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# Diffusion-influenced reaction rates for active "sphere-prolate spheroid" pairs and Janus dimers

Sergey D. Traytak<sup>1,a)</sup> and Denis S. Grebenkov<sup>2,3,b),c)</sup> <sup>1</sup>Institute of Applied Mechanics of the Russian Academy of Sciences, 32-a Lenin Avenue, Moscow 117334, Russia <sup>2</sup>Laboratoire de Physique de la Matière Condensée (UMR 7643), CNRS–Ecole Polytechnique, University Paris-Saclay, 91128 Palaiseau, France <sup>3</sup>Interdisciplinary Scientific Center Poncelet (ISCP), Bolshoy Vlasyevskiy Pereulok 11, 119002 Moscow, Russia (Received 26 September 2017; accepted 20 December 2017; published online 10 January 2018)

The purpose of this paper is twofold. First, we provide a concise introduction to the generalized method of separation of variables for solving diffusion problems in canonical domains beyond conventional arrays of spheres. Second, as an important example of its application in the theory of diffusion-influenced reactions, we present an exact solution of the axially symmetric problem on diffusive competition in an array of two active particles (including Janus dumbbells) constructed of a prolate spheroid and a sphere. In particular, we investigate how the reaction rate depends on sizes of active particles, spheroid aspect ratio, particles' surface reactivity, and distance between their centers. *Published by AIP Publishing*. https://doi.org/10.1063/1.5006544

## I. INTRODUCTION

The year 2017 marks the centenary of the seminal Smoluchowski paper which became the cornerstone of the modern theory of diffusion-influenced reactions.<sup>1,2</sup> In particular, the Smoluchowski theory concerns the pseudo-first-order irreversible bulk contact reactions

$$A + B \xrightarrow{k} A + P \tag{1}$$

between point-like diffusing reactants (reactive particles) *B* and static sinks *A* of finite size and infinite capacity (e.g., catalytic germs) immersed in the inert bulk liquid, resulting in inert products *P* (these reactions are often termed as the diffusion trapping model).<sup>3,4</sup> When the characteristic relaxation time for diffusion processes occurring in the system is small enough to ignore the transient effects, the kinetics is essentially determined by the *observed* reaction rate constant (or steady-state reaction rate coefficient) k.<sup>2</sup> In the particular case of stationary diffusion of *B* particles towards a single perfectly absorbing spherical sink of radius *R*, the Smoluchowski rate constant is

$$k_S = 4\pi RD,\tag{2}$$

where *D* is the translational diffusion coefficient of reactants *B*. The scaling of the reaction rate with the linear size of the sink is a remarkable feature of diffusion-controlled reactions, which contradicts the intuitively expected scaling with the area of the sink (given that the reaction occurs at the surface).<sup>2</sup> Note that Eq. (2) is only valid when the surface reaction rate constant is much larger than the characteristic velocity of diffusion *D/R*.

In the following, we will consider a general situation with an arbitrary surface reaction rate constant.

Diffusion-influenced reactions are widely encountered in natural and technological processes, playing a significant role in a broad and diversified range of physical, chemical, and biological systems.<sup>2,4</sup> As a rule, these systems comprise a mixture of particles or obstacles varying in sizes, shapes, and chemical activities on their surfaces. The mathematical description of diffusion-influenced reactions is based on the diffusion equation with respect to local concentration  $n_B(x)$ of diffusing solute particles B in a three-dimensional domain outside the array of static particles A under appropriate boundary conditions that account for the surface chemical activity. One can distinguish particles by the surface chemical activity as inert, partially absorbing, ideally absorbing (B disappears immediately when touching A), inert with some active sites, permeable, partially permeable, etc. In general, an active particle (AP) can be defined as a pair { $\Omega(\mathbf{x}_0), \kappa(\mathbf{s})$ }, where  $\Omega(\mathbf{x}_0)$  is a three-dimensional domain associated with the point  $x_0 \in \mathbb{R}^3$ and represents a particle of sort A and  $\kappa(s)$  (with  $s \in \partial \Omega$ ) stands for the intrinsic reaction rate coefficient for the absorption process (or surface reactivity) on the particle surface denoted by  $\partial \Omega$ . In general  $\kappa(s): \partial \Omega \to [0, \infty)$  is a piecewise continuous function on  $\partial \Omega$ . For instance,  $\{B_R(x_0), 0\}$ is an inert spherical obstacle of radius R centered at  $x_0$ , whereas  $\{B_R(\mathbf{x}_0), \infty\}$  is an ideal spherical sink. Hereafter  $B_R(\mathbf{x}_0) = \{\mathbf{x} \in \mathbb{R}^3 : ||\mathbf{x} - \mathbf{x}_0|| < R\}$  is an open ball of radius R and center  $x_0$ , where ||y - z|| stands for the distance between points  $y, z \in \mathbb{R}^3$ . The primary task of the theory is the derivation of the pseudo-first-order reaction rate constant k for a given array of APs.

In contrast to the Smoluchowski solution for a single spherical particle, the diffusion problem for an array of two or more APs is much more involved. Indeed, the concentration  $n_B(x)$  in the vicinity of any AP is affected by the presence of

<sup>&</sup>lt;sup>a)</sup>Electronic mail: sergtray@mail.ru

b)Electronic mail: denis.grebenkov@polytechnique.edu

cJISCP: International Joint Research Unit–UMI 2615 CNRS/IUM/IITP RAS/ Steklov MI RAS/Skoltech/HSE, Moscow, Russian Federation.

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all other APs from a given array. This effect is often called the *diffusive interaction* (DI), in analogy to the hydrodynamics interaction for many particle systems in Stokes flow.<sup>5</sup> The literature also reveals other terms for this phenomenon, e.g., *competitive interaction* (or just *competition*)<sup>6,7</sup> and *diffusion screening*, in analogy with electrostatic screening.<sup>8</sup> From the mathematical point of view, DI effects are stipulated by the disconnectedness of the boundary, consisting of the reaction surfaces formed by the given array of APs.

From both theoretical and practical points of view, the diffusion-influenced reactions on two APs are of special current interest. In particular, the problem of two ideally or partially absorbing spherical APs has been a subject of long standing interest among theoreticians (see, e.g., Refs. 2 and 3). Different methods have been used to address this problem. In the scope of the method of orthogonal curvilinear coordinates,<sup>9</sup> the bispherical coordinate system was perhaps the most widely used for handling different problems of potential theory and related topics in applications with two spheres. Samson and Deutch pioneered the application of bispherical coordinates to the exact solution for the diffusion-controlled rate into a pair of reacting spherical sinks "... in order to provide a basis for comparison to the more general theories."10 Later many authors used the bispherical coordinates to obtain the analytical solutions for diffusion-influenced reactions on two spherical APs.<sup>7,11–13</sup> In particular, the analysis of the DI between two burning or evaporating fuel drops with different sizes and surface activities was accomplished.<sup>14–16</sup> Until now, the method of bispherical coordinates is still widely used to describe diffusion reaction kinetics on the surface of geometrically and chemically axially symmetric Janus dumbbell particles consisting of two spherical APs.<sup>17-19</sup> In addition, a numerical investigation of the diffusion-controlled reaction between diffusing charged particles B and a system of two oppositely charged static spherical sinks has been successfully performed.<sup>20</sup>

In spite of these advances, the method of bispherical coordinates has several disadvantages (see Appendix for details). In particular, for almost touching spheres or spheres in contact (dumbbells), solutions contain secular terms and, therefore, the problem becomes singularly perturbed. To avoid this difficulty, several regularization procedures have been proposed (see, e.g., Refs. 21 and 22 and references therein), whereas the degenerate bispherical coordinate system may be used to describe the array of touching spheres.<sup>9</sup> We emphasize however that the bispherical coordinate system is only suitable for *two spherical* APs.

To overcome these limitations, in particular, to deal with arrays comprising many spherical APs, other methods have been proposed. For instance, diffusion interactions in an array of two non-spherical APs were studied by a modified image method elaborated by Labowsky<sup>23</sup> and much later by a bound-ary collocation method by Labowsky and Fahmy.<sup>24</sup> Recently McCammon *et al.* have investigated diffusion-influenced reactions on an array of several sinks by solving numerically the Laplace equation by means of a finite element method.<sup>25</sup> To describe diffusion-controlled reactions on a finite number of ideal spherical sinks, Beenakker and Ross applied the induced sources method<sup>26</sup> which originally was developed for

problems on hydrodynamics interactions in the Stokes flow. The method of irreducible Cartesian tensors has been suggested by Traytak for solving similar problems<sup>14</sup> (note that these two approaches appear to be equivalent since both lead to the same second kind infinite set of linear algebraic equations with respect to unknown coefficients). Many other theoretical methods such as variational estimates and perturbative analysis have been employed to study diffusion among static APs.<sup>4,27–35</sup> Generalization of the Wilemski-Fixman-Weiss decoupling approximation elaborated by Lee *et al.* deserves special attention as a very powerful and general technique to investigate DI in arrays containing multiple APs of different sizes, shapes, and reactivities.<sup>36</sup> Finally, Monte Carlo simulations have been often used for computing the reaction rate and other diffusion characteristics in arrays of spheres.<sup>37–39</sup>

In this paper, we advocate for another method that was originally developed for diffraction problems and called the generalized method of separation of variables (GMSV).<sup>40</sup> The GMSV should not be confused with "the method of generalized separation of variables" proposed by Polyanin and Zhurov.<sup>79</sup> For the axially symmetric DI problems, a particular version of this method has been employed by Goodrich in 1967 to find the steady-state diffusion field in the neighborhood of two identical ideal spherical sinks (drops).<sup>41</sup> Later Mattern and Felderhof treated the more general case of diffusion-controlled reactions in a random array of spherical sinks by means of the GMSV.<sup>42</sup> Much later Traytak and Tachiya studied the DI between two sinks trapping charged diffusing reactants B in an external electric field E with the help of the GMSV for the modified Helmholtz equation.<sup>43</sup> It is clear that the general formulas obtained there for the reaction rates lead to the corresponding formulas in the case of pure diffusion as  $\mathbf{E} \rightarrow 0$ . By means of the axially symmetric GMSV for solid spherical harmonics, the free energy change of the electron transfer reaction, including the effect of an external electric field, was calculated rigorously.<sup>44</sup> Using the same approach, Tsao obtained the reaction rates for diffusion uptake of B particles by two spherical APs of different reactivity and size.<sup>45</sup> Then Strieder and co-authors used the GMSV to study reactions on two different spherical sinks and a spherical source and sink.<sup>6,46</sup> It is worth noting that the latter case of DI between the source and sink is of special interest for applications. Within the scope of the GMSV, Felderhof used so-called addition theorems for arbitrary solid spherical harmonics to study diffusion-controlled reactions in a regular array of spheres.<sup>47</sup> Galanti *et al.* applied the most general form of the GMSV for computing the reaction rate in an array of non-overlapping spherical APs with arbitrary sizes, locations, and chemical activities.<sup>48</sup>

All these former studies involving the GMSV have been exclusively focused on various arrays of *spherical* APs. In the past years, however, considerable progress has been made towards micro- and nanoparticle syntheses including a great variety of building blocks of different shapes, compositions, patterns, and functionalities.<sup>49,50</sup> For example, recent investigations of artificial antenna systems have awakened keen interest of researchers (see, e.g., Refs. 51 and 52 and references therein). A typical antenna system may be modeled as an immobile target (or a specific site) which is attached to a straight one-dimensional non-reactive rod of some finite length

embedded in the three-dimensional space. Although such an antenna might be approximated as an array of spheres, a more natural geometric model for the antenna system is an active sphere in contact with a non-reactive prolate spheroid of large enough aspect ratio. In addition, many useful effects of Janus particles (e.g., their self-propulsion, see Ref. 53 and references therein) have inspired studies of heteronuclear sticky Janus dumbbells and Janus prolate spheroidal APs.<sup>54–58</sup> While trapping of point-like diffusing particles *B* by an isolated ideally or partially absorbing spheroidal AP was well investigated, <sup>59–62</sup> the case of an array of two "sphere-prolate spheroid" APs has remained unexplored.

Bearing in mind the growing interest in the analysis of diffusion-influenced reactions in arrays of non-spherical APs, we have selected the "sphere-prolate spheroid" geometric configuration as an important example to illustrate how the GMSV can be used for generic canonical domains. The main objective of our study is to familiarize the readers with this rather powerful general technique and some peculiarities related to its implementation and application to a number of problems often arising in the theory of diffusion-influenced reactions. We present the semi-analytical solution of the steady-state diffusion problem for an array of two APs: a sphere and a prolate spheroid (whose principal axis goes through the center of the sphere). In particular, this solution allows us to investigate the effect of shape and surface reactivity on the overall reaction rate. The obtained result may be used to construct models of diffusion-controlled reactions on axially symmetric microbodies.

This paper is organized as follows. In Sec. II, the mathematical model is formulated in terms of the boundary value problem for the steady-state diffusion equation. The basic description of the generalized method of separation of variables for canonical domains is given in Sec. III. Section IV contains a detailed solution of the axially symmetric problem on diffusion competition between two active particles of the "sphere-prolate spheroid" array. Section V presents the analysis of the screening effect of one active particle on the other and of the respective roles of the shape and surface reactivity. In particular, the cases of both ideally absorbing sinks and one absorbing/one reflecting particle are discussed. We also consider the case of Janus dumbbells which consist of a touching sphere and prolate spheroid. This is followed by the conclusions in Sec. VI. Appendix summarizes the expressions for the reaction rate in the particular case of an array comprising two spherical active particles.

### **II. STATEMENT OF THE PROBLEM**

As already noted, we consider here the steady-state diffusion of point-like particles *B* towards an axially symmetric array of two static non-overlapping APs { $\Omega_i(\mathbf{x}_0^i), \kappa_i(s_i)$ }:  $\Omega_1(\mathbf{x}_0^1) \equiv B_R(\mathbf{x}_0^1)$  is the ball of radius *R*, centered at the point  $\mathbf{x}_0^1 = (0, 0, -L)$ , and  $\Omega_2(\mathbf{x}_0^2)$  is a prolate spheroid with the minor semi-axis *a* and the major semi-axis *b* (*b* > *a*), centered at the origin  $\mathbf{x}_0^2 = O = (0, 0, 0)$ . By construction, the centers of two APs are located on the *z* axis and separated by distance  $L \ge R + b$  (see Fig. 1). In this study, we treat spheroidal APs of arbitrary aspect ratio  $\epsilon = b/a \in (1, \infty)$ ,



FIG. 1. Schematic view of two active particles: (1) a sphere of radius R and (2) a prolate spheroid with the minor semi-axis a and the major semi-axis b. The major axis of the spheroid goes through the center of the sphere (axial symmetry). The distance between centers of two APs is L.

ranging between the limiting cases of spheres ( $\epsilon = 1$ ) and needles ( $\epsilon \to \infty$ ). The reaction in (1) occurs when reactants *B* reach the total reaction surface  $\partial \Omega^- = \partial \Omega_1 \cup \partial \Omega_2$ , and we assume that  $\kappa_i(s_i) = \kappa_i = const$  anywhere on each surface  $s_i \in \partial \Omega_i$ . Although for our illustrative purposes we formulate the problem for the particular case of two "sphereprolate spheroid" APs, this formulation has a straightforward extension to any finite number of arbitrary non-overlapping canonical domains (see Sec. III).

In mathematical terms, we are interested in finding the steady-state local concentration field of diffusing reactants *B*, i.e., a function  $n_B(\mathbf{x})$ :  $\Omega^- \to [0, \infty)$ , where the domain  $\Omega^- = \mathbb{R}^3 \setminus (\overline{\Omega}_1 \cup \overline{\Omega}_2)$  is the exterior of the above two APs. From the geometrical point of view,  $\Omega^-$  is a spatial domain in  $\mathbb{R}^3$  with disconnected boundary  $\partial\Omega^-$  consisting of two connected components  $\partial\Omega_1$  and  $\partial\Omega_2$  such that  $\partial\Omega_1 \cap \partial\Omega_2 = \emptyset$ .

The desired field  $n_B(\mathbf{x})$  obeys the Laplace equation

$$\nabla^2 n_B = 0 \quad \text{in} \quad \Omega^- \tag{3}$$

under appropriate boundary conditions.

(a) In the general partially diffusion-controlled regime  $(0 < \kappa_i < \infty)$ , the Robin boundary condition is imposed,  $^{2,63,64}$ 

$$-(D\partial_{\mathbf{n}}n_B)|_{\partial\Omega_i} = \kappa_i n_B|_{\partial\Omega_i},\tag{4}$$

where  $\partial_{\mathbf{n}}$  is the normal derivative at the *i*th AP boundary  $\partial \Omega_i$  directed outwards the domain  $\Omega^-$  and *D* is the translational diffusion coefficient. Condition (4) means that the local diffusive flux towards the boundary (the lefthand side) is equal to the "reaction" flux at the boundary (the right-hand side).

(b) For the fully diffusion-controlled regime  $(\kappa_i \rightarrow \infty)$ , the boundary condition (4) turns into the Dirichlet one as the reaction occurs when a reactant *B* reaches the surface,

$$n_B|_{\partial\Omega_i} = 0. \tag{5}$$

This condition describes an ideal sink when solute particles *B* react instantaneously after contact with any point of the AP surface. (c) In the case of an inert particle ( $\kappa_i = 0$ ), we deal with the Neumann boundary condition

$$(\partial_{\mathbf{n}} n_B)|_{\partial \Omega_i} = 0, \tag{6}$$

which implies that the surface of the given AP is impermeable and inert for particles *B*.

Since different types of boundary conditions can be imposed on different active particles, one faces the so-called improper mixed boundary value problem, in contrast to proper mixed boundary value problems when different boundary conditions are imposed on disjoint parts of the same AP boundary.<sup>17,65</sup>

In addition, we impose the regularity condition at infinity, i.e., the local concentration  $n_B(x)$  approaches its constant bulk value  $n_0$  at infinity,

$$n_B|_{\|\mathbf{x}\| \to \infty} \to n_0. \tag{7}$$

Since Eq. (3) with any of the boundary conditions (a)-(c) and regularity condition at infinity (7) forms a well posed exterior boundary value problem,<sup>66,67</sup> it possesses a regular solution. Once the local concentration  $n_B(\mathbf{x})$  is found, one can deduce the total flux of diffusing particles *B* onto the *i*th AP

$$J_{i} = \int_{\partial \Omega_{i}} (-D\partial_{\mathbf{n}} n_{B}) |_{\partial \Omega_{i}} ds_{i}, \qquad (8)$$

where  $ds_i$  stands for the incremental surface area on the surface  $\partial \Omega_i$ . One can also write it in the form of the microscopic absorption rate

$$k_i = \frac{J_i}{n_0} \,. \tag{9}$$

Note that, strictly speaking, the microscopic absorption rate (9) in the case of two or more APs does not coincide with the macroscopic rate constant k.<sup>5</sup>

To study the diffusion interaction, it is expedient to introduce the reduced *B* particles' concentration field

$$u(\boldsymbol{x}) = 1 - \frac{n_B(\boldsymbol{x})}{n_0},$$

which varies between 0 and 1, vanishes at infinity, and obeys the following exterior Robin boundary value problem:

$$\nabla^2 u = 0 \quad (\boldsymbol{x} \in \Omega^-), \tag{10}$$

$$(\Lambda_i \partial_{\mathbf{n}} u + u)|_{\partial \Omega_i} = 1, \tag{11}$$

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

where  $\Lambda_i = D/\kappa_i$  (*i* = 1, 2) has units of length. The solution to the boundary value problem (10)–(12) takes into account the DI effects and gives a complete *microscopic description* of the diffusion trapping model under consideration.

## **III. METHOD OF SOLUTION**

In this section, for the sake of generality, we consider the arrays comprising N APs. Thus here we assume that B particles diffuse in the exterior domain outside APs

$$\Omega^{-} = \mathbb{R}^{3} \setminus \bigcup_{i=1}^{N} \overline{\Omega}_{i}, \quad \partial \Omega^{-} = \bigcup_{i=1}^{N} \partial \Omega_{i}$$
(13)

under the condition of mutually disjoint AP domains:  $\overline{\Omega}_i \cap \overline{\Omega}_i = \emptyset$  for  $(i \neq j)$ . The most commonly used analytical and numerical methods for solving boundary value problems for the Laplace equation given on  $\Omega^-$  are<sup>68</sup>

- the method of images;
- the method of reflections;
- Green's function method;
- the method of induced forces;
- the method of irreducible Cartesian tensors;
- direct methods in the calculus of variations;
- the method of surface integral equations;
- the method of fundamental solutions;
- the domain decomposition method;
- a fat boundary method;
- finite difference and finite elements methods;
- Monte Carlo simulations.

Despite a number of inherent advantages, all above approaches have also weaknesses as compared to the generalized method of separation of variables. This method allows one to overcome many difficulties of existing methods and to provide a clear and powerful semi-analytical approach to solve the problem for systems comprising many different active particles.

For further description, we recall the definition of the canonical domain. A three-dimensional domain  $\Omega\, \subset\, \mathbb{R}^3$  is called canonical for a given partial differential equation if the classical solution to this equation may be expanded on  $\Omega$  into an absolutely and uniformly convergent series with respect to relevant basis solutions in the Hilbert space  $L_2(\partial \Omega)$ . Due to the rather complicated geometry of the exterior domain  $\Omega^-$  for N > 2, it is not possible to reduce the Laplace equation (10) even to some equation with  $\mathcal{R}$ -separable variables globally in the whole  $\Omega^{-.80}$  On the other hand, taking into account the symmetry of the Laplace equation under translations, problem (10)–(12) may be solved analytically in the whole  $\Omega^{-}$  if one uses the relevant local curvilinear orthogonal coordinates associated with the surfaces  $\partial \Omega_i$ , where  $\Omega_i$   $(i = \overline{1, N})$  are the canonical domains. In our example, domains  $\Omega_1$  (a ball) and  $\Omega_2$  (a prolate spheroid) are canonical.

The main idea of the GMSV for *N* canonical domains relies on Green's representation of any harmonic function,  $u(\mathbf{x})$ , which is regular at infinity, at any interior point  $\mathbf{x} \in \Omega^{-}$  as<sup>66</sup>

$$u(\mathbf{x}) = \int_{\partial \Omega^{-}} \left[ u(s)\partial_{\mathbf{n}} \mathcal{G}(\mathbf{x},s) - \mathcal{G}(\mathbf{x},s)\partial_{\mathbf{n}} u \right] ds, \qquad (14)$$

where  $\mathcal{G}(\mathbf{x}, \mathbf{y}) = 1/(4\pi ||\mathbf{x} - \mathbf{y}||)$  is the Newton potential (or electrostatic potential in three dimensions). By means of the Riemann integral additivity with respect to the surface of integration  $\partial \Omega^-$  and relation (13), Eq. (14) leads to the unique decomposition

$$u(\mathbf{x}) = \sum_{i=1}^{N} u_i(\mathbf{x}) \quad \text{in} \quad \Omega^-, \tag{15}$$

where

$$u_{i}(\boldsymbol{x}) \coloneqq \int_{\partial \Omega_{i}} \left[ u(\boldsymbol{s}) \partial_{\mathbf{n}} \mathcal{G}(\boldsymbol{x}, \boldsymbol{s}) - \mathcal{G}(\boldsymbol{x}, \boldsymbol{s}) \partial_{\mathbf{n}} u \right]_{\partial \Omega_{i}} d\boldsymbol{s}_{i}$$
(16)

is termed the partial solution corresponding to the AP concentrated in  $\Omega_i$ . Applying the boundary conditions, one gets a set of integral equations on functions  $u_i|_{\partial\Omega_i}$  that can be resolved by different methods. In particular, for each  $\partial \Omega_i$ , one can decompose the Newton potential  $\mathcal{G}(x,s)$  in Eq. (16) on the basis of appropriate functions in the local coordinates of the AP in  $\Omega_i$ . This decomposition decouples x and s variables and yields an expansion of the partial solution  $u_i(\mathbf{x})$  on that basis. The unknown coefficients of the expansion are then fixed by the boundary conditions, which are exactly satisfied by substitution accompanied by the use of appropriate re-expansion formulas (in diffraction theory commonly termed as "addition theorems").<sup>40</sup> In other words, one looks for the classical solution of problem (10)–(12) as a superposition of N implicit expansions into basis solutions of the Laplace equation in each orthogonal curvilinear coordinate system connected with the APs of the array. As a result, the original boundary value problem with respect to a harmonic function is reduced to a Fredholm second kind infinite set of linear algebraic equations (ISLAE) in the Hilbert space of sequences  $\ell_2^N$  with respect to the sequences of unknown coefficients. Provided that the relevant matrix operator of the ISLAE is compact, the system can be truncated and numerically solved. The practical implementation of this general scheme is illustrated in Sec. IV for the particular case of two "sphere-prolate spheroid" APs.

## **IV. SOLUTION TO THE PROBLEM**

In order to solve the boundary value problem (10)–(12), we use the local curvilinear coordinates associated with the symmetries of two APs. The local spherical coordinates  $(O_1; r, \theta, \phi)$  are related to the local Cartesian coordinates  $(O_1; x_1, y_1, z_1)$  as

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = r \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix},$$
(17)

where  $0 < r < \infty$ ,  $0 < \theta < \pi$ ,  $0 < \phi < 2\pi$ , and

$$\begin{pmatrix} r\\ \theta\\ \phi \end{pmatrix} = \begin{pmatrix} +\sqrt{x_1^2 + y_1^2 + z_1^2}\\ \tan^{-1}\left[\sqrt{x_1^2 + y_1^2}/z_1\right]\\ \tan^{-1}\left(y_1/x_1\right) \end{pmatrix}.$$
 (18)

In turn, the local prolate spheroidal coordinates ( $O_2$ ;  $\alpha$ ,  $\beta$ ,  $\phi$ ) are related to the local Cartesian coordinates ( $O_2$ ;  $x_2$ ,  $y_2$ ,  $z_2$ ) as<sup>66,69</sup>

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = a_E \begin{pmatrix} \sinh \alpha \sin \beta \cos \phi \\ \sinh \alpha \sin \beta \sin \phi \\ \cosh \alpha \cos \beta \end{pmatrix},$$
(19)

where  $0 < \alpha < \infty$ ,  $0 < \beta < \pi$ ,  $0 < \phi < 2\pi$ , and

$$\begin{pmatrix} \alpha \\ \beta \\ \phi \end{pmatrix} = \begin{pmatrix} \cosh^{-1} \left[ (r_+ + r_-) / (2a_E) \right] \\ \cos^{-1} \left[ (r_+ - r_-) / (2a_E) \right] \\ \tan^{-1} \left( y_2 / x_2 \right) \end{pmatrix},$$
(20)

where

$$r_{\pm} = \sqrt{x_2^2 + y_2^2 + (z_2 \pm a_E)^2}$$
(21)

are the distances to the two foci located at points  $(0, 0, \pm a_E)$  and

$$a_E = \sqrt{b^2 - a^2} \tag{22}$$

is half of the focal distance. Note that local prolate spheroidal coordinates  $(O_2; \alpha, \beta, \phi)$  are dimensionless and  $a_E$  is the only scale factor which has the dimension of length.

Finally, the local Cartesian coordinates  $(O_1; x_1, y_1, z_1)$ and  $(O_2; x_2, y_2, z_2)$  are related by translation,

$$x_2 = x_1, \quad y_2 = y_1, \quad z_2 = z_1 + L.$$
 (23)

The above formulas allow one to "switch" between local coordinates of two APs that will be the key property in the following derivation.

In local coordinates, the two APs domains are defined as

$$\Omega_1(\boldsymbol{x}_0^1) = \left\{ \boldsymbol{x} \in \mathbb{R}^3 : 0 < r < R \right\},$$
$$\Omega_2(\boldsymbol{x}_0^2) = \left\{ \boldsymbol{x} \in \mathbb{R}^3 : 0 < \alpha < \alpha_0 \right\}$$

where  $\alpha_0$  determines the boundary of the second AP,

$$\partial \Omega_2 = \{ \alpha = \alpha_0 : 0 < \beta < \pi, 0 < \phi < 2\pi \}$$

with

$$\alpha_0 = \cosh^{-1}\left(\frac{b}{a_E}\right).$$

The general solution to problem (10)–(12) may be given as the superposition

$$u(\mathbf{x}) = u_1(r,\theta) + u_2(\alpha,\beta). \tag{24}$$

Due to the axial symmetry of the domain  $\Omega^-$ , the solution  $u(\mathbf{x})$  does not depend on  $\phi$  which will be omitted in the remaining text. In Eq. (24), the partial solutions corresponding to the sphere,  $u_1(r, \theta)$ , and to the prolate spheroid,  $u_2(\alpha, \beta)$ , satisfying the regularity condition at infinity (12), read<sup>66,69</sup>

$$u_1(r,\theta) = \sum_{n=0}^{\infty} A_n^{(1)} r^{-n-1} P_n(\cos\theta),$$
 (25)

$$u_2(\alpha,\beta) = \sum_{n=0}^{\infty} A_n^{(2)} Q_n(\cosh\alpha) P_n(\cos\beta), \qquad (26)$$

where  $P_n(x)$  and  $Q_n(x)$  are the Legendre functions of the first and second kinds, respectively. To find the unknown coefficients  $A_n^{(1)}$  and  $A_n^{(2)}$ , we use the re-expansion formulas<sup>40</sup> for the "sphere-prolate spheroid" array,

$$r^{-n-1} P_n(\cos \theta) = \sum_{k=0}^{\infty} U_{nk}^{12} P_k(\cosh \alpha) P_k(\cos \beta), \qquad (27)$$

where the so-called mixed-basis matrix elements are

$$U_{nk}^{12} = \frac{(-1)^{n+k}(2k+1)a_E^{-n-1}}{n!(\sigma^2 - 1)^{n/2}} Q_k^n(\sigma) \quad (\sigma > 1), \qquad (28)$$

and for prolate spheroid/sphere,

$$Q_n(\cosh \alpha)P_n(\cos \beta) = \sum_{k=0}^{\infty} U_{nk}^{21} r^k P_k(\cos \theta), \qquad (29)$$

where the reciprocal mixed-basis matrix elements read

$$U_{nk}^{21} = \frac{(-1)^{k+n} a_E^{-k}}{k! (\sigma^2 - 1)^{k/2}} Q_n^k(\sigma) \quad (\sigma > 1),$$
(30)

with  $\sigma = L/a_E$ ,  $k = \overline{0, \infty}$ ,  $n = \overline{0, \infty}$ , and  $Q_n^k$  is the associated Legendre function of the second kind, which can also be expressed in terms of the Gauss hypergeometric function,

$$Q_n^k(\zeta) = \frac{(-1)^k \sqrt{\pi(n+k)!}}{2^{n+1} \Gamma(n+3/2) \zeta^{n+k+1}} (\zeta^2 - 1)^{k/2} \\ \times {}_2F_1\left(\frac{n+k}{2} + 1, \frac{n+k+1}{2}; n+\frac{3}{2}; \zeta^{-2}\right).$$

Using representations (25) and (26), we search for the coefficients  $A_n^{(1)}$  and  $A_n^{(2)}$  to satisfy the boundary conditions (11). We get on the boundary of the sphere,

$$I = (\Lambda_1 \partial_n u + u)|_{\partial \Omega_1}$$
  
=  $\sum_{n=0}^{\infty} A_n^{(1)} q_n^{(1)} P_n(\cos \theta) + \sum_{n=0}^{\infty} A_n^{(2)} \sum_{k=0}^{\infty} U_{nk}^{21} p_k^{(1)} P_k(\cos \theta),$   
(31)

where

$$p_n^{(1)} = (1 - n\lambda_1)R^n, \tag{32}$$

$$q_n^{(1)} = \left[1 + (n+1)\lambda_1\right] R^{-n-1},\tag{33}$$

with  $\lambda_1 = \Lambda_1/R = D/(R\kappa_1)$ . Multiplying this relation by  $P_m(\cos \theta) \sin \theta$  and integrating over  $\theta$  from 0 to  $\pi$ , we get for any  $m = \overline{0, \infty}$  the infinite system of equations

$$A_m^{(1)} q_m^{(1)} + \sum_{n=0}^{\infty} A_n^{(2)} U_{nm}^{21} p_m^{(1)} = \delta_{m,0}.$$
 (34)

Similarly, the boundary condition at the boundary of the spheroid reads

$$1 = (\Lambda_2 \partial_{\mathbf{n}} u + u)|_{\partial \Omega_2}$$
  
=  $\sum_{n=0}^{\infty} A_n^{(1)} \sum_{k=0}^{\infty} U_{nk}^{12} p_k^{(2)} P_k(\cos \beta) + \sum_{n=0}^{\infty} A_n^{(2)} q_n^{(2)} P_n(\cos \beta),$   
(35)

where

$$p_n^{(2)} = P_n(\cosh \alpha_0) + \Lambda_2 (\partial_{\mathbf{n}} P_n(\cosh \alpha))_{\alpha_0}$$
  
=  $P_n(\cosh \alpha_0) - \frac{\Lambda_2 \sinh \alpha_0}{h_{\alpha_0}} P'_n(\cosh \alpha_0),$  (36)

$$q_n^{(2)} = Q_n(\cosh \alpha_0) + \Lambda_2 \left( \partial_{\mathbf{n}} Q_n(\cosh \alpha) \right)_{\alpha_0}$$
  
=  $Q_n(\cosh \alpha_0) - \frac{\Lambda_2 \sinh \alpha_0}{h_{\alpha_0}} Q'_n(\cosh \alpha_0), \quad (37)$ 

and we represented the normal derivative as

$$\partial_{\mathbf{n}} f(\alpha) = -\frac{1}{h_{\alpha}} \partial_{\alpha} f(\alpha),$$
 (38)

where

$$h_{\alpha} = a_E \sqrt{\sinh^2(\alpha) + \sin^2(\beta)}$$
(39)

is the corresponding scale factor. In contrast to the spherical sink, the coefficients  $p_n^{(2)}$  and  $q_n^{(2)}$  depend on the angular coordinate  $\beta$  if  $\Lambda_2 > 0$ .

For the Dirichlet case ( $\Lambda_2 = 0$ ), the multiplication of Eq. (35) by  $P_m(\cos\beta)\sin\beta$  and integration over  $\beta$  from 0 to  $\pi$  yield another infinite set of linear equations

$$\sum_{n=0}^{\infty} A_n^{(1)} U_{nm}^{12} p_m^{(2)} + A_m^{(2)} q_m^{(2)} = \delta_{m,0}.$$
 (40)

For the Neumann case, Eq. (35) is multiplied by  $-(h_{\alpha_0}/\sinh \alpha_0)P_m(\cos \beta)\sin \beta/\Lambda_2$  and integrated over  $\beta$  from 0 to  $\pi$ . In the limit  $\Lambda_2 \to \infty$ , one gets

$$\sum_{n=0}^{\infty} A_n^{(1)} U_{nm}^{12} \, \tilde{p}_m^{(2)} + A_m^{(2)} \, \tilde{q}_m^{(2)} = 0, \tag{41}$$

with

$$\tilde{p}_n^{(2)} = P'_n(\cosh \alpha_0), \qquad \tilde{q}_n^{(2)} = Q'_n(\cosh \alpha_0).$$
 (42)

Finally, in the intermediate Robin case, the integration of Eq. (35), multiplied by  $P_m(\cos\beta)\sin\beta$ , results in the infinite set of linear equations

$$\sum_{n=0}^{\infty} \left\{ A_n^{(2)} Q_{mn} + \left( \sum_{k=0}^{\infty} A_k^{(1)} U_{kn}^{12} \right) P_{mn} \right\} = \delta_{m,0}, \qquad (43)$$

with

$$Q_{mn} = \delta_{mn} Q_n (\cosh \alpha_0) - \lambda_2 \sinh \alpha_0 Q'_n (\cosh \alpha_0) I_{mn},$$
  

$$P_{mn} = \delta_{mn} P_n (\cosh \alpha_0) - \lambda_2 \sinh \alpha_0 P'_n (\cosh \alpha_0) I_{mn},$$
(44)

which involve the integrals

$$I_{mn} = (m+1/2) \int_{0}^{\pi} d\beta \sin\beta \frac{P_m(\cos\beta)P_n(\cos\beta)}{\sqrt{\sinh^2\alpha_0 + \sin^2\beta}}.$$
 (45)

These integrals can be computed numerically. However, in the rest of this paper, we focus on the Dirichlet and Neumann cases, for which these integrals are not needed.

Combining Eq. (34) with either Eq. (40) for  $\Lambda_2 = 0$  or Eq. (41) for  $\Lambda_2 = \infty$  or Eq. (43) for  $0 < \Lambda_2 < \infty$ , one gets a closed ISLAE that can be written in the matrix form as

$$\underbrace{\begin{pmatrix} \mathbf{W}^{(11)} & \mathbf{W}^{(12)} \\ \mathbf{W}^{(21)} & \mathbf{W}^{(22)} \end{pmatrix}}_{\mathbf{W}} \begin{pmatrix} \mathbf{A}^{(1)} \\ \mathbf{A}^{(2)} \end{pmatrix} = \begin{pmatrix} \mathbf{B}^{(1)} \\ \mathbf{B}^{(2)} \end{pmatrix},$$
(46)

where  $\mathbf{B}^{(1)} = \mathbf{B}^{(2)} = (1, 0, 0, ...)^{\mathrm{T}}$  and

$$(\mathbf{W}^{(11)})_{kn} = \delta_{nk} q_k^{(1)}, \qquad (\mathbf{W}^{(12)})_{kn} = U_{nk}^{21} p_k^{(1)}, (\mathbf{W}^{(21)})_{kn} = U_{nk}^{12} p_k^{(2)}, \qquad (\mathbf{W}^{(22)})_{kn} = \delta_{nk} q_k^{(2)}.$$

$$(47)$$

In the Neumann case  $(\Lambda_2 = \infty)$ , one uses  $\mathbf{B}^{(2)} = (0, 0, 0, ...)^{\mathrm{T}}$ , and  $p_k^{(2)}$  and  $q_k^{(2)}$  are replaced by  $\tilde{p}_k^{(2)}$  and  $\tilde{q}_k^{(2)}$ . Inverting the matrix **W**, one gets the coefficients  $A_n^{(1)}$  and  $A_n^{(2)}$ .

The analytical solutions (24)–(26) with these coefficients are the main theoretical results of this paper. In practice, the infinite series in Eqs. (25) and (26) are truncated at some order,  $n_{\text{max}} - 1$ , yielding the  $n_{\text{max}}$ -pole approximate solution with any desired accuracy controlled by  $n_{\text{max}}$ . Consequently, infinite-dimensional matrices  $\mathbf{W}^{(ij)}$  are truncated to a finite size  $n_{\text{max}} \times n_{\text{max}}$ , and the coefficients  $A_n^{(1)}$  and  $A_n^{(2)}$  are found by inverting a  $2n_{\text{max}} \times 2n_{\text{max}}$  matrix  $\mathbf{W}$ . Since the computation of coefficients implies the numerical step, the solution is called semi-analytical. The significant advantage of this solution is the analytical dependence on coordinates and a very fast convergence with  $n_{\text{max}}$ : for most applications, it is enough to take the truncation size  $n_{\text{max}}$  between 5 and 10. 024107-7 S. D. Traytak and D. S. Grebenkov

The diffusive flux onto the spherical sink can be obtained as

$$J_{1} = -Dn_{0} \int_{\partial\Omega_{1}} \sum_{n=0}^{\infty} \left[ -(n+1)A_{n}^{(1)}R^{-n-2}P_{n}(\cos\theta) + \sum_{k=0}^{\infty} U_{nk}^{21}kR^{k-1}P_{k}(\cos\theta) \right] ds_{1} = 4\pi Dn_{0}A_{0}^{(1)}, \quad (48)$$

where  $ds_1 = R^2 \sin \theta d\theta d\varphi$ , and the other terms vanished due to the orthogonality of Legendre polynomials  $P_n$ . Similarly, we get the diffusive flux onto the spheroid as

$$J_{2} = -Dn_{0} \int_{\partial\Omega_{2}} \sum_{n=0}^{\infty} \left\{ A_{n}^{(2)} \frac{\sinh \alpha_{0}}{h_{\alpha_{0}}} Q_{n}^{\prime}(\cosh \alpha_{0}) P_{n}(\cos \beta) + A_{n}^{(1)} \sum_{k=0}^{\infty} U_{nk}^{12} \frac{\sinh \alpha_{0}}{h_{\alpha_{0}}} P_{k}^{\prime}(\cosh \alpha_{0}) P_{k}(\cos \beta) \right\} ds_{2}$$
$$= 4\pi Dn_{0} a_{E} A_{0}^{(2)}, \qquad (49)$$

where  $ds_2 = a_E h_\alpha \sinh \alpha \sin \beta d\beta d\varphi$ ,

$$Q_0(z) = \frac{1}{2} \ln \frac{z+1}{z-1}$$
 and  $Q'_0(z) = \frac{1}{1-z^2}$ .

Expression (49) is only valid for the Dirichlet case. For the Neumann case, the flux is zero:  $J_2 = 0$ . An extension to the Robin case can also be derived.

Note that the classical solution for a single sphere (without the spheroid) can be obtained by setting  $u_2 = 0$  (and thus  $A_n^{(2)} = 0$ ), from which Eq. (34) yields immediately

$$A_n^{(1)} = \delta_{n,0} \frac{R}{1 + \lambda_1} \,. \tag{50}$$

As a consequence, we have

$$u = \frac{1}{1 + \lambda_1} \frac{R}{r}, \qquad (51)$$



and the total diffusive flux is

$$J_1^0 = \frac{4\pi D n_0 R}{1 + \lambda_1} = \frac{4\pi D n_0 R}{1 + D/(R\kappa_1)},$$
 (52)

in agreement with the Collins-Kimball solution.<sup>2,63</sup> In the Dirichlet case  $\Lambda_1 = \lambda_1 = 0$ , one retrieves the Smoluchowski diffusive flux.<sup>1</sup> The superscript 0 highlights that this flux corresponds to the particular case of a single sphere.

Similarly, the solution for a single spheroid (without the sphere) is obtained by setting  $u_1 = 0$  (and thus  $A_n^{(1)} = 0$ ), from which Eq. (40) yields  $A_n^{(2)} = \delta_{n,0}/q_0$  and thus

$$u_2(\alpha, \beta) = \frac{Q_0(\cosh \alpha)}{q_0^{(2)}} \,. \tag{53}$$

For the Dirichlet case, the diffusive flux is then

$$J_2^0 = \frac{4\pi D n_0 a_E}{q_0^{(2)}} = \frac{4\pi D n_0 a_E}{Q_0(\cosh \alpha_0)} = \frac{8\pi D n_0 a_E}{\ln\left(\frac{1+a_E/b}{1-a_E/b}\right)}.$$
 (54)

In the limit  $a \to b$ , one has  $a_E \to 0$  and recovers the flux onto the sphere of radius b. In turn, when  $a \to 0$ , one has  $a_E \to b$ so that

$$J \simeq \frac{4\pi D n_0 b}{\ln(2b/a)}.$$
(55)

As expected, the flux vanishes logarithmically in the limit when the prolate spheroid becomes an infinitely thin rod.

## V. THE DIFFUSIVE INTERACTION EFFECTS AND THE ROLE OF THE SHAPE

0.8

0.6

0.4

0.2

0.8

0.6

0.4

0.2

0.8

0.6

0.4

0.2

It is well known that the DI appeared to be the most profound in the steady-state regime when the interaction becomes long ranged and affects the entire array.<sup>5</sup> So one can treat results obtained for the steady-state reaction rate as a lower bound of the relevant time-dependent rate due to diffusive interaction. We aim here at quantifying the DI effect of one

FIG. 2. Solution *u* of the problem in the XZ plane, for three types of boundary conditions: DD (Dirichlet on both APs, top row), DN (Dirichlet on the sphere, Neumann on the spheroid, middle row), and ND (Neumann on the sphere, Dirichlet on the spheroid, bottom row), with a = 1 (left), a = 0.5 (middle), and a = 0.1 (right) and b = 1, R = 1, and L = 3 (APs are separated by distance 1). We used  $n_{max} = 10$ .





FIG. 3. Solution *u* of the problem in the XZ plane, for Janus dimers with three types of boundary conditions: DD (Dirichlet on both APs, top row), DN (Dirichlet on the sphere, Neumann on the spheroid, middle row), and ND (Neumann on the sphere, Dirichlet on the spheroid, bottom row), with a = 1 (left), a = 0.5 (middle), and a = 0.1 (right) and b = 1, R = 1, and L = 2 (touching APs). We used  $n_{\text{max}} = 10$ .

AP on the other. The reference point is the case of two spheres. We compare three settings: (i) two perfect sinks ( $\kappa_1 = \kappa_2 = \infty$ , DD), (ii) absorbing sphere with a reflecting spheroid ( $\kappa_1 = \infty$ ,  $\kappa_2 = 0$ , DN), and (iii) reflecting sphere with an absorbing spheroid ( $\kappa_1 = 0$ ,  $\kappa_2 = \infty$ , ND).

Figures 2 and 3 illustrate how the local concentration of B particles depends on the shapes of two APs, whereas the normalized diffusive fluxes onto two APs are summarized in Table I.

For two well separated APs, Fig. 2 shows that the diffusive interaction is strong enough to treat the whole DD array as an effective ideal sink. In turn, both cases DN and ND indicate that the DI becomes much weaker, provided that one of the two APs is reflecting. Moreover, the analysis of the corresponding infinite systems of equations reveals that the diffusive interaction arises starting from monopole terms for ideally absorbing APs, whereas this interaction is rather weak

TABLE I. Normalized diffusive fluxes  $J_1^n = J_1/J_1^0$  and  $J_2^n = J_2/J_2^0$  onto two sinks (the sphere and the spheroid), divided by the fluxes  $J_1^0$  and  $J_2^0$  onto a single sphere and a single spheroid, for three types of boundary conditions: DD (Dirichlet on both sinks), DN (Dirichlet on the sphere, Neumann on the spheroid), and ND (Neumann on the sphere, Dirichlet on the spheroid), with three values of a(1, 0.5, 0.1), b = 1, R = 1, and two values of L(3 and 2). We used  $n_{\text{max}} = 10$ . One has  $J_1^0/(Dn_0R) = 12.5664, J_2^0(a = 0.5)/(Dn_0b) = 8.2636$ , and  $J_2^0(a = 0.1)/(Dn_0b) = 4.1772$ .

L	Туре	<i>a</i> = 1		<i>a</i> = 0.5		<i>a</i> = 0.1	
		$J_1^n$	$J_2^n$	$J_1^n$	$J_2^n$	$J_1^n$	$J_2^n$
2	DD	0.6931	0.6931	0.8154	0.6033	0.9180	0.5196
	DN	0.9628	0	0.9901	0	0.9996	0
	ND	0	0.9628	0	0.9505	0	0.9578
3	DD	0.7572	0.7572	0.8436	0.7180	0.9234	0.6840
	DN	0.9929	0	0.9984	0	0.9999	0
	ND	0	0.9929	0	0.9942	0	0.9968

and emerges starting from dipole terms only for reflecting APs.

A similar behavior of the local concentration field is observed for Janus dimers depicted in Fig. 3. Note that the last picture for the DN row in Fig. 3 corresponds to the above-mentioned model of an antenna system.<sup>51,52</sup>

The DI effects are especially well seen in Fig. 4 which shows how the flux onto an absorbing prolate spheroid in the presence of a large sphere depends on its aspect ratio. Here we fix the minor semi-axis a = 0.1 and change the major semi-axis b from a to 2 (note that the radius of the reflecting sphere is R = 1). Solid and dashed lines show the results in the presence of a reflecting/absorbing large sphere. For comparison, we also present the flux from Eq. (54) for a single spheroid (without the large sphere). One can see that the effect of the large reflecting sphere is minor. In turn, the large absorbing sphere captures some B particles that would otherwise come to the spheroid and thus reduces the flux. This is a clear manifestation of the diffusive interaction effect.



FIG. 4. The diffusive flux onto Janus dimers: an absorbing prolate spheroid in the presence of a large reflecting sphere (solid line), in the presence of a large absorbing sphere (dashed line), and without a large sphere (dotted line) as a function of the larger semi-axis *b*, with R = 1, a = 0.1, and L = R + b (touching APs). We used  $n_{\text{max}} = 15$ .

#### **VI. CONCLUSION**

We presented the basic principles and an example of practical implementation of the generalized method of separation of variables. This approach had been successfully applied for many decades to diffusion, electrostatic and hydrodynamic problems in arrays of spherical active particles. We demonstrated how this powerful semi-analytical technique can be extended to arbitrary canonical domains (e.g., spheroids, circular and elliptic cylinders, cones) and their finite number of non-overlapping unions that opens conceptually new horizons for the analysis of diffusion-influenced reactions with complicated molecules and composite materials. For the sake of simplicity, we illustrated the formulation and implementation of the GMSV for an important example of a two-particle "sphere-prolate spheroid" array. The semi-analytical solution of the steady-state diffusion equation allowed us to investigate in depth the diffusive interaction effects of one active particle on the other. In particular, we studied the respective roles of the shape and surface chemical activities on the reaction rates and the concentration profile.

It is important to emphasize that although the considered setting with two active particles looks simple, a numerical solution of the underlying exterior problem is rather difficult. Standard numerical solvers are not well adapted to exterior problems as one needs to impose a distant artificial outer boundary, either for discretizing the domain (finite difference and finite element methods) or for restricting the motion of random walkers (for Monte Carlo algorithms). However, the presence of this artificially imposed boundary may significantly affect the solution due to strong long-range diffusion interactions. In order to reduce this effect, the artificial outer boundary should be set very far away from the APs that slow down simulations. By contrast, the GMSV, which operates with decaying at infinity basis functions, does not require any artificial outer boundary at all. As a matter of fact, the GMSV uses the most appropriate basis functions which are specifically adapted to the considered array of APs. This implementation ensures its superior efficiency as compared to other numerical methods.

Future extensions of the present work may include the case of various systems consisting of two or more APs, e.g., "sphere-oblate spheroid" and different variations of "spheroid-spheroid" arrays. Moreover, the generalized method of separation of variables allows us to solve all steady-state diffusion problems for arrays of two or more arbitrary APs shaped as canonical domains. Note that the proposed solution can be easily extended to the case of one prolate spheroid and multiple spheres of different radii (with the co-axial symmetry). Although an extension to multiple spheroids with different locations is feasible as well, it would require additional re-expansion formulas.

Moreover, using the appropriate dual series (integral) equation technique,<sup>65</sup> a number of exterior and interior problems for diffusion and chemically anisotropic diffusioninfluenced reactions in complex geometries containing both two-dimensional surfaces with smooth boundaries and without them (e.g., spheres with circular holes or with circular active patches) become tractable semi-analytically. Among them, it is worth noting a number of important problems on diffusion escape through narrow openings.<sup>70–75</sup> Finally, the GMSV may be naturally extended to treat time-dependent effects of diffusion interaction between active particles,<sup>76</sup> and, furthermore, it may also be employed for similar problems in Stokes hydrodynamics of suspensions.

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## APPENDIX: THE CASE OF TWO ACTIVE SPHERES

As a reference point, we recall the main results for two spherical ideal sinks of the same radius.

#### 1. The method of bispherical coordinates

First we recall that the bispherical coordinate system  $(O; \xi, \eta, \phi)$  is related to the global Cartesian coordinates (O; x, y, z) as<sup>66,67</sup>

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{a}{\cosh \xi - \cos \eta} \begin{pmatrix} \sin \eta \cos \phi \\ \sin \eta \sin \phi \\ \sinh \xi \end{pmatrix},$$
(A1)

whereas the inverse relation is

$$\begin{pmatrix} \xi \\ \eta \\ \phi \end{pmatrix} = \begin{pmatrix} \sinh^{-1}(2az/Q) \\ \cos^{-1}((R^2 - a^2)/Q) \\ \tan^{-1}(y/x) \end{pmatrix},$$
 (A2)

where  $-\infty < \xi < \infty, 0 < \eta < \pi, 0 < \phi < 2\pi, R = \sqrt{x^2 + y^2 + z^2}$ , and  $Q = \sqrt{(R^2 + a^2)^2 - (2az)^2}$ .

The bispherical coordinate parameter *a* (sometimes termed as the interfocal distance) has units of length and is given as  $a = R \sinh \xi_0$ , where  $\xi_0 = \cosh^{-1}(L/(2R))$ . Therefore, *a* is fixed by the distance between the centers of the sinks *L* and by their radius *R* and for our case reads

$$a = \frac{1}{2}\sqrt{L^2 - 4R^2} \,.$$

In bispherical coordinates, the exterior of two spheres,  $\Omega^-$ , is simply described by the inequality  $|\xi| < \xi_0$ .

The Laplace equation is multiplicatively  $\mathcal{R}$ -separable in bispherical coordinates with the modulation factor  $\sqrt{2} (\cosh \xi - \cos \eta)$ .<sup>66</sup> That is the reason why this coordinate system was successfully used to obtain the exact solution to Laplace or Stokes equations in the exterior of two spheres. With the aid of bispherical coordinates, Samson and Deutch<sup>10</sup> solved exactly the axially symmetric steady-state diffusion problem for two identical absorbing spheres of radii *R*, located at  $\mathbf{x}_0^1 = (0, 0, -L/2)$  and  $\mathbf{x}_0^2 = (0, 0, L/2)$ , while Tachiya used this solution to find the escape probability.<sup>77</sup> The local concentration of *B* particles is governed by the following formula:<sup>10</sup>

$$u(\xi,\eta) = 1 - \sqrt{2(\cosh\xi - \cos\eta)}$$
$$\times \sum_{m=0}^{\infty} C_m \cosh\left[\left(m + \frac{1}{2}\right)\xi\right] P_m(\cos\eta), \qquad (A3)$$

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where  $P_m(\cos \eta)$  are Legendre polynomials and

$$C_m = \frac{\exp\left[-\left(m + \frac{1}{2}\right)\xi_0\right]}{\cosh\left[\left(m + \frac{1}{2}\right)\xi_0\right]}.$$

The normalized flux to each sink is given by the series

$$\frac{k_1}{k_S} = \frac{k_2}{k_S} = 2\sum_{m=0}^{\infty} \frac{\sinh \xi_0}{1 + \exp\left[(2m+1)\,\xi_0\right]},\qquad(A4)$$

where  $k_S$  is given by Eq. (2). One can rewrite this expression in the alternative form

$$\frac{k_1}{k_S} = \frac{k_2}{k_S} = \sum_{m=1}^{\infty} (-1)^{m-1} \frac{\sinh \xi_0}{\sinh m\xi_0} \,. \tag{A5}$$

In the case of an ideal sink dimer ( $\xi_0 \rightarrow 0$ ), series (A5) yields the well-known exact value  $k_1/k_s = \ln 2.^{9,10,41}$ 

We used this analytical solution for checking the accuracy of our semi-analytical results for two spheres, in particular, for determining an appropriate choice of the truncation size  $n_{\text{max}}$ . In particular, for L = 3 and R = b = 1, the maximal error between two solutions was around  $10^{-6}$  for  $n_{\text{max}} = 10$ .

In contrast to the above explicit results for the Dirichlet boundary condition, the method of bispherical coordinates becomes more difficult for other boundary conditions due to the modulation factor, which leads to the systems of recurrence relations with respect to unknown coefficients.<sup>7,11,12</sup> By means of Green's function for the difference equations, Love managed to obviate the above difficulties, but this procedure is rather cumbersome to use.<sup>78</sup> In turn, the GMSV is free of these difficulties and allows one to investigate much more general geometric settings.

#### 2. The generalized method of separation of variables

The generalized method of separation of variables appeared to be free of the aforementioned restrictions that are inherent for the method of bispherical coordinates.<sup>41</sup>

The solution for one sphere and one spheroid is not easily reducible to the case of two spheres because the focal distance  $a_E$  vanishes when  $a \rightarrow b$ . For this reason, we separately write the solution for two spheres of radii R and b, located, respectively, at points  $\mathbf{x}_0^1 = (0, 0, -L)$  and  $\mathbf{x}_0^2 = (0, 0, 0)$ . The derivation follows the same lines; the only difference is that for the exterior of  $\Omega_2(\mathbf{x}_0^2)$ , the prolate spheroidal coordinates are replaced by the spherical coordinates,

$$u_2(r_2,\theta_2) = \sum_{n=0}^{\infty} A_n^{(2)} r_2^{-n-1} P_n(\cos\theta_2).$$
 (A6)

We emphasize that  $(O_2; r_2, \theta_2)$  are the local coordinates in the system of coordinates of the second sphere. For the exterior of the first sphere  $\Omega_1(\mathbf{x}_0^1)$ , we will write  $(O_1; r_1, \theta_1)$  instead of previously used  $(O_1; r, \theta)$ . The re-expansion formulas are

$$r_1^{-n-1} P_n(\cos \theta_1) = \sum_{k=0}^{\infty} U_{nk}^{12} r_2^k P_k(\cos \theta_2) \qquad (r_2 < L),$$
 (A7)

with the mixed-basis matrix elements

$$U_{nk}^{12} = \frac{(-1)^k}{L^{n+k+1}} \,\frac{(n+k)!}{n!\,k!}\,,\tag{A8}$$

and

$$r_2^{-n-1} P_n(\cos \theta_2) = \sum_{k=0}^{\infty} U_{nk}^{21} r_1^k P_k(\cos \theta_1) \qquad (r_1 < L), \quad (A9)$$

with the reciprocal mixed-basis matrix elements

$$U_{nk}^{21} = \frac{(-1)^n}{L^{n+k+1}} \frac{(n+k)!}{n!\,k!} \,. \tag{A10}$$

One gets the same infinite set of linear equations with

$$p_n^{(2)} = (1 - n\lambda_2)b^n,$$
  

$$q_n^{(2)} = [1 + (n+1)\lambda_2]b^{-n-1},$$
(A11)

and  $\lambda_2 = \Lambda_2/b$ .

- <sup>1</sup>M. Smoluchowski, Z. Phys. Chem. **92**, 129 (1917).
- <sup>2</sup>S. A. Rice, *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).
- <sup>3</sup>G. H. Weiss, J. Stat. Phys. **42**, 3 (1986).
- <sup>4</sup>S. Torquato, Random Heterogeneous Materials: Microstructure and Macroscopic Properties (Springer-Verlag, NY, 2002).
- <sup>5</sup>S. D. Traytak, Chem. Phys. **193**, 351 (1995).
- <sup>6</sup>N. McDonald and W. Strieder, J. Chem. Phys. 121, 7966 (2004).
- <sup>7</sup>V. M. Bluett and N. J. B. Green, J. Phys. Chem. A **110**, 4738 (2006).
- <sup>8</sup>B. Sapoval, Phys. Rev. Lett. **73**, 3314 (1994).
- <sup>9</sup>N. N. Lebedev, I. P. Skal'skaya, and Ya. S. Uflyand, *Problems in Mathematical Physics* (Pergamon Press, Oxford, 1966).
- <sup>10</sup>R. Samson and J. M. Deutch, J. Chem. Phys. 67, 847 (1977).
- <sup>11</sup>G. Zoia and W. Strieder, J. Chem. Phys. 108, 3114 (1998).
- <sup>12</sup>W. Strieder and S. Saddawi, J. Chem. Phys. 113, 10818 (2000).
- <sup>13</sup>F. Piazza, P. De Los Rios, D. Fanelli, L. Bongini, and U. Skoglund, Eur. Biophys. J. 34, 899 (2005).
- <sup>14</sup>S. D. Traytak, Theor. Found. Chem. Eng. **24**, 473 (1990).
- <sup>15</sup>V. I. Dubinko, A. A. Turkin, A. V. Tur, and V. V. Yanovskiy, Phys. Met. Metall. 68, 17 (1989).
- <sup>16</sup>A. Umemura, S. Ogawa, and N. Oshima, Combust. Flame 43, 111 (1981).
- <sup>17</sup>S. Michelin and E. Lauga, Sci. Rep. **7**, 42264 (2017).
- <sup>18</sup>M. N. Popescu, M. Tasinkevych, and S. Dietrich, Europhys. Lett. 95, 28004 (2011).
- <sup>19</sup>S. Y. Reigh and R. Kapral, Soft Matter **11**, 3149 (2015).
- <sup>20</sup>S. D. Traytak, A. V. Barzykin, and M. Tachiya, J. Chem. Phys. **126**, 144507 (2007).
- <sup>21</sup>D. J. Jeffrey, IMA J. Appl. Math. 22, 337 (1978).
- <sup>22</sup>J. Lekner, Proc. R. Soc. A 468, 2829 (2012).
- <sup>23</sup>M. Labowsky, Chem. Eng. Sci. 31, 803 (1976).
- <sup>24</sup>M. Labowsky and T. M. Fahmy, Chem. Eng. Sci. 74, 114 (2012).
- <sup>25</sup>C. Eun, P. M. Kekenes-Huskey, and J. A. McCammon, J. Chem. Phys. **139**, 044117 (2013).
- <sup>26</sup>C. W. J. Beenakker and J. Ross, J. Chem. Phys. 84, 3857 (1986).
- <sup>27</sup>R. F. Kayser and J. B. Hubbard, Phys. Rev. Lett. **51**, 79 (1983).
- <sup>28</sup>R. F. Kayser and J. B. Hubbard, J. Chem. Phys. 80, 1127 (1984).
- <sup>29</sup>A. M. Berezhkovskii and Yu. A. Makhnovskii, Chem. Phys. Lett. **175**, 499 (1990).
- <sup>30</sup>A. M. Berezhkovskii, Yu. A. Makhnovskii, L. V. Bogachev, and S. A. Molchanov, Phys. Rev. E 47, 4564 (1993).
- <sup>31</sup>G. Oshanin and A. Blumen, J. Chem. Phys. 108, 1140 (1998).
- <sup>32</sup>M. Yang, S. Lee, and K. J. Shin, J. Chem. Phys. 108, 117 (1998).
- <sup>33</sup>A. A. Kipriyanov, I. V. Gopich, and A. B. Doktorov, Phys. A 255, 347 (1998).
- <sup>34</sup>A. V. Barzykin, K. Seki, and M. Tachiya, Adv. Colloid Interface Sci. 89-90, 47–140 (2001).
- <sup>35</sup>B. T. Nguyen and D. S. Grebenkov, J. Stat. Phys. 141, 532–554 (2010).
- <sup>36</sup>J. Uhm, J. Lee, C. Eun, and S. Lee, J. Chem. Phys. **125**, 054911 (2006).
- <sup>37</sup>L. H. Zheng and Y. C. Chiew, J. Chem. Phys. **90**, 322 (1989).
- <sup>38</sup>H.-K. Tsao, S.-Y. Lu, and C.-Y. Tseng, J. Chem. Phys. **115**, 3827 (2001).
- <sup>39</sup>A. R. Kansal and S. Torquato, J. Chem. Phys. **116**, 10589 (2002).
- <sup>40</sup>E. A. Ivanov, Diffraction of Electromagnetic Waves on Two Bodies (Washington Springfield, 1970).
- <sup>41</sup>F. C. Goodrich, Kolloid Z. Z. Polym. **219**, 156 (1967).
- <sup>42</sup>K. Mattern and B. U. Felderhof, Phys. A **143**, 1 (1987).
- <sup>43</sup>S. D. Traytak and M. Tachiya, J. Chem. Phys. **107**, 9907 (1997).
- <sup>44</sup>K. Seki, S. D. Traytak, and M. Tachiya, J. Chem. Phys. 118, 669 (2003).
- <sup>45</sup>H.-K. Tsao, Phys. Rev. E **66**, 011108 (2002).

- <sup>46</sup>N. McDonald and W. Strieder, J. Chem. Phys. 118, 4598 (2003).
- <sup>47</sup>B. U. Felderhof, Phys. A **130**, 34–56 (1985).
- <sup>48</sup>M. Galanti, D. Fanelli, S. D. Traytak, and F. Piazza, Phys. Chem. Chem. Phys. **18**, 15950 (2016).
- <sup>49</sup>F. Ungaro, I. d'Angelo, A. Miro, M. I. La Rotonda, and F. Quaglia, J. Pharm. Pharmacol. **64**, 1217 (2012).
- <sup>50</sup>S. C. Glotzer and M. J. Solomon, Nat. Mater. 6, 557 (2007).
- <sup>51</sup>U. A. K. Chude-Okonkwo, R. Malekian, and B. T. Maharaj, EURASIP J. Adv. Signal Process. 2015, 1.
- <sup>52</sup>O. A. Vasilyev, L. Lizana, and G. Oshanin, J. Phys. A: Math. Theor. 50, 264004 (2017).
- <sup>53</sup>G. Oshanin, M. N. Popescu, and S. Dietrich, J. Phys. A: Math. Theor. 50, 134001 (2017).
- <sup>54</sup>W. Li and J. D. Gunton, Langmuir **29**, 8517 (2013).
- <sup>55</sup>G. Munaò, P. O'Toole, T. S. Hudson, D. Costa, C. Caccamo, F. Sciortino, and A. Giacometti, J. Phys.: Condens. Matter 27, 234101 (2015).
- <sup>56</sup>D. Gazzillo, G. Munao, and S. Prestipino, J. Chem. Phys. **144**, 234504 (2016).
- <sup>57</sup>D. W. Kang, W. Ko, B. Lee, and B. Jun, Materials 9, 664 (2016).
- <sup>58</sup>D. P. Ruth, J. D. Gunton, J. M. Rickman, and W. Li, J. Chem. Phys. **1419**, 214903 (2014).
- <sup>59</sup>S. Torquato and F. Lado, J. Chem. Phys. **94**, 4453 (1991).
- <sup>60</sup>C. A. Miller, I. C. Kim, and S. Torquato, J. Chem. Phys. **94**, 5592 (1991).
- <sup>61</sup>S.-Y. Lu, J. Chem. Phys. **113**, 6906 (2000).
- <sup>62</sup>A. M. Berezhkovskii and A. V. Barzykin, J. Chem. Phys. **126**, 106102 (2007).
- <sup>63</sup>F. C. Collins and G. E. Kimball, J. Colloid Sci. 4, 425 (1949).
- <sup>64</sup>H. Sano and M. Tachiya, J. Chem. Phys. 71, 1276 (1979).

- <sup>65</sup>S. D. Traytak and W. S. Price, J. Chem. Phys. 127, 184508 (2007).
- <sup>66</sup>P. M. Morse and H. Feshbach, *Methods of Theoretical Physics, Part II* (McGraw-Hill, 1953).
- <sup>67</sup>P. Moon and D. E. Spencer, Field Theory Handbook: Including Coordinate Systems, Differential Equations and Their Solutions (Springer, 1971).
- <sup>68</sup>S. D. Traytak, J. Compos. Mech. Design 9, 495 (2003) (in Russian).
- <sup>69</sup>I. V. Komarov, L. I. Ponomarev, and S. Yu. Slavyanov, Spheroidal and Coulomb Spheroidal Functions (Nauka, Moscow, 1976) (in Russian).
- <sup>70</sup>S. Redner, A Guide to First Passage Processes (Cambridge University Press, Cambridge, 2001).
- <sup>71</sup> First-Passage Phenomena and Their Applications, edited by R. Metzler, G. Oshanin, and S. Redner (World Scientific, Singapore, 2014).
- <sup>72</sup>O. Bénichou and R. Voituriez, Phys. Rep. **539**, 225–284 (2014).
- <sup>73</sup>D. Holcman and Z. Schuss, SIAM Rev. **56**, 213–257 (2014).
- <sup>74</sup>D. S. Grebenkov and J.-F. Rupprecht, J. Chem. Phys. **146**, 084106 (2017).
- <sup>75</sup>D. S. Grebenkov and G. Oshanin, Phys. Chem. Chem. Phys. **19**, 2723–2739 (2017).
- <sup>76</sup>S. D. Traytak, Chem. Phys. Lett. **453**, 212 (2008).
- <sup>77</sup>M. Tachiya, J. Chem. Phys. **69**, 2375 (1978).
- <sup>78</sup>J. Love, J. Chem. Soc., Faraday Trans. 2 **73**, 669 (1977).
- <sup>79</sup>A. D. Polyanin and A. I. Zhurov, Theor. Found. Chem. Eng. **36**, 201 (2002).
- <sup>80</sup>A second-order partial differential equation in a domain  $\Omega \subset \mathbb{R}^3$  is said to be multiplicatively  $\mathcal{R}$ -separable for coordinates  $(O; \xi_1, \xi_2, \xi_3)$  in  $\Omega$ , if its solutions can be represented as a multiplicative ansatz

$$u(\xi_1,\xi_2,\xi_3) = R(\xi_1,\xi_2,\xi_3) v_{\alpha\beta}^1(\xi_1) v_{\alpha\beta}^2(\xi_2) v_{\alpha\beta}^3(\xi_3),$$

where the modulation factor  $R(\xi_1, \xi_2, \xi_3) \neq const$  and the constants of separation  $\alpha$  and  $\beta$  are some complex numbers.