Exact solution for anisotropic diffusion-controlled reactions with partially reflecting conditions

Sergey D. Traytak
Institute of Applied Mechanics, Russian Academy of Sciences, 32a Lenin Avenue, GSP-1, 119991 Moscow, Russia

William S. Price
Nanoscale Organisation and Dynamics Group, College of Health and Science, University of Western Sydney, Penrith South, NSW 1797, Australia

(Received 18 April 2007; accepted 28 August 2007; published online 13 November 2007)

We investigate a generalization of the model of Solc and Stockmayer to describe the diffusion-controlled reactions between chemically anisotropic reactants taking into account the partially reflecting conditions on two parts of the reaction surface. The exact solution of the relevant mixed boundary-value problem was found for different ratios of the intrinsic rate constants. The results obtained may be used to test numerical programs that describe diffusion-controlled reactions in real systems of particles with anisotropic reactivity. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2786452]

I. INTRODUCTION

Diffusion-controlled reactions very often display chemically anisotropic behavior; i.e., the reaction depends on only limited region of the reaction surface. The part of the reaction surface where the reaction occurs is called the active site and the rest of the surface is said to be an inert site. Such reactions play important roles in many different applications, particularly in biophysical processes, e.g., in processes of ligand-protein binding,[1–10] the encounter reaction between an antibody and its antigen.[11]

In such cases the reaction rate constant is less than the relevant Smoluchowski one because of the chemical anisotropy of the reactants. This reduction in the case of steady state reactions is usually described by the so-called effective steric factor (ESF) $f<1$ which is defined as

$$f = k/k_S, \tag{1}$$

where $k_S=4\pi RD$ is the Smoluchowski rate constant for reactants A and B with spherically symmetric reactivity, $R=R_A+R_B$ is the radius of the reaction sphere where R_A and R_B are the radii of reactants A and B, respectively, and $D=D_A+D_B$ is the relative translational diffusion coefficient. So the theoretical problem consists in the determination of the value of the ESF as a function of the active site parameters.

Mathematically the diffusion-controlled reactions between chemically anisotropic reactants are described by proper mixed boundary value problems.[12–14] On the reaction surface $\partial\Omega$ of a chemically anisotropic reactant one should give a linear combination of a function (local concentration, distribution function of diffusing reactants) and its normal derivative of the general form

$$\alpha(\mathbf{x})\ \frac{\partial u}{\partial \mathbf{n}} + \beta(\mathbf{x})u\Big|_{\partial\Omega} = \psi(\mathbf{x}), \quad \mathbf{x}\in\partial\Omega. \tag{2}$$

This condition is called a mixed boundary condition if the functions $\alpha(\mathbf{x})$ and $\beta(\mathbf{x})$ are piecewise continuous and $\psi(\mathbf{x})$ is continuous on $\partial\Omega$. In particular, if $\alpha(\mathbf{x})=0$, $\beta(\mathbf{x})\neq 0$ on $\partial\Omega_1\subset\partial\Omega$ and $\beta(\mathbf{x})=0$, $\alpha(\mathbf{x})\neq 0$ on $\partial\Omega_2\subset\partial\Omega$ (for the sake of simplicity we assume that $\partial\Omega=\partial\Omega_1\cup\partial\Omega_2$ such that $\partial\Omega_1\cap\partial\Omega_2=\varnothing$) condition (2) gives

$$u|_{\partial\Omega_1} = \psi_1(\mathbf{x}), \quad \mathbf{x}\in\partial\Omega_1, \tag{3}$$

$$\frac{\partial u}{\partial \mathbf{n}}\Big|_{\partial\Omega_2} = \psi_2(\mathbf{x}), \quad \mathbf{x}\in\partial\Omega_2, \tag{4}$$

where $\psi_1(\mathbf{x})=\psi(\mathbf{x})/\beta(\mathbf{x})$ and $\psi_2(\mathbf{x})=\psi(\mathbf{x})/\alpha(\mathbf{x})$. Thus, in this case we have the Dirichlet boundary condition on $\partial\Omega_1$ and the Neumann condition on the remainder of the boundary $\partial\Omega_2$.[12] Usually it is very difficult to investigate mixed boundary value problems both analytically and numerically and very often one faces unstable or slowly converging procedures. Moreover the Dirichlet-Robin boundary condition leads to a more complicated analytical solution than the corresponding mixed Dirichlet-Neumann problem.

It is known that the exact solution of the mixed boundary value problems may be found only for some simple models. In particular, diffusion-controlled reactions between chemically isotropic particles and particles with an axially symmetric circular absorbing patch may be treated exactly. There are many theoretical works on approximate analytical and numerical methods to describe diffusion-controlled reactions between chemically anisotropic reactants (see Refs. 15–18 and references therein). Recently an interesting approach for the approximate analytical solution of the problem at issue was described in Ref. 19.

The exact solutions to model boundary value problems are widely used to test different numerical and analytical approaches.[15,16,20–23] However, only a few exact results have been obtained for this problem.[24–27] The mixed Robin-Neumann and Dirichlet-Neumann boundary value problems were considered numerically using the finite element method in recent papers.[3,4] In this work the software package SMOL

 © 2007 American Institute of Physics

was validated by comparison with an appropriate spherically symmetric test boundary value problem. However, this test problem does not give the main features which arose due to the mixed boundary conditions. To perform a reliable comparison with numerical calculations, it is necessary to have exact results for the mixed Robin-Robin and Dirichlet-Robin boundary value problems. Here we investigate the simple Solc-Stockmayer model for diffusion-controlled protein-ligand binding without interaction potential in order to find its exact solution in the case of partially reflecting (Robin-Robin) boundary conditions for different intrinsic rate constants. We apply the method of dual series relations[12,13] to the case where the partially reflecting boundary conditions hold true on the reaction surface. Moreover we derive a sufficient condition for convergence of the truncation method in order to solve the obtained infinite set of linear algebraic equations and, therefore, prove that the value of the ESF may be found with any desired accuracy. Moreover the exact solution allows us to find at least qualitative estimates of the effect of chemical anisotropy in the case of partially reflecting boundary conditions.

The paper outline is as follows. In Sec. I we present the general formulation of the problem at issue. The limiting cases which correspond to the cases when the reaction occurs on an almost chemically symmetric reaction sphere with almost partial reflection and almost ideally absorbing reaction surfaces are studied in Sec. II. The most important case of strong asymmetric reactivity is considered in Sec. III. The main conclusions of the paper are given in Sec. IV. The Appendix contains the proof on solvability of the infinite system of linear algebraic equations describing the case of strong asymmetric reactivity.

II. STATEMENT OF THE PROBLEM

We shall investigate the diffusion-controlled reactions of the form $A+B\to P$ assuming that the relaxation time for the diffusive flux is small.[24] Thus we can treat the reaction in the steady state regime. Steady state translational diffusion of chemically isotropic particles B towards the reaction surface of a test chemically anisotropic particle A reads

$$\nabla^2 C_B = 0 \quad \text{in } \Omega^*, \tag{5}$$

where C_B is the local concentration of B particles and $\Omega^* = \mathbb{R}^3 \backslash \bar{\Omega}$. We assume that the reaction surface $\partial\Omega^*$ is a sphere of radius R which consists of two capped parts $\partial\Omega_1 \subset \partial\Omega^*$ and $\partial\Omega_2 = \partial\Omega^* \backslash \partial\Omega_1$ (see Fig. 1); i.e., in spherical coordinates connected with the center of the reaction surface we have

$$\partial\Omega_1 = \{r = R, 0 \leqslant \theta \leqslant \theta_0, 0 \leqslant \phi < 2\pi\},$$

$$\partial\Omega_2 = \{r = R, \theta_0 < \theta < \pi, 0 \leqslant \phi < 2\pi\}.$$

Let us suppose that on the site $\partial\Omega_i$ the following partially reflecting boundary conditions hold:

$$\left[4\pi R^2 D \frac{\partial C_B}{\partial r} - \kappa_i C_B\right]\Bigg|_{\partial\Omega_i} = 0, \quad i = 1,2, \tag{6}$$

where $\kappa_i > 0$ are the intrinsic reaction rate constants which determine the character of the reaction occurring on each site

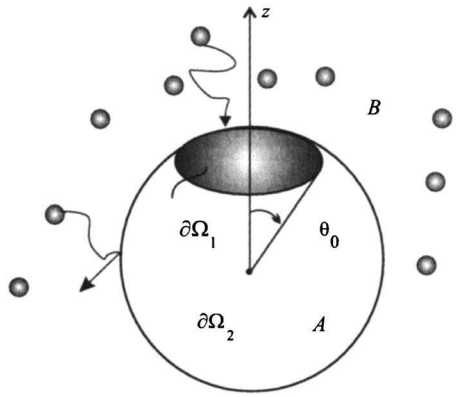

FIG. 1. Geometric sketch of the problem.

$\partial\Omega_i$. Note that in mathematical physics these conditions are also called Robin boundary conditions. One should also pose the condition at infinity

$$C_B|_{r\to\infty} \to C_0, \tag{7}$$

where C_0 is the bulk concentration of B particles. So mathematically we deal with the Robin axially symmetric mixed boundary value problem (5)–(7).

The reaction rate constant is defined by the formula

$$k(\theta_0) = \frac{D}{C_0}\int_{\partial\Omega^*} \left(\frac{\partial C_B}{\partial r}\right)\Bigg|_{\partial\Omega^*} dS \tag{8}$$

and one can see that the ESF is

$$f(\theta_0) = k(\theta_0)/k(\pi). \tag{9}$$

Hereafter this relation will define the ESF.

It is convenient to introduce a new dimensionless function $u = 1 - C_B/C_0$ and the dimensionless spatial variable $\xi = r/R$. So the posed boundary value problem is rewritten as follows:

$$\nabla^2 u = 0 \quad \text{in } \Omega^*, \tag{10}$$

$$\left[\frac{\partial u}{\partial \xi} + h_i(1-u)\right]\Bigg|_{\xi=1} = 0 \quad \text{in } \partial\Omega_i, \tag{11}$$

$$u|_{\xi\to\infty} \to 0, \tag{12}$$

where $h_i = \kappa_i/k_S$ are the dimensionless intrinsic rate constants. Note that using Green's identity one can easily prove the uniqueness of solution to the problem (10)–(12) provided $h_i \geqslant 0$.[28]

It is clear that the general solution to Eq. (10) satisfying the condition at infinity [Eq. (12)] is

$$u(\xi,\theta,\phi) = \sum_{l=0}^{\infty} \frac{A_l}{\xi^{l+1}} P_l(\mu), \tag{13}$$

where A_l are unknown constants to be determined from the boundary conditions (11) and $P_n(\mu)$ are Legendre polynomials with $\mu = \cos\theta$.

One can see that the ESF is $f = A_0$ and, therefore, our main objective is to calculate this coefficient in expression (13).

III. ALMOST SYMMETRIC REACTIVITY

First we investigate the more simple limiting cases which correspond to almost uniform Robin (when $h_1 \neq h_2$ are finite and close to each other) or Dirichlet (e.g., $h_1 \to \infty$ and $h_2 \gg 1$) boundary conditions, i.e., when the reaction occurs on an almost chemically symmetric reaction sphere with almost partial reflection and almost ideally absorbing reaction surfaces, respectively.

A. Almost uniform Robin conditions

Consider the case when both parts of the reaction surface, $\partial\Omega_1$ and $\partial\Omega_2$, are partially reflecting but with different intrinsic rate constants. Without loss of generality we can suppose that $h_1 > h_2$ and h_1 is a finite value. Substitution of the general solution (13) into boundary conditions (11) gives

$$\sum_{l=0}^{\infty} (1+l+h_2)A_l P_l(\mu) = h_2 + (h_1 - h_2)\Theta(\theta_0 - \theta) \times \left(1 - \sum_{m=0}^{\infty} A_m P_m(\mu)\right) \quad \text{in } \partial\Omega_1 \cup \partial\Omega_2, \tag{14}$$

where

$$\Theta(z) = \begin{cases} 0 & \text{if } z < 0, \\ 1 & \text{if } z \geqslant 0 \end{cases}$$

is the Heaviside step function. Multiplying Eq. (14) by $P_m(\mu)$ and integrating over the interval $(-1,1)$ one obtains the infinite set of linear algebraic equations

$$A_l + \sum_{m=0}^{\infty} G_{lm} A_m = b_l. \tag{15}$$

Here we use the notation

$$G_{lm} = (h_1 - h_2)\frac{(l+1/2)}{(1+l+h_2)} \int_{\mu_0}^{1} P_l(\mu)P_m(\mu)d\mu, \tag{16}$$

$$b_l = \frac{1}{1+h_2}\left[h_2 + \frac{1}{2}(h_1 - h_2)(1-\mu_0)\right]\delta_{l0} + \frac{1}{2}\frac{(h_1 - h_2)}{1+l+h_2}[P_{l-1}(\mu_0) - P_{l+1}(\mu_0)](1-\delta_{l0}),$$

and $\mu_0 = \cos\theta_0$. In particular, when $h_1 = h_2 = h$ we obtain the well-known result for a chemically symmetric reactant with the reflecting boundary condition, $A_l = \delta_{l0} h/(1+h)$.

Following from the theory of infinite systems of linear algebraic equations,[29] the solution of the system (15) may be found only asymptotically in the following cases: (a) as $\theta_0 \to 0$ and $h_1 - h_2 = \mathcal{O}(1)$, $h_2 = \mathcal{O}(1)$; (b) if θ_0, $h_2 = \mathcal{O}(1)$ and $h_1 \to h_2$; (c) θ_0, $h_1 - h_2 = \mathcal{O}(1)$ and $h_2 \to \infty$; and (d) $\theta_0 = \mathcal{O}(1)$ as $h_1 - h_2 \to 0$ and $h_2 \to 0$. Note that in the present case the ESF is

$$f(\theta_0, h_1) = A_0(1+h_1)/h_1.$$

In Fig. 2 we present numerical calculations for the ESF at $h_2 = 1$ and various values of h_1. One can see that the greater the value of intrinsic rate constant on site $\partial\Omega_1$ the less ESF is.

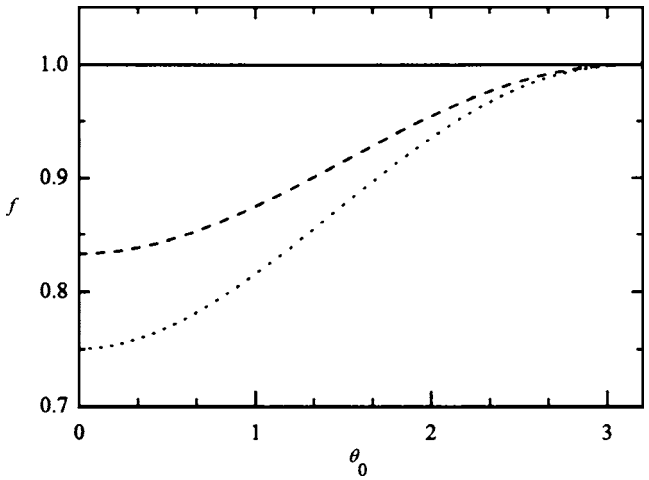

FIG. 2. Effective steric factor as a function of θ_0 for the almost uniform Robin boundary conditions at $h_2 = 1$ for $h_1 = 1.0$ (solid line), $h_1 = 1.5$ (dashed line), and $h_1 = 2.0$ (dotted line).

B. Almost uniform Dirichlet conditions

Consider now another quasiisotropic case, when $\partial\Omega_1$ is ideally absorbing (in the theory of diffusion-controlled reactions, this is often called the Smoluchowski boundary condition) and $\partial\Omega_2$ is almost ideally absorbing (i.e., as $h_1 \to \infty$ and $h_2 \gg 1$). In this case substitution of the general solution (13) into boundary conditions (11) leads to an equation of Dirichlet form

$$\sum_{l=0}^{\infty} A_l P_l(\mu) = 1 - [1 - \Theta(\theta_0 - \theta)] \times \sum_{l=0}^{\infty} (l+1)\frac{1}{h_2} A_l P_l(\mu) \quad \text{in } \partial\Omega_1 \cup \partial\Omega_2. \tag{17}$$

Multiplying Eq. (17) by $P_m(\mu)$ and integrating over the interval $(-1,1)$ the solution of this equation is reduced to the solution of the following infinite system of linear equations:

$$A_l + \sum_{m=0}^{\infty} W_{lm} A_m = \delta_{l0}, \tag{18}$$

where

$$W_{lm} = \frac{1}{h_2}(l+1/2)(m+1)\int_{-1}^{\mu_0} P_l(\mu)P_m(\mu)d\mu \tag{19}$$

and δ_{lm} is the Kronecker delta.

One can see that again the infinite systems of linear algebraic equation (18) has the asymptotic solution for $\theta_0 = \mathcal{O}(1)$ as $h_2 \to \infty$ or as $\theta_0 \to 0$ and $h_2 = \mathcal{O}(1)$. It is evident that integrals in Eqs. (16) and (19) are connected by the normalization property of the Legendre polynomials

$$\int_{-1}^{\mu_0} P_l(\mu)P_m(\mu)d\mu + \int_{\mu_0}^{1} P_l(\mu)P_m(\mu)d\mu = \frac{2\delta_{lm}}{2l+1}.$$

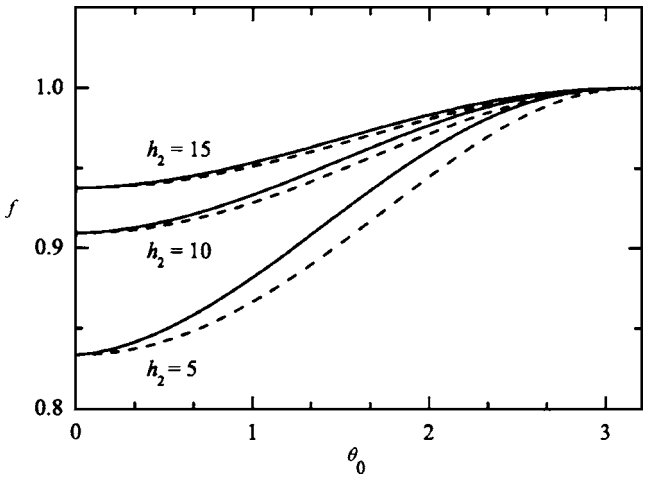

FIG. 3. Effective steric factor as a function of θ_0 for the almost uniform Dirichlet boundary conditions ($h_1 \to \infty$) for large but finite values h_2. The corresponding monopole approximations (20) are given as dashed lines.

For the monopole approximation as $\theta_0 \to 0$ we have a very simple formula for the ESF, viz.,

$$f(\theta_0,h_2) = A_0 \sim A_{0mon} = \left(1 + \frac{1+\mu_0}{2h_2}\right)^{-1}, \tag{20}$$

nevertheless this formula works well even for small finite θ_0. One can see from Fig. 3 that the simple monopole approximation for the ESF if $h_2 \gg 1$ but finite. It is worth noting that the accuracy of the monopole approximation (20) increases when the parameter h_2 increases.

IV. CASE OF STRONG ASYMMETRIC REACTIVITY

A. Dual series relations

Suppose now that the intrinsic rate constant $h_1 \to \infty$ and the Robin boundary condition on $\partial\Omega_1$ is reduced to the Dirichlet one. Hereafter we denote $h_2 = h$ and consider the case when $0 \leqslant h \leqslant 1$. In this case the problem becomes more complicated and needs another approach. After substitution of the general solution (13) into conditions (11) we obtain the so-called dual series relations[12] (DSRs),

$$\sum_{l=0}^{\infty} A_l P_l(\mu) = 1 \quad \text{in } \partial\Omega_1, \tag{21}$$

$$\sum_{l=0}^{\infty} (1+l+h) A_l P_l(\mu) = h \quad \text{in } \partial\Omega_2. \tag{22}$$

Introducing new unknown coefficients X_l by the formula

$$X_l = \frac{(1+l+h)}{(l+1/2)} A_l,$$

we can represent the DSRs (21) and (22) in the following canonical form:

$$\sum_{l=0}^{\infty} (1-q_l) X_l P_l(\mu) = 1 \quad \text{in } \partial\Omega_1, \tag{23}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) X_l P_l(\mu) = h \quad \text{in } \partial\Omega_2, \tag{24}$$

where $q_l(h) = (1+2h)/2(1+l+h)$.

It is clear that for the ESF one has

$$f(\theta_0,h) = \frac{1}{2(1+h)} X_0. \tag{25}$$

B. Reduction to an infinite system of linear equations

Consider the inhomogeneous DSR of the general form

$$\sum_{l=0}^{\infty} (1-q_l) X_l P_l(\mu) = g_1(\theta) \quad \text{in } \partial\Omega_1, \tag{26}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) X_l P_l(\mu) = g_2(\theta) \quad \text{in } \partial\Omega_2, \tag{27}$$

where $g_1(\theta)$ and $g_2(\theta)$ are some continuous functions on θ on the interval $(0,\pi)$. When $g_1(\theta) \equiv 1$ and $g_2(\theta) \equiv h$ this DSR reverts to Eqs. (23) and (24). Using the expansion of $g_2(\theta)$ in Legendre polynomials

$$g_2(\theta) = \sum_{l=0}^{\infty} B_l P_l(\mu), \quad \theta \in (0,\pi) \tag{28}$$

we can introduce new coefficients as follows:

$$Y_l = X_l - \frac{B_l}{(l+1/2)}. \tag{29}$$

Therefore the DSRs (26) and (27) are reduced to

$$\sum_{l=0}^{\infty} (1-q_l) Y_l P_l(\mu) = g_1^*(\theta) \quad \text{in } \partial\Omega_1, \tag{30}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) Y_l P_l(\mu) = 0 \quad \text{in } \partial\Omega_2, \tag{31}$$

where

$$g_1^*(\theta) = g_1(\theta) - \sum_{l=0}^{\infty} \frac{(1-q_l)}{(l+1/2)} B_l P_l(\mu).$$

Thus we have shown that inhomogeneous DSR may be reduced to a homogeneous form.

Consider now Eqs. (30) and (31) at $q_l(h) \equiv 0$,

$$\sum_{l=0}^{\infty} Y_l^* P_l(\mu) = g_1^*(\theta) \quad \text{in } \partial\Omega_1, \tag{32}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) Y_l^* P_l(\mu) = 0 \quad \text{in } \partial\Omega_2. \tag{33}$$

It is known that these DSRs possess the exact solution[12]

$$Y_l^* = \frac{\sqrt{2}}{\pi}\int_0^{\theta_0} dt \cos\left(1+\frac{1}{2}\right)t \frac{d}{dt}\int_0^t d\tau \frac{g_1^*(\tau)\sin\tau}{\sqrt{\cos\tau - \cos t}}. \quad (34)$$

Let us represent Eq. (30) in the form

$$\sum_{l=0}^{\infty} Y_l P_l(\mu) = G^*(\theta) \quad \text{in } \partial\Omega_1, \quad (35)$$

where

$$G^*(\theta) = g_1^*(\theta) + \sum_{l=0}^{\infty} q_l Y_l P_l(\mu).$$

Using formula (34) we find

$$Y_l = \frac{\sqrt{2}}{\pi}\int_0^{\theta_0} dt \cos\left(1+\frac{1}{2}\right)t \frac{d}{dt}\int_0^t d\tau \frac{G^*(\tau)\sin\tau}{\sqrt{\cos\tau - \cos t}}. \quad (36)$$

Performing the integrations in this relation we get the following infinite set of linear algebraic equations:

$$Y_l - \sum_{m=0}^{\infty} M_{lm} Y_m = b_l^*, \quad (l \geqslant 0). \quad (37)$$

Here $M_{lm}=q_m(h)Q_{lm}$, where matrix

$$Q_{lm}(\theta_0) = \frac{1}{\pi}\left\{\frac{\sin[(l+m+1)\theta_0]}{(l+m+1)} + \frac{\sin[(l-m)\theta_0]}{(l-m)} \times(1-\delta_{lm}) + \theta_0\delta_{lm}\right\}, \quad (38)$$

and $b_l^*=[1-2h(1-q_0)]Q_{l0}$.

It is clear that the corresponding ESF is given by

$$f(\theta_0,h) = \left(h+\tfrac{1}{2}Y_0\right)/(1+h). \quad (39)$$

The general solution for the local concentration is defined by expression (13), where

$$A_l = (1-q_l)\left(\frac{B_l}{(l+1/2)} + Y_l\right).$$

In particular, for the problems (10)–(12) under consideration [when $h_1\to\infty$ and $h_2=O(1)$] this formula is simplified to

$$A_l = (1-q_l)(2h\delta_{l0} + Y_l). \quad (40)$$

The obtained infinite set of Eq. (37) may be solved by truncation. We present the evidence for the method of truncation for the case of system (37) in the Appendix.

The solution to the corresponding truncated system of equations may be found by iteration to any required accuracy and therefore it may be treated as the exact solution. Curves for the ESF at different values of the intrinsic rate coefficient h are shown in Fig. 4.

C. Approximations

It is convenient to represent the obtained infinite set of linear Eq. (37) in the matrix form

$$(\mathbf{E}+\mathbf{M})\mathbf{Y} = \mathbf{B}^*, \quad (41)$$

where $\mathbf{E}$ is the infinite unit matrix. Providing the solution of the matrix Eq. (42) exists we have

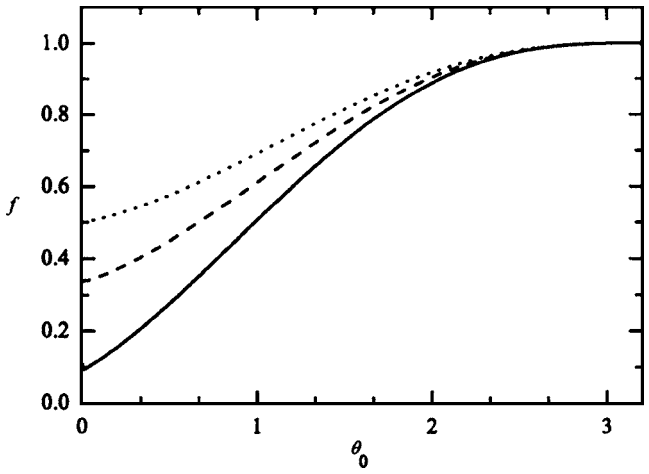

FIG. 4. Effective steric factor as a function of θ_0 for the case of strong asymmetric reactivity ($h_1\to\infty$ and $h_2=h\in[0,1]$) for $h=0.1$ (solid line), $h=0.5$ (dashed line), and $h=1.0$ (dotted line).

$$\mathbf{Y} = (\mathbf{E}+\mathbf{M})^{-1}\mathbf{B}^*.$$

On the other hand if $\|\mathbf{M}\|_\infty < 1$ system (37) (a) may be truncated to

$$(\mathbf{E}^{(n)} + \mathbf{M}_{(n)})\mathbf{Y}^{(n)} = \mathbf{B}^{*(n)}, \quad (42)$$

and (b) its solution may be found by iteration, i.e.,

$$\mathbf{Y}^{(n)} = \left(\sum_{k=0}^{\infty}(-1)^k \mathbf{M}_{(n)}^k\right)\mathbf{B}^{*(n)} = \sum_{k=0}^{\infty}\mathbf{A}_k. \quad (43)$$

Here $\mathbf{E}^{(n)}$ and $\mathbf{M}_{(n)}$ are finite $n\times n$ matrices corresponding to the infinite ones $\mathbf{E}$ and $\mathbf{M}$, respectively. It is evident that $\mathbf{A}_k=-\mathbf{M}_{(n)}\mathbf{A}_{k-1}$ for $k\in\mathbb{N}$ at $\mathbf{A}_0=\mathbf{B}^{*(n)}$.

Let us consider the zero order truncated system

$$Y_0^{(0)} - M_{00}Y_0^{(0)} = b_0^*. \quad (44)$$

For small θ_0, even zero order iteration for this simplest truncation

$$Y_0^{(0)} = b_0^* \quad (45)$$

leads to a small angle approximation

$$f^{(0)}(\theta_0,h) \sim k_h(\pi) + \frac{k_h^2(\pi)}{h^2} f^{(0)}(\theta_0) \quad \text{as } \theta_0\to 0, \quad (46)$$

where $k_h(\pi)=h/(1+h)$, $f^{(0)}(\theta_0)\equiv f^{(0)}(\theta_0,0)=(1/2\pi)(\theta_0+\sin\theta_0)$ is the zeroth order approximation of the ESF when part $\partial\Omega_2$ of the reaction surface is inert ($h=0$).[25]

$$Y_0^{(0)} = (1-M_{00})^{-1}b_0^*, \quad (47)$$

where $M_{00}=1/2\pi(\theta_0+\sin\theta_0)(1+2h)/(1+h)$. It is evident that approximation (45) is the expansion of the approximation (47) as $\theta_0\to 0$. The corresponding ESF is

$$f^{(1)}(\theta_0,h) = \left[h+\tfrac{1}{2}(1-M_{00})^{-1}b_0^*\right]/(1+h). \quad (48)$$

Moreover we can obtain one more so-called "diagonal" approximation,[25] solving the truncated system (44) exactly

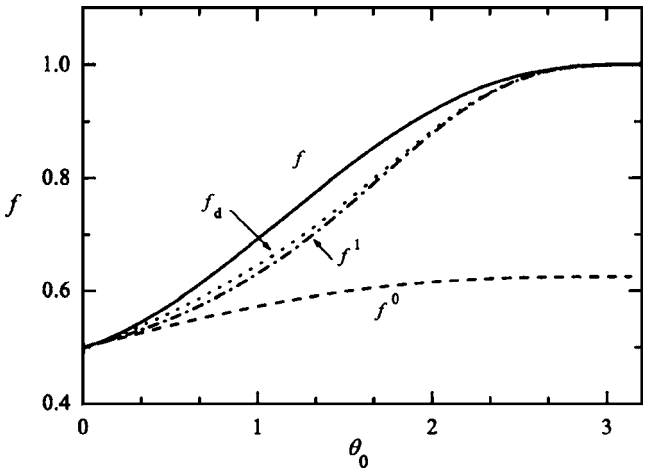

FIG. 5. Comparison of the different approximations for the effective steric factor as a function of θ_0 at $h=1.0$. The solid line corresponds to the exact solution, the dashed line corresponds to Eq. (46), the chain line corresponds to Eq. (48), and the dotted line corresponds to the "diagonal" approximation (49).

$$Y_0^{(d)} = b_0^* + \sum_{m=0}^{\infty} M_{0m}\tilde{Y}_m,$$

where

$$\tilde{Y}_m = \frac{b_m^*}{1 - M_{mm}}.$$

Thus the diagonal approximation for the ESF is

$$f_d(\theta_0,h) = \left(h + \tfrac{1}{2}Y_0^{(d)}\right)/(1+h). \tag{49}$$

In Fig. 5 we compare the different approximations for the ESF with its exact values at $h=1$. One can see that contrary to the case $h\to\infty$ the diagonal approximation f_d amended the previous approximation $f^{(1)}$ (44) slightly.

V. CONCLUDING REMARKS

The well known model of Solc and Stockmayer describing the diffusion-controlled reactions between chemically anisotropic reactants has been investigated. We assumed that the reaction surface has two sites with different intrinsic rate constants and took into account the corresponding partially reflecting conditions on these parts.

We considered the three cases: (1) when both parts of the reaction surface are partially reflecting but at different intrinsic rate constants; (2) when $\partial\Omega_1$ is ideally absorbing and $\partial\Omega_2$ is almost ideally absorbing (i.e., as $h_1\to\infty$ and $h_2\gg 1$); and (3) when the boundary condition on $\partial\Omega_1$ is reduced to the ideally absorbing one. For these cases we have found the conditions when the corresponding infinite set of linear algebraic equations is solvable and we solved them by the method of truncation.

The results obtained may be used for estimates of the rate coefficients in biophysical applications and to test numerical programs that describe diffusion-controlled reactions in real systems of particles with anisotropic reactivity. In particular we pointed out that simple formula (40) gives the exact effective steric factor for the case $h=-1/2$.

Our result may be easily generalized to the case of rotational diffusion.[16] Actually rotational diffusion leads to a more symmetric reaction surface and in this way it increases the value of the effective steric factor. Note also that using a similar analytical approach the practically important case of several active sites that covered the reaction surface may be treated as well.

ACKNOWLEDGMENTS

The NSW State Government is acknowledged for support through a Biofirst Award to one of the authors (W.S.P.).

APPENDIX: SOLVABILITY OF THE INFINITE SYSTEM (37)

Definition 1. *A sequence* $\{Y_l\}$ *such that for all* $l=\overline{0,\infty}$, *the series* $\Sigma_{m=0}^{\infty}(\delta_{lm}-M_{lm})Y_m$ *converge and their sums coincide with the constant term* $\{b_l^*\}$, *is termed a solution of the infinite set of linear algebraic equations (37).*[29]

Definition 2. *The infinite set of linear algebraic equations (37) is called fully regular, if there exists a positive number* $q<1$ *such that*

$$\sum_{m=0}^{\infty} |M_{lm}| \leqslant q \quad \text{for all } l=\overline{0,\infty}. \tag{A1}$$

Definition 3. *Truncation of the infinite set (37) is said to be the corresponding set of finite order*

$$Y_l^{(n)} - \sum_{m=0}^{n} M_{lm}Y_m^{(n)} = b_l^*, \quad (l=\overline{0,n}). \tag{A2}$$

Lemma. *Condition (A1) is sufficient for the system (37) to be solved by truncation (A2) such that*

$$\lim_{n\to\infty} Y_l^{(n)} = Y_l \quad \text{for all } l=\overline{0,\infty}$$

is the solution of the system (37).

The proof of this lemma may be found elsewhere (see, e.g., Ref. 29).

Let us derive now the regularity condition (A1) for the obtained infinite system of linear algebraic equations (37) as a function of the angular size of the active site θ_0. The following result holds true.

Theorem. *The infinite system (37) may be solved by truncation if*

$$0 \leqslant \theta_0 < \frac{2\pi}{1+2h} - 3. \tag{A3}$$

Proof. According to *Lemma* to prove the solvability of system (37) by truncation one should investigate the regularity condition (A1) for the matrix of the system (37). It is clear that Eq. (A1) holds if

$$s_l < 1 \quad \text{for all } l=\overline{0,\infty},$$

where

$$s_l = \sum_{m=0}^{\infty} |M_{lm}|.$$

The parameter $q_l(h)$ may be recast as

$$q_l(h) = q_l^0\left(\frac{1+2h}{1+2hq_l^0}\right),$$

where $q_l^0 \equiv q_l(0) = 1/2(1+l)$ and for all real $h \geqslant 0$ and integer $l \geqslant 0$ the following inequality holds true:

$$\frac{1}{1+2hq_l^0} \leqslant 1.$$

The latter inequality means that to find the regularity condition at $h \neq 0$ we can consider the specific case at $h=0$ and multiply the final estimate by the factor $1+2h$. It is evident that

$$s_l \leqslant \frac{1}{2\pi(l+1)}\left[\sum_{m=0}^{\infty}\frac{1}{(m+1)(l+m+1)} + \frac{1}{(l+1)}\theta_0 + \sum_{m(\neq l)=0}^{\infty}\frac{1}{(m+1)|l-m|}\right]. \quad \text{(A4)}$$

For the first sum on the right-hand side we have

$$\sum_{m=0}^{\infty}\frac{1}{(m+1)(l+m+1)} = \frac{1}{l}\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+l}\right).$$

This sum may be estimated using the integral representation[30]

$$\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+\gamma}\right) = \int_0^1 \frac{1-t^{\gamma}}{1-t}dt. \quad \text{(A5)}$$

Performing an estimate of this integral one obtains the inequality

$$\frac{1}{l}\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+1}\right) \leqslant \frac{1}{l}\sup_{t\in(0,1)}\left(\frac{1-t^l}{1-t}\right) = 1. \quad \text{(A6)}$$

For the second sum in (A4) we find

$$\sum_{m(\neq l)=0}^{\infty}\frac{1}{(m+1)|l-m|} = \sum_{m(<l)=0}^{l-1}\frac{1}{(m+1)(l-m)} + \sum_{m(>l)=l+1}^{\infty}\frac{1}{(m+1)(m-l)} \quad \text{(A7)}$$

and employing estimate (A6) for the second term on the right-hand side of Eq. (A7) we get

$$\sum_{m(>l)=l+1}^{\infty}\frac{1}{(m+1)(m-l)} = \sum_{\nu=1}^{\infty}\frac{1}{\nu(\nu+l+1)} = \frac{1}{l+1}\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+l+1}\right) \leqslant 1.$$

For the first term on the right-hand side of Eq. (A7) we have

$$\sum_{m=0}^{l-1}\frac{1}{(m+1)(l-m)} = \frac{1}{l+1}\sum_{m=0}^{l-1}\left(\frac{1}{m+1} + \frac{1}{l-m}\right) = \frac{1}{l+1}\left(\sum_{\nu=1}^{l}\frac{1}{\nu} + \sum_{m=0}^{l-1}\frac{1}{l-m}\right) = \frac{2}{l+1}\sum_{\nu=1}^{l}\frac{1}{\nu} \equiv \alpha_l.$$

Thus we obtain the estimate

$$\sum_{m(\neq l)=0}^{\infty}\frac{1}{(m+1)|l-m|} < 1 + \alpha_l$$

and finally the following inequality:

$$s_l < \frac{(1+2h)}{2\pi(l+1)}\left[2 + \frac{\theta_0}{(l+1)} + \alpha_l\right] \quad \text{for all } l = \overline{0,\infty}. \quad \text{(A8)}$$

One can see that the sequence $\{\alpha_l\}$ decreases monotonically for all $l \in \mathbb{N}$ and, therefore, $\alpha_l < \alpha_1 = 1$. Taking the upper boundary in inequality (A8) we arrive at

$$\|M\|_{\infty} = \sup_l\left(\sum_{m=0}^{\infty}|M_{lm}|\right) < \frac{(1+2h)}{2\pi}(3+\theta_0).$$

Therefore, the desired range of values θ_0 when $\|\mathbf{M}\|_{\infty} < 1$ is determined by the inequality

$$\frac{(1+2h)}{2\pi}(3+\theta_0) < 1$$

or the desired inequality (A3).

Corollary. *It follows from inequality (A3) that the condition of regularity holds uniformly in* $(0,\pi)$ *if*

$$0 \leqslant h \leqslant \frac{\pi-3}{2(3+\pi)}. \quad \text{(A9)}$$

Remark 1. *Condition (A9) means that the system (37) is solvable by the truncation method for all* $\theta_0 \in (0,\pi)$ *in the case of the mixed Dirichlet-Neumann boundary-value problem (10)–(12) when* $h_1 \to \infty$ *and* $h_2 = 0$. *This is the rigorous basis for the results of Ref. 25.*

Remark 2. *The estimate derived is rather rough and the convergence of the solution* $\{Y_l^{(n)}\}$ *of the truncated system (A2) to the exact solution occurs over a wider range of parameter h, at least for* $h \in (0,1)$.

[1] M. Maalmi, W. Strieder, and A. Varma, Chem. Eng. Sci. **56**, 5609 (2001).
[2] A. H. Elcock, D. Sept, and J. A. McCammon, J. Phys. Chem. B **105**, 1504 (2001).
[3] Y. Song, Y. Zhang, T. Shen, C. L. Bajaj, and J. A. McCammon, Biophys. J. **86**, 2017 (2004).
[4] D. Zhang, J. Suen, Y. Zhang, Y. Song, Z. Radic, P. Taylor, M. J. Holst, C. Bajaj, N. A. Baker, and J. A. McCammon, Biophys. J. **88**, 1659 (2005).
[5] A. Nag and A. R. Dinner, Biophys. J. **90**, 896 (2006).
[6] Y. Song, Y. Zhang, C. L. Bajaj, and N. A. Baker, Biophys. J. **87**, 1558 (2004).
[7] W. S. Price, F. Tsuchiya, and Y. Arata, J. Am. Chem. Soc. **121**, 11503 (1999).
[8] W. S. Price, Aust. J. Chem. **56**, 855 (2003).
[9] S. Lee and M. Kurplus, J. Chem. Phys. **86**, 1904 (1987).
[10] K. L. Ivanov, A. V. Yurkovskaya, P. J. Hore, and N. N. Lukzen, Mol.

Phys. **104**, 1687 (2006).
[11] F. Piazza, P. De Los Rios, D. Fanelli, L. Bongini, and U. Skoglund, Eur. Biophys. J. **80**, 2062 (2005).
[12] I. N. Sneddon, *Mixed Boundary Value in Potential Theory* (North-Holland, Amsterdam, 1966).
[13] V. A. Kudinov, E. M. Kartashov, and V. V. Kalashnikov, *Analytical Solutions of the Heat, Mass Transfer and Thermoelasticity for the Sandwich Structures* (Vysshaya Shkola, Moscow, 2005) (in Russian).
[14] If the boundary conditions differ on different parts of a given connected component of a boundary these conditions are called proper mixed boundary conditions. Provided different boundary conditions are posed on different connected components they are termed improper mixed boundary conditions.
[15] A. V. Barzykin and A. I. Shushin, Biophys. J. **80**, 2062 (2001).
[16] A. I. Shushin and A. V. Barzykin, Biophys. J. **81**, 3137 (2001).
[17] A. I. Shushin, J. Chem. Phys. **110**, 12044 (1999).
[18] A. I. Shushin, J. Chem. Phys. **113**, 4305 (2000).
[19] A. Grassi, G. M. Lombardo, and A. Raudino, J. Math. Chem. **25**, 321 (1999).
[20] H.-X. Zhou, Biophys. J. **97**, 2441 (1997).
[21] C.-O. Hwang, J. A. Given, and M. Masagni, J. Comput. Phys. **174**, 925 (2001).
[22] M. Masagni and C.-O. Hwang, Math. Comput. Simul. **63**, 93 (2003).
[23] M. Masagni and N. A. Simonov, SIAM J. Sci. Comput. **26**, 339 (2004).
[24] S. D. Traytak, J. Phys. Chem. **98**, 7419 (1994).
[25] S. D. Traytak, Chem. Phys. **192**, 1 (1995).
[26] S. D. Traytak and M. Tachiya, J. Chem. Phys. **102**, 2760 (1995).
[27] S. D. Traytak and M. Tachiya, J. Chem. Phys. **102**, 9240 (1995).
[28] P. Moon and D. E. Spencer, *Field Theory for Engineers* (Van Nostrand, New York, 1961).
[29] L. V. Kantorovich and V. I. Krylov, *Approximate Methods of Higher Analysis* (Interscience, New York, 1964).
[30] C. Jordan, *Calculus of Finite Differences* (Chelsea, New York, 1950).

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see http://ojps.aip.org/jcpo/jcpcr/jsp

Exact solution for anisotropic diffusion-controlled reactions with partially reflecting conditions

Sergey D. Traytak
Institute of Applied Mechanics, Russian Academy of Sciences, 32a Lenin Avenue, GSP-1, 119991 Moscow, Russia

William S. Price
Nanoscale Organisation and Dynamics Group, College of Health and Science, University of Western Sydney, Penrith South, NSW 1797, Australia

(Received 18 April 2007; accepted 28 August 2007; published online 13 November 2007)

We investigate a generalization of the model of Solc and Stockmayer to describe the diffusion-controlled reactions between chemically anisotropic reactants taking into account the partially reflecting conditions on two parts of the reaction surface. The exact solution of the relevant mixed boundary-value problem was found for different ratios of the intrinsic rate constants. The results obtained may be used to test numerical programs that describe diffusion-controlled reactions in real systems of particles with anisotropic reactivity. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2786452]

I. INTRODUCTION

Diffusion-controlled reactions very often display chemically anisotropic behavior; i.e., the reaction depends on only limited region of the reaction surface. The part of the reaction surface where the reaction occurs is called the active site and the rest of the surface is said to be an inert site. Such reactions play important roles in many different applications, particularly in biophysical processes, e.g., in processes of ligand-protein binding,[1–10] the encounter reaction between an antibody and its antigen.[11]

In such cases the reaction rate constant is less than the relevant Smoluchowski one because of the chemical anisotropy of the reactants. This reduction in the case of steady state reactions is usually described by the so-called effective steric factor (ESF) $f<1$ which is defined as

$$f = k/k_S, \tag{1}$$

where $k_S=4\pi RD$ is the Smoluchowski rate constant for reactants A and B with spherically symmetric reactivity, $R=R_A+R_B$ is the radius of the reaction sphere where R_A and R_B are the radii of reactants A and B, respectively, and $D=D_A+D_B$ is the relative translational diffusion coefficient. So the theoretical problem consists in the determination of the value of the ESF as a function of the active site parameters.

Mathematically the diffusion-controlled reactions between chemically anisotropic reactants are described by proper mixed boundary value problems.[12–14] On the reaction surface $\partial\Omega$ of a chemically anisotropic reactant one should give a linear combination of a function (local concentration, distribution function of diffusing reactants) and its normal derivative of the general form

$$\alpha(\mathbf{x})\ \frac{\partial u}{\partial \mathbf{n}} + \beta(\mathbf{x})u\Big|_{\partial\Omega} = \psi(\mathbf{x}), \quad \mathbf{x}\in\partial\Omega. \tag{2}$$

This condition is called a mixed boundary condition if the functions $\alpha(\mathbf{x})$ and $\beta(\mathbf{x})$ are piecewise continuous and $\psi(\mathbf{x})$ is continuous on $\partial\Omega$. In particular, if $\alpha(\mathbf{x})=0$, $\beta(\mathbf{x})\neq 0$ on $\partial\Omega_1\subset\partial\Omega$ and $\beta(\mathbf{x})=0$, $\alpha(\mathbf{x})\neq 0$ on $\partial\Omega_2\subset\partial\Omega$ (for the sake of simplicity we assume that $\partial\Omega=\partial\Omega_1\cup\partial\Omega_2$ such that $\partial\Omega_1\cap\partial\Omega_2=\varnothing$) condition (2) gives

$$u|_{\partial\Omega_1} = \psi_1(\mathbf{x}), \quad \mathbf{x}\in\partial\Omega_1, \tag{3}$$

$$\frac{\partial u}{\partial \mathbf{n}}\Big|_{\partial\Omega_2} = \psi_2(\mathbf{x}), \quad \mathbf{x}\in\partial\Omega_2, \tag{4}$$

where $\psi_1(\mathbf{x})=\psi(\mathbf{x})/\beta(\mathbf{x})$ and $\psi_2(\mathbf{x})=\psi(\mathbf{x})/\alpha(\mathbf{x})$. Thus, in this case we have the Dirichlet boundary condition on $\partial\Omega_1$ and the Neumann condition on the remainder of the boundary $\partial\Omega_2$.[12] Usually it is very difficult to investigate mixed boundary value problems both analytically and numerically and very often one faces unstable or slowly converging procedures. Moreover the Dirichlet-Robin boundary condition leads to a more complicated analytical solution than the corresponding mixed Dirichlet-Neumann problem.

It is known that the exact solution of the mixed boundary value problems may be found only for some simple models. In particular, diffusion-controlled reactions between chemically isotropic particles and particles with an axially symmetric circular absorbing patch may be treated exactly. There are many theoretical works on approximate analytical and numerical methods to describe diffusion-controlled reactions between chemically anisotropic reactants (see Refs. 15–18 and references therein). Recently an interesting approach for the approximate analytical solution of the problem at issue was described in Ref. 19.

The exact solutions to model boundary value problems are widely used to test different numerical and analytical approaches.[15,16,20–23] However, only a few exact results have been obtained for this problem.[24–27] The mixed Robin-Neumann and Dirichlet-Neumann boundary value problems were considered numerically using the finite element method in recent papers.[3,4] In this work the software package SMOL

 © 2007 American Institute of Physics

was validated by comparison with an appropriate spherically symmetric test boundary value problem. However, this test problem does not give the main features which arose due to the mixed boundary conditions. To perform a reliable comparison with numerical calculations, it is necessary to have exact results for the mixed Robin-Robin and Dirichlet-Robin boundary value problems. Here we investigate the simple Solc-Stockmayer model for diffusion-controlled protein-ligand binding without interaction potential in order to find its exact solution in the case of partially reflecting (Robin-Robin) boundary conditions for different intrinsic rate constants. We apply the method of dual series relations[12,13] to the case where the partially reflecting boundary conditions hold true on the reaction surface. Moreover we derive a sufficient condition for convergence of the truncation method in order to solve the obtained infinite set of linear algebraic equations and, therefore, prove that the value of the ESF may be found with any desired accuracy. Moreover the exact solution allows us to find at least qualitative estimates of the effect of chemical anisotropy in the case of partially reflecting boundary conditions.

The paper outline is as follows. In Sec. I we present the general formulation of the problem at issue. The limiting cases which correspond to the cases when the reaction occurs on an almost chemically symmetric reaction sphere with almost partial reflection and almost ideally absorbing reaction surfaces are studied in Sec. II. The most important case of strong asymmetric reactivity is considered in Sec. III. The main conclusions of the paper are given in Sec. IV. The Appendix contains the proof on solvability of the infinite system of linear algebraic equations describing the case of strong asymmetric reactivity.

II. STATEMENT OF THE PROBLEM

We shall investigate the diffusion-controlled reactions of the form $A+B\to P$ assuming that the relaxation time for the diffusive flux is small.[24] Thus we can treat the reaction in the steady state regime. Steady state translational diffusion of chemically isotropic particles B towards the reaction surface of a test chemically anisotropic particle A reads

$$\nabla^2 C_B = 0 \quad \text{in } \Omega^*, \tag{5}$$

where C_B is the local concentration of B particles and $\Omega^* = \mathbb{R}^3 \backslash \bar{\Omega}$. We assume that the reaction surface $\partial\Omega^*$ is a sphere of radius R which consists of two capped parts $\partial\Omega_1 \subset \partial\Omega^*$ and $\partial\Omega_2 = \partial\Omega^* \backslash \partial\Omega_1$ (see Fig. 1); i.e., in spherical coordinates connected with the center of the reaction surface we have

$$\partial\Omega_1 = \{r = R, 0 \leqslant \theta \leqslant \theta_0, 0 \leqslant \phi < 2\pi\},$$

$$\partial\Omega_2 = \{r = R, \theta_0 < \theta < \pi, 0 \leqslant \phi < 2\pi\}.$$

Let us suppose that on the site $\partial\Omega_i$ the following partially reflecting boundary conditions hold:

$$\left[4\pi R^2 D \frac{\partial C_B}{\partial r} - \kappa_i C_B\right]\Bigg|_{\partial\Omega_i} = 0, \quad i = 1,2, \tag{6}$$

where $\kappa_i > 0$ are the intrinsic reaction rate constants which determine the character of the reaction occurring on each site

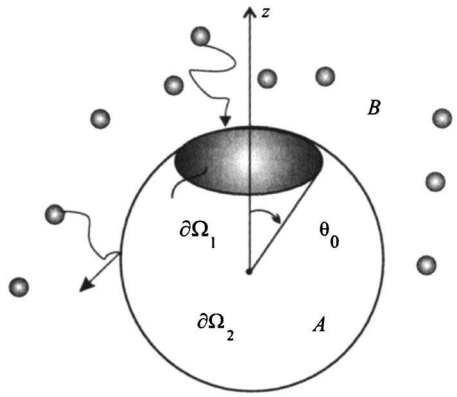

FIG. 1. Geometric sketch of the problem.

$\partial\Omega_i$. Note that in mathematical physics these conditions are also called Robin boundary conditions. One should also pose the condition at infinity

$$C_B|_{r\to\infty} \to C_0, \tag{7}$$

where C_0 is the bulk concentration of B particles. So mathematically we deal with the Robin axially symmetric mixed boundary value problem (5)–(7).

The reaction rate constant is defined by the formula

$$k(\theta_0) = \frac{D}{C_0}\int_{\partial\Omega^*} \left(\frac{\partial C_B}{\partial r}\right)\Bigg|_{\partial\Omega^*} dS \tag{8}$$

and one can see that the ESF is

$$f(\theta_0) = k(\theta_0)/k(\pi). \tag{9}$$

Hereafter this relation will define the ESF.

It is convenient to introduce a new dimensionless function $u = 1 - C_B/C_0$ and the dimensionless spatial variable $\xi = r/R$. So the posed boundary value problem is rewritten as follows:

$$\nabla^2 u = 0 \quad \text{in } \Omega^*, \tag{10}$$

$$\left[\frac{\partial u}{\partial \xi} + h_i(1-u)\right]\Bigg|_{\xi=1} = 0 \quad \text{in } \partial\Omega_i, \tag{11}$$

$$u|_{\xi\to\infty} \to 0, \tag{12}$$

where $h_i = \kappa_i/k_S$ are the dimensionless intrinsic rate constants. Note that using Green's identity one can easily prove the uniqueness of solution to the problem (10)–(12) provided $h_i \geqslant 0$.[28]

It is clear that the general solution to Eq. (10) satisfying the condition at infinity [Eq. (12)] is

$$u(\xi,\theta,\phi) = \sum_{l=0}^{\infty} \frac{A_l}{\xi^{l+1}} P_l(\mu), \tag{13}$$

where A_l are unknown constants to be determined from the boundary conditions (11) and $P_n(\mu)$ are Legendre polynomials with $\mu = \cos\theta$.

One can see that the ESF is $f = A_0$ and, therefore, our main objective is to calculate this coefficient in expression (13).

III. ALMOST SYMMETRIC REACTIVITY

First we investigate the more simple limiting cases which correspond to almost uniform Robin (when $h_1 \neq h_2$ are finite and close to each other) or Dirichlet (e.g., $h_1 \to \infty$ and $h_2 \gg 1$) boundary conditions, i.e., when the reaction occurs on an almost chemically symmetric reaction sphere with almost partial reflection and almost ideally absorbing reaction surfaces, respectively.

A. Almost uniform Robin conditions

Consider the case when both parts of the reaction surface, $\partial\Omega_1$ and $\partial\Omega_2$, are partially reflecting but with different intrinsic rate constants. Without loss of generality we can suppose that $h_1 > h_2$ and h_1 is a finite value. Substitution of the general solution (13) into boundary conditions (11) gives

$$\sum_{l=0}^{\infty} (1+l+h_2)A_l P_l(\mu) = h_2 + (h_1 - h_2)\Theta(\theta_0 - \theta) \times \left(1 - \sum_{m=0}^{\infty} A_m P_m(\mu)\right) \quad \text{in } \partial\Omega_1 \cup \partial\Omega_2, \tag{14}$$

where

$$\Theta(z) = \begin{cases} 0 & \text{if } z < 0, \\ 1 & \text{if } z \geqslant 0 \end{cases}$$

is the Heaviside step function. Multiplying Eq. (14) by $P_m(\mu)$ and integrating over the interval $(-1,1)$ one obtains the infinite set of linear algebraic equations

$$A_l + \sum_{m=0}^{\infty} G_{lm} A_m = b_l. \tag{15}$$

Here we use the notation

$$G_{lm} = (h_1 - h_2)\frac{(l+1/2)}{(1+l+h_2)} \int_{\mu_0}^{1} P_l(\mu)P_m(\mu)d\mu, \tag{16}$$

$$b_l = \frac{1}{1+h_2}\left[h_2 + \frac{1}{2}(h_1 - h_2)(1-\mu_0)\right]\delta_{l0} + \frac{1}{2}\frac{(h_1 - h_2)}{1+l+h_2}[P_{l-1}(\mu_0) - P_{l+1}(\mu_0)](1-\delta_{l0}),$$

and $\mu_0 = \cos\theta_0$. In particular, when $h_1 = h_2 = h$ we obtain the well-known result for a chemically symmetric reactant with the reflecting boundary condition, $A_l = \delta_{l0} h/(1+h)$.

Following from the theory of infinite systems of linear algebraic equations,[29] the solution of the system (15) may be found only asymptotically in the following cases: (a) as $\theta_0 \to 0$ and $h_1 - h_2 = \mathcal{O}(1)$, $h_2 = \mathcal{O}(1)$; (b) if θ_0, $h_2 = \mathcal{O}(1)$ and $h_1 \to h_2$; (c) θ_0, $h_1 - h_2 = \mathcal{O}(1)$ and $h_2 \to \infty$; and (d) $\theta_0 = \mathcal{O}(1)$ as $h_1 - h_2 \to 0$ and $h_2 \to 0$. Note that in the present case the ESF is

$$f(\theta_0, h_1) = A_0(1+h_1)/h_1.$$

In Fig. 2 we present numerical calculations for the ESF at $h_2 = 1$ and various values of h_1. One can see that the greater the value of intrinsic rate constant on site $\partial\Omega_1$ the less ESF is.

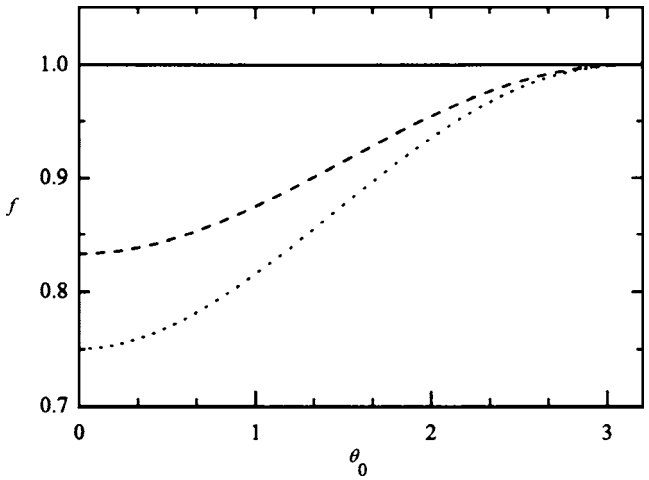

FIG. 2. Effective steric factor as a function of θ_0 for the almost uniform Robin boundary conditions at $h_2 = 1$ for $h_1 = 1.0$ (solid line), $h_1 = 1.5$ (dashed line), and $h_1 = 2.0$ (dotted line).

B. Almost uniform Dirichlet conditions

Consider now another quasiisotropic case, when $\partial\Omega_1$ is ideally absorbing (in the theory of diffusion-controlled reactions, this is often called the Smoluchowski boundary condition) and $\partial\Omega_2$ is almost ideally absorbing (i.e., as $h_1 \to \infty$ and $h_2 \gg 1$). In this case substitution of the general solution (13) into boundary conditions (11) leads to an equation of Dirichlet form

$$\sum_{l=0}^{\infty} A_l P_l(\mu) = 1 - [1 - \Theta(\theta_0 - \theta)] \times \sum_{l=0}^{\infty} (l+1)\frac{1}{h_2} A_l P_l(\mu) \quad \text{in } \partial\Omega_1 \cup \partial\Omega_2. \tag{17}$$

Multiplying Eq. (17) by $P_m(\mu)$ and integrating over the interval $(-1,1)$ the solution of this equation is reduced to the solution of the following infinite system of linear equations:

$$A_l + \sum_{m=0}^{\infty} W_{lm} A_m = \delta_{l0}, \tag{18}$$

where

$$W_{lm} = \frac{1}{h_2}(l+1/2)(m+1)\int_{-1}^{\mu_0} P_l(\mu)P_m(\mu)d\mu \tag{19}$$

and δ_{lm} is the Kronecker delta.

One can see that again the infinite systems of linear algebraic equation (18) has the asymptotic solution for $\theta_0 = \mathcal{O}(1)$ as $h_2 \to \infty$ or as $\theta_0 \to 0$ and $h_2 = \mathcal{O}(1)$. It is evident that integrals in Eqs. (16) and (19) are connected by the normalization property of the Legendre polynomials

$$\int_{-1}^{\mu_0} P_l(\mu)P_m(\mu)d\mu + \int_{\mu_0}^{1} P_l(\mu)P_m(\mu)d\mu = \frac{2\delta_{lm}}{2l+1}.$$

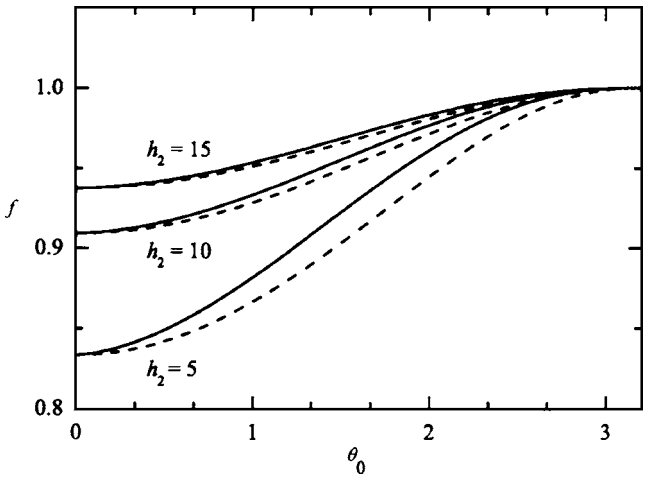

FIG. 3. Effective steric factor as a function of θ_0 for the almost uniform Dirichlet boundary conditions ($h_1 \to \infty$) for large but finite values h_2. The corresponding monopole approximations (20) are given as dashed lines.

For the monopole approximation as $\theta_0 \to 0$ we have a very simple formula for the ESF, viz.,

$$f(\theta_0,h_2) = A_0 \sim A_{0mon} = \left(1 + \frac{1+\mu_0}{2h_2}\right)^{-1}, \tag{20}$$

nevertheless this formula works well even for small finite θ_0. One can see from Fig. 3 that the simple monopole approximation for the ESF if $h_2 \gg 1$ but finite. It is worth noting that the accuracy of the monopole approximation (20) increases when the parameter h_2 increases.

IV. CASE OF STRONG ASYMMETRIC REACTIVITY

A. Dual series relations

Suppose now that the intrinsic rate constant $h_1 \to \infty$ and the Robin boundary condition on $\partial\Omega_1$ is reduced to the Dirichlet one. Hereafter we denote $h_2 = h$ and consider the case when $0 \leqslant h \leqslant 1$. In this case the problem becomes more complicated and needs another approach. After substitution of the general solution (13) into conditions (11) we obtain the so-called dual series relations[12] (DSRs),

$$\sum_{l=0}^{\infty} A_l P_l(\mu) = 1 \quad \text{in } \partial\Omega_1, \tag{21}$$

$$\sum_{l=0}^{\infty} (1+l+h) A_l P_l(\mu) = h \quad \text{in } \partial\Omega_2. \tag{22}$$

Introducing new unknown coefficients X_l by the formula

$$X_l = \frac{(1+l+h)}{(l+1/2)} A_l,$$

we can represent the DSRs (21) and (22) in the following canonical form:

$$\sum_{l=0}^{\infty} (1-q_l) X_l P_l(\mu) = 1 \quad \text{in } \partial\Omega_1, \tag{23}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) X_l P_l(\mu) = h \quad \text{in } \partial\Omega_2, \tag{24}$$

where $q_l(h) = (1+2h)/2(1+l+h)$.

It is clear that for the ESF one has

$$f(\theta_0,h) = \frac{1}{2(1+h)} X_0. \tag{25}$$

B. Reduction to an infinite system of linear equations

Consider the inhomogeneous DSR of the general form

$$\sum_{l=0}^{\infty} (1-q_l) X_l P_l(\mu) = g_1(\theta) \quad \text{in } \partial\Omega_1, \tag{26}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) X_l P_l(\mu) = g_2(\theta) \quad \text{in } \partial\Omega_2, \tag{27}$$

where $g_1(\theta)$ and $g_2(\theta)$ are some continuous functions on θ on the interval $(0,\pi)$. When $g_1(\theta) \equiv 1$ and $g_2(\theta) \equiv h$ this DSR reverts to Eqs. (23) and (24). Using the expansion of $g_2(\theta)$ in Legendre polynomials

$$g_2(\theta) = \sum_{l=0}^{\infty} B_l P_l(\mu), \quad \theta \in (0,\pi) \tag{28}$$

we can introduce new coefficients as follows:

$$Y_l = X_l - \frac{B_l}{(l+1/2)}. \tag{29}$$

Therefore the DSRs (26) and (27) are reduced to

$$\sum_{l=0}^{\infty} (1-q_l) Y_l P_l(\mu) = g_1^*(\theta) \quad \text{in } \partial\Omega_1, \tag{30}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) Y_l P_l(\mu) = 0 \quad \text{in } \partial\Omega_2, \tag{31}$$

where

$$g_1^*(\theta) = g_1(\theta) - \sum_{l=0}^{\infty} \frac{(1-q_l)}{(l+1/2)} B_l P_l(\mu).$$

Thus we have shown that inhomogeneous DSR may be reduced to a homogeneous form.

Consider now Eqs. (30) and (31) at $q_l(h) \equiv 0$,

$$\sum_{l=0}^{\infty} Y_l^* P_l(\mu) = g_1^*(\theta) \quad \text{in } \partial\Omega_1, \tag{32}$$

$$\sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) Y_l^* P_l(\mu) = 0 \quad \text{in } \partial\Omega_2. \tag{33}$$

It is known that these DSRs possess the exact solution[12]

$$Y_l^* = \frac{\sqrt{2}}{\pi}\int_0^{\theta_0} dt \cos\left(1+\frac{1}{2}\right)t \frac{d}{dt}\int_0^t d\tau \frac{g_1^*(\tau)\sin\tau}{\sqrt{\cos\tau - \cos t}}. \quad (34)$$

Let us represent Eq. (30) in the form

$$\sum_{l=0}^{\infty} Y_l P_l(\mu) = G^*(\theta) \quad \text{in } \partial\Omega_1, \quad (35)$$

where

$$G^*(\theta) = g_1^*(\theta) + \sum_{l=0}^{\infty} q_l Y_l P_l(\mu).$$

Using formula (34) we find

$$Y_l = \frac{\sqrt{2}}{\pi}\int_0^{\theta_0} dt \cos\left(1+\frac{1}{2}\right)t \frac{d}{dt}\int_0^t d\tau \frac{G^*(\tau)\sin\tau}{\sqrt{\cos\tau - \cos t}}. \quad (36)$$

Performing the integrations in this relation we get the following infinite set of linear algebraic equations:

$$Y_l - \sum_{m=0}^{\infty} M_{lm} Y_m = b_l^*, \quad (l \geqslant 0). \quad (37)$$

Here $M_{lm}=q_m(h)Q_{lm}$, where matrix

$$Q_{lm}(\theta_0) = \frac{1}{\pi}\left\{\frac{\sin[(l+m+1)\theta_0]}{(l+m+1)} + \frac{\sin[(l-m)\theta_0]}{(l-m)} \times(1-\delta_{lm}) + \theta_0\delta_{lm}\right\}, \quad (38)$$

and $b_l^*=[1-2h(1-q_0)]Q_{l0}$.

It is clear that the corresponding ESF is given by

$$f(\theta_0,h) = \left(h+\tfrac{1}{2}Y_0\right)/(1+h). \quad (39)$$

The general solution for the local concentration is defined by expression (13), where

$$A_l = (1-q_l)\left(\frac{B_l}{(l+1/2)} + Y_l\right).$$

In particular, for the problems (10)–(12) under consideration [when $h_1\to\infty$ and $h_2=O(1)$] this formula is simplified to

$$A_l = (1-q_l)(2h\delta_{l0} + Y_l). \quad (40)$$

The obtained infinite set of Eq. (37) may be solved by truncation. We present the evidence for the method of truncation for the case of system (37) in the Appendix.

The solution to the corresponding truncated system of equations may be found by iteration to any required accuracy and therefore it may be treated as the exact solution. Curves for the ESF at different values of the intrinsic rate coefficient h are shown in Fig. 4.

C. Approximations

It is convenient to represent the obtained infinite set of linear Eq. (37) in the matrix form

$$(\mathbf{E}+\mathbf{M})\mathbf{Y} = \mathbf{B}^*, \quad (41)$$

where $\mathbf{E}$ is the infinite unit matrix. Providing the solution of the matrix Eq. (42) exists we have

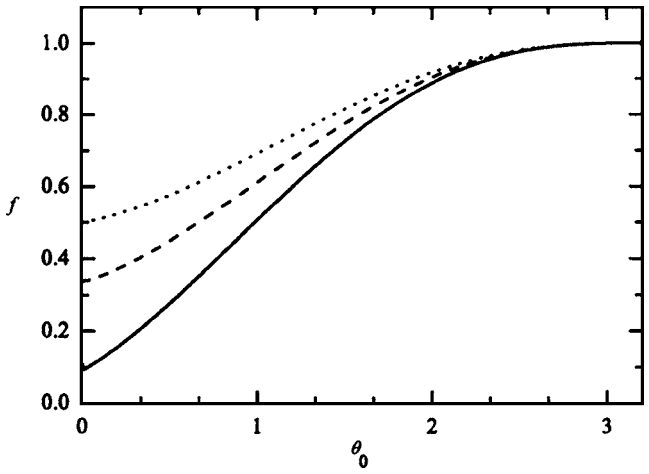

FIG. 4. Effective steric factor as a function of θ_0 for the case of strong asymmetric reactivity ($h_1\to\infty$ and $h_2=h\in[0,1]$) for $h=0.1$ (solid line), $h=0.5$ (dashed line), and $h=1.0$ (dotted line).

$$\mathbf{Y} = (\mathbf{E}+\mathbf{M})^{-1}\mathbf{B}^*.$$

On the other hand if $\|\mathbf{M}\|_\infty < 1$ system (37) (a) may be truncated to

$$(\mathbf{E}^{(n)} + \mathbf{M}_{(n)})\mathbf{Y}^{(n)} = \mathbf{B}^{*(n)}, \quad (42)$$

and (b) its solution may be found by iteration, i.e.,

$$\mathbf{Y}^{(n)} = \left(\sum_{k=0}^{\infty}(-1)^k \mathbf{M}_{(n)}^k\right)\mathbf{B}^{*(n)} = \sum_{k=0}^{\infty}\mathbf{A}_k. \quad (43)$$

Here $\mathbf{E}^{(n)}$ and $\mathbf{M}_{(n)}$ are finite $n\times n$ matrices corresponding to the infinite ones $\mathbf{E}$ and $\mathbf{M}$, respectively. It is evident that $\mathbf{A}_k=-\mathbf{M}_{(n)}\mathbf{A}_{k-1}$ for $k\in\mathbb{N}$ at $\mathbf{A}_0=\mathbf{B}^{*(n)}$.

Let us consider the zero order truncated system

$$Y_0^{(0)} - M_{00}Y_0^{(0)} = b_0^*. \quad (44)$$

For small θ_0, even zero order iteration for this simplest truncation

$$Y_0^{(0)} = b_0^* \quad (45)$$

leads to a small angle approximation

$$f^{(0)}(\theta_0,h) \sim k_h(\pi) + \frac{k_h^2(\pi)}{h^2} f^{(0)}(\theta_0) \quad \text{as } \theta_0\to 0, \quad (46)$$

where $k_h(\pi)=h/(1+h)$, $f^{(0)}(\theta_0)\equiv f^{(0)}(\theta_0,0)=(1/2\pi)(\theta_0+\sin\theta_0)$ is the zeroth order approximation of the ESF when part $\partial\Omega_2$ of the reaction surface is inert ($h=0$).[25]

$$Y_0^{(0)} = (1-M_{00})^{-1}b_0^*, \quad (47)$$

where $M_{00}=1/2\pi(\theta_0+\sin\theta_0)(1+2h)/(1+h)$. It is evident that approximation (45) is the expansion of the approximation (47) as $\theta_0\to 0$. The corresponding ESF is

$$f^{(1)}(\theta_0,h) = \left[h+\tfrac{1}{2}(1-M_{00})^{-1}b_0^*\right]/(1+h). \quad (48)$$

Moreover we can obtain one more so-called "diagonal" approximation,[25] solving the truncated system (44) exactly

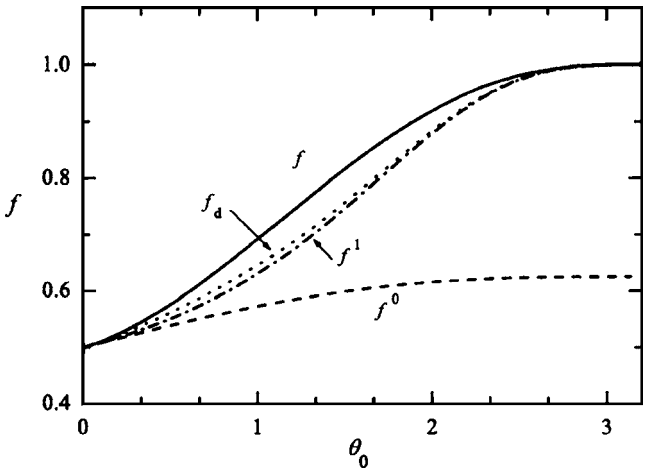

FIG. 5. Comparison of the different approximations for the effective steric factor as a function of θ_0 at $h=1.0$. The solid line corresponds to the exact solution, the dashed line corresponds to Eq. (46), the chain line corresponds to Eq. (48), and the dotted line corresponds to the "diagonal" approximation (49).

$$Y_0^{(d)} = b_0^* + \sum_{m=0}^{\infty} M_{0m}\tilde{Y}_m,$$

where

$$\tilde{Y}_m = \frac{b_m^*}{1 - M_{mm}}.$$

Thus the diagonal approximation for the ESF is

$$f_d(\theta_0,h) = \left(h + \tfrac{1}{2}Y_0^{(d)}\right)/(1+h). \tag{49}$$

In Fig. 5 we compare the different approximations for the ESF with its exact values at $h=1$. One can see that contrary to the case $h\to\infty$ the diagonal approximation f_d amended the previous approximation $f^{(1)}$ (44) slightly.

V. CONCLUDING REMARKS

The well known model of Solc and Stockmayer describing the diffusion-controlled reactions between chemically anisotropic reactants has been investigated. We assumed that the reaction surface has two sites with different intrinsic rate constants and took into account the corresponding partially reflecting conditions on these parts.

We considered the three cases: (1) when both parts of the reaction surface are partially reflecting but at different intrinsic rate constants; (2) when $\partial\Omega_1$ is ideally absorbing and $\partial\Omega_2$ is almost ideally absorbing (i.e., as $h_1\to\infty$ and $h_2\gg 1$); and (3) when the boundary condition on $\partial\Omega_1$ is reduced to the ideally absorbing one. For these cases we have found the conditions when the corresponding infinite set of linear algebraic equations is solvable and we solved them by the method of truncation.

The results obtained may be used for estimates of the rate coefficients in biophysical applications and to test numerical programs that describe diffusion-controlled reactions in real systems of particles with anisotropic reactivity. In particular we pointed out that simple formula (40) gives the exact effective steric factor for the case $h=-1/2$.

Our result may be easily generalized to the case of rotational diffusion.[16] Actually rotational diffusion leads to a more symmetric reaction surface and in this way it increases the value of the effective steric factor. Note also that using a similar analytical approach the practically important case of several active sites that covered the reaction surface may be treated as well.

ACKNOWLEDGMENTS

The NSW State Government is acknowledged for support through a Biofirst Award to one of the authors (W.S.P.).

APPENDIX: SOLVABILITY OF THE INFINITE SYSTEM (37)

Definition 1. *A sequence* $\{Y_l\}$ *such that for all* $l=\overline{0,\infty}$, *the series* $\Sigma_{m=0}^{\infty}(\delta_{lm}-M_{lm})Y_m$ *converge and their sums coincide with the constant term* $\{b_l^*\}$, *is termed a solution of the infinite set of linear algebraic equations (37).*[29]

Definition 2. *The infinite set of linear algebraic equations (37) is called fully regular, if there exists a positive number* $q<1$ *such that*

$$\sum_{m=0}^{\infty} |M_{lm}| \leqslant q \quad \text{for all } l=\overline{0,\infty}. \tag{A1}$$

Definition 3. *Truncation of the infinite set (37) is said to be the corresponding set of finite order*

$$Y_l^{(n)} - \sum_{m=0}^{n} M_{lm}Y_m^{(n)} = b_l^*, \quad (l=\overline{0,n}). \tag{A2}$$

Lemma. *Condition (A1) is sufficient for the system (37) to be solved by truncation (A2) such that*

$$\lim_{n\to\infty} Y_l^{(n)} = Y_l \quad \text{for all } l=\overline{0,\infty}$$

is the solution of the system (37).

The proof of this lemma may be found elsewhere (see, e.g., Ref. 29).

Let us derive now the regularity condition (A1) for the obtained infinite system of linear algebraic equations (37) as a function of the angular size of the active site θ_0. The following result holds true.

Theorem. *The infinite system (37) may be solved by truncation if*

$$0 \leqslant \theta_0 < \frac{2\pi}{1+2h} - 3. \tag{A3}$$

Proof. According to *Lemma* to prove the solvability of system (37) by truncation one should investigate the regularity condition (A1) for the matrix of the system (37). It is clear that Eq. (A1) holds if

$$s_l < 1 \quad \text{for all } l=\overline{0,\infty},$$

where

$$s_l = \sum_{m=0}^{\infty} |M_{lm}|.$$

The parameter $q_l(h)$ may be recast as

$$q_l(h) = q_l^0\left(\frac{1+2h}{1+2hq_l^0}\right),$$

where $q_l^0 \equiv q_l(0) = 1/2(1+l)$ and for all real $h \geqslant 0$ and integer $l \geqslant 0$ the following inequality holds true:

$$\frac{1}{1+2hq_l^0} \leqslant 1.$$

The latter inequality means that to find the regularity condition at $h \neq 0$ we can consider the specific case at $h=0$ and multiply the final estimate by the factor $1+2h$. It is evident that

$$s_l \leqslant \frac{1}{2\pi(l+1)}\left[\sum_{m=0}^{\infty}\frac{1}{(m+1)(l+m+1)} + \frac{1}{(l+1)}\theta_0 + \sum_{m(\neq l)=0}^{\infty}\frac{1}{(m+1)|l-m|}\right]. \quad \text{(A4)}$$

For the first sum on the right-hand side we have

$$\sum_{m=0}^{\infty}\frac{1}{(m+1)(l+m+1)} = \frac{1}{l}\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+l}\right).$$

This sum may be estimated using the integral representation[30]

$$\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+\gamma}\right) = \int_0^1 \frac{1-t^{\gamma}}{1-t}dt. \quad \text{(A5)}$$

Performing an estimate of this integral one obtains the inequality

$$\frac{1}{l}\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+1}\right) \leqslant \frac{1}{l}\sup_{t\in(0,1)}\left(\frac{1-t^l}{1-t}\right) = 1. \quad \text{(A6)}$$

For the second sum in (A4) we find

$$\sum_{m(\neq l)=0}^{\infty}\frac{1}{(m+1)|l-m|} = \sum_{m(<l)=0}^{l-1}\frac{1}{(m+1)(l-m)} + \sum_{m(>l)=l+1}^{\infty}\frac{1}{(m+1)(m-l)} \quad \text{(A7)}$$

and employing estimate (A6) for the second term on the right-hand side of Eq. (A7) we get

$$\sum_{m(>l)=l+1}^{\infty}\frac{1}{(m+1)(m-l)} = \sum_{\nu=1}^{\infty}\frac{1}{\nu(\nu+l+1)} = \frac{1}{l+1}\sum_{\nu=1}^{\infty}\left(\frac{1}{\nu} - \frac{1}{\nu+l+1}\right) \leqslant 1.$$

For the first term on the right-hand side of Eq. (A7) we have

$$\sum_{m=0}^{l-1}\frac{1}{(m+1)(l-m)} = \frac{1}{l+1}\sum_{m=0}^{l-1}\left(\frac{1}{m+1} + \frac{1}{l-m}\right) = \frac{1}{l+1}\left(\sum_{\nu=1}^{l}\frac{1}{\nu} + \sum_{m=0}^{l-1}\frac{1}{l-m}\right) = \frac{2}{l+1}\sum_{\nu=1}^{l}\frac{1}{\nu} \equiv \alpha_l.$$

Thus we obtain the estimate

$$\sum_{m(\neq l)=0}^{\infty}\frac{1}{(m+1)|l-m|} < 1 + \alpha_l$$

and finally the following inequality:

$$s_l < \frac{(1+2h)}{2\pi(l+1)}\left[2 + \frac{\theta_0}{(l+1)} + \alpha_l\right] \quad \text{for all } l = \overline{0,\infty}. \quad \text{(A8)}$$

One can see that the sequence $\{\alpha_l\}$ decreases monotonically for all $l \in \mathbb{N}$ and, therefore, $\alpha_l < \alpha_1 = 1$. Taking the upper boundary in inequality (A8) we arrive at

$$\|M\|_{\infty} = \sup_l\left(\sum_{m=0}^{\infty}|M_{lm}|\right) < \frac{(1+2h)}{2\pi}(3+\theta_0).$$

Therefore, the desired range of values θ_0 when $\|\mathbf{M}\|_{\infty} < 1$ is determined by the inequality

$$\frac{(1+2h)}{2\pi}(3+\theta_0) < 1$$

or the desired inequality (A3).

Corollary. *It follows from inequality (A3) that the condition of regularity holds uniformly in* $(0,\pi)$ *if*

$$0 \leqslant h \leqslant \frac{\pi-3}{2(3+\pi)}. \quad \text{(A9)}$$

Remark 1. *Condition (A9) means that the system (37) is solvable by the truncation method for all* $\theta_0 \in (0,\pi)$ *in the case of the mixed Dirichlet-Neumann boundary-value problem (10)–(12) when* $h_1 \to \infty$ *and* $h_2 = 0$. *This is the rigorous basis for the results of Ref. 25.*

Remark 2. *The estimate derived is rather rough and the convergence of the solution* $\{Y_l^{(n)}\}$ *of the truncated system (A2) to the exact solution occurs over a wider range of parameter h, at least for* $h \in (0,1)$.

[1] M. Maalmi, W. Strieder, and A. Varma, Chem. Eng. Sci. **56**, 5609 (2001).
[2] A. H. Elcock, D. Sept, and J. A. McCammon, J. Phys. Chem. B **105**, 1504 (2001).
[3] Y. Song, Y. Zhang, T. Shen, C. L. Bajaj, and J. A. McCammon, Biophys. J. **86**, 2017 (2004).
[4] D. Zhang, J. Suen, Y. Zhang, Y. Song, Z. Radic, P. Taylor, M. J. Holst, C. Bajaj, N. A. Baker, and J. A. McCammon, Biophys. J. **88**, 1659 (2005).
[5] A. Nag and A. R. Dinner, Biophys. J. **90**, 896 (2006).
[6] Y. Song, Y. Zhang, C. L. Bajaj, and N. A. Baker, Biophys. J. **87**, 1558 (2004).
[7] W. S. Price, F. Tsuchiya, and Y. Arata, J. Am. Chem. Soc. **121**, 11503 (1999).
[8] W. S. Price, Aust. J. Chem. **56**, 855 (2003).
[9] S. Lee and M. Kurplus, J. Chem. Phys. **86**, 1904 (1987).
[10] K. L. Ivanov, A. V. Yurkovskaya, P. J. Hore, and N. N. Lukzen, Mol.

Phys. **104**, 1687 (2006).
[11] F. Piazza, P. De Los Rios, D. Fanelli, L. Bongini, and U. Skoglund, Eur. Biophys. J. **80**, 2062 (2005).
[12] I. N. Sneddon, *Mixed Boundary Value in Potential Theory* (North-Holland, Amsterdam, 1966).
[13] V. A. Kudinov, E. M. Kartashov, and V. V. Kalashnikov, *Analytical Solutions of the Heat, Mass Transfer and Thermoelasticity for the Sandwich Structures* (Vysshaya Shkola, Moscow, 2005) (in Russian).
[14] If the boundary conditions differ on different parts of a given connected component of a boundary these conditions are called proper mixed boundary conditions. Provided different boundary conditions are posed on different connected components they are termed improper mixed boundary conditions.
[15] A. V. Barzykin and A. I. Shushin, Biophys. J. **80**, 2062 (2001).
[16] A. I. Shushin and A. V. Barzykin, Biophys. J. **81**, 3137 (2001).
[17] A. I. Shushin, J. Chem. Phys. **110**, 12044 (1999).
[18] A. I. Shushin, J. Chem. Phys. **113**, 4305 (2000).
[19] A. Grassi, G. M. Lombardo, and A. Raudino, J. Math. Chem. **25**, 321 (1999).
[20] H.-X. Zhou, Biophys. J. **97**, 2441 (1997).
[21] C.-O. Hwang, J. A. Given, and M. Masagni, J. Comput. Phys. **174**, 925 (2001).
[22] M. Masagni and C.-O. Hwang, Math. Comput. Simul. **63**, 93 (2003).
[23] M. Masagni and N. A. Simonov, SIAM J. Sci. Comput. **26**, 339 (2004).
[24] S. D. Traytak, J. Phys. Chem. **98**, 7419 (1994).
[25] S. D. Traytak, Chem. Phys. **192**, 1 (1995).
[26] S. D. Traytak and M. Tachiya, J. Chem. Phys. **102**, 2760 (1995).
[27] S. D. Traytak and M. Tachiya, J. Chem. Phys. **102**, 9240 (1995).
[28] P. Moon and D. E. Spencer, *Field Theory for Engineers* (Van Nostrand, New York, 1961).
[29] L. V. Kantorovich and V. I. Krylov, *Approximate Methods of Higher Analysis* (Interscience, New York, 1964).
[30] C. Jordan, *Calculus of Finite Differences* (Chelsea, New York, 1950).

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see http://ojps.aip.org/jcpo/jcpcr/jsp