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## The Diffusion-Controlled Energy Transfer Rate for a Paired Sink Distribution and Donor–Acceptor Interaction

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The kinetics of the diffusion-controlled energy transfer,  $A + B \rightarrow B$ , between mobile donors A and sinks (acceptors) B is studied for the case when energy acceptors are not uniformly distributed in space, as usually assumed, but are paired. Use of the Kirkwood superposition interaction permits to solve this problem easily, and to treat also the effect of particle Coulomb interaction.

### 1. Introduction

The diffusion-controlled kinetics of energy transfer in solids between mobile donors A and unsaturable sinks B,  $A + B \rightarrow B$ , remains to be of considerable interest [1, 2, 3]. Several papers deal with the effects of a non-uniform sink distribution, e.g., the case of a *paired sink distribution*. The latter problem was solved exactly in [4] using a bi-spherical coordinate system. Recently, in [5] the Kirkwood superposition approximation has been very successfully applied to the energy transfer kinetics with arbitrary spatial sink distribution. In this paper we will generalize results obtained in [5] through incorporation of donor–acceptor *interaction*.

### 2. Basic Equations

Following the approach described in [5], let us consider the steady-state three-dimensional diffusion equation for interacting particles AB and an arbitrary distribution of sinks B  $\eta_{BB}$ :

$$D \Delta_r^\Phi \eta_{AB}(r) + k(\infty) n_B \eta_{AB}(r) [1 - I(r, r_0)] = 0, \quad (1)$$

$$I(r, r_0) = \frac{1}{2rr_0} \int_{r-r_0}^{r+r_0} \eta_{BB}(r') r' dr', \quad (2)$$

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

where  $D$  is the donor diffusion coefficient,  $\eta_{AB}(r)$  the correlation function “sink-donor”,  $\Phi(r)$  the interaction potential between donors and acceptors,  $k(\infty)$  the reaction rate in the quasi-stationary case ( $t \rightarrow \infty$ ) and, lastly,  $n_B$  the concentration of sinks B. The reaction rate sought for is obtained from the flux of A particles through the reaction surface

around the sink B,

$$k(\infty) = 4\pi D r_0^2 \left[ \frac{\partial \eta_{AB}(r)}{\partial r} \right]_{r=r_0}, \quad (3)$$

where  $r_0$  is the radius of the sink at which the reaction  $A + B \rightarrow B$  instantly occurs. The relevant Smoluchowski boundary condition

$$\eta_{AB}(r = r_0) = 0, \quad (4)$$

and additional condition of the particle correlation weakening at infinity

$$\eta_{AB}(r \rightarrow \infty) = 1 \quad (5)$$

are used. For describing the AB particle interaction we restrict ourselves to the dimensionless model potential

$$\Phi_{\text{eff}}(r) = \beta U_{\text{eff}}(r) = -2 \ln \left( 1 + \frac{R_0}{r} \right), \quad (6)$$

where  $\beta = (k_B T)^{-1}$ ,  $R_0$  the parameter proportional to the so-called Onsager radius  $R_0 \simeq e^2/(\varepsilon k_B T)$ . Equation (6) behaves like a Coulomb potential as  $r \rightarrow \infty$ , but is limited at short distances.

### 3. Reaction Rate Calculation

We consider two paired sinks B described by the distribution function

$$\eta_{BB}(r') = \frac{\delta(r' - l)}{4\pi r'^2 n_B}, \quad (7)$$

where  $l$  is the distance between the centers of two sinks. Using Eq. (1), we obtain the following set of equations

$$D \Delta_r \eta_{1AB}(r) = 0, \quad r_0 \leq r < l - r_0, \quad (8)$$

$$D \Delta_r \eta_{2AB}(r) + k(\infty) n_B \eta_{2AB}(r) \left[ 1 - \frac{1}{8\pi l r_0 n_B} \right] = 0, \quad l - r_0 \leq r \leq l + r_0, \quad (9)$$

$$D \Delta_r \eta_{3AB}(r) = 0, \quad l + r_0 \leq r < \infty. \quad (10)$$

We can neglect the second term in Eq. (9) since  $Sl^2/r_0^2 \ll 1$ , where  $S$  is the volume fraction occupied by sinks,  $S = 4/3\pi r_0^3 n_B$ . Making the substitution

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

and introducing the dimensionless reaction rate,  $k' = k(\infty)/(4\pi D r_0)$ , we get a simple set of equations

$$\frac{d^2 \beta_1(r)}{dr^2} = 0, \quad r_0 \leq r < l - r_0, \quad (11)$$

$$\frac{d^2 \beta_2(r)}{dr^2} - \chi^2 \beta(r) = 0, \quad l - r_0 \leq r \leq l + r_0, \quad (12)$$

$$\frac{d^2 \beta_3(r)}{dr^2} = 0, \quad l + r_0 \leq r < \infty. \quad (13)$$

Parameter  $\varkappa$  is defined by the equation:

$$\varkappa^2 = \frac{k'}{2l^2}. \tag{14}$$

One can rewrite the boundary conditions as

$$\begin{aligned} \beta_1(r_0) &= 0, \\ \beta_3(r \rightarrow \infty) &= r \end{aligned} \tag{15}$$

and the equation for the reaction rate

$$k' = \left[ \frac{\partial \beta_1}{\partial r} \right]_{r=r_0} \left( 1 + \frac{R_0}{r_0} \right). \tag{16}$$

Using Eq. (15), an internal boundary conditions, and Eq. (16) we obtain finally the reaction rate sought for

$$k' = \frac{1 + \frac{R_0}{r_0}}{\text{ch} \left( \frac{r_0}{l} \sqrt{2k'} \right) + \left( 1 - \frac{2r_0}{l} \right) \sqrt{\frac{k'}{2}} \text{sh} \left( \frac{r_0}{l} \sqrt{2k'} \right)}, \tag{17}$$

where ch, sh are the hyperbolic sine and cosine.

#### 4. Particular Cases

The following particular cases are of special interest.

A. One isolated sink ( $l \rightarrow \infty, n_B \rightarrow 0$ ) with the potential, Eq. (6). From Eq. (17) we get immediately

$$k = k_0 \left( 1 + \frac{R_0}{r_0} \right) \tag{18}$$

where we denote as  $k_0 = 4\pi D r_0$  the reaction rate well-known for a random particle distribution (dilute sink solution) [1, 2].

B. Two sinks without any interaction ( $R_0 = 0$ ). The reaction rate reads now

$$k = \frac{k_0}{\text{ch} \left( \frac{r_0}{l} \sqrt{2} \right) + \frac{1}{\sqrt{2}} \left( 1 - \frac{2r_0}{l} \right) \text{sh} \left( \frac{r_0}{l} \sqrt{2} \right)}. \tag{19}$$

(We used in the derivation the zero approximation for  $k'$  under the square root,  $(k')^0 = 1$ .) Retaining the first two terms of the expansion for the hyperbolic functions we arrive at:

$$k = \frac{k_0}{1 + \frac{r_0}{l} - \left( \frac{r_0}{l} \right)^2}. \tag{20}$$

As  $r_0/l$  is small, Eq.(20) reads (see also [4, 5])

$$k = k_0 \left[ 1 - \frac{r_0}{l} + \left( \frac{r_0}{l} \right)^2 \right]. \tag{21}$$

C. Another extreme situation occurs when the two sinks touch each other, i.e.,  $l = 2r_0$ . From Eq. (20) an interesting result appears:

$$k_2 = 0.8k_0. \tag{22}$$

This means that one sink B is *screened* by the other and the effective flux of particles A to *each* of the sinks turns out to be 20% less than the flux to one isolated sink,  $k_0$ .

Another estimate of the combined flux into two touching sinks could be obtained by approximating the two touching spheres by a spheroid with the small axes  $a = b = r_0$  and the long axis  $c = 2r_0$  based on the equation given, e.g., in [1],

$$k_{\text{spheroid}} = \frac{\sqrt{c^2 - a^2}}{F\left(\sqrt{\frac{c^2 - b^2}{c^2 - a^2}}, \arcsin \sqrt{1 - \frac{a^2}{c^2}}\right)} k_0, \quad (23)$$

where  $F$  is the incomplete elliptic integral of first kind. The flux divided by a factor of two (for getting the flux per sphere) gives the dimensionless reaction rate sought for  $k_{\text{spheroid}}/2k_2 = 0.81$ , i.e. the effective flux per each sink is reduced *additionally* by 19%. This is very close to the ratio of the spheroid surface to that of the two isolated spheres ( $s_{\text{spheroid}}/s_{\text{sink}} = 0.85$ ).

D. For the two sinks and Coulomb interaction let us consider the situation when  $R_0 \gg r_0, l \gg r_0, l > R_0$  (strong interaction and well-separated sinks). From Eq. (17) using an expansion of hyperbolic sine and cosine, we arrive at

$$k = \frac{k_0 \left(1 + \frac{R_0}{r_0}\right)}{1 + \frac{R_0}{l}}.$$

## 5. Conclusion

The iterative equation for the energy transfer rate in the case of paired sinks (acceptors) has been derived. Taking into account Coulomb-like reactant interaction, the reaction rate for the following cases is analyzed: an isolated sink with potential interaction, paired sinks without interaction, paired sinks with interaction (under conditions  $R_0 \gg r_0, l \gg r_0, l > R_0$ , where  $R_0$  is the Onsanger radius),  $r_0$  the sink radius,  $l$  the distance between two sinks). In the limit of paired sinks without interaction the obtained reaction rate coincides with the well-known result [4]. This study demonstrates clearly the flexibility and efficiency of the Kirkwood superposition approximation in the complicated chemical and physical kinetics.

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