffusion-controlled luminescence quenching, $A+B\rightarrow B$, under a permanent donor A production has been discussed in several papers [1–4]. These studies have demonstrated that the quasi-steady ($t \rightarrow \infty$) reaction rate is

$$k(\infty) = k_0 \left(1 + \sqrt{3S} \right), \quad (1)$$

where $k_0 = 4\pi D r_0$ is the so-called Smoluchowski reaction rate, $D = D_A + D_B$ is the relative diffusion coefficient, $S = \frac{4}{3}\pi r_0^3 n_B$ is a fraction of the reaction volume covered by unsaturable luminescence quenchers (sinks) B and r_0 is the reaction radius. This $\sqrt{n_B}$ correction results in a deviation from the standard Stern–Volmer law known for dilute quencher solutions. Such an effect has been observed more than once for fluorescence quenching in DNA, polymer and other concentrated solutions (see review articles [4,5] and ref-

erences therein). Reactants A and B can be both neutral and oppositely charged. The former case takes place, e.g. for the reaction of a repressor molecule R with a target site on a DNA molecule [6]. Relevant experiments show that the reaction rate exceeds the “standard” value, k_0 , by three orders of magnitude which has been interpreted as the sink concentration effect [7].

The fluorescence studies of $^*Os(5\text{-Cl-pen})_3^{2+} - Fe(CN)_6^{4-}$ and $^*Ru(bpy)_3^{2+} - Fe(CN)_6^{4-}$ complexes can serve as examples of reactions between charged reactants (see Ref. [8] for more examples and details). The quencher concentration corrections for the reaction rate between charged reactants have been considered in several papers [9–11], employing mean-field theory and the special “tilde-space method”. This study shows that for the Coulomb interaction

$$U_{AB} = \frac{e^2 Z_1 Z_2}{4\pi\epsilon\epsilon_0 r}$$

Eq. (1) remains valid with S changed to $\tilde{S} = \frac{4}{3}\pi R_0^3 n_B$, where R_0 is the effective so-called *Onsager radius*

$$R_0 = \frac{e^2 Z_1 Z_2}{4\pi\epsilon\epsilon_0 k_B T}. \quad (2)$$

Z_1 , Z_2 are the reactant charges and T is the temperature.

As is well known, the donor-quencher relative spatial distribution at the moment of the donor creation, $\lambda(r)$, under a permanent or pulsed excitation (used in steady-state or fluorescence decay experiments, respectively) is inhomogeneous [9]. Typical examples are donor generation by photoionization and by ionizing radiation. Up to now, no attempts have been undertaken to analyze how this inhomogeneity could affect the reaction rate under study.

In this Letter, instead of a complicated theory [9] we employ a much simpler Smoluchowski-type formalism and study a model potential for the reactant interaction which allows an analytical solution of the problem. We show that the reaction rate greatly depends not only on the interaction potential between donors A and sinks (quenchers) B but also on the spatial distribution of donors with respect to quenchers at the moment of their creation (the initial distribution function).

2. Basic equations

Let us consider the steady-state diffusion equation where the donors A are generated with the permanent rate $\lambda(r)$ per unit time [3]

$$D\Delta_r \eta_{AB}(r) - k(\infty)n_B \eta_{AB}(r) + \frac{\lambda(r)}{n_A(\infty)} = 0, \quad (3)$$

where the first, second and third terms describe diffusion, bimolecular reaction and donor generation, respectively, in terms of the *correlation function* of dissimilar AB reactants $\eta_{AB}(r)$; the quantity $\eta_{AB}(r) n_B n_A(\infty)$ gives the number of AB pairs separated by the relative distance r , $n_A(\infty) = n_A(t \rightarrow \infty)$ is the macroscopic concentration of particles A at saturation and n_B is the concentration of unsaturable sinks B. From Eq. (3) in the $r \rightarrow \infty$ limit one gets for the generation rate:

$$\lambda(\infty) = k(\infty)n_B n_A(\infty). \quad (4)$$

The *reaction rate* is obtained from the flux of reactants A over the reaction sphere of radius r_0 around sinks B:

$$k(\infty) = 4\pi D r_0^2 \left[\frac{\partial \eta_{AB}(r)}{\partial r} \right]_{r=r_0}. \quad (5)$$

The boundary condition for $\eta_{AB}(r)$ at infinity comes from the absence of particle correlation at long relative distances, $r \rightarrow \infty$, and its normalization:

$$\eta_{AB}(r \rightarrow \infty) = 1. \quad (6)$$

This is accompanied by the Smoluchowski boundary condition of an instant reaction at radius r_0

$$\eta_{AB}(r = r_0) = 0. \quad (7)$$

In the case of the reactant AB interaction defined by the dimensionless potential $\Phi(r) = U_{AB}/k_B T$, instead of the usual diffusion operator

$$\Delta_r = \frac{1}{r} \frac{d}{dr} r^2 \frac{d}{dr}. \quad (8)$$

Eq. (3) contains the operator

$$\Delta_r^\Phi = \frac{1}{r} \frac{d}{dr} r^2 e^{-\Phi(r)} \frac{d}{dr} e^{\Phi(r)}. \quad (9)$$

3. Effect of the donor–sink interaction

Let us now consider the particle interaction in terms of the following dimensionless model potential:

$$\Phi_{\text{eff}}(r) = \frac{U_{\text{eff}}(r)}{k_B T} = -2 \ln \left(1 + \frac{R_0}{r} \right), \quad (10)$$

where R_0 is the Onsager radius, Eq. (2). This potential is limited at short distances r but behaves as a Coulomb potential as $r \rightarrow \infty$. Using the substitution

$$\eta(r) = \frac{\beta(r)}{R_0 + r} \exp(-\Phi_{\text{eff}}(r)). \quad (11)$$

into Eqs. (3), (6), (7) we obtain the following diffusion equation and the boundary conditions:

$$\frac{d^2 \beta(r)}{dr^2} - \alpha^2 \beta = -\frac{\alpha^2 r^2}{R_0 + r}, \quad (12)$$

$$\beta(r = r_0) = 0, \quad \beta(r \rightarrow \infty) = r, \quad (13)$$

where $\alpha^2 = k(\infty)n_B/D$. The solution of Eqs. (12), (13) reads

$$\beta(r) = \frac{\alpha}{2} \left[\exp(-\alpha r) \int_{r_0}^r \frac{\exp(\alpha r) r^2}{r + R_0} dr - \exp(\alpha r) \int_{r_0}^r \frac{\exp(-\alpha r) r^2}{r + R_0} dr \right] + C_1 \exp(-\alpha r) + C_2 \exp(\alpha r), \quad (14)$$

where the constants C_1 and C_2 are

$$C_1 = -C_2 \exp(2\alpha r_0),$$

$$C_2 = \frac{\alpha R_0^2}{2} \int_{r_0}^{\infty} \frac{\exp(-\alpha r)}{r + R_0} dr + \frac{(\alpha r_0 + 1) \exp(-\alpha r_0)}{2\alpha} - \frac{R_0 \exp(-\alpha r_0)}{2}.$$

For the reaction rate we have a general expression

$$k(\infty) = 4\pi D r_0 \left[\frac{\partial \beta(r)}{\partial r} \right]_{r=r_0} \left(1 + \frac{R_0}{r_0} \right). \quad (15)$$

Inserting the solution Eq. (14) into Eq. (15), one gets the reaction rate

$$k_{\text{eff}}(\infty) = 4\pi D (R_0 + r_0) \times [1 + \alpha^2 R_0^2 \exp[\alpha(R_0 + r_0)] \times E_1[\alpha(R_0 + r_0)] - \alpha(R_0 - r_0)], \quad (16)$$

where the $E_1(\alpha)$ function is defined by the equation

$$E_1(\alpha) = \int_1^{\infty} \frac{\exp(-\alpha z)}{z} dz. \quad (17)$$

For noninteracting reactants, $R_0 \rightarrow 0$, we obtain the standard Eq. (1). Note the useful expansion for $E_1(\alpha)$ in powers of $\alpha \gg 1$

$$E_1(\alpha) = \frac{\exp(-\alpha)}{\alpha} \left(1 - \frac{1}{\alpha} + \frac{2}{\alpha^2} - \dots \right). \quad (18)$$

With Eq. (18) and substituting into α the zero approximation of reaction rate, $k_{\text{eff}}(\infty) = 4\pi D (R_0 + r_0)$, one gets for $\tilde{S} \gg 1$ the first nontrivial correction to the reaction rate

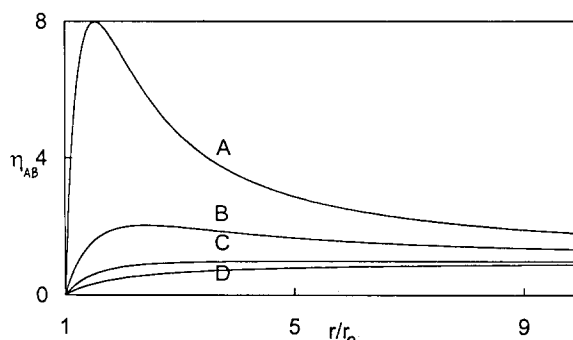


Fig. 1. Joint correlation functions of dissimilar reactants (AB) for the sink volume fraction $S = 0.3$: curve A: a model interaction potential, Eq. (10) with parameters $R_0/r_0 = 3.5$ and the generation function $\lambda(r) = \text{const} \times \exp(\Phi_{\text{eff}}(r))$,

$\eta_{AB}(r) = (1 + (R_0/r_0)/(r/r_0))(1 + (R_0/r_0)/(r/r_0) - (1 + R_0/r_0)/(r/r_0) \exp(\sqrt{3S}(1 + R_0/r_0)(1 - r/r_0)))$, non-interacting particles: curve B: $\lambda(r) = 1 + R_0/r$, $\eta_{AB}(r) = 1 + (R_0/r_0)/(r/r_0) - (1 + R_0/r_0)/(r/r_0) \times \exp(\sqrt{3S}(1 - r/r_0))$, curve C: $\lambda(r) = \text{const}$, $\eta_{AB}(r) = 1 - 1/(r/r_0) \exp(\sqrt{3S}(1 - r/r_0))$, curve D: $\lambda(r) = 1 - r_0/r$, $\eta_{AB}(r) = 1 - 1/(r/r_0)$.

$$k_{\text{eff}} = 4\pi D (R_0 + r_0) \left[1 + \sqrt{3S} \sqrt{\frac{r_0}{R_0}} \left(1 + \frac{r_0}{R_0} \right) \right]. \quad (19)$$

4. Different reactant generation functions

(i) Consider now the particle interaction combined with different A-particle generation functions $\lambda(r)$ shown in Fig. 1. We discuss their effect on the reaction rate.

In the case of noninteracting particles, $\Phi(r) = 0$, and homogeneous particle generation, $\lambda = \text{const}$ (curve C in Fig. 1), we obtain

$$\frac{D}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \eta_{AB}(r) \right] - k(\infty) n_B \eta_{AB}(r) + \frac{\lambda}{n_A(\infty)} = 0, \quad (20)$$

$$\eta_{AB}(r) = 1 - \frac{r_0}{r} \times \exp \left(-\sqrt{\frac{k(\infty) n_B}{D}} (r - r_0) \right), \quad (21)$$

which leads to the trivial result, Eq. (1).

(ii) Consider next the Boltzmann-like generation function $\lambda^*(r) = \lambda \exp(-\Psi(r))$ which satisfies the diffusion equation

$$\frac{D}{r^2} \frac{d}{dr} \left[r^2 e^{-\phi(r)} \frac{d}{dr} e^{\phi(r)} \eta_{AB}(r) \right] - k(\infty) n_B \eta_{AB}(r) + \frac{\lambda^*(r)}{n_A(\infty)} = 0, \quad (22)$$

and boundary conditions

$$\begin{aligned} \eta_{AB}(r = r_0) &= 0, \\ \eta_{AB}(r \rightarrow \infty) &= 1. \end{aligned} \quad (23)$$

For a further quantitative comparison with the earlier formalism [9] we choose $\Psi(r)$ in the generation function to have exponential form (which models a strong initial correlation of reactants). (Despite the fact that the generation function has the same mathematical form as the interaction potential $\Phi(r)$, Eq. (10) (curve A in Fig. 1) these two functions have quite different physical meaning.) When doing so, we obtain

$$\frac{d^2 \beta(r)}{dr^2} - \alpha^2 \beta = -\alpha^2 (R_0 + r), \quad (24)$$

$$\beta(r) = R_0 + r + C_1 \exp(-\alpha r) + C_2 \exp(\alpha r), \quad (25)$$

where

$$C_1 = -(R_0 - r_0) \exp(\alpha r_0), \quad C_2 = 0.$$

Using the relation $\alpha^2 = k(\infty) n_B / D$, one finally gets

$$\begin{aligned} k_{\text{eff}}(\infty) &= 4\pi D (R_0 + r_0) \\ &\times \left[1 + (R_0 + r_0) \sqrt{\frac{k_{\text{eff}}(\infty) n_B}{D}} \right]. \end{aligned} \quad (26)$$

Using the approximation

$$k_{\text{eff}} \approx k_{\text{eff}}^0 = 4\pi D (R_0 + r_0)$$

under the square root, we arrive at

$$k_{\text{eff}}(\infty) = 4\pi D (R_0 + r_0) \left[1 + \sqrt{3\tilde{S}} \right]. \quad (27)$$

This result can be obtained just by replacing the reaction radius r_0 in Eq. (1) by the effective radius $R_0 + r_0$. This hides the fact that we have used a source term

with the Boltzmann distribution function for the generation function. It is evident that in the case of overlapping spheres of radius R_0 our treatment of the problem becomes incorrect, i.e. Eq. (27) is valid for $R_0^3 n_B < 1$ only. Otherwise the attraction of donors to several sinks would partly compensate each other and particles A would not feel the potential field $\Phi_{\text{eff}}(r)$ but another field, $\Phi_{\text{eff}}(r) - \Phi_{\text{eff}}(\bar{R})$. For $\tilde{S} = \frac{4}{3}\pi R_0^3 n_B < 1$, i.e. not very large sink concentrations n_B , there is a small number of particles B in the system, which are paired. As we have shown in Eq. (21), for the homogeneous particle generation function the reaction rate is a function of S but with the Boltzmann-like distribution the reaction rate turns out to be a function of \tilde{S} . In other words, the \tilde{S} factor arises due to the exponential particle generation function $\lambda^*(r)$ but not due to the many-particle effect.

(iii) Consider now the case shown in Fig. 1, curve B, neutral particles with the generation function containing $\Psi(r) = -\ln(1 + R_0/r)$. In this case $\lambda^*(r)$ has a maximum at $r = R_0$. The diffusion equation

$$\begin{aligned} \frac{D}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \eta_{AB}(r) \right] \\ - k(\infty) n_B \eta_{AB}(r) + \frac{\lambda^*(r)}{n_A(\infty)} = 0 \end{aligned} \quad (28)$$

has a solution

$$\begin{aligned} \eta_{AB}(r) &= 1 + \frac{R_0}{r} - (R_0 + r_0) \\ &\times \frac{\exp[-\alpha(r - r_0)]}{r}. \end{aligned} \quad (29)$$

We can easily obtain the reaction rate which is a combination of the *two* contributions:

$$k_{\text{eff}}(\infty) = 4\pi D r_0 \left[1 + \sqrt{3\tilde{S}} + \sqrt{3\tilde{S}} \sqrt{\frac{r_0}{R_0}} \right]. \quad (30)$$

(iv) Let us modify the generation function taking it in the form $\Psi(r) = -\ln(1 - r_0/r)$ (particles A are not created in the vicinity of sinks, curve D in Fig. 1). We obtain immediately

$$\eta_{AB}(r) = 1 - \frac{r_0}{r}, \quad (31)$$

and the relevant reaction rate well known for dilute quencher solutions [12]

$$k_{\text{eff}}(\infty) = 4\pi D r_0. \quad (32)$$

From the above results Eqs. (27), (30), (32) we see that the $\sqrt{3S}$ or $\sqrt{3\tilde{S}}$ factors appear purely as a result of the spatial distribution of particles under their generation but not a particular particle interaction potential. If no A particles are generated close to the recombination spheres the $\sqrt{3S}$ factor disappears. On the contrary, a large term $\sqrt{3\tilde{S}}$ arises due to a large A particle density created in the vicinity of the sinks B. Inclusion of the particle interaction in the discussed cases (i)–(iii) will result qualitatively in the correlation function increasing at short relative distances, similar to curve A in Fig. 1 (case (ii)).

5. Comparison with “mean-field” approach

Let us compare our Eq. (22) with the equation derived in the “mean-field” approach [4,9,13]

$$D\Delta_r^\phi [n(r) - n_{\text{eq}}(r)] - k(\infty)n_B [n(r) - n_{\text{eq}}(r)] = 0, \quad (33)$$

where $n_{\text{eq}}(r)$ is the density equilibrium value in the absence of a reaction, and $n_{\text{eq}}(r) = \exp(R_0/r)$. For this purpose we can rewrite Eq. (33) in the form of Eq. (22):

$$\frac{D}{r^2} \frac{d}{dr} \left[r^2 e^{-\phi(r)} \frac{d}{dr} e^{\phi(r)} (\eta_{AB}(r) - e^{-\psi(r)}) \right] = k(\infty)n_B (\eta_{AB}(r) - e^{-\psi(r)}). \quad (34)$$

Only in the case when $\lambda^*(r)$ contains the Boltzmann-like factor, i.e. $\Psi(r) = \Phi(r)$, are these two equations equivalent. This means that the mean-field approach is not correct for an arbitrary generation function. In the general case one should use Eq. (22) with the corresponding generation rate (source term) function for donors. As a result of the large difference between the equilibrium function $n_{\text{eq}}(r)$ and nonequilibrium $n(r)$ caused by the fact that the reaction changes the $n_{\text{eq}}(r)$ function drastically, a range of the applicability of the “mean-field” approximation is restricted.

6. Conclusion

We have demonstrated in this Letter that the generally accepted quencher concentration corrections in

the reaction rate are determined by a particular form of the chosen generation (source) function $\lambda(r)$ of the donors A. This correction disappears for $\lambda(r)$ having a depletion at $r \geq r_0$, whereas for $\lambda(r)$ having a maximum close to r_0 it turns out to be a combination of the two corrections, $\sqrt{3S}$ and $\sqrt{3\tilde{S}}$, Eq. (30). Since for charged reactants usually $\tilde{S} \gg S$, the conclusion suggests that the central result of Ref. [9], $k_{\text{eff}}(\infty) = (1 + \sqrt{3\tilde{S}})$, comes mainly from the shape of the generation function for donors A rather than from the Coulomb reactant interaction. Moreover, we have also shown that the same result, $k_{\text{eff}} \propto \tilde{S}^{1/2}$, also holds for a non-Coulomb potential, Eq. (10).

Our theory allows us to make (at least qualitatively) a conclusion on the shape of the donor-quencher initial distribution: for neutral reactants and a homogeneous distribution Eq. (1) holds whereas for a strongly correlated distribution the reaction rate is larger, Eq. (30), due to an additional term which could be calculated and compared with the experimental reaction rate.

An experimental check of our theoretical predictions (valid for a broad class of chemical reactions revealing fluorescence quenching) is of great interest.

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