Diffusion and reversible reaction in a medium with penetrable sinks[a]

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A theory of diffusion controlled reactions with randomly distributed penetrable sinks is presented. The model considered includes a reversible reaction between a diffusing species, and a fixed reactive sink. For low reactivity, both steady state and initial value problems are discussed. The dependence on the sink concentration of the rate coefficients and the diffusion coefficients is found. By considering the limit of fast irreversible reaction, the connection is made with previous work.

I. INTRODUCTION

Recently there has been considerable interest in concentration effects on diffusion controlled reactions.[1-9] The problem of central concern is the determination of the effective rate and diffusion coefficients for solute species that react with statistically distributed sinks.

Up to the present attention has been restricted to perfectly absorbing sinks, where reaction takes place instantaneously upon contact of the solute species with the stationary sink. There will be many cases where this perfectly absorbing, irreversible behavior may not be an adequate representation. In particular, one would like to describe reverse reactions and the attainment of kinetic equilibrium within the framework of the diffusion controlled reaction model.

In this paper we develop a new formalism for attacking this problem and discuss several new aspects. First, we present a simple model of diffusion controlled reactions in a homogeneous medium containing many "reaction centers" (they are no longer perfect "sinks") where the *reversible* reaction

$$A \rightleftharpoons B \tag{1.1}$$

takes place *within* the fixed reaction centers. For a steady state situation, we discuss how diffusional effects can modify the observed rate coefficients and how reaction effects can modify the observed diffusion coefficients. We also examine the long time properties of the corresponding initial value problem. For an irreversible reaction, we discuss the modification of existing results due to penetrable sinks, and demonstrate that the results for inpenetrable sinks can be obtained within our formalism, when the absorption rate is made very large. We close with a brief recapitulation of our results and a discussion of the relevant experimental situations.

II. FORMALISM AND CALCULATION OF THE GREEN'S FUNCTION

We consider kinetic equations of the general form

$$\frac{\partial C_A}{\partial t} = D_A \nabla^2 C_A - \lambda_A(\mathbf{r}) C_A + \lambda_B(\mathbf{r}) C_B + S_A(\mathbf{r}, t) ,$$

$$\frac{\partial C_B}{\partial t} = D_B \nabla^2 C_B + \lambda_A(\mathbf{r}) C_A - \lambda_B(\mathbf{r}) C_B + S_B(\mathbf{r}, t) . \tag{2.1}$$

The two chemical species A and B are diffusing through a medium. The chemical reaction

$$A \rightleftharpoons B$$

occurs locally with forward rate λ_A and reverse rate λ_B. Additional (external) sources of species A and B are introduced by the source terms $S_A(\mathbf{r}, t)$ and $S_B(\mathbf{r}, t)$, respectively.

Several problems may be treated using this description. For example, setting $\lambda_B = 0$, reduces Eq. (2.1) to the irreversible removal of particles of type A at the sinks. Specification of λ_A, λ_B, and the source terms determine the physical model. In the model we will investigate, the reaction will be allowed to proceed only within one or more spherical reaction sinks which are in fixed locations. Assuming the reaction rate is uniform within the sink and the same for all sinks, we have

$$\lambda_A(\mathbf{r}) = \lambda_A \sum_{i=1}^{N} \theta(|\mathbf{r} - \mathbf{r}_i| - a) ,$$

$$\lambda_B(\mathbf{r}) = \lambda_B \sum_{i=1}^{N} \theta(|\mathbf{r} - \mathbf{r}_i| - a) , \tag{2.2}$$

where $\mathbf{r}_i$ is the location of the center of the ith sink, $\theta(|\mathbf{r} - \mathbf{r}_i| - a)$ is the Heaviside step function, and all sinks are taken to have equal radius.

We shall consider the case of reaction centers randomly distributed in space and we define the average $\langle f(\mathbf{r}) \rangle$ as an ensemble average over all possible center configurations. The quantities we will determine are $\langle C_A(\mathbf{r}, t) \rangle$ and $\langle C_B(\mathbf{r}, t) \rangle$.

We introduce the notation

$$\mathsf{C} = \begin{bmatrix} C_A \\ C_B \end{bmatrix} ,$$

$$\mathsf{D} = \begin{bmatrix} D_A & 0 \\ 0 & D_B \end{bmatrix} ,$$

$$\lambda = \begin{bmatrix} \lambda_A(\mathbf{r}) & -\lambda_B(\mathbf{r}) \\ -\lambda_A(\mathbf{r}) & \lambda_B(\mathbf{r}) \end{bmatrix} , \tag{2.3}$$

$$\mathsf{S} = \begin{bmatrix} S_A(\mathbf{r}, t) \\ S_B(\mathbf{r}, t) \end{bmatrix}$$

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so that $\mathbf{c}(\mathbf{r}, t)$ obeys

$$\frac{\partial \mathrm{C}}{\partial t} = \nabla^2 \mathbf{D} \cdot \mathrm{C} - \boldsymbol{\lambda} \cdot \mathrm{C} + \mathrm{S} \ . \tag{2.4}$$

It is convenient to Laplace–Fourier transform this equation. Defining

$$\hat{\hat{f}} = \int_0^\infty e^{-zt} \int_V e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}, t) d^3\mathbf{r}\, dt \ , \tag{2.5}$$

Eq. (2.4) becomes

$$z\hat{\hat{\mathrm{C}}}(\mathbf{k}, z) - \hat{\mathrm{C}}(\mathbf{k}, t=0)$$
$$= -k^2 \mathbf{D} \cdot \mathrm{C} - \frac{1}{(2\pi)^3} \int \boldsymbol{\lambda}(\mathbf{k}-\mathbf{k}') \cdot \hat{\mathrm{C}}(k', z) d^3k' + \hat{\hat{\mathrm{S}}}(k, z) \ . \tag{2.6}$$

We define the convolution operation by

$$\mathbf{f} * \mathbf{g} = \frac{1}{(2\pi)^3} \int \mathbf{f}(\mathbf{k}-\mathbf{k}') \cdot \mathbf{g}(\mathbf{k}') d^3\mathbf{k}' \tag{2.7}$$

and formally express Eq. (2.6) as

$$z\hat{\hat{\mathrm{C}}} - \hat{\mathrm{C}}(\mathbf{k}, t=0) = -k^2 \mathbf{D} \cdot \hat{\hat{\mathrm{C}}} - \boldsymbol{\lambda} * \hat{\hat{\mathrm{C}}} + \hat{\hat{\mathrm{S}}}(\mathbf{k}, z) \tag{2.8}$$

or

$$[z\mathbf{I} + \mathbf{D}k^2] \cdot \hat{\hat{\mathrm{C}}} = -\boldsymbol{\lambda} * \hat{\hat{\mathrm{C}}} + [(\hat{\hat{\mathrm{S}}}(\mathbf{k}, t=0) + \hat{\mathrm{C}}(\mathbf{k}, t=0)] \ . \tag{2.9}$$

To derive an equation for $\langle c(r, t)\rangle$, we introduce the projection operators P and Q where

$$Pf = \langle f \rangle \tag{2.10}$$

and

$$Qf = (1-P) f = f - \langle f \rangle \tag{2.11}$$

and the "unperturbed Green's function"

$$\mathbf{G}^\circ(\mathbf{k}, z) = [z\mathbf{I} + k^2\mathbf{D}]^{-1} \ . \tag{2.12}$$

We consider, initially, the case that the sources, and initial conditions, are uncorrelated with the reaction center locations. This implies

$$P\mathbf{s}' = \langle \mathbf{s}' \rangle = \mathbf{s}' \ ,$$

$$Q\mathbf{s}' = 0 \ ,$$

where $\mathbf{s}' = \hat{\hat{\mathbf{s}}}(\mathbf{k}, t) + \hat{\mathbf{c}}(\mathbf{k}, t=0)$.

Applying the projection operators to Eq. (2.9), we obtain

$$[z\mathbf{I} + k^2\mathbf{D}] P\hat{\hat{\mathbf{c}}} = -P\boldsymbol{\lambda} * [P\hat{\hat{\mathbf{c}}} + Q\hat{\hat{\mathbf{c}}}] + \mathbf{s}' \tag{2.13}$$

and

$$[z\mathbf{I} + k^2\mathbf{D}] Q\hat{\hat{\mathbf{c}}} = -Q\boldsymbol{\lambda} * [Q\hat{\hat{\mathbf{c}}} + P\hat{\hat{\mathbf{c}}}] \tag{2.14}$$

which may be written as

$$Q\hat{\hat{\mathbf{c}}} = -\mathbf{G}^\circ \cdot \boldsymbol{\lambda} * [Q\hat{\hat{\mathbf{c}}} + P\hat{\hat{\mathbf{c}}}] \ , \tag{2.15}$$

where

$$\mathbf{G}^\circ = [z\mathbf{I} + k^2\mathbf{D}]^{-1} \ . \tag{2.16}$$

Accordingly one finds

$$Q\hat{\hat{\mathbf{c}}} = -[\mathbf{I} + \mathbf{G}^\circ \cdot Q\boldsymbol{\lambda} *]^{-1} \mathbf{G}^\circ Q\boldsymbol{\lambda} * P\hat{\hat{\mathbf{c}}} \ . \tag{2.17}$$

The "inverse convolution" formally indicated in Eq. (2.17) is defined

$$\int [\mathbf{A}*]^{-1}(\mathbf{k}-\mathbf{k}') \cdot \mathbf{A}(\mathbf{k}'-\mathbf{k}'') d^3k' = \delta^3(\mathbf{k}-\mathbf{k}'') \ . \tag{2.18}$$

We may combine Eqs. (2.13) and (2.17) to obtain

$$[z\mathbf{I} + k^2\mathbf{D}] \cdot P\hat{\hat{\mathbf{c}}} = -P\boldsymbol{\lambda} * \{\mathbf{I} - [\mathbf{I} + \mathbf{G}^\circ Q\boldsymbol{\lambda} *]^{-1} \cdot \mathbf{G}^\circ \cdot Q\boldsymbol{\lambda}\} P\hat{\hat{\mathbf{c}}} + \mathbf{s}'$$
$$= P\boldsymbol{\lambda} * [\mathbf{I} + \mathbf{G}^\circ Q\boldsymbol{\lambda} *]^{-1} P\hat{\hat{\mathbf{c}}} + \mathbf{s}' \ . \tag{2.19}$$

We define the operator $\boldsymbol{\Gamma}_{\mathrm{op}}$ by

$$\boldsymbol{\Gamma}_{\mathrm{op}} = \langle \boldsymbol{\lambda} * [\mathbf{I} + \mathbf{G}^\circ \cdot Q\boldsymbol{\lambda}]^{-1} \rangle$$
$$= \left\langle \boldsymbol{\lambda} * \sum_{n=0}^{\infty} (-\mathbf{G}^\circ \cdot Q\boldsymbol{\lambda} *)^n \right\rangle \tag{2.20}$$
$$= \left\langle \sum_{n=0}^{\infty} (-\lambda * \mathbf{G}^\circ Q)^n \cdot \lambda \right\rangle$$

so that

$$\boldsymbol{\Gamma}_{\mathrm{op}} \langle \hat{\mathbf{c}} \rangle = \frac{1}{(2\pi)^3} \int \left\langle \sum_{n=0}^{\infty} (-\lambda \cdot \mathbf{G}^\circ Q)^n \lambda \right\rangle * \langle \hat{\mathbf{c}}(\mathbf{k}', z) \rangle d^3k'$$
$$= \frac{1}{(2\pi)^3} \int \boldsymbol{\Gamma}(\mathbf{k}, \mathbf{k}') \cdot \langle \hat{\mathbf{c}}(\mathbf{k}', z) \rangle d^3\mathbf{k}' \ ,$$

where the matrix $\boldsymbol{\Gamma}$ is

$$\boldsymbol{\Gamma}(\mathbf{k}, \mathbf{k}') = \sum_{n=0}^{\infty} \langle (-\lambda * \mathbf{G}^\circ Q)^n \cdot \lambda \rangle \ . \tag{2.21}$$

If the reaction centers are uniformly distributed in space, i.e., overlap is permitted, the quantity $\boldsymbol{\Gamma}(\mathbf{k}, \mathbf{k}')$ will simplify to

$$\boldsymbol{\Gamma}(\mathbf{k}, \mathbf{k}') = (2\pi)^3 \delta^3(\mathbf{k}-\mathbf{k}') \boldsymbol{\Gamma}(\mathbf{k}) \tag{2.22}$$

which yields

$$\boldsymbol{\Gamma}_{\mathrm{op}} \cdot \langle \hat{\mathbf{c}} \rangle = \boldsymbol{\Gamma}(k) \cdot \hat{\mathbf{c}}(\mathbf{k}, z) \ .$$

This result permits us to write a simple formal expression for the Green's function for the averaged concentration

$$\mathbf{G}(\mathbf{k}, z) = [z\mathbf{I} + k^2\mathbf{D} + \boldsymbol{\Gamma}(\mathbf{k})] \tag{2.23}$$

with

$$\boldsymbol{\Gamma}(\mathbf{k}) = \sum_{n=0}^{\infty} \langle (-\lambda * \mathbf{G}^\circ Q)^n \lambda \rangle \ . \tag{2.24}$$

Equation (2.24) is exact, subject only to the conditions that the reaction centers be uniformly distributed in space and the sources and initial conditions be uncorrelated from the location of the centers. We discuss relaxing the second assumption later.

For our model for the reaction center, $\boldsymbol{\lambda}(\mathbf{r})$ will be

$$\boldsymbol{\lambda} = \begin{bmatrix} \lambda_A & -\lambda_B \\ -\lambda_A & \lambda_B \end{bmatrix} * \int \sum_i \delta^3(\mathbf{r}_i - \mathbf{r}') \theta(|\mathbf{r}-\mathbf{r}'| - a) d^3\mathbf{r}' \tag{2.25}$$

or

$$\hat{\hat{\boldsymbol{\lambda}}} = \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i} 4\pi \frac{\sin(ka) - ka\cos(ka)}{k^3} \begin{bmatrix} \lambda_A & -\lambda_B \\ -\lambda_B & \lambda_A \end{bmatrix}$$
$$= \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \Pi(\mathbf{k}) \ , \tag{2.26}$$

where

$$\Pi(\mathbf{k}) = \begin{bmatrix} \lambda_A & -\lambda_B \\ -\lambda_A & \lambda_B \end{bmatrix} 4\pi \left[\frac{\sin(ka) - ka\cos(ka)}{k^3}\right] .$$

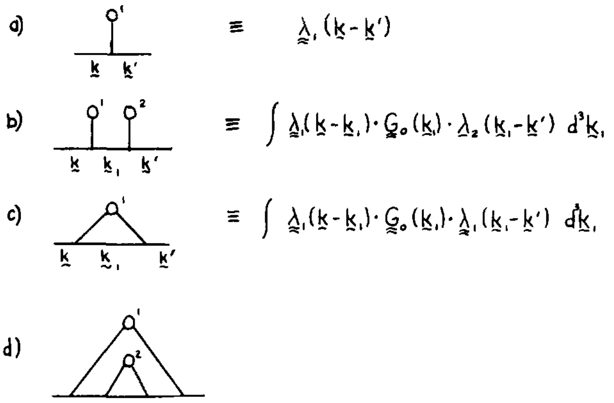

FIG. 1. Diagrammatic representation of the terms in Eq. (2.24).

Although we have already noted that the convolution contained in Γ_{op} is not necessary for uniform systems, it turns out to be convenient, at this stage, to discuss the quantity $\Gamma(\mathbf{k},\mathbf{k}')$. The first term in the summation in Eq. (2.21) is

$$\langle\lambda(\mathbf{k}-\mathbf{k}')\rangle \,.$$

For randomly distributed sinks one finds

$$\langle\lambda(\mathbf{k}-\mathbf{k}')\rangle=\Big\langle\sum_i \exp(i\mathbf{k}\cdot\mathbf{r}_i-i\mathbf{k}'\cdot\mathbf{r}_i)\Big\rangle\Pi(\mathbf{k}-\mathbf{k}')$$
$$=2\pi^3\frac{N}{V}\,\delta^3(\mathbf{k}-\mathbf{k}')\,\Pi(0)$$

since

$$\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}=\frac{N}{V}\int e^{i\mathbf{k}\cdot\mathbf{r}}\,d^3\mathbf{r}\ . \qquad (2.27)$$

Thus, the first term is

$$\langle\lambda(\mathbf{k}-\mathbf{k}')\rangle=(2\pi)^3\,\delta^3(\mathbf{k}-\mathbf{k}')\,\frac{N}{V}\frac{4\pi a^3}{3}\begin{bmatrix}\lambda_A & -\lambda_B\\ -\lambda_A & \lambda_B\end{bmatrix}\ . \qquad (2.28)$$

The second term in Eq. (2.21) is

$$-\langle\lambda*\mathbf{G}^\circ Q\lambda\rangle=-[\langle\lambda*\mathbf{G}^\circ\cdot\lambda\rangle-\langle\lambda\rangle*\mathbf{G}^\circ*\langle\lambda\rangle]$$
$$=-\frac{1}{(2\pi)^3}\int\langle\lambda(\mathbf{k}-\mathbf{k}'')\cdot\mathbf{G}^\circ(\mathbf{k}'',z)\cdot\lambda(\mathbf{k}''-\mathbf{k}')\rangle d^3\mathbf{k}''-\frac{1}{(2\pi)^3}\int\langle\lambda(\mathbf{k}-\mathbf{k}'')\rangle\cdot\mathbf{G}^\circ(\mathbf{k}'',z)\cdot\langle\lambda(\mathbf{k}'-\mathbf{k})\rangle d^3k''\ . \qquad (2.29)$$

We evaluate the first term as the right-hand side of Eq. (2.29):

$$\langle\lambda(\mathbf{k}-\mathbf{k}'')\cdot\mathbf{G}^\circ(k,z)\cdot\lambda(\mathbf{k}''-\mathbf{k}')\rangle$$
$$=\sum_{ij}\langle\exp[i(\mathbf{k}-\mathbf{k}'')\cdot\mathbf{r}_i]\exp[i(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{r}_j]\rangle\Pi(\mathbf{k}-\mathbf{k}'')\cdot\mathbf{G}^\circ(k'',z)\cdot\Pi(k''-k') \qquad (2.30)$$
$$=\left[\frac{N(N-1)}{V^2}(2\pi)^6\,\delta^3(\mathbf{k}-\mathbf{k}'')\,\delta^3(\mathbf{k}''-\mathbf{k}')+(2\pi)^3\frac{N}{V}\,\delta^3(\mathbf{k}-\mathbf{k}')\right]\cdot\Pi(k-k'')\cdot\mathbf{G}^\circ(k'',z)\cdot\Pi(k''-k')\ .$$

When the second term on the right-hand side of Eq. (2.29) is evaluated there is a cancellation so that

$$-\langle\lambda*\mathbf{G}^\circ\lambda\rangle=-\frac{N}{V}\frac{1}{(2\pi)^3}\int\Pi(\mathbf{k}-\mathbf{k}')\,\mathbf{G}^\circ(k',z)\cdot\Pi(\mathbf{k}'-\mathbf{k})\,d^3\mathbf{k}'\ . \qquad (2.31)$$

The projection operator removes contributions due to two uncorrelated reaction centers.

It is convenient to introduce a diagrammatic notation for the terms in Eq. (2.21). The notation we use is based on that used in studies of electronic structure in disordered systems.[8] Examples are shown in Fig. 1. A diagram is read from left to right, with the horizontal line representing $\mathbf{G}^\circ$. The vertices above the line represent the traps and a vertical line connecting a vertex i to the horizontal line indicates a factor of λ_i. We have labeled the vertices and shown the corresponding wave vectors in $\mathbf{G}^\circ$, to aid in understanding the representation.

The averaging process and the presence of the projection operator Q in the summation reduce greatly the number of diagrams that are included. The averaging process can be summarized by the following rules for evaluating diagrams.

(1) Sum all k's entering any vertex, subtract all k's leaving a vertex.

(2) Replace all $\lambda_i(\mathbf{k})$ by $\Pi(\mathbf{k})$ and the average by a product of delta functions of the sums from step 1 and multiply each delta function by $(2\pi)^3$.

For example, the diagram labeled d shown in Fig. 1 will be

$$\frac{1}{(2\pi)^{12}}\iiint\langle\lambda_1(\mathbf{k}_0-\mathbf{k}_1)\cdot\mathbf{G}^\circ(\mathbf{k}_1,z)\,\lambda_2(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{G}^\circ(\mathbf{k}_2,z)\,\lambda_2(\mathbf{k}_2-\mathbf{k}_3)\cdot\mathbf{G}^\circ(\mathbf{k}_3,z)\cdot\lambda(\mathbf{k}_3-\mathbf{k}_4)\rangle d^3\mathbf{k}_1d^3\mathbf{k}_2d^3\mathbf{k}_3$$
$$=\frac{\rho^2}{(2\pi)^6}\iiint\Pi(\mathbf{k}_0-\mathbf{k}_1)\cdot\mathbf{G}^\circ(\mathbf{k}_1,z)\cdot\Pi(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{G}^\circ(\mathbf{k}_2,z)\cdot\Pi(\mathbf{k}_2-\mathbf{k}_3)$$
$$\cdot\mathbf{G}^\circ(\mathbf{k}_3,z)\cdot\Pi(\mathbf{k}_3-\mathbf{k}_4)\,\delta^3(\mathbf{k}_0-\mathbf{k}_1+\mathbf{k}_3-\mathbf{k}_4)\,\delta^3(\mathbf{k}_1-\mathbf{k}_3)\,d^3\mathbf{k}_1d^3\mathbf{k}_2d^3\mathbf{k}_3 \qquad (2.32)$$
$$=\frac{\rho^2}{(2\pi)^6}\,\delta^3(\mathbf{k}_0-\mathbf{k}_4)\iint\Pi(\mathbf{k}_0-\mathbf{k}_1)\cdot\mathbf{G}^\circ(\mathbf{k}_1,z)\cdot\Pi(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{G}^\circ(\mathbf{k}_2,z)\cdot\Pi(\mathbf{k}_2-\mathbf{k}_1)\cdot\mathbf{G}^\circ(\mathbf{k}_1,z)\cdot\Pi(\mathbf{k}_1-\mathbf{k}_4)\,d^3\mathbf{k}_1d^3\mathbf{k}_2\ .$$

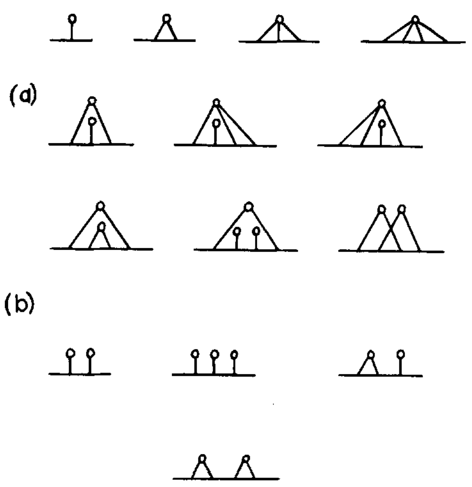

FIG. 2. Diagrams to fourth order in scattering. (a) Admissible diagrams. (b) Nonadmissible diagrams.

We now need to sum all admissible diagrams. Due to the presence of the projection operator, it is necessary to sum only those diagrams where no vertical line can be drawn through the diagrams such that all the vertices on the right of the line are disconnected from all the vertices on the left of the line. Figure 2(a) shows examples of diagrams that are allowed; Fig. 2(b) shows diagrams that are not allowed.

From the rules for evaluating diagrams, we can immediately see that the incoming k on the left-most vertext must equal the outgoing k on the right-most vertex. This is simply a restatement of our previous point that the homogeneity of the reaction center distribution allows us to remove the convolution in $\mathbf{\Gamma}_{op}$. For evaluation of the diagrams, it is convenient to retain the distinction.

The quantities of interest are the observed rate coefficient matrix and the observed diffusion coefficient matrix. These quantities are determined according to

$$\lambda_{obs} = \lim_{\substack{\mathbf{k}\to 0\\ z\to 0}} \mathbf{\Gamma}(\mathbf{k}, z) \ , \tag{2.33}$$

$$\mathbf{D}_{obs} = \mathbf{D} + \lim_{\substack{\mathbf{k}\to 0\\ z\to 0}} \tfrac{1}{2}\, \nabla_{\mathbf{k}}^2 \mathbf{\Gamma}(\mathbf{k}, z) \ . \tag{2.34}$$

It has been pointed out by Felderhof, Deutch, and Titulaer[7] that this definition of the effective diffusion coefficient will contain contributions that may be more properly included as a k^2 contribution to the rate coefficient.

III. RESULTS FOR SYSTEMS WITH LOW REACTIVITY

The expression we have derived is an expansion with the reaction rate as the expansion parameter. This formalism is hence convenient for situations where λ is small. We will consider three cases: (1) steady state; (2) the long time behavior of an initial value problem; and (3) the effect of correlation between the initial conditions and the location of the reaction center.

A. Steady state

In this case we are interested in results for the limit $z=0$. We need to evaluate all the all the admissible diagram with

$$\mathbf{G}^\circ(\mathbf{k}) = \begin{bmatrix} \dfrac{1}{D_A k^2} & 0 \\ 0 & \dfrac{1}{D_B k^2} \end{bmatrix} . \tag{3.1}$$

Our objective is to evaluate the sum displayed formally in Eq. (2.21). In the limit $z\to 0$ certain classes of diagrams are divergent. These are shown in Fig. 3. Ordering the diagrams by powers of λ, the first diagram in each row of Fig. 3 are found to be the most strongly divergent. This class of diagrams can, however, be resummed to yield a convergent result:

$$\mathbf{\Gamma}_{DH}(\mathbf{k}) = \rho\lambda(\mathbf{k}) - \frac{\rho}{(2\pi)^3}\int \Pi(\mathbf{k}-\mathbf{q})\cdot\mathbf{G}^\circ(\mathbf{q}) \cdot [\mathbf{I}+\rho\Pi(0)\cdot\mathbf{G}^\circ(\mathbf{q})]^{-1}\cdot\Pi(\mathbf{q}-\mathbf{k})\, d^3\mathbf{q} \ . \tag{3.2}$$

Because the series summed is similar to the summation used in the Debye–Huckel theory of electrolytes,[11] we have used the subscript DH. Muthukumar and Cukier[4] have found a similar series of divergent contributions in their treatment of the perfectly absorbing case.

Combining Eq. (3.2) with Eq. (2.39) leads to the following expression for the rate coefficient

$$\lim_{k\to 0}\mathbf{\Gamma}_{DH}(\mathbf{k}) = \begin{bmatrix} \lambda_A & -\lambda_B \\ -\lambda_A & \lambda_B \end{bmatrix} \times\left\{\phi - 8\rho a^3\gamma^2\int_0^\infty \frac{(\sin l - l\cos l)^2}{l^4}\,\frac{1}{l^2+\gamma^2\phi}\, dl\right\} , \tag{3.3}$$

where

$$\gamma^2 = a^2\left(\frac{\lambda_A}{D_A}+\frac{\lambda_B}{D_B}\right) \tag{3.4}$$

and

$$\phi = \rho\,\frac{4\pi a^3}{3} \ . \tag{3.5}$$

Performing the integration, we find

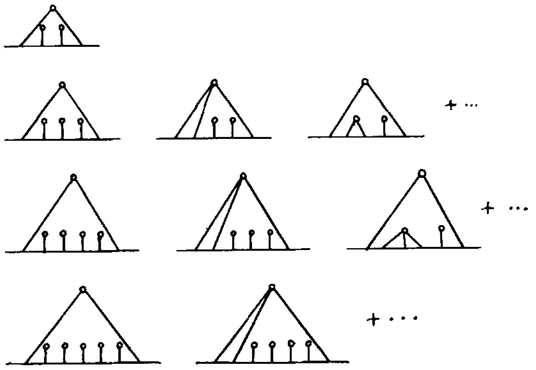

FIG. 3. Divergent diagrams.

$$\mathbf{\Gamma}_{\rm DH}(0)=\begin{bmatrix}\lambda_A & -\lambda_B\\ -\lambda_A & \lambda_B\end{bmatrix}\left\{\phi-\left[1+\frac{3}{2}\,\frac{[1-\exp(-2\gamma\sqrt{\phi}]-2\gamma\sqrt{\phi}\exp(-2\gamma\sqrt{\phi})-\gamma^2\phi[1+\exp(-2\gamma\sqrt{\phi})]}{\gamma^3\phi^{3/2}}\right]\right\}. \tag{3.6}$$

For low densities, the rate per reaction center is

$$\frac{1}{\rho}\,\mathbf{\Gamma}_{\rm DH}(0)\cong\frac{4\pi a^3}{3}\begin{bmatrix}\lambda_A & -\lambda_B\\ -\lambda_A & \lambda_B\end{bmatrix}\left(1-\tfrac{2}{5}\gamma^2+\tfrac{1}{3}\sqrt{\phi}\,\gamma^2+\cdots\right). \tag{3.7}$$

This rate coefficient depends, to leading order, on the square root of the occupied volume fraction. Studies[1–4] of perfectly absorbing sinks have also found a square root dependence.

The diffusion coefficient matrix, obtained from Eqs. (3.2) and (2.34), is

$$\begin{aligned}\mathbf{D}_{\rm DH}&=\mathbf{D}+\frac{4\pi\rho a^5}{30}\begin{bmatrix}-\lambda_A & \lambda_B\\ \lambda_A & -\lambda_B\end{bmatrix}+\begin{bmatrix}-\lambda & \lambda_B\\ \lambda_A & -\lambda_B\end{bmatrix}8\rho a^5\gamma^2\int_0^\infty\frac{(-l^4+16l^2+\frac{21}{2})\cos(2l)+(6l^3-21l)\sin(2l)+\frac{21}{2}}{l^6(l^2+\phi\gamma^2)}\,dl \\ &=\mathbf{D}+\begin{bmatrix}-\lambda_A a^2 & \lambda_B a^2\\ \lambda_A a^2 & -\lambda_B a^2\end{bmatrix}\times\left(\frac{\phi}{10}+3\phi\gamma^2\left\{\frac{17}{3\phi\gamma^2}+\frac{1}{\phi\gamma^2}\left[-5\gamma^2\phi-2\gamma\sqrt{\phi}+\tfrac{21}{2}\right.\right.\right. \\ &\qquad\left.\left.\left.+\exp(-2\gamma\sqrt{\phi})(-\phi^2\gamma^4-6\phi^{3/2}\gamma^3-16\phi\gamma^2+21\gamma\sqrt{\phi}+\tfrac{21}{2})\right]\right\}\right).\end{aligned} \tag{3.8}$$

For small $\gamma^2\phi$ one finds

$$\mathbf{D}_{\rm DH}\cong\begin{bmatrix}D_A-\lambda_A a^2\left(\frac{\phi}{10}+9\phi\gamma^2+\cdots\right) & \lambda_B a^2\left(\frac{\phi}{10}+9\phi\gamma^2+\cdots\right)\\ \lambda_A a^2\left(\frac{\phi}{10}+9\phi\gamma^2+\cdots\right) & D_B-\lambda_B a^2\left(\frac{\phi}{10}+9\phi\gamma^2+\cdots\right)\end{bmatrix}. \tag{3.9}$$

The effective diffusion coefficient matrix contains off diagonal terms, and these off diagonal terms are not equal. In the extreme case that the reaction is irreversible, $\lambda_B=0$, and to first order only one off diagonal term will be nonzero. The effective diffusion coefficient matrix then reflects the fact that a particle diffuses as a reactant molecule until it becomes a product molecule at some point in space.

B. Initial value problem

Some situations are more accurately modeled by an initial value problem, rather than the steady state situation considered in the previous section. Here we consider the situation where the initial condition for the spatial arrangement of the concentration is uncorrelated to the positions of the reaction centers:

$$\mathbf{c}(\mathbf{r},t=0)=\mathbf{c}_0$$

or (3.10)

$$\hat{\mathbf{c}}(k,t=0)=\mathbf{c}_0\,\delta^3(\mathbf{k})\ .$$

If this initial value is completely uncorrelated with the location of the reaction centers, we must solve

$$[z\mathbf{I}+\mathbf{D}k^2+\mathbf{\Gamma}(k,z)]\cdot\hat{\mathbf{c}}(k,z)=\hat{\mathbf{c}}(k,t=0) \tag{3.11}$$

or

$$\hat{\mathbf{c}}(\mathbf{k},z)=[z\mathbf{I}+\mathbf{D}k^2+\mathbf{\Gamma}(k,t)]^{-1}\cdot\hat{\mathbf{c}}(k,t=0)\ . \tag{3.12}$$

Since $\mathbf{c}_0$ is uniform

$$\hat{\mathbf{c}}(r,z)=[z\mathbf{I}+\mathbf{\Gamma}(k=0,z)]^{-1}\cdot\mathbf{c}_0 \tag{3.13}$$

and $\hat{\mathbf{c}}(\mathbf{r},z)=\mathbf{c}(z)$ is uniform in space. In this case $\mathbf{c}(t)$ will decay uniformly because we have averaged our reaction center locations, with time scales related to the pole structure of $\mathbf{\Gamma}(0,z)$.

In the limit at long times, or small values of z, the diagrams considered in the previous section remain divergent and hence, still dominate the sum in Eq. (2.21). We need then to evaluate

$$\mathbf{\Gamma}_{\rm DH}(k=0,z)=\rho\lambda(0)-\frac{\rho}{(2\pi)^3}\int\lambda(q)\cdot\mathbf{G}^\circ(q,z)\cdot\left[\mathbf{I}+\frac{\rho}{(2\pi)^3}\lambda(0)\cdot\mathbf{G}^\circ(q,z)\right]^{-1}\cdot\lambda(q)\,d^3\mathrm{q}\ , \tag{3.14}$$

where

$$\mathbf{G}^\circ(\mathrm{q},z)=\begin{bmatrix}\dfrac{1}{z+D_Aq^2} & 0\\ 0 & \dfrac{1}{z+D_Bq^2}\end{bmatrix}. \tag{3.15}$$

One finds the result,

$$\mathbf{\Gamma}(k=0,t)=\begin{bmatrix}\lambda_A & -\lambda_B\\ -\lambda_B & \lambda_A\end{bmatrix}\times\left\{\phi-\frac{2\rho}{\pi}\int_0^\infty\frac{[\sin(qa)-qa\cos(qa)]^2}{q^6}\times\frac{\lambda_A(z+D_Bq^2)+\lambda_B(z+D_Aq^2)}{(z+D_Aq^2)(z+D_Bq^2)+\phi[\lambda_A(z+D_B)+\lambda_B(z+D_Aq^2)]}\,dq\right\}. \tag{3.16}$$

This expression can be evaluated in the same manner as used in the previous section. For simplicity, we will consider the case $D_A=D_B$ in which case

$$\mathbf{\Gamma}_{\rm DH}(k=0,t)=\begin{bmatrix}\lambda_A & -\lambda_B\\ -\lambda_A & \lambda_B\end{bmatrix}\times\left\{\phi-\tfrac{3}{2}\,y_0^2\ \frac{2}{3y^2}+\frac{(1-e^{-2y})-2ye^{-2y}-y^2(1+e^{-2y})}{y^5}\right\}, \tag{3.17}$$

where

$$y(z)=\sqrt{\frac{z+\phi(\lambda_A+\lambda_B)}{D/a^2}} \quad \text{and} \quad y_0=y(0)\ . \tag{3.18}$$

For small y, one finds

$$\mathbf{\Gamma}_{\mathrm{DH}} \cong \begin{bmatrix} \lambda_A & -\lambda_B \\ -\lambda_A & \lambda_B \end{bmatrix} (\phi-\tfrac{2}{5}\,y_0^2+\tfrac{1}{3}\,y\,y_0^2+\cdots)\ . \tag{3.19}$$

The observed relaxation is found by the matrix inversion

$$[z\mathbf{I}+\mathbf{\Gamma}(\mathrm{k}=0,z)]^{-1}=\frac{1}{z[z+A(\lambda_A+\lambda_B)]}\begin{bmatrix} z+A\lambda_B & A\lambda_B \\ A\lambda_A & z+A\lambda_A \end{bmatrix}, \tag{3.20}$$

where

$$A=(\phi-\tfrac{2}{5}\,y_0^2+\tfrac{1}{3}\,y\,y_0^2+\cdots).$$

In this expression y, and hence A, is still a function of z. To obtain the time evolution we must invert the Laplace transform.

The denominator in Eq. (3.20) is, for small λ_A, λ_B, and z,

$$z\,[z+A(\lambda_A+\lambda_B)] \simeq z\left[z+(\lambda_A+\lambda_B)\,\phi-\frac{2}{5}\frac{(\lambda_A+\lambda_B)^2}{D/a^2}\,\phi + \frac{1}{3}\frac{(\lambda_A+\lambda_B)^2}{D/a^2}\,\phi\sqrt{\frac{z+\phi(\lambda_A+\lambda_B)}{D/a^2}}\,\right]. \tag{3.21}$$

To lowest order in z, there are two important contributions. First, there is a simple pole at $z=0$ which is the equilibrium concentration of the two species

$$\frac{1}{\lambda_A+\lambda_B}\begin{bmatrix} \lambda_B & \lambda_B \\ \lambda_A & \lambda_A \end{bmatrix}. \tag{3.22}$$

There is also a contribution from the pole at $z=-\phi(\lambda_A+\lambda_B)$. Because of the nonanalytic behavior of A (or y) as a function of z, this contribution is complicated. For very long times, where only the small z behavior needs to be considered, and we find

$$\begin{bmatrix} -\phi\lambda_A & \phi\lambda_B \\ \phi\lambda_A & -\phi\lambda_B \end{bmatrix} \frac{\exp[-\phi(\lambda_A+\lambda_B)t]}{[\phi(\lambda_A+\lambda_B)]^{3/2}}\,\frac{D}{a^2}\left(\frac{25}{12}\right)t^{-3/2}\ . \tag{3.23}$$

This behavior is different than would be expected from a uniform medium with rate coefficients $\phi\lambda_A$ and $\phi\lambda_B$ at all points in space. In such a system the medium, where decay would be given by

$$\begin{bmatrix} -\phi\lambda_A & \phi\lambda_B \\ \phi\lambda_A & -\phi\lambda_B \end{bmatrix} \frac{\exp[-\phi(\lambda_A+\lambda_B)t]}{\lambda_A+\lambda_B}\ . \tag{3.24}$$

The difference in behavior is due to screening. The screening effects manifest themselves by speeding the approach to equilibrium. The nonexponential decay will only appear for times much greater than $\phi(\lambda_A+\lambda_B)$ so in the limit of very small ϕ, this "diffusive tail" will not be observable.

Kirkpatrick[5] has obtained results similar to Eq. (3.22) for the case of perfectly absorbing spheres. He has, however, argued that the expression is valid only for small values of z (for long times) and that the square root term should be expanded to yield (for our problem)

$$z\,[z+A(\lambda_A+\lambda_B)] \sim z\left\{z+(\lambda_A+\lambda_B)\,\phi-\frac{2}{5}\frac{(\lambda_A+\lambda_B)^2}{D/a^2}\,\phi + \tfrac{1}{3}\,(\gamma_A+\gamma_B)\left[\frac{(\lambda_A+\lambda_B)\phi}{D/a^2}\right]^{3/2}\right\}. \tag{3.25}$$

This corresponds to simple exponential decay in time, with the decay rate given by

$$\lambda_{\mathrm{eff}}=(\lambda_A+\lambda_B)\,\phi[1-\tfrac{2}{5}\,\gamma^2+\tfrac{1}{3}\sqrt{\phi}\,\gamma^3+\cdots]\ . \tag{3.26}$$

This expression has the same lowest order γ and ϕ dependence as the steady state rate [Eq. (3.7)]. A recent scaling analysis by Tokuyama and Cukier[8] of perfectly absorbing spheres supports the interpretation represented by Eq. (3.26). However, the true nature of the long time behavior is far from settled. The complicated, nonanalytic dependence of the various averaged quantities on the Laplace transform variable and the parameters (e.g., Felderhof and Deutch[1] find corrections of order $\phi\ln\phi$) suggests the true time dependence will be considerably more complicated than simple exponential decay, and that nonperturbative methods of analysis should be applied to this problem. A recent step in this direction has been made by Grassberger and Procaccia.[9]

C. Initial conditions correlated to the positions of the reaction centers

In the derivation of Eq. (2.19), we have assumed that the sources or the initial values were uncorrelated with the reaction centers so that

$$P\langle \mathbf{s}'\rangle=\mathbf{s}'\ . \tag{3.27}$$

If we relax that requirement we find that the source (or initial value) term in Eq. (2.19) is replaced by

$$\hat{\mathbf{s}}_{\mathrm{eff}}(k,z)=\left\langle \sum_{n=0}^{\infty}[-\lambda*\mathbf{G}^{\circ}Q]^n\cdot\mathbf{s}'\right\rangle. \tag{3.28}$$

This implies that even if there are no external sources, $\mathbf{s}'=\hat{\mathbf{c}}(\mathrm{k},t=0)$, correlations may build up and introduce an effective source in the averaged equation with some complicated time (or z) dependence.

To examine the importance of these terms, we considered a system where all the reactants are initially located within the reaction centers. For the slow reaction case, it can be demonstrated that the corrections to the long time behavior are an order of magnitude (in terms of γ) smaller than the leading order contribution determined in Sec. III B.

IV. HIGHLY REACTIVE SYSTEMS

Our previous results are valid only for slowly reacting systems; the quantity γ must be small. In this section we discuss the extension of our model to more reactive systems. Specifically we consider a single irreversible reaction at steady state in the limit of large γ.

Because we will be interested in the limit of large γ we must consider a different and larger set of diagrams. Direct evaluation of the diagrams is mathematically difficult and also unproductive since large numbers of the diagrams are divergent.

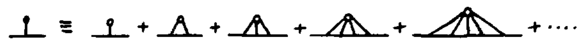

FIG. 4. The renormalized vertex is the sum of all interactions with a single site.

We begin, instead, by defining a new, "renormalized" vertex $v(\mathbf{q},\mathbf{q}')$. This vertex is the summation of all diagrams that include only a single sink as shown in Fig. 4. We will demonstrate shortly that the new vertex is well behaved in the limit of large λ and that it is nonzero as q and q' go to zero. The allowed diagrams are shown in Fig. 5. There are again divergent diagrams and we must resum a series of divergent diagrams (now expressed in terms of the modified vertex) to obtain a finite result. The series of diagrams is shown in Fig. 5(b). The diagrams included in this sum are the most strongly divergent to a given order in the sink density. The series is again similar to the Debye–Huckel sum [cf. Eq. (3.2)]. The result is

$$\Gamma_{\mathrm{DH}}(q)=\rho v(\mathbf{q},q')$$
$$-\frac{\rho^2}{(2\pi)^3}\int\frac{v(\mathbf{q},q')\,G_0(\mathbf{q}')\,v(\mathbf{q}',\mathbf{q}')\,G_0(q')\,v(q',q)}{1+\rho G_0(q')\,v(q',q')}\,d^3q\ . \qquad (4.1)$$

To proceed with the calculation we need an expression for $v(q,q')$. We find such an expression by considering a single sink problem. For a single sink

$$[z+Dq^2]\,\hat{c}_s=-\lambda*\hat{c}_s+\hat{s} \qquad (4.2)$$

which has the solution

$$\hat{c}_s=[1+G_0\lambda*]^{-1}G_0\,\hat{s} \qquad (4.3)$$

or

$$[z+Dq^2]\,\hat{c}_s=\sum_{n=0}^{\infty}(-\lambda*G_0)^n\,\hat{s} \qquad (4.4)$$

or

$$-\lambda*\hat{c}_s+\hat{s}=\sum_{n=0}^{\infty}(-\lambda*G^{\circ})^n\,\hat{s}\ . \qquad (4.5)$$

The new vertex will be defined as the sum of all interactions with a single sink,

$$v(\mathbf{q},\mathbf{q}')=\sum_{n=0}^{\infty}(-\lambda*G_0)^n\lambda\ . \qquad (4.6)$$

If we solve the single sink problem with a source term given by

$$s(\mathbf{r})=\lambda\theta(|\mathbf{r}|-a)\,e^{i\mathbf{q}\cdot\mathbf{r}} \qquad (4.7)$$

the new vertex is simply Eq. (4.8),

$$v(\mathbf{q},\mathbf{q}')=[-\lambda*\hat{c}_s+\hat{s}]\ . \qquad (4.8)$$

The quantity $c_s(\mathbf{r})$, will obey the inverse Fourier transform of Eq. (4.2), together with Eq. (4.7) which is

$$D\nabla^2c_s(\mathbf{r})-\lambda c_s(r)=\lambda e^{i\mathbf{q}\cdot\mathbf{r}}\ ,\quad r<a\ ,$$
$$D\nabla^2c_s(\mathbf{r})=0\ ,\quad r>a\ . \qquad (4.9)$$

Our renormalized vertex is the single body t matrix for this problem. Ghosh, Zhao, and Huber,[12] and Huber and Ghosh[12] have also calculated this t matrix in modeling fluorescence in solids. They considered the average t-matrix approximation (ATA), which corresponds to including only the first term in Eq. (4.1). The ATA does not contain the resummed divergent terms, and hence does not show any nonanalytic dependence on the density.

It is interesting to note that the problem has sources *within* the sinks. Previous calculations that have used a T-matrix formalism and perfectly absorbing sinks have had difficulties that appear to arise from the possibility of the sources overlapping the sinks.[3,7] Our approach avoids such problems.

The solution to Eq. (4.9) can be written as

$$c_s(r)=\sum_{n=0}^{\infty}\frac{\lambda(2n+1)\,i^n}{Dq^2+\lambda}\,\frac{j_n(qa)+\dfrac{a}{(n+1)}j_n'(qa)}{i_n(\alpha a)+\dfrac{\alpha a}{n+1}i_n'(\alpha a)}$$
$$\times i_n(\alpha r)P_n(\cos\theta')+\frac{\lambda e^{+i\mathbf{q}\cdot\mathbf{r}}}{Dq^2+\lambda}\ ,\quad r<a \qquad (4.10)$$
$$=\sum_{n=0}^{\infty}\frac{\lambda(2n+1)\,i^n}{Dq^2+\lambda}\,\frac{q\,i_n(\alpha a)\,j_n'(qa)-\alpha i_n'(\alpha a)\,j_n(qa)}{i_n(\alpha a)+\dfrac{\alpha a}{(n+1)}i_n'(\alpha a)}$$
$$\times\frac{a^{n+2}}{r^{n+1}}P_n(\cos\theta)\ ,\quad r>a\ ,$$

where $\alpha^2=(\lambda/D)$ and $\cos(\theta')=\mathbf{q}\cdot\mathbf{r}$, here j_n and i_n are the spherical and modified spherical Bessel functions.[13] The renormalized vertex is found from Eqs. (4.8) and (4.10) to be

$$v(\mathbf{q},\mathbf{q}')=\lambda^2\sum_{n=0}^{\infty}(-)^n\left\{\frac{(2n+1)}{Dq^2+\lambda}\,\frac{j_n(q'a)+\dfrac{q'a}{(n+1)}j_n'(q'a)}{i_n(\alpha a)+\dfrac{\alpha a}{(n+1)}i_n'(\alpha a)}P_n(\cos\theta)\right.$$
$$\left.\times\frac{a}{q^2+\alpha^2}\,[qa\,j_{n+1}(qa)\,i_n(\alpha a)-\alpha a\,j_n(qa)\,i_{n+1}(\alpha a)]\right\} \qquad (4.11)$$
$$+\frac{\lambda Dq^2}{Dq^2+\lambda}\,4\pi a^2\,\frac{j_1(|\mathbf{q}-\mathbf{q}'|a)}{|\mathbf{q}-\mathbf{q}'|}\ ,$$

where $\cos\theta=\mathbf{q}\cdot\mathbf{q}'$.

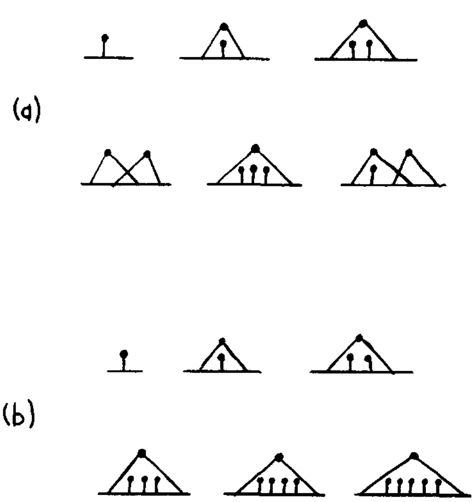

FIG. 5. (a) Admissible diagrams with the renormalized vertex; (b) diagrams included in Γ_{DH}.

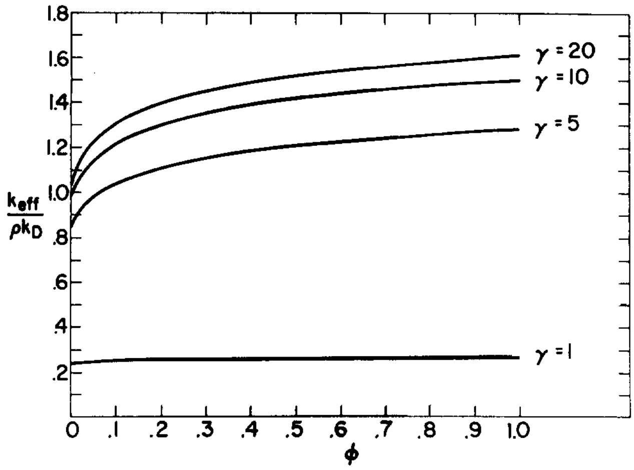

FIG. 6. The rate coefficients as a function of volume fraction of sinks for various values of γ.

The expression for $\Gamma_{DH}(q)$ is rather formidable. We will focus on the effective rate and diffusion coefficients in the low k limit as defined by Eqs. (2.33). The rate coefficient is given by

$$k_{eff} = \rho\, 4\pi Da\left[1 - \frac{\tanh(\gamma)}{\gamma}\right] - \frac{\rho^2}{(2\pi)^3}\int \frac{v^2(0,q)\, G_0^{\circ 2}(\mathbf{q})\, v(\mathbf{q},\mathbf{q})}{1+\rho G^\circ(\mathbf{q})\, v(\mathbf{q},\mathbf{q})}\, d^3\mathbf{q}\ , \qquad (4.12)$$

where

$$v(0,\mathbf{q}) = \frac{4\pi Da}{Dq^2+\lambda}\,\frac{\lambda}{Dq^2+\lambda}\left[\frac{\sin qa}{qa} - \cos(qa)\,\frac{\tanh(\gamma)}{\gamma}\right]$$

and

$$\gamma = a\sqrt{\frac{\lambda}{D}}\ . \qquad (4.13)$$

The integral is too complicated to evaluate analytically. To proceed, we make the "monopole approximation" for $v(\mathbf{q},\mathbf{q})$,

$$v(\mathbf{q},\mathbf{q}) \approx \lim_{q\to 0} v(\mathbf{q},\mathbf{q}) = k_0\left[1 - \frac{\tanh(\gamma)}{\gamma}\right], \qquad (4.14)$$

where

$$k_0 = 4\pi Da\ . \qquad (4.15)$$

With this approximation, the rate coefficient is

$$\lambda_{eff} = \rho k_0\left[1 - \frac{\tanh(\gamma)}{\gamma}\right] \times\left\{1 + 3\phi\,\frac{2}{\pi}\int_0^\infty \frac{\gamma^4}{(l^2+\gamma^2)^2}\left[\frac{\sin(l)}{l} - \cos(l)\,\frac{\tanh(\gamma)}{\gamma}\right]^2 \times \frac{1}{l^2 + 3\phi\left[1 - \frac{\tanh(\gamma)}{\gamma}\right]}\, dl\right\}. \qquad (4.16)$$

In the limit of high reactivity (λ large), this reduces to

$$\lambda_{eff} = \rho k_0\left[1 + 3\phi\,\frac{2}{\pi}\int_0^\infty \left(\frac{\sin l}{l}\right)^2 \frac{1}{l^2+3\phi}\, dl\right] \qquad (4.17)$$

which is equivalent to the expression given by Muthukumar and Cukier[4] for the perfectly absorbing sinks with the monopole approximation.

We can perform the integration to obtain an expression for the rate coefficient valid for all reactivities

$$\lambda_{eff} = \rho k_0\left[1 - \frac{\tanh(\gamma)}{\gamma}\right]\left(1 + 3\phi\left\{\frac{1-T(\gamma)}{\epsilon^2}\,\frac{\gamma^4}{2(\gamma^2-\epsilon^2)^2\epsilon^3}\,[(1-e^{-2\epsilon}) - 2\epsilon T(\gamma)\, e^{-2\epsilon} - T^2(\gamma)\epsilon^2(1+e^{-2\epsilon})] + \frac{-\gamma T^2(\gamma) + e^{-2\gamma}\,[1 + 2\gamma T(\gamma) + \gamma^2 T^2(\gamma) - T(\gamma) - \gamma T^2(\gamma)]}{2(\epsilon^2-\gamma^2)}\right\}\right), \qquad (4.18)$$

where

$$\epsilon^2 = 3\phi\,[1 - T(\gamma)] \quad \text{and} \quad T(\gamma) = \frac{\tanh(\gamma)}{\gamma}\ . \qquad (4.19)$$

This result is plotted in Fig. 6. In the limit $\gamma\to\infty$ ($\lambda\to\infty$) we find

$$\lambda_{eff} = \rho k_0\left[2 - \frac{[1 - \exp(-2\sqrt{3\phi})]}{2\sqrt{3\phi}}\right], \qquad (4.20)$$

for small ϕ,

$$\lambda_{eff} \approx \rho k_0\ [1 + \sqrt{3\phi} + \cdots]\ . \qquad (4.21)$$

This agrees with the results of Felderhof and Deutch,[1] as well as later workers. The full expression for $v(\mathbf{q},\mathbf{q}')$ should be introduced when diffusion and reaction can occur on the same time scale.

The effective diffusion coefficient has a similar structure. From Eqs. (2.33) and (4.1) we find

$$D_{eff} = D_0 - \lim_{q\to 0}\rho\,\frac{1}{2}\,\frac{d^2}{eq^2}\, v(q,q) + \frac{2\rho^2}{(2\pi)^3}\lim_{q\to 0}\int\left[\frac{\partial v(q,q')}{\partial q}\right]^2 \frac{G^{\circ 2}(q')\, v(q',q')}{1+\rho G^\circ(q')\, v(q',q')}\, d^3q' + \frac{2\rho^2}{(2\pi)^3}\lim_{q\to 0}\int \frac{\partial^2 v(q,q')}{\partial q^2}\,\frac{G^{\circ 2}(q') v(q',q')}{1+\rho G^\circ(q') v(q',q')}\, d^3q'\ . \qquad (4.22)$$

The first term is

$$\frac{1}{2}\left[\frac{d^2}{dq^2}v(q,q)\right]_{q=0}=D_0\phi\left\{2+\frac{3\tanh(\gamma)}{\gamma}-\frac{12}{\gamma^2}\left[1-\frac{\tanh(\gamma)}{\gamma}\right]+\frac{3}{\gamma}\left[\frac{1}{\gamma}-\coth(\gamma)\right]\right\} \tag{4.23}$$

Using the monopole approximation for $v(\mathbf{q}',\mathbf{q}')$ [Eq. (4.14)], the integrals in Eq. (4.22) reduce to

$$-D_0\phi^2\frac{6}{\pi}\int_0^\infty\left(\frac{\gamma^2}{l^2+\gamma^2}\right)^2\left[\left(\cos l\left\{\frac{6}{\gamma^2}\left[1-\frac{\tanh(\gamma)}{\gamma}\right]\right\}-\frac{3\tanh(\gamma)}{\gamma}\right)+j_0(l)-2j_2(l)\right]\left[j_0(l)-\frac{\tanh(\gamma)}{\gamma}\cos(l)\right]\frac{1}{l^2+\epsilon^2}\,dl$$
$$+D_0\frac{54\phi^2}{\pi}\int_0^\infty\left(\frac{\gamma^2}{l^3+\gamma^2}\right)^2\left\{\frac{\sin l}{l}\left[\frac{1}{\gamma}-\coth(\gamma)\right]+j_1(l)\right\}^2\frac{1}{l^2+\epsilon^2}\,dl\ . \tag{4.24}$$

In order to compare our result to the perfectly absorbing case take the limit $\lambda\to\infty$, and we find

$$D_{\mathrm{eff}}=D_0\left\{1+2\phi-6\phi^2\frac{1}{\pi}\int_0^\infty\frac{j_0(l)\left[j_0(l)-2j_2(l)\right]}{l^2+3\phi}\,dl+54\phi^2\frac{1}{\pi}\int_0^\infty\frac{j_1^2(l)}{l^2+3\phi}\,dl\right\}\ . \tag{4.25}$$

This expression differs from that given by Muthukumar and Cukier[4] by the term

$$D_0\frac{12\phi}{\pi}\int_0^\infty\frac{j_0(l)\,j_2(l)}{l^2+3\phi}\,dl\ . \tag{4.26}$$

For small volume fractions our result is

$$D_{\mathrm{eff}}=D_0\left[1+2\phi-\sqrt{3}\,\phi^{3/2}+\tfrac{16}{5}\phi^2+\cdots\right], \tag{4.27}$$

whereas Muthukumar and Cukier[4] find

$$D_{\mathrm{eff}}=D_0\left[1+2\phi-\sqrt{3}\,\phi^{3/2}+\tfrac{8}{5}\phi^2+\cdots\right]\ . \tag{4.28}$$

The difference between the two results is not significant since nondivergent terms of order ϕ^2 were not completely included in the calculation.

The result for all values of the reactivity is rather complicated. It is

$$D_{\mathrm{eff}}=D_0\Bigg[1+2\phi+3T(\gamma)-\frac{12}{\gamma^2}\left[1-T(\gamma)\right]+\frac{3}{\gamma}G(\gamma)+\tfrac{27}{2}\gamma^4\phi^2\Bigg(\frac{6(\gamma)+\frac{2}{3}}{\gamma^4\epsilon^2}+\frac{(1-e^{-2\epsilon})}{\epsilon^4(\gamma^2-\epsilon^2)}\left\{\left[1-\epsilon^2G(\gamma)\right]^2-2\epsilon\left[1-\epsilon^2G(\gamma)\right]e^{-2\epsilon}\right.$$
$$\left.-\epsilon^2(1+e^{-2\epsilon})\right\}+\frac{1}{\gamma^6(\epsilon^2-\gamma^2)}\left\{e^{-2\gamma}\left[-\gamma^2\coth(\gamma)+\gamma\coth(\gamma)-2\gamma^2\coth(\gamma)-2+\gamma-\gamma^2\right]+\left[1-\gamma\coth(\gamma)\right]\left[\coth(\gamma)+\gamma\right]\right\}\Bigg)$$
$$-\tfrac{2}{3}\gamma^4\phi^2\Bigg(\frac{1}{\gamma^2\epsilon^2}\left[2-3T(\gamma)+3F(\gamma)\right]-\frac{1}{(\epsilon^2-\gamma^2)^2}\frac{1}{\epsilon^5}\left\{(3\epsilon^2+6)(1-e^{-2\epsilon})+\left[3\epsilon^4F(\gamma)-6\epsilon^2\right]T(\gamma)\,(1+e^{-2\epsilon})\right.$$
$$\left.+\left[3\epsilon^3F(\gamma)-3\epsilon^3T(\gamma)-6\epsilon-T(\gamma)\,6\epsilon\right]e^{-2\epsilon}+6\epsilon\left[T(\gamma)-1\right]\right\}+\left[\frac{1}{\gamma^6}\frac{1}{\epsilon^2-\gamma^2}-\frac{1}{2\gamma^4(\epsilon^2-\gamma^2)^2}\right]6\left[T(\gamma)-1\right]\Bigg)$$
$$-\tfrac{2}{3}\gamma^4\phi^2\Bigg\{\left[\frac{15}{4}\frac{1}{\gamma^2}\frac{1}{(\epsilon^2-\gamma^2)}-\frac{1}{2\gamma^5}\frac{1}{(\epsilon^2-\gamma^2)^2}\right]*\left[-(\gamma^2+2)(1-e^{-2\epsilon})-\left[\gamma^4F(\gamma)-2\gamma^2\right]T(\gamma)\,(1+e^{-2\gamma})\right.$$
$$+e^{-2\gamma}\left[\gamma^3F(\gamma)-\gamma^3T(\gamma)-2\gamma-2\gamma T(\gamma)\right]+\left(\frac{1}{\epsilon^2-\gamma^2}\frac{1}{4\gamma^6}\right)\left[2\gamma(1-e^{-2\gamma})+2(\gamma^2+2)\,e^{-2\gamma}\right]+\left[4\gamma^3F(\gamma)-4\gamma\right]T(\gamma)(1+e^{-2\gamma})$$
$$-2\left[\gamma^4F(\gamma)-2\gamma^2\right]T(\gamma)\,e^{-2\gamma}+\left[3\gamma^2F(\gamma)-3\gamma^2T(\gamma)-2-2T(\gamma)\right]e^{-2\gamma}+2\left[\gamma^3F(\gamma)-\gamma^3T(\gamma)-2\gamma-2\gamma\,T(\gamma)\right]e^{-2\gamma}\Bigg\}\Bigg], \tag{4.29}$$

where

$$T(\gamma)=\frac{\tanh(\gamma)}{\gamma}\ , \tag{4.30}$$

$$G(\gamma)=\frac{1}{\gamma^2}-\frac{\coth(\gamma)}{\gamma}\ , \tag{4.31}$$

and

$$F(\gamma)=\frac{2}{\gamma^2}\left[1-\frac{\tanh(\gamma)}{\gamma}\right]-\frac{\tanh(\gamma)}{\gamma}\ . \tag{4.32}$$

A plot of D_{eff} is given in Fig. 7.

V. SUMMARY AND DISCUSSION

We have shown that the penetrable sink model of diffusion controlled reactions can lead to interesting new results. We have, for the first time, included back re-

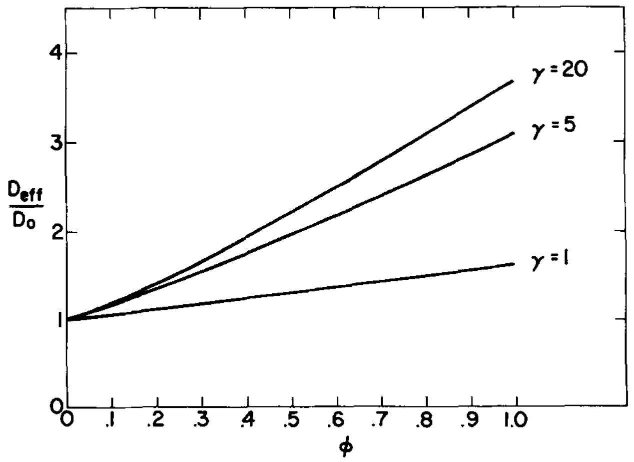

FIG. 7. The diffusion coefficient as a function of volume fraction of sinks for various values of γ.

action, and have seen a square-root dependence on the concentration in the observed rate and an asymmetry in the diffusion coefficient matrix which reflects coupling between reaction and diffusion. We have also shown that the long time behavior of this system is not a purely exponential decay. Finally, we have demonstrated that the impenetrable sink results[4] can be recovered as a limit to our theory.

We have also seen that both the rate and diffusion coefficients depend less strongly on the sink concentration as their reactivity is decreased. This behavior has also been reported by Cukier[14] in a recent calculation of properties of partially absorbing, impenetrable spherical sinks.

Much of the behavior we have observed in our model mirrors that found in the impenetrable sink calculations. A recent reexamination of fluorescence quenching data by Baird and Escott[15] has given support for the square root dependence in the observed rate. Our calculations suggest these effects may be seen in other situations, such as reaction–diffusion systems in micellar solutions or microemulsions where reaction proceeds more rapidly in one of the phases.

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