The Journal of Chemical Physics

RESEARCH ARTICLE | AUGUST 15 2024

The generalized method of separation of variables for diffusion-influenced reactions: Irreducible Cartesian tensor technique

Sergey D. Traytak

J. Chem. Phys. 161, 074101 (2024)
https://doi.org/10.1063/5.0226416

AIP Publishing

The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

The generalized method of separation of variables for diffusion-influenced reactions: Irreducible Cartesian tensor technique

Cite as: J. Chem. Phys. 161, 074101 (2024); doi: 10.1063/5.0226416
Submitted: 1 July 2024 • Accepted: 1 August 2024 •
Published Online: 15 August 2024

Sergey D. Traytak[a)]

AFFILIATIONS

Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygina St., 119991 Moscow, Russian Federation

[a)]Author to whom correspondence should be addressed: sergtray@mail.ru

ABSTRACT

Motivated by the various applications of the trapping diffusion-influenced reaction theory in physics, chemistry, and biology, this paper deals with irreducible Cartesian tensor (ICT) technique within the scope of the generalized method of separation of variables (GMSV). We provide a survey from the basic concepts of the theory and highlight the distinctive features of our approach in contrast to similar techniques documented in the literature. The solution to the stationary diffusion equation under appropriate boundary conditions is represented as a series in terms of ICT. By means of proved translational addition theorem, we straightforwardly reduce the general boundary value diffusion problem for N spherical sinks to the corresponding resolving infinite set of linear algebraic equations with respect to the unknown tensor coefficients. These coefficients exhibit an explicit dependence on the arbitrary three-dimensional configurations of N sinks with different radii and surface reactivities. Our research contains all relevant mathematical details such as terminology, definitions, and geometrical structure, along with a step by step description of the GMSV algorithm with the ICT technique to solve the general diffusion boundary value problem within the scope of Smoluchowski's trapping model.

I. INTRODUCTION

A. Motivation

It is presently accepted that for the most part, chemical reactions in micro-heterogeneous liquid media are *contact diffusion-influenced*.[1–4] The latter means that the rate of these reactions is determined significantly by the rate of encounter of reactants due to diffusion; that is, the reaction rate is not controlled by only the chemical requirement of overcoming an activation energy barrier.

Due to their high abundance, diffusion-influenced reactions play a decisive role for a wide and diversified range of applications often occurring in physics, chemistry, biology, and nanotechnology. Examples include excitation quenching of donors by acceptors, heterogeneous catalysis, crystal defect annealing, crystal growth, Ostwald ripening, evaporation or burning of liquid droplets, nutrient consumption by living cells, and cell metabolism to name just a few.

To describe the microphysics of diffusion-influenced reactions theoretically, the so-called *Smoluchowski's trapping model* is often used; this model assumes that particles diffuse in a continuum medium containing immobile uniformly distributed absorbing sinks. Smoluchowski's theory is essentially a one-sink theory, which does not account for the influence of the neighboring sinks. The presence of neighboring absorbing sinks clearly decreases the local concentration of diffusing particles, causing each sink to capture fewer particles than it would if it were isolated. This, obviously, implies that many-sink effects should be incorporated into theoretical analysis. According to accepted terminology, many-sink effects are called the diffusive interaction (for an extended discussion, see Sec. II). The corresponding problems are well-defined; however, the theoretical description of the diffusive interaction is often so complex that solving these problems analytically, even approximately, is very difficult, if not impossible.

Here, we will investigate a micro-heterogeneous medium in which spherical obstacles, including absorbing sinks of different radii, are distributed within the second distinct continuous phase. The dispersed obstacles are assumed to be non-overlapping and impenetrable.

It has been shown explicitly that diffusive interaction effects are most pronounced in the steady state.[5,6] A number of different analytical approaches proposed earlier to solve the posed diffusion problems for the steady state were reviewed in Ref. 7. The most complete list of the commonly used analytical and numerical methods to solve the posed problems along with some comments was given later in Refs. 8 and 9.

Here, we consider a modification of the generalized method of separation of variables (GMSV) that goes back to Rayleigh's seminal paper on the conductivity of heat and electricity in a medium comprising cylindrical or spherical sink systems[10] (see Sec. V). Although the GMSV by means of irreducible Cartesian tensors (ICT) seems to be fairly convenient, at least for numerical calculations, it still did not draw due attention of researchers. This work extends our previous studies via the GMSV[7–9,11,12] to the general case of the steady-state diffusion-influenced processes. We focus on developing a detailed theory of the diffusive interaction effects (see a survey in Sec. II) by means of the ICT technique within the framework of microscopic Smoluchowski's trapping model. It turns out that solution in terms of ICT elucidates rather subtle mathematical facets of the multipole method and, what is more important, it significantly simplifies the calculation of the diffusion field and the corresponding reaction rates.

This research contains all the pertinent mathematical details, including terminology, definitions, geometrical structure, along with a step by step description of the GMSV algorithm with the ICT technique to solve the general diffusion boundary value problem within the scope of Smoluchowski's trapping model.

Therefore, the main purpose of this research is twofold. First, we intend to pose rigorously and in full detail the boundary value problem for the most general case of boundary conditions, describing the small particles' diffusion and absorption in a medium comprising both static inert obstacles and reactive sinks. Second, providing the overall view onto the GMSV, we solve the posed problem by means of the ICT technique, keeping in mind its practical aspects. Since reviews of the problem are lacking in the existing literature, we aim to provide a rather comprehensive overview of the current research activities in the field. Brief literature surveys on the relevant subjects will also be included at appropriate points in the text.

B. Physical background

To study diffusion-influenced reactions theoretically, the so-called *trapping model* is often used.[13] It considers diffusion of very small (point-like) reactants B in heterogeneous media, in which the disperse phase behaves as a collection of immobile obstacles immersed in an inert continuous medium commonly known as *host medium*. This is justified, e.g., when obstacles diffuse much more slowly than reactants (they are of much larger size). Provided an arbitrary but a finite number of obstacles are regularly or randomly distributed within a given region of the surrounding host medium, for this system of obstacles, the terms "ensemble" or "array" are usually used.

Standard treatments of the theory of diffusion-influenced reactions generally assume that the host medium is unbounded (open system[14]), quiescent, isotropic, and homogeneous; therefore, mathematically, it is well modeled by the 3D Euclidean space $\mathbb{R}^3$ (called *physical space* below). In turn, reactants are assumed to be identical non-interacting point-like *Brownian particles* (from now on called *B-particles* or *B-reactants*) diffusing among 3D non-overlapping immobile spherical obstacles embedded in some domains of the physical space. In considering microscopic kinetics of diffusion-influenced reactions, it is necessary to distinguish between obstacles. Each obstacle is characterized by its geometrical and physicochemical parameters, which drastically influence the reaction kinetics. Any particle of kind A refers to the absorbing obstacle usually called a *trap* or a *sink*.[15] For clarity, we will use the term "obstacles" to refer exclusively to fully reflecting entities. Otherwise, we will use the more common term "sinks." Despite its relative simplicity, the trapping problem is fundamental for understanding the kinetics of diffusion-influenced reactions.[2,16]

In this paper, we deal with irreversible bulk contact diffusion-influenced reactions described by the simplest reaction scheme,[2]

$$A + B \xrightarrow{k} A \cdot B \xrightarrow{k_{in}} A + Products. \tag{1}$$

Here, $A \cdot B$ is the so-called *encounter pair*; k and k_{in} stand for the *reaction rate constant* and the *intrinsic reaction rate constant* for the reaction of the encounter pair $A \cdot B$ to form inert products, respectively.[2] Clearly, the rate k_{in} describes the surface reactivity of sinks A,[17] which we assume to be spherically symmetric.

It should be emphasized that one can assume infinite capacity approximation for sinks A provided the initial concentration of B-particles appreciably exceeds that of sinks. In other words, reactions (1) are of the catalytic type,[18] when the activity of the catalyst A remains unchanged.

II. MATHEMATICAL METHODS TO STUDY DIFFUSIVE INTERACTION

The absorbing rate coefficient of B-particles on a given sink surface is of primary importance for the microscopic theory of diffusion-influenced reactions (1). In his pioneering work of 1917, Smoluchowski, on the basis of the Fick laws of diffusion, proposed a rather simple calculation of the reaction rate coefficient k to describe the absorption of B-particles by the surface of a given fully absorbing spherical sink often referred to as a test sink.[2,19] In passing, it should be mentioned that initially Smoluchowski's theory was developed for coagulation of colloids.[16]

Subsequently, one-sink diffusion theory was generalized in many aspects. This section focuses on previous theoretical studies developing the above theory to account for the diffusive interaction between sinks.

Smoluchowski's theory leads to the total flux of B's into the whole ensemble of N identical uncharged sinks as the additive sum $\Phi_N = N\Phi_1(R)$.[20] Here, $\Phi_1(R)$ is the total flux of B-particles on the test sink of radius R. Nevertheless, over the years, it has been realized that this theory faces challenges to understand various reaction–diffusion phenomena in systems comprising many sinks with small sink–sink separations. Indeed, each sink, due to chemical reaction (1) occurring upon its surface, affects B's concentration field around other sinks. Simply speaking, an influence arises between the sinks as a result of the fact that any sink "feels" the self-consistent diffusion field of B-particles, determined by the entire array of sinks.

This is caused by the law of conservation of *B*-particles in a host medium.

It must be recognized that, up to now, there has been no established terminology for the above effects. The reason is that since these effects have wide applications in various fields, various technical languages, including definitions and notations, were used. The following multitude of terms is used in the literature just to define this kind of interaction: (1) competition,[21–27] (2) diffusive (diffusional) interaction,[11,12,14,28–33] (3) effect of multiparticle interaction,[34–36] (4) Laplace's interaction,[37] (5) concentration effects,[38] (6) collective effects,[39–41] (7) reactive interference,[42] (8) shielding effects,[43] (9) cooperative effects,[44] and even (10) chemical interaction.[40] Throughout this paper, we shall clarify some of the relevant terms that are used in the literature.

The use of the term "collective effects" seems an unfortunate one because of its frequent utilization in particle accelerator physics. At the same time, we believe that among other terms, the term "Laplace interaction" (or, generally speaking, "Laplacian transport"[45]) best describes the essence of the interaction under consideration for the steady-state diffusion, heat transfer, and Stokes hydrodynamics.[46] Nonetheless, for definiteness, we, as before, will only use the term *diffusive interaction*, keeping in mind that the obtained results may be applied to the another counterpart.[32]

As far as we know, Frisch and Collins pioneered in studying "competition among sinks for the diffusing molecules" in the diffusion-influenced processes, particularly the growth of aerosol particles by condensation.[21] Among early approaches, it is also worth mentioning Ham's theory based on the Wigner–Seitz cell model.[22] Applying a variational procedure, Reck and Prager had first established rigorous upper and lower bounds on the rate of diffusion-controlled reactions.[47] A detailed description of this approach with applications can be found in Ref. 17.

Later, during many years, a serious effort has been mounted toward calculation of the microscopic reaction rates, taking into account multisink effects. The monopole and dipole approximations for the steady state diffusion and reactions of *B*-particles in dense ensembles of fully absorbing spherical sinks have been extensively investigated by many authors.[2,19,23,27,30,40,48–56] However, it was noted long ago: ". . .the interactions between sinks for the competitive consumption of the solutes are not exactly accounted for in these approximations."[57] Using the moment scattering, Bonnecaze and Brady derived analytically the reaction rate for cubic arrays of sinks up to the quadrupole level.[58] Incidentally, they have emphasized there: "to accurately compute the effective reaction rate at high volume fractions, higher order many-body multipole interactions are required."

Much attention has been concentrated on an important particular case of two sinks, while the above illustration relied on an example with two spherical sinks that could alternatively be solved analytically by using bispherical coordinates.[2,25]

For $N > 2$, the problem was solved by the methods of images and reflections analytically.[23,34] It is worth noting that the connection between the method of images and the method of reflections was discovered in Ref. 7. An important point is that within the framework of the classical method of images, the corresponding compensating solutions are based on point charge potentials inside sinks and, thereby, allow us to obviate the need for the use of addition theorems for solid harmonics.[7]

Concerning theoretical methods to attack the multi-particle diffusion problem, Ratke and Voorhees (Ref. 59) noted: "we shall develop a solution to the diffusion problem that is consistent with the particles having a spherical morphology. This can be done in a self-consistent manner using multiple scattering theory,[51] using irreducible Cartesian tensor,[60] or using boundary integrals and multipole expansions."[61] In this context, we note that the multiple scattering theory[51] based on the microscopic monopole approximation and multipole expansions method was applied in spherical coordinates.[61] In its turn, the irreducible Cartesian tensor approach[60] is nothing more but a scalar version of the well-known induced force method.

Later on, the influence of many neighboring sinks on diffusion-controlled reactions was theoretically investigated in Ref. 26. A particular focus has been given there to the fact that ". . .in most analytical works, only two-sphere cases were mainly considered in the calculations of physical quantities such as rate constant. This is because of difficulty in solving differential equations with more than three spheres (or with many local boundary conditions)." On this basis, authors, "to avoid the mathematical difficulty encountered in analytical approach," have solved the corresponding boundary value problem for the 3D diffusion equation by means of the finite element method.[26] However, it turns out that the diffusive interaction is harder to describe by this method especially in the case of fully reflecting obstacles.

We emphasize that interest to the study of the diffusive interaction was revived past decades due to problems on crowded systems and active transport.[42,62] More recently, there has been a growing interest in theoretical and experimental investigations on the diffusive interaction effects of neighboring droplets during their evaporation on a surface (substrate). Particularly in recent experiments, there was evidence that ". . .neglecting the diffusive interactions can lead to severe inaccuracies in the measurement of droplet concentration. . ."[33] This circumstance has significant practical implications, bearing in mind the fact that "droplet evaporation on surfaces is ubiquitous in nature and plays a key role in a wide range of industrial and scientific applications. . ."[33] Note in passing that quasi-steady-state diffusion to an assembly of slowly growing truncated sphere on a substrate may also be treated with the help of spherical multipoles.[63]

For years the complexity of the problem under consideration caused well reasoned pessimism among many researchers. For example, in Ref. 140, we read: "When there are more than two static sinks in an isotropic medium, it seems nearly impossible to obtain exact analytical expressions. . ."

Early studies on the diffusive interaction were comprehensively reviewed in Ref. 64, whereas the current status of research on this subject can be found in the recent survey.[32]

Thus, an accurate theoretical description of the problems involving diffusive interaction in multi-particle ensembles of spherical obstacles and sinks is a long-standing challenge due to their many-body nature.

III. STATEMENT OF THE GENERAL PROBLEM

As we pointed out above, the diffusive interaction is the most manifested in the steady state regime. Accordingly, when studying the diffusive interaction, this circumstance allows us to simplify

significantly the mathematical problem, ignoring the time-dependent effects.

A rigorous formulation of the problems on the microscopic theory of diffusion-influenced reactions comprises the following: (a) specifying the geometry of the configuration manifold, (b) taking into account the reactants' properties and the host medium involved, (c) using an adequate diffusion system of the continuity equations and constitutive relation, and (d) prescribing appropriate boundary conditions. It is important to note from the outset that by solution to the diffusion–reaction problem, we mean solely its classical solution.

Our mathematical statement of the problem is similar to that given in Ref. 26 (attention is drawn to the fact that sinks and diffusing particles are denoted there as B and A, respectively).

The diffusive interaction substantially depends on a given configuration of reactive and inert boundaries,[32] so first of all, we specify the geometrical part of the problem.

A. Domains' definition

As is customary, let $\partial\Omega$ denote the closed boundary of a 3D domain $\Omega \subset \mathbb{R}^3$ such that its closure is $\overline{\Omega} = \Omega \cup \partial\Omega$.

Consider a collection of arbitrary but finitely many $N \geq 1$ microscopic spherical sinks of different radii R_i, immersed within an unbounded host fluid medium $\mathbb{R}^3$. Geometrically, we treat the ith sink as a 3D body occupying a spherical domain (open ball) $\Omega_i \subset \mathbb{R}^3$. Denote by $\overline{\Omega}_i$ the corresponding closed bounded spherical domain, assuming that all $\overline{\Omega}_i$ are non-intersecting or non-touching, i.e., $\overline{\Omega}_i \cap \overline{\Omega}_j = \emptyset$ for $i(\neq j) = \overline{1,N}$. So, the total domain occupied by an array of N sinks is $\Omega^+ := \bigcup_{i=1}^N \Omega_i$. Clearly, this domain has multiply connected boundary $\partial\Omega^+ = \bigcup_{i=1}^N \partial\Omega_i$, where the corresponding boundary $\partial\Omega_i$ (ith sink reaction surface[2]) is the ith *connected component* of the total boundary $\partial\Omega^+$.

Meanwhile, it is apparent that the diffusion problem should be posed on the whole 3D physical space $\mathbb{R}^3$ excluding the total domain occupied by sinks, i.e., in the sink-free region.[17] Hence, the required domain outside all sinks is the *exterior domain* with respect to sinks: $\Omega^- := \mathbb{R}^3 \backslash \overline{\Omega}^+ \subset \mathbb{R}^3$ and the whole physical space $\mathbb{R}^3$ can be naturally partitioned into two complementary subdomains Ω^+ and Ω^-.

Plainly, Ω^- is the set of accessible configurations for B's, so we term this domain as a *configuration manifold*. It is evident that diffusive interaction is highly affected by the geometry of the configuration manifold Ω^-.

Example III.1. For instance, consider two sinks labeled i and j with radii R_i and R_j, as depicted in Fig. 1. Here, we placed a particle B into an arbitrary point P of the configuration manifold $\Omega^- := \mathbb{R}^3 \backslash \left(\overline{\Omega}_i \cup \overline{\Omega}_j\right)$.

Let $\mathbf{r} := \overrightarrow{OP}$ be a vector that represents the position of the current point P in Ω^- with respect to some fixed point O. Introduce a global Cartesian coordinate system, taking point O as the origin: $\{O;\, \mathbf{r}\}$, and attach the standard orthonormal Cartesian basis $\{\mathbf{e}_\alpha\}_{\alpha=1}^3$ to this origin. The related components of the position vector $\mathbf{r}$ are denoted by r_α $(\alpha = 1, 2, 3)$ or in ordered triple form by (r_1, r_2, r_3).

Using the global coordinates, we designate by $\mathbf{r}_0^i$ the position of the center of the ith sink and by $\mathbf{L}_{ij} := \overrightarrow{O_jO_i} = \mathbf{r}_0^i - \mathbf{r}_0^j$ the separation vector between the two sink centers, pointing from the jth sink toward the ith sink (see Fig. 1).

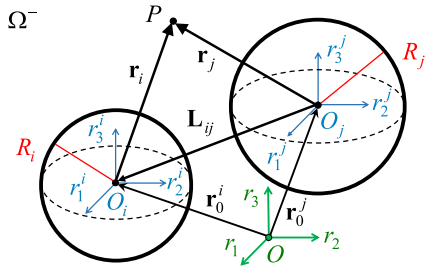

FIG. 1. Definition sketch for the two-sink array. The configuration manifold $\Omega^- \subset \mathbb{R}^3$ corresponds to the given microstructure $X^{(2)}$ with a B particle located at point $P \in \Omega^-$. Cartesian coordinate systems: global $\{O;\, \mathbf{r}\}$ (green); local in ith sink $\{O_i;\, \mathbf{r}_i\}$ and in jth sink $\{O_j;\, \mathbf{r}_j\}$ (blue); and sink radii R_i and R_j (red).

Clearly, any ith sink spherical domain is $\Omega_i = \{\mathbf{r} \in \mathbb{R}^3 : \|\mathbf{r} - \mathbf{r}_0^i\| < R_i\}$ with the boundary $\partial\Omega_i = \{\mathbf{r} \in \mathbb{R}^3 : \|\mathbf{r} - \mathbf{r}_0^i\| = R_i\}$, where $\|\cdot\|$ stands for the common Euclidean norm.

We shall consider diffusion of B's in the configuration manifold Ω^- formed by an arbitrary but a finite ensemble of N spherical sinks with fixed radii $\{R_i\}_{i=1}^N$ centered at positions $\{\mathbf{r}_0^i\}_{i=1}^N$ immersed in the 3D host medium. Hence, the geometry of this manifold is completely determined by the *N-sink configuration*[17] or briefly *microstructure*,[65]

$$X^{(N)} := \left\{\left(\mathbf{r}_0^i, R_i\right)\right\}_{i=1}^N. \tag{2}$$

Introduce open complements of the sink domains Ω_i in the physical space $\mathbb{R}^3$, which play an important role in our study: $\Omega_i^- = \mathbb{R}^3 \backslash \overline{\Omega}_i$. It is clear that for all arrays $(N \geq 1)$, we have $\Omega^- = \bigcap_{i=1}^N \Omega_i^- \subseteq \Omega_i^-$.

Consider the position vector $\mathbf{r}_i(r_1^i, r_2^i, r_3^i)$ of point $P \in \Omega_i^-$. These three real numbers are called *local coordinates of point P in* Ω_i^-. The corresponding local Cartesian coordinate system for any ith sink can be conveniently defined by $\{O_i; r_1^i, r_2^i, r_3^i\} \equiv \{O_i; \mathbf{r}_i\}$ with the same orientation as the global one and the origin $O_i(\mathbf{r}_0^i)$ at the center of the ith sink (see Fig. 1). So, for any fixed i, we can choose standard local orthonormal Cartesian basis $\{\mathbf{e}_\alpha^i\}_{\alpha=1}^3$ attached to the origin $O_i(\mathbf{r}_0^i)$ such that r_α^i are coordinates in this basis. The introduced local coordinates are useful for computation of the diffusion field in arrays with microstructure (2).

Let us take the above position vector $\mathbf{r}$ for the point P and consider it with respect to two local Cartesian coordinate systems $\{O_i;\, \mathbf{r}_i\}$ and $\{O_j;\, \mathbf{r}_j\}$. The corresponding point P position vectors are

$$\mathbf{r}_i = \mathbf{r} - \mathbf{r}_0^i \quad \text{and} \quad \mathbf{r}_j = \mathbf{r} - \mathbf{r}_0^j. \tag{3}$$

The transition between these local coordinates is given by the following rule (see Fig. 1):

$$\mathbf{r}_j = \mathbf{r}_i + \mathbf{L}_{ij}. \tag{4}$$

In this work, we also use the corresponding unit vector $\widehat{\mathbf{L}}_{ij} := \mathbf{L}_{ij}/L_{ij}$, where L_{ij} is the distance between centers $L_{ij} = \|\mathbf{L}_{ij}\| = \|\mathbf{r}_0^i - \mathbf{r}_0^j\| = \|\mathbf{r}_i - \mathbf{r}_j\|$.

Remark III.1. Note that simple linear connection between local coordinates (4) arose due to the use of Cartesian coordinates. Really,

the application of polar spherical coordinate systems leads to the corresponding nonlinear dependence.

An additional point to emphasize is that theoretical calculations often used the distance between the surfaces of domains Ω_i and Ω_j, i.e., $h_{ij} := L_{ij} - (R_i + R_j)$ (see Fig. 1). Hence, the condition describing the configurations of N sinks, which are not intersecting or touching may be written explicitly as

$$h_{ij} > 0 \quad \text{for all} \quad i(\neq j) = \overline{1,N}. \tag{5}$$

Finally, note that in Refs. 7 and 66, we have shown that the 3D smooth manifold is a relevant mathematical concept to describe diffusion-influenced reactions in domains with multiply connected boundaries.

B. Governing equation

To describe the steady state microscopic diffusion–reaction model and introduce a local concentration (number density) of B-reactants, $n : \Omega^- \to \mathbb{R}_+$ depends on a given microstructure $X^{(N)}$ (2) and also different reactivities of sinks. Moreover, to describe reactions, it is convenient to introduce the *set of sink reactivities* $k_{in}^{(N)} := \{k_{in}^i\}_{i=1}^N$, where the rate k_{in}^i corresponds to the ith sink reactivity. Thus, in a fixed global Cartesian coordinate system $\{O;\ \mathbf{r}\}$, extending notations of Refs. 17 and 19, one can write this function as $n\left(P; X^{(N)},\ k_{in}^{(N)}\right)$, which for short we denote just by $n_N(P)$. Often, function $n_N(P)$ is scaled with its bulk concentration of B's c_B so that $n_N(P)(r)/c_B$ treated.[2,26]

However, we are going to use another function, namely *complementary normalized local concentration*, which seems to be more appropriate to subsequently diffusive interaction effects,

$$u_N : \Omega^- \to (0,1), \quad \text{where} \quad u_N(P) = 1 - \frac{n_N(P)}{c_B}. \tag{6}$$

For brevity, we will still call this function local concentration, if there is no confusion to be appeared.

Assuming that the rescaled Fick's local diffusion flux constitutive relation holds,[2]

$$\mathbf{j} = D\nabla u_N(P) \quad \text{in} \quad \Omega^-, \tag{7}$$

where D is the translation diffusion coefficient. The local concentration $u_N(P)$ is governed by the B-particle conservation law, which leads to the Laplace equation as follows:

$$\nabla^2 u_N(P) = 0 \quad \text{in} \quad \Omega^-. \tag{8}$$

Hereinafter, as usual, $\nabla := \sum_{\alpha=1}^3 \mathbf{e}_\alpha \partial_\alpha$ and ∇^2 stand for the gradient operator and the Laplacian on $\mathbb{R}^3$, respectively. For brevity, henceforth, we use the notation ∂_ς for the partial derivative $\partial/\partial\varsigma$ with respect to the independent variable ς.

To describe the diffusion–reaction phenomena, Eq. (8) should be subjected to the appropriate boundary conditions on the sink surfaces $\partial\Omega_i$ and condition at infinity.

C. Boundary conditions

The present work is concerned with the whole possible range of the intrinsic rate constants $0 \le k_{in}^i < +\infty$, and in general case, we can impose the local form of inhomogeneous Robin boundary conditions,

$$\left[4\pi R_i^2 D\ \hat{\mathbf{n}}_i \cdot \nabla u_N - k_{in}^i(1 - u_N)\right]\big|_{\partial\Omega_i} = 0, \quad i = \overline{1,N}, \tag{9}$$

where $\hat{\mathbf{n}}_i$ is the outer-pointing unit normal vector with respect to the ith sink boundary $\partial\Omega_i$.

For applications, it is expedient to distinguish two important particular cases of the general boundary conditions (9).

(i) In the case when $k_{in}^i \to 0$ conditions (9) give homogeneous Neumann boundary conditions,

$$4\pi R_i^2 D\hat{\mathbf{n}}_i \cdot \nabla u_N|_{\partial\Omega_i} = 0. \tag{10}$$

(ii) Provided $k_{in}^i \to +\infty$, conditions (9) are reduced to inhomogeneous Dirichlet boundary conditions,

$$u_N|_{\partial\Omega_i} = 1. \tag{11}$$

For uniqueness of a solution to Laplace's equation (8) under conditions (9), one should require satisfying the regularity conditions at infinity: $u_N(P) = \mathcal{O}(\|\mathbf{r}\|^{-1})$ and $\nabla u_N(P) = \mathcal{O}(\|\mathbf{r}\|^{-2})$ as $\|\mathbf{r}\| \to \infty$.[67,68] These conditions are equivalent to the following *regularity condition at infinity*:

$$u_N(P)|_{\|\mathbf{r}\|\to\infty} \rightrightarrows 0, \tag{12}$$

and it uniquely determines the function $u_N(P)$, which is harmonic in the infinite domain Ω^-.[67] Hereafter, the sign $\rightrightarrows$ denotes the uniform limit. Note in passing that in the physical literature, condition (12) is commonly referred to as the *outer boundary condition*.[26,69]

Thus, the exterior inhomogeneous Robin boundary value problems (8), (9), and (12) are entirely formulated.

D. Physical meaning of the boundary conditions

Specific values of k_{in}^i should be known experimentally or by means of more detailed kinetic theory, e.g., based on the Fokker–Planck–Klein–Kramers equation.[2] Provided magnitudes of k_{in}^i are positive and finite, we deal with *diffusion-influenced reactions* on the so-called *partially reflecting (absorbing) sinks*.[70,71] In the case of very large values of k_{in}^i (i.e., as $k_{in}^i \to +\infty$), the sinks are called *fully (perfectly) absorbing*, and the corresponding reactions, occurring on them, are known as *fully diffusion-controlled*.[2] Physically, that means that the activation barrier appeared to be very small.[72] Particular attention should be given to the case of *fully reflecting obstacles* (when $k_{in}^i = 0$), which becomes also important for dense arrays of sinks and obstacles. Formally speaking, we can treat a fully reflecting obstacle as a sink with the zero intrinsic rate.

Of special interest in many applications is the case when sinks possess different surface reactivities for a microstructure $X^{(N)}$. To put it another way, intrinsic rate constants $k_{in}^i|_{\partial\Omega_i} = const$ are different for at least some numbers from a given set $\{1 < i \le N\}$. Generally, arrays consisting of three kinds of chemically distinct sinks can occur: partially reflecting, fully absorbing, and fully reflecting. Provided different boundary conditions are posed on different connected components of the total boundary, they are termed *improper mixed boundary conditions*.[73] At first glance, it would seem that this

case is described by boundary conditions (9) automatically. However, solution of the boundary value problems (8), (9), and (12) may face subtle mathematical difficulties.[68]

In concluding this subsection, we note that crowding and geometrical constraint effects on diffusion-influenced reactions[42] may be treated if one considers microstructures $X^{(N)}$ containing $1 \le N_0 \le N$ inert obstacles. The presence of fully reflecting obstacles might strongly influence the reaction rate when the number of these obstacles is large enough.[26,42]

IV. THE DIMENSIONLESS FORMULATION OF THE PROBLEM

Before subsequent mathematical study, it is expedient to reduce the original boundary value problem to a non-dimensional form. In its turn, for spatial dimensionless independent variables, we shall utilize the corresponding local Cartesian coordinates $(O_i; \mathbf{r}_i)$ at the ith sink of radius R_i as a characteristic unit,

$$\boldsymbol{\xi}_i = \mathbf{r}_i/R_i, \qquad \boldsymbol{\xi}^i_0 = \mathbf{r}^i_0/R_i \qquad \xi^i_\nu = r^i_\nu/R_i, \qquad \xi_i = \|\boldsymbol{\xi}_i\|. \tag{13}$$

Besides these dimensionless local coordinates for any pair of sinks i and $j(\neq i)$, the following important parameters[74]

$$\varepsilon_{ji} = R_i/L_{ij} < 1, \qquad \varepsilon_{ij} = R_j/L_{ij} < 1 \tag{14}$$

are naturally arisen. Clearly, parameters (14) are totally determined by a given microstructure $X^{(N)}$ (2), and in general case, they obey the condition $\varepsilon_{ij} \neq \varepsilon_{ji}$. Moreover, the unit sphere centered at a point $\boldsymbol{\xi}^i_0$ we henceforth designate by

$$\partial\Omega^1_i \equiv \partial\Omega_i\big(\boldsymbol{\xi}^i_0; 1\big) := \{\boldsymbol{\xi}_i \in \Omega^-_i : \xi_i = 1\}. \tag{15}$$

Here, it should be especially noted that the performed normalization (13) holds only locally in Ω^-_i and does not hold in the whole manifold Ω^-. Note also that in the interest of readability for all domains Ω^-_i, transformed according to Eq. (13), we retain the same designations.

It is expedient now to write the diffusion problem immediately in the local coordinates $\{O_i;\ \boldsymbol{\xi}_i\}$. However, sometimes to emphasize the fact that we deal with the field on a manifold coordinateless form, $u_N(P)$ will be used. Clearly, the basic equation governing the exterior steady-state equation (8) under partially reflecting boundary conditions (9) and regularity condition at infinity (12) with respect to the local concentration $u_N(\boldsymbol{\xi}_i)$ $(i = \overline{1,N})$ and dimensionless variables (13) reads

$$\nabla^2_{\boldsymbol{\xi}_i} u_N(\boldsymbol{\xi}_i) = 0 \quad \text{in} \quad \Omega^-_i, \tag{16}$$

$$-\partial_{\xi_i} u_N(\boldsymbol{\xi}_i)\big|_{\partial\Omega^1_i} = \kappa_i\Big[1 - u_N(\boldsymbol{\xi}_i)\big|_{\partial\Omega^1_i}\Big] > 0, \tag{17}$$

$$u_N(\boldsymbol{\xi}_i)\big|_{\xi_i\to\infty} \rightrightarrows 0. \tag{18}$$

Hereafter, $\nabla^2_{\boldsymbol{\xi}_i}$ stands for the corresponding dimensionless Laplacian written in local coordinates $\{O_i;\ \boldsymbol{\xi}_i\}$.

In addition, we introduce the corresponding dimensionless set of sink reactivities: $\boldsymbol{\kappa}^{(N)} := \{\kappa_i\}_{i=1}^N$ with $\kappa_i = k^i_{in}/k^i_S \in [0, +\infty)$, where $k^i_S = 4\pi R_i D$ is the Smoluchowski rate constant for the fully absorbing ith sink.

Thus, from a mathematical viewpoint, we deal with the exterior Robin boundary value problem given by Eqs. (16)–(18) in an unbounded 3D manifold Ω^- with N-connected boundary $\partial\Omega^-$. An additional point to emphasize is that the boundary conditions (17), being posed on all connected components $\partial\Omega_i$ of the boundary $\partial\Omega^-$, are integral, which reflects the important fact that the diffusive interaction between sinks is not pairwise additive.

A. The microscopic trapping rate

For the theory of diffusion-influenced reactions, the most important value is the *microscopic trapping rate* for the ith sink defined as $k_i := \Phi_i/c_B$, where Φ_i stands for ,the total flux of B's on the ith sink surface. In turn. with the help of known solution $n_N(P)$, the total microscopic trapping rate on the reaction surface $\partial\Omega_i$ can be calculated straightforwardly,

$$k_i = \oint_{\partial\Omega_i} \hat{\mathbf{n}}_i \cdot \mathbf{j}|_{\partial\Omega_i} dS_i, \tag{19}$$

where dS_i is the ith surface element. Then, recasting (19) with respect to $u_N(\boldsymbol{\xi}_i)$ in an exterior neighborhood of the ith sink surface, one can easily obtain the desired microscopic trapping rate (19) by the surface integral over the unit sphere,

$$k_i(X^{(N)}; \boldsymbol{\kappa}^{(N)}) = -\oint_{\partial\Omega^1_i} \partial_{\xi_i} u_N|_{\partial\Omega^1_i} d\hat{\boldsymbol{\xi}}_i. \tag{20}$$

Hence, for dense enough sink arrays when diffusive interaction effects become important, it is necessary to determine the appropriate correction factors to the absorption rates on all N sinks. Therefore the above rate (20) is sought in the following form:

$$k_i(X^{(N)}; \boldsymbol{\kappa}^{(N)}) = k^i_S J^i_0(\kappa_i) J_i(X^{(N)}; \boldsymbol{\kappa}^{(N)}), \tag{21}$$

where the ith dimensionless Collins–Kimball rate given by[2]

$$J^i_0(\kappa_i) = \kappa_i/(1 + \kappa_i) \quad \text{for} \quad i = \overline{1,N} \tag{22}$$

generalizes one-sink expression. Below, to simplify notations, we omitted the corresponding parameters. Evidently, J^i_0 is unperturbed by the diffusive interaction Collins–Kimball trapping rate for the ith sink normalized by k^i_S.

In representation (21), the magnitudes J_i are commonly called the *screening coefficients*[75] (rate correction factors[34]). It is absolutely clear that due to dependence on configuration of sinks $X^{(N)}$ and their reactivities $\boldsymbol{\kappa}^{(N)}$, the screening coefficient J_i (usually, for simplicity, we shall omit arguments in the function notation) expresses the effect of the diffusive interaction between a given ith sink and other $N-1$ sinks. It emerges from the physical standpoint that the diffusive interaction reduces the reaction rate of either sink compared with that of a single one. Hence, the stronger the diffusive interaction, the smaller the J_i is, and the following relations hold true:

$$0 < J_i < 1, \quad \lim_{\varepsilon_{ij}\to 0} J_i = 1 \quad \text{for all} \quad i(\neq j) = \overline{1,N}. \tag{23}$$

Limit (23) simply means that the diffusive interaction disappears at large separations between sinks.

It is significant that, generally speaking, the microscopic trapping rate (20) for $N \geq 2$ does not coincide with the reaction rate constant k defined by Eq. (1), which is a macroscopic value.[76] So, investigating diffusive interaction effects in systems with $N \geq 2$ sinks, we cannot use the term "rate constant" for k_i given by Eq. (20) any more.[12]

V. METHOD OF SOLUTION

The present section is devoted to an overall description of the generalized method of separation of variables, which is a powerful tool for the solution of the Robin boundary value diffusion problem given by Eqs. (16)–(18).

However, before starting to discuss this topic, we briefly highlight the application of the *boundary integral equation method*.[9,77] One can reduce the above diffusion problem given by Eqs. (16)–(18) to solution of a system of Fredholm boundary integral equations of the II kind. It turned out that this system of integral equations may be reduced to the corresponding infinite system of linear algebraic equations.[78] However, this method for the diffusion problem given by Eqs. (16)–(18) involves a number of disadvantages compared to the approach at issue, and, therefore, it would not be considered here.

A. Generalized method of separation of variables

The *generalized method of separation of variables* (GMSV)[7–9,32] naturally stems from the standard method of separation of variables and its incipience goes back to the classic studies by Maxwell[79] and Basset.[80] However, most clearly, this idea was expressed in Rayleigh's seminal paper on the conductivity of heat and electricity in a medium with cylindrical or spherical sinks arranged in a rectangular array.[10] At present, this approach is referred to as the Rayleigh multipole method.

Since then, the GMSV had been intensively developed and found numerous applications in electrostatics, hydrodynamics, mechanics, heat transfer, diffraction theory, and many other fields. Surprisingly, these advances typically remained "hidden" within each discipline and unknown to the researchers, worked in other fields. Such a parallel development led to multiple "rediscoveries" of the same results in different fields. Wherein, various names were given to the GMSV by different authors. It is also widely known as the "generalized Fourier method."[81,82] Guz' and Golovchan treated the method as essentially a particular case of the "method of series."[83] Finally, in micromechanics of heterogeneous materials, mainly the term "multipole expansion approach" is used.[84]

Note that all the above-mentioned names capture only some features of the method under consideration. As this method relies on the separation of variables in local curvilinear coordinates, following Ivanov, it can be called "generalized method of separation of variables."[85]

Among the numerous studies devoted to the development of GMSV, Ivanov's book holds a special place.[85] For the first time, Ivanov presented the scheme of the GMSV in full detail and, moreover, he derived a number of new and reviewed known then addition theorems for the sets of basis solutions to the Helmholtz equation, written in different curvilinear coordinate systems.[85] Although Ivanov used the method to solve various problems concerning diffraction theory for two particles, it is clear that the same approach is also valid for a finite number of particles.

The basic idea of the GMSV consists in reducing the original boundary value problem posed in the configuration manifold Ω^- to the corresponding N boundary value problems in domains Ω_i^-. These N problems are coupled through the boundary conditions, prescribed on the whole disconnected boundary $\partial\Omega^-$. Thus, the GMSV is actually the method of separation of variables on the 3D manifold.[7,66]

B. Outline of approach

The application of the GMSV to the boundary value problem given by Eqs. (16)–(18) may be formulated as the *GMSV algorithm*, which in turn can be divided up into the following main steps:

1. Proof of the well-posedness of the solution to the posed boundary value problem;
2. Decomposition of the desired solution in the form of the sum of partial solutions by means of the general linear superposition principle;
3. Determination of the appropriate basis solutions to the diffusion boundary value problem posed in the given canonical domains with disconnected boundary;
4. Determination of relevant addition theorems to obtain local regular expansions of partial solutions in a neighborhood of corresponding connected components of boundary;
5. Application of the addition theorems in order to satisfy the boundary conditions;
6. Reduction of the problem to a resolving self-consistent infinite system of linear algebraic equations;
7. Solution of the resolving infinite system of linear algebraic equations; and
8. Calculation of the microscopic reaction rate.

One can see that the *linearity* of the boundary value problem is one of the primary requirements for the GMSV algorithm. Furthermore, contrary to the standard method of separation of variables, the GMSV algorithm requires two supplementary rather non-trivial mathematical tools: the appropriate addition theorems for the basis solutions along with methods to solve the resolving infinite system of linear algebraic equations.

We have to emphasize that here a particular case of the GMSV for the sinks of the same form (spherical) will be utilized. So, we shall not apply the *re-expansion theorems* connecting different basis functions corresponding to the different shapes of sinks.

VI. THE GMSV WITH IRREDUCIBLE CARTESIAN TENSORS

Previously, by means of GMSV for 3D domains with N disconnected spherical boundaries, we presented the detailed derivation of the Laplacian Green functions for both the exterior and interior Dirichlet and Robin problems along with the Green function for the relevant conjugate (transmission) boundary value problem.[9] Some facets of the GMSV applications to the theory of stationary bulk diffusion-influenced reactions on spherical sinks were also studied and discussed in Refs. 9, 32, and 86. However, it is important that

all analytical and numerical calculations were performed there using the local spherical coordinate systems.

Plainly, the general solution algorithm is feasible in two ways: by means of either solid spherical harmonics with respect to a polar spherical coordinate system or, alternatively, with the help of the ICT (for details, see the Appendix). The wide use of solid harmonics in the theory of diffusion-influenced reactions is a matter of common knowledge (see, e.g., Refs. 24 and 87–90 and references cited there). In the meantime, studies devoted to similar applications of ICT are only very few.[7,11,12,60,71,91] This seems surprisingly, taking into account the facts that the ICT formalism has a number important advantages against standard solid harmonics approach (see Sec. IX). In this connection, it is particularly remarkable that recent decades investigations have inspired a renewed interest for use of the ICT technique to study a number of problems in systems with N-sphere microstructure (2).[92–102]

Against these recent trends, the lack of new studies concerning the applications of the ICT in diffusion-influenced reaction theory is especially noticeable.

To our knowledge, Lebenhaft and Kapral were the first who successfully applied the ICT technique to the diffusion problem given by Eqs. (16)–(18).[71] Subsequently, an explicit form of the GMSV with the aid of ICT was carried out in our paper (Ref. 11), where we utilized this form of the GMSV to solve problems on Ostwald ripening, taking into account multipole corrections. It should be stressed that our approach stems from the *method of Cartesian ansatz* suggested in 1978 by Schmitz and Felderhof.[103] Although Ref. 103 studied a hydrodynamic problem, the authors also treated the Robin boundary value problem for Laplace's equation in the unbounded domain exterior to a sphere. In that regard, it is pertinent to cite here the above paper: "we solve this problem by making an ansatz in Cartesian coordinates, rather than following the usual method of introducing spherical coordinates."

Note in passing that the so-called *self-consistent field method* is another version of the above method of Cartesian ansatz.[95] A method of reflections with the help of ICT used in Ref. 104 to solve the problem of the spherical particle motion due to a temperature gradient is also worth mentioning here. It is important to mention that some approaches used just different modifications of the GMSV in terms of the above-treated version with the help of the ICT.[56,105]

In Ref. 60, a scalar version of the well-known induced force method has been applied to the theory of diffusion-controlled reactions for the first time. It turns out, however, that both the induced force method and the GMSV by means of the ICT lead to the same second kind ISLAE with respect to unknown tensor constants involved.[7,78]

VII. THE ADDITION THEOREM IN TERMS OF IRREDUCIBLE CARTESIAN TENSORS

Due to the fact that the Laplace equation (16) remains invariant under the action of the group of Euclidean motions,[106] *irregular solid harmonics* (see definitions in the Appendix) written in local coordinates of any domain Ω_i^- (Ω_j^-) can be recast in terms of *regular solid harmonics* written in local coordinates of another domain Ω_j^- (Ω_i^-).

One of the key points of the GMSV algorithm is the transformation of the solid harmonics under the action of subgroup of translations.[32,107] Provided domains Ω_i^- and Ω_j^- possess the same form (complements of spheres in the present paper), the appropriate transformation formulas of that kind it is expedient to call *irregular to regular translation addition theorems* (I → R TAT).

The goal of this section is to present a proof of the I → R TAT within the scope of the GMSV in terms of ICT. We note in passing that, strictly speaking, we deal here with scalar translation addition theorems only.

Before starting presenting the main material of this section, it only remains to recall the basic terminology and notations concerning the Cartesian tensors given on $\mathbb{R}^3$.

A real tensor field of nth order defined on $\mathbb{R}^3$ we denote by $\boldsymbol{T}_n(\mathbf{r})$ in coordinate-free notation. The same tensor field can also be described by its components with respect to a fixed orthonormal basis $\{\mathbf{e}_\alpha\}_{\alpha=1}^3$ given in coordinates $\{O;\ \mathbf{r}\}$, i.e., $\boldsymbol{T}_n(\mathbf{e}_{\gamma_1},\ldots,\mathbf{e}_{\gamma_n}) = T_{\gamma_1\ldots\gamma_n}(\mathbf{r})$. Here and in the following, $T_{\gamma_1\ldots\gamma_n}(\mathbf{r})$ are 3^n components of the n-rank generic Cartesian tensor field $\boldsymbol{T}_n(\mathbf{r})$. It is clear that the action of the nabla operator with $\partial_{r_\mu} := \nabla_\mu$ to a field, which is a tensor of rank l, yields a tensor of rank $l+1$. We recall in passing that one should not distinguish between co- and contravariant indices due to the duality of Cartesian basis.[108]

The product symbol $\odot^q$ represents a *full tensorial contraction of multiplicity* q or shortly the *q-fold contraction* between two tensors with the convention $\boldsymbol{S}_0 \odot \boldsymbol{T}_0 := \boldsymbol{T}_0$. In particular, for tensors $\boldsymbol{S}_n$ and $\boldsymbol{T}_m$ and $q \le n, m$, we have a tensor

$$\boldsymbol{S}_n \odot^q \boldsymbol{T}_m := \sum_{\gamma_1} \ldots \sum_{\gamma_q} S_{\gamma_1\ldots\gamma_n} \odot^q T_{\mu_1\ldots\mu_m}$$

of rank $n+m-2q$, whereas it is a scalar if $n = m = q$.

A. The degenerate translation addition theorem

First, let us focus our treatment on a particular case of the I → R TAT, which plays a key role in the subsequent proof of the general TAT.

Assume that $r > \|\mathbf{r}_0^i\|$, where $r = \|\mathbf{r}\|$ is the distance between the global origin O and a current point P (see Fig. 1).

Thereby, we can write the known Taylor's expansion as follows:

$$\frac{1}{\|\mathbf{r}_i\|} = \frac{1}{\|\mathbf{r} - \mathbf{r}_0^i\|} = \exp\left(-\mathbf{r}_0^i \cdot \nabla\right)\frac{1}{r}, \tag{24}$$

where the so-called *translation operator* is represented by[107]

$$\exp\left(-\mathbf{r}_0^i \cdot \nabla\right) := \sum_{k=0}^{\infty} \frac{(-1)^k}{k!}\left(\mathbf{r}_0^i \cdot \nabla\right)^k.$$

Clearly, series (24) converges absolutely and uniformly for all $r > 0$.[67]

Function $1/r$ is often termed the *generating function*. Traditionally, Eq. (24) is referred to as the *multipole expansion of the (global) fundamental solution* of the Laplacian at the pole point $\mathbf{r}_0^i$ in powers of r^{-1} (see, e.g., Ref. 67).

For the further consideration, it is convenient to recast expansion (24) in terms of ICT defined by Eq. (A1).[97] This fact allows us to formulate the so-called *degenerate translation addition theorem* for solid harmonics

Theorem VII.1. *For all $r > 0$, the fundamental solution of the Laplacian by means of the ICT may be expanded in an absolutely and uniformly convergent series,*

$$\frac{1}{\|\mathbf{r}-\mathbf{r}_0^i\|}=\sum_{k=0}^{\infty}\omega_k r^{-(2k+1)}\,\overline{r_{\gamma_1}\dots r_{\gamma_k}}\odot^k\overline{r_{\gamma_1}^{0i}\dots r_{\gamma_k}^{0i}}, \tag{25}$$

where $\omega_k := (2k-1)!!/k!$, and r_{γ_ν} and $r_{\gamma_m}^{0i}$ are the Cartesian coordinates of vectors $\mathbf{r}$ and $\mathbf{r}_0^i$, respectively.

This form of multipole expansion is very broadly utilized across various scalar fields of physical and chemical sciences. Moreover, (25) plays a key role in the derivation of the translation addition theorem and that is why it is also called the degenerate addition theorem.

B. The translation addition theorem

It has been known that I → R TAT holds true for solid harmonics $\psi_{nm}^{\pm}(\mathbf{r})$ defined in polar spherical coordinates (see, e.g., Ref. 9 and references therein). Here, we present a derivation of the similar I → R TAT in terms of ICT $\boldsymbol{X}_n^{\pm}$ (see the Appendix), which was given in Refs. 11 and 12 without a proof.

For our problem, the connection between local coordinates (4) plays a key role, so let us start with an important general.

Definition VII.1. Any two given local curvilinear coordinate systems $\{O_i;\ \boldsymbol{\zeta}_i\}$ and $\{O_j;\ \boldsymbol{\zeta}_j\}$ are said to be consistent if there exists a translation with vector $\mathbf{a}$ such that $\boldsymbol{\zeta}_j = \boldsymbol{\zeta}_i + \mathbf{a}$.

This definition immediately brings to the following assertion. Any two local Cartesian coordinate systems $\{O_i;\ \mathbf{r}_i\}$ and $\{O_j;\ \mathbf{r}_j\}$ are consistent if and only if: (a) they are positively oriented and (b) all their axes are pairwise parallel with respect to the global Cartesian coordinates. One can see that local Cartesian coordinates $\{O_i;\ \mathbf{r}_i\}$ and $\{O_j;\ \mathbf{r}_j\}$ depicted in Fig. 1 are consistent. Note in passing that some authors prefer to use the term "parallel coordinate systems" rather than "consistent coordinate systems."[107]

Definition VII.2. A translation addition theorem for a given smooth function $u:\Omega^-\to\mathbb{R}_+$ is a formula expressing its value $u(\mathbf{r}+\mathbf{a})$ in terms of values $u(\mathbf{r})$ and $u(\mathbf{a})$, where $\mathbf{r},\mathbf{r}+\mathbf{a}\in\Omega^-$, and also their derivatives.

Definition VII.3. The translation addition theorem I → R yields an explicit formula for converting an irregular ICT $\boldsymbol{X}_n^-$ given in one origin O_j into a local expansion with respect to the corresponding regular ICT $\boldsymbol{X}_n^+$ about a shifted origin O_i.

The meaning of the addition theorems is to derive the corresponding addition formulas.

Now, we can state and prove our main result in this section.

Theorem VII.2. *The irregular to regular translation addition theorem for the irreducible Cartesian tensors holds true,*

$$r_j^{-(2n+1)}\,\overline{r_{\gamma_1}^j\dots r_{\gamma_n}^j}=\sum_{k=0}^{\infty}U^{ij}_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}\left(\widehat{\mathbf{L}}_{ij}\right)\odot^k\overline{r_{\mu_1}^i\dots r_{\mu_k}^i}, \tag{26}$$

where the mixed-basis matrix[106] elements read

$$U^{ij}_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}\left(\widehat{\mathbf{L}}_{ij}\right)=\sigma_{kn}L_{ij}^{-(n+k+1)}\Lambda_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}\left(\widehat{\mathbf{L}}_{ij}\right),$$
$$\sigma_{kn}=(-1)^n\frac{[2(k+n)-1]!!}{k!\,(2n-1)!!},$$
$$\Lambda_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}\left(\widehat{\mathbf{L}}_{ij}\right)=\overline{\hat{L}^{ij}_{\gamma_1}\dots\hat{L}^{ij}_{\gamma_n}\hat{L}^{ij}_{\mu_1}\dots\hat{L}^{ij}_{\mu_k}},$$
$$\hat{L}^{ij}_{\mu_m}=L^{ij}_{\mu_m}/L_{ij},$$

wherein series (26) converges uniformly and absolutely if inequalities (14) hold true.

Proof. Rewriting Eq. (4) in the relevant local Cartesian coordinates of jth and ith spheres, we have

$$r_{\gamma_\nu}^j=r_{\gamma_\nu}^i+L_{\gamma_\nu}^{ij}, \tag{27}$$

where $L_{\gamma_\nu}^{ij}$ are the coordinates of vector $\mathbf{L}_{ij}$ ($\gamma_\nu=\overline{1,3}$). Linear dependence (27) leads to the evident relations $\partial_{r_{\gamma_\nu}^j}=\partial_{r_{\gamma_\nu}^i}$. Using them in Eq. (A1), one readily obtains

$$r_j^{-(2n+1)}\,\overline{r_{\gamma_1}^j\dots r_{\gamma_n}^j}=\frac{(-1)^n}{(2n-1)!!}\partial_{r_{\gamma_1}^i}\dots\partial_{r_{\gamma_n}^i}\left(\frac{1}{\|\mathbf{r}_i-\mathbf{L}_{ij}\|}\right)$$

or, taking into account that $\partial_{r_{\gamma_\nu}^i}=-\partial_{L_{\gamma_\nu}^{ij}}$, one has the relation

$$r_j^{-(2n+1)}\,\overline{r_{\gamma_1}^j\dots r_{\gamma_n}^j}=\frac{1}{(2n-1)!!}\partial_{L_{\gamma_1}^{ij}}\dots\partial_{L_{\gamma_n}^{ij}}\left(\frac{1}{\|\mathbf{r}_i-\mathbf{L}_{ij}\|}\right). \tag{28}$$

Theorem VII.1 yields

$$\frac{1}{\|\mathbf{r}_i-\mathbf{L}_{ij}\|}=\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}\partial_{L_{\gamma_1}^{ij}}\dots\partial_{L_{\gamma_k}^{ij}}\left(\frac{1}{L_{ij}}\right)\odot^k\overline{r_{\gamma_1}^i\dots r_{\gamma_k}^i}. \tag{29}$$

Substituting this expansion into Eq. (28) and taking into consideration the uniform convergence of the series (29), we arrive at the required translation addition theorem (26). □

For further investigation of the problem given by Eqs. (16)–(18), it is expedient to recast expression (26) in a dimensionless form as follows:

$$\xi_j^{-(2n+1)}\,\overline{\xi_{\gamma_1}^j\dots\xi_{\gamma_n}^j}=\sum_{k=0}^{\infty}\widetilde{U}^{ij}_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}\odot^k\overline{\xi_{\mu_1}^i\dots\xi_{\mu_k}^i}, \tag{30}$$

where dimensionless mixed-basis matrix elements are

$$\widetilde{U}^{ij}_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}:=\sigma_{kn}\varepsilon_{ij}^{n+1}\varepsilon_{ji}^{k}\Lambda_{\gamma_1\dots\gamma_n\mu_1\dots\mu_k}\left(\widehat{\mathbf{L}}_{ij}\right).$$

In particular, the dimensionless form of the degenerate translation addition theorem (25) reads

$$\xi_j^{-1}=\sum_{k=0}^{\infty}\widetilde{U}^{ij}_{\mu_1\dots\mu_k}\odot^k\overline{\xi_{\mu_1}^i\dots\xi_{\mu_k}^i}. \tag{31}$$

The above presented proof of I → R TAT in terms of ICT seems to be the simplest among previously known theorems for solid harmonics in terms of polar spherical coordinates.[109,110] It is important to stress that using connection between spherical solid harmonics and ICT (see the Appendix), the proved addition theorem (26) can be reduced to that for the spherical solid harmonics written in a spherical coordinate system.

Finally, note that to solve diffusion problems under proper mixed boundary conditions,[73] when intrinsic rates are functions

on the angular local coordinates $\kappa_i(\theta_i, \phi_i)$, we need the *rotational addition theorem for the ICT*. The latter theorem may be proved in entirely similar way.

VIII. SOLUTION TO THE PROBLEM

Here, we implement the GMSV algorithm described in Sec. V using the ICT technique. Moreover, we shall develop here the version of the GMSV elaborated previously in Refs. 11, 12, and 91.

A. The GMSV algorithm implementation

For clarity sake, we organize our treatment according to the method outline distinguishing eight steps inherent in the GMSV.

Step 1. The mixed boundary value problem given by Eqs. (16)–(18) is well posed and has a unique classical solution.[67,68,111]

Step 2. First, we can apply the superposition principle. Decompose the general solution $u_N(P)$ of the above diffusion problem given by Eqs. (16)–(18) with respect to the ith sink, considering the set of *partial solutions* to Eq. (16), which are defined as $\{u_i(\boldsymbol{\xi}_i)\}_{i=1}^N$ $(u_i : \Omega_i^- \to (0, 1])$. Thus, in the local Cartesian coordinates $\{O_i; \boldsymbol{\xi}_i\}$, we can write

$$u_N(\boldsymbol{\xi}_i) = u_i(\boldsymbol{\xi}_i) + \sum_{j(\neq i)=1}^{N} u_j\big(\boldsymbol{\xi}_j\big) \quad \text{in} \quad \Omega_i^-. \tag{32}$$

Here, by virtue of Eqs. (4) and (14), one has evident relations: $\boldsymbol{\varepsilon}_{ij}\boldsymbol{\xi}_j = \boldsymbol{\varepsilon}_{ji}\boldsymbol{\xi}_i + \widehat{\mathbf{L}}_{ij}$ (see Fig. 1). From the physical standpoint, representation (32) means that to find the desired reaction rate on the ith sink, we need to know only the local behavior of the field $u_N(P)$ in a vicinity of this sink.

Clearly, by definition, functions $u_i(\boldsymbol{\xi}_i)$ are harmonic in domains Ω_i^-, i.e.,

$$\nabla^2_{\boldsymbol{\xi}_i} u_i(\boldsymbol{\xi}_i) = 0, \tag{33}$$

$$u_i(\boldsymbol{\xi}_i)|_{\xi_i \to \infty} \rightrightarrows 0. \tag{34}$$

Therefore, the original diffusion boundary value problem given by Eqs. (16)–(18) in the manifold Ω^- (intersection of all domains Ω_i^-) is reduced to N coupled problems for $u_i(\boldsymbol{\xi}_i)$ in simpler domains Ω_i^-, with the advantages of the local Cartesian coordinates $\{O_i; \boldsymbol{\xi}_i\}$.

Alternatively, for inhomogeneous partially reflecting boundary conditions (17) in an exterior ε-neighborhood of the boundary $\partial\Omega_i$: $\Omega_i^-(\varepsilon) := \{\boldsymbol{\xi}_i : 1 < \xi_i < 1 + \varepsilon\} \subset \Omega_i^-$, it is convenient to recast solution $u_N(\boldsymbol{\xi}_i)$ as

$$u_N(\boldsymbol{\xi}_i) = u^i_{(0)}(\xi_i) + \delta u_i(\boldsymbol{\xi}_i) \quad \text{in} \quad \Omega_i^-(\varepsilon), \tag{35}$$

where $u^i_{(0)}(\xi_i)$ is the unperturbed one-sink solution and $\delta u_i(\boldsymbol{\xi}_i)$ is a perturbation due to the influence of each from other $N-1$ sinks for $j(\neq i) = \overline{1, N}$. Owing to Eq. (17), we assume that these solutions obey inhomogeneous and homogeneous partially reflecting boundary conditions, respectively,

$$-\left(\partial_{\xi_i} u^i_{(0)} - \kappa_i u^i_{(0)}\right)\big|_{\partial\Omega_i^1} = \kappa_i, \tag{36}$$

$$\left(\partial_{\xi_i}\delta u_i - \kappa_i \delta u_i\right)\big|_{\partial\Omega_i^1} = 0. \tag{37}$$

Therewith, the unperturbed by diffusive interaction solution

$$u^i_{(0)}(\xi_i) = J^i_0 \xi_i^{-1} \tag{38}$$

obeys inhomogeneous boundary condition (36). Here, J^i_0 is the ith Collins–Kimball rate (22).

One important point to emphasize is that Eqs. (32) and (35) are, respectively, the global and local representations of the same function defined on the manifold: $u_N : \Omega^- \to (0, 1]$.

Step 3. It can be shown that tensor fields introduced by Eqs. (A6) and (A7) are families of irregular $\{\mathbf{X}_n^-(\boldsymbol{\xi}_i)\}_{n=0}^\infty$ and regular $\{\mathbf{X}_n^+(\boldsymbol{\xi}_i)\}_{n=0}^\infty$ solid Cartesian harmonics, which form the desired basis functions (complete and orthogonal sets) in domains Ω_i^- and Ω_i^+, respectively. Thus, we can represent a partial solution $u_i(\boldsymbol{\xi}_i)$ with the help of the irregular ICT, satisfying the regularity condition at infinity,

$$u_i(\boldsymbol{\xi}_i) = \sum_{n=0}^{\infty} \xi_i^{-(2n+1)} A^i_{\gamma_1\ldots\gamma_n} \odot^n \overbrace{\boldsymbol{\xi}^i_{\gamma_1}\ldots\boldsymbol{\xi}^i_{\gamma_n}} \quad \text{in} \quad \Omega_i^-. \tag{39}$$

Meanwhile, in an exterior neighborhood of ith sink boundary $\partial\Omega_i$, we can represent the perturbation function in Eq. (32) as a series with respect to the regular ICT,

$$\sum_{j(\neq i)=1}^{N} u_j(\boldsymbol{\xi}_j) = \sum_{n=0}^{\infty} B^i_{\gamma_1\ldots\gamma_n} \odot^n \overbrace{\boldsymbol{\xi}^i_{\gamma_1}\ldots\boldsymbol{\xi}^i_{\gamma_n}}. \tag{40}$$

In Eqs. (39) and (40) $A^i_{\gamma_1\ldots\gamma_n}$ and $B^i_{\gamma_1\ldots\gamma_n}$ are tensor coefficients to be determined from the boundary conditions (17).

Step 4. Theorem VII.2 in the dimensionless form (30) gives the required translation addition theorem to tackle the diffusion problem given by Eqs. (16)–(18).

Step 5. Now, by means of the dimensionless translation addition theorem (30), we satisfy the Robin boundary conditions (17). Hence, taking advantage of the ICT linear independence, we can express the coefficients $A^i_{\gamma_1\ldots\gamma_n}$ in terms of $B^i_{\gamma_1\ldots\gamma_n}$,

$$A^i_0 = J^i_0\left(1 - B^i_0\right) \quad \text{for} \quad n = 0, \tag{41}$$

$$A^i_{\gamma_1\ldots\gamma_n} = \frac{n - \kappa_i}{1 + n + \kappa_i} B^i_{\gamma_1\ldots\gamma_n} \quad \text{for} \quad n \in \mathbb{N}. \tag{42}$$

With the aid of these connections, formula (35) for the perturbed diffusion field in an exterior neighborhood of the surface $\partial\Omega_i$ $(i = \overline{1, N})$ yields

$$\delta u_i(\boldsymbol{\xi}_i) = \sum_{k=0}^{\infty}\left[1 + \left(\frac{k - \kappa_i}{1 + k + \kappa_i}\right)\xi_i^{-(2k+1)}\right] \times B^i_{\gamma_1\ldots\gamma_k} \odot^k \overbrace{\boldsymbol{\xi}^i_{\gamma_1}\ldots\boldsymbol{\xi}^i_{\gamma_k}}. \tag{43}$$

One can easily verify that this solution obeys homogeneous partially reflecting boundary condition (37).

In addition, using Eq. (39) under relationships (41) and (42) for domain Ω_j^-, we immediately write down an auxiliary relation,

$$\sum_{j(\neq i)=1}^{N} u_j(\xi_j) = \sum_{j(\neq i)=1}^{N} u_{(0)}^j(\xi_j) + \sum_{j(\neq i)=1}^{N} \sum_{k=0}^{\infty} \left(\frac{k-\kappa_j}{1+k+\kappa_j} \right) \xi_j^{-(2k+1)} B^j_{\gamma_1 \ldots \gamma_k} \odot^k \overline{\xi^j_{\gamma_1} \ldots \xi^j_{\gamma_k}}. \tag{44}$$

It is worth noting that all terms here satisfy the regularity condition at infinity (18) as opposed to the local expression (43).

Step 6. Now in the local Cartesian coordinates $\{O_i;\ \boldsymbol{\xi}_i\}$, one can carry out a *self-consistent procedure* to find unknown tensor coefficients $B^i_{\gamma_1 \ldots \gamma_k}$ appearing in formulas (43) and (44). First, we apply the dimensionless translation addition theorem (30) including its degenerate form (31) to the right-hand side of Eq. (44) in order to recast it in the local coordinates $\{O_i;\ \boldsymbol{\xi}_i\}$. Then, with allowance made for expression (40) and orthogonality property of the ICT on the unit spheres $\partial\Omega_i^1$ (A5), we derive the required self-consistent *infinite system of linear algebraic equations* (ISLAE) of the II kind with respect to unknown tensor coefficients $B^i_{\gamma_1 \ldots \gamma_k}$. We should note that these infinite systems are commonly referred to as the *resolving ISLAE*.[84,112] According to the statement of the diffusion problem given in Sec. III, we should distinguish three particular cases of the resolving ISLAE.

(a) For partially reflecting sinks (when $0 < \kappa_i < +\infty$), the resolving ISLAE is

$$B^i_{\gamma_1 \ldots \gamma_k} = B^{i(0)}_{\gamma_1 \ldots \gamma_k} + \sum_{j(\neq i)=1}^{N} \sum_{l=0}^{\infty} \left(\frac{k-\kappa_j}{1+k+\kappa_j} \right) \times \widetilde{U}^{ij}_{\gamma_1 \ldots \gamma_k \mu_1 \ldots \mu_l} \odot^l B^j_{\mu_1 \ldots \mu_l}, \quad k = \overline{0, \infty}. \tag{45}$$

Hereinafter, for short, we denoted

$$B^{i(0)}_{\gamma_1 \ldots \gamma_k} = \sum_{j(\neq i)=1}^{N} J_0^j \widetilde{U}^{ij}_{\gamma_1 \ldots \gamma_k}. \tag{46}$$

Another two important ISLAE are special cases of (45).

(b) In case of fully absorbing sinks (when $\kappa_i \to +\infty$), the resolving ISLAE is simplified to

$$B^i_{\gamma_1 \ldots \gamma_k} = B^{i(0)}_{\gamma_1 \ldots \gamma_k} - \sum_{j(\neq i)=1}^{N} \sum_{l=0}^{\infty} \widetilde{U}^{ij}_{\gamma_1 \ldots \gamma_k \mu_1 \ldots \mu_l} \odot^l B^j_{\mu_1 \ldots \mu_l}, \tag{47}$$

where $k = \overline{0, \infty}$.

(c) For fully reflecting (when $\kappa_i \to 0$), the resolving ISLAE (45) obviously yields

$$B^i_{\gamma_1 \ldots \gamma_k} = \left(\frac{k}{1+k} \right) \sum_{j(\neq i)=1}^{N} \sum_{l=0}^{\infty} \widetilde{U}^{ij}_{\gamma_1 \ldots \gamma_k \mu_1 \ldots \mu_l} \odot^l B^j_{\mu_1 \ldots \mu_l}, \tag{48}$$

where $k = \overline{1, \infty}$.

Step 7. Consider here the most general case of arrays with partially reflecting sinks. In other words, to find $B^i_{\gamma_1 \ldots \gamma_k}$, system (45) requires the inversion of the corresponding infinite-dimensional matrix.[32,86] So, we deal with a typical problem that may be solved by the methods of functional analysis.[113,114] For instance, provided the ISLAE (45) is of *normal Poincare–Koch type*, it implies that the *Fredholm–Hilbert alternative* holds true.[113] Hence, a unique solution of (45) exists and it may be found by the *method of reduction* to any degree of accuracy.[112] The latter means that the resolving ISLAE (45) should be truncated and then inverted obtained finite system numerically to get approximations of the coefficients $B^i_{\gamma_1 \ldots \gamma_k}$. Under some conditions, the resolving ISLAE (45) possesses solution, which may be obtained by means of simple iterations.[86] Obviously, the zero and the first iterations for B_0^i are

$$B_0^{i(0)} = \sum_{j(\neq i)=1}^{N} J_0^j \widetilde{U}_0^{ij}, \tag{49}$$

$$B_0^{i(1)} = B_0^{i(0)} - \sum_{j(\neq i)=1}^{N} J_0^j \widetilde{U}_0^{ij} B_0^{j(0)} - \sum_{j(\neq i)=1}^{N} \sum_{l=1}^{\infty} J_0^j \widetilde{U}^{ij}_{\mu_1 \ldots \mu_l} \odot^l B^{j(0)}_{\mu_1 \ldots \mu_l}. \tag{50}$$

Here and below, $\widetilde{U}_0^{ij}$ is the monopole approximation to the mixed-basis matrix. Interestingly, in the course of solving the ISLAE (45) by simple iterations, angular dependence arises starting from terms $\mathcal{O}(\varepsilon^4)$.

We suggest the readers who are interested in questions concerning the convergence of the GMSV procedure to address Ref. 66 and references therein.

Step 8. Once the local concentration $u_N(P)$ is found, one can deduce the total flux of diffusing particles B onto the ith sink. At that, one should utilize the local representation (35) of function $u_N(P)$. Due to the orthogonality condition for the ICT (A5), explicit surface integration on the unit sphere in the general formula (20) will yield the desired rates (21).

B. Main results obtained by using the ICT technique

Within this subsection, we present our main results, which are conveniently to formulate in a form of two theorems.

Thus, for an arbitrary sinks microstructure $X^{(N)}$ and reactivities set $\kappa^{(N)}$, we have proved the following assertions:

(a) On global representation of the solution $u_N(P)$.

Theorem VIII.1. *Using the local Cartesian coordinates* $\{O_j;\ \boldsymbol{\xi}_j\}$ $(j = \overline{1, N})$, *the solution* $u_N(P)$ $(P \in \Omega^-$, *see Fig. 1) to the exterior Robin boundary value problem given by Eqs. (16)–(18) may be represented as follows:*

$$u_N(P) = \sum_{j=1}^{N} \left[J_0^j \left(1 - B_0^j \right) \xi_j^{-1} + \sum_{k=0}^{\infty} \left(\frac{k-\kappa_j}{1+k+\kappa_j} \right) \times \xi_j^{-(2k+1)} B^j_{\gamma_1 \ldots \gamma_k} \odot^k \overline{\xi^j_{\gamma_1} \ldots \xi^j_{\gamma_k}} \right], \tag{51}$$

where tensor coefficients $B^i_{\gamma_1\ldots\gamma_k}$ $(k=\overline{0,\infty})$ *are solution of the resolving ISLAE (45).*

(b) On local representation of the solution $u_N(P)$.

Theorem VIII.2. *Solution* $u_N(\boldsymbol{\xi}_i)$ *to the exterior Robin boundary value problem given by Eqs. (16)–(18) in a small exterior* ε*-neighborhood of the unit sphere* $\partial\Omega_i^1$ *with respect to the local Cartesian coordinates* $\{O_i;\ \boldsymbol{\xi}_i\}$ *reads*

$$u_N(\boldsymbol{\xi}_i)=J_0^i\xi_i^{-1}+\sum_{k=0}^{\infty}\left[1+\left(\frac{k-\varkappa_i}{1+k+\varkappa_i}\right)\xi_i^{-(2k+1)}\right]\times B^i_{\gamma_1\ldots\gamma_k}\odot^k\overbrace{\boldsymbol{\xi}^i_{\gamma_1}\ldots\boldsymbol{\xi}^i_{\gamma_k}}\quad in\quad\Omega_i^-(\varepsilon)\quad i=\overline{1,N};\tag{52}$$

where tensor coefficients $B^i_{\gamma_1\ldots\gamma_k}$ $(k=\overline{0,\infty})$ *are solution of the resolving ISLAE (45).*

So, if we know the solution $u_N(\boldsymbol{\xi}_i)$ in an exterior neighborhood adjacent to the ith reaction surface (52), we can calculate the B-particles flux on the ith sink and, therefore, the corresponding absorbing rate and, in this way, screening coefficient (21). Thus, taking advantage of Theorem VIII.2, one can readily prove the following important corollary.

Corollary 1. For the exterior Robin boundary value problem given by Eqs. (16)–(18), the screening coefficient in Eq. (21) has the following form:

$$J_i=1-B_0^i\quad\text{and}\quad 0\le B_0^i<1,\tag{53}$$

where coefficients B_0^i *are determined by means of solution to the resolving ISLAE (45).*

It is worth noting here that in Ref. 115, Krasovitov thoroughly reproduced the notation, derivations, and even misprints of our paper.[11] However, he has been the first who kept all terms comprising $B^i_{\gamma_1\ldots\gamma_n}$ $(n\in\mathbb{N})$ in the series with respect to the orthogonal system of ICT after integration over the unit sphere (20) (see a detailed discussion of these points in Ref. 91).

C. General remarks on the obtained solution

In Sec. II, we already stated that exact solution to the diffusion boundary value problem given by Eqs. (16)–(18) is possible only for two fully absorbing sinks by means of bispherical coordinates.[25,28,29,116] Using the bispherical coordinates for the problem under partially reflecting boundary conditions (17) leads to rather cumbersome recurrence relations and therefore does not provide any advantages compared to other methods. On the contrary, for our approach, the kind of boundary conditions does not matter. Moreover, the calculation of the diffusion field $u_N(P)$ from the boundary value problem given by Eqs. (16)–(18) in general case of N sinks microstructure (2), when $N>2$ is a far too complicated task to be solved analytically in closed form.

A comparison of the general resolving ISLAE (45) with that (47) for fully absorbing sinks shows the weakening of the diffusive interaction effects in arrays comprising the partially reflecting sinks. Clearly, the diffusive interaction vanishes for the fully reflecting obstacles.

An N-sink calculation reveals that the pure diffusion field of B-particle around any ith sink $u^i_{(0)}(\xi_i)$ (38) is influenced by a contribution mediated by all other $N-1$ sinks (52), leading, in turn, to the screening effects similar to that in electrostatics.[23]

We emphasize that discussed in Sec. III mixed diffusion boundary value problems with three kinds of obstacles may be treated straightforwardly by the GMSV in terms of ICT.

The GMSV in terms of ICT may also be applied to catalytically activated diffusion-influenced trapping reactions occurring in host media comprising arrays of both finitely many sinks and immobile catalytic domains.[18]

Finally, it is worth noting that the stationary diffusion equation under the so-called conjugate boundary conditions[9,112,117] may also be tackled with the above-mentioned method quite similarly.

IX. DISCUSSION

This section contains discussion of some distinctive characteristics of the method under consideration and some important conclusions of its application for the description of the diffusive interaction between sinks.

First, point out that regardless of its technical implementation, the GMSV belongs to the class of methods, when the corresponding approximate solution satisfies the diffusion equation (16) and regularity at infinity (18), while the boundary conditions (17) are obeyed only approximately. This fact is of primary concern to theoretical modeling of the diffusion-influenced reactions in an arbitrary ensemble of N sinks. Here, it is worth noting that, for example, performing solution of the exterior elliptic boundary value problems in unbounded domains by grid methods, one faces serious difficulties concerning condition at infinity.

A. Advantages of the ICT technique

We have solved the problem on the diffusive interaction between spherical sinks by means of local Cartesian coordinate systems, rather than by introducing polar spherical coordinates. As it might be appeared at first sight, Cartesian coordinates serve well to solve diffusion problems for rectangular geometries, and not for the problems containing spherical domains. However, it turns out that the above assertion generally is not a case. In connection with this, it is significant that Hinsen and Felderhof claimed the following: "…the spherical harmonics have disadvantages in numerical calculations" and below they continued: "in both analytical and numerical calculations the Cartesian moments are often more convenient."[118]

It appears that applying of irreducible Cartesian tensor technique leads to rather fast convergence of the local concentration expansion (52). In addition, this approach, contrary to standard one based on the irregular solid spherical harmonics $\psi_n^-(r_i,\theta_i,\phi_i)$,[9,32,86] allows us to perform all numerical calculations for the real-valued functions only. Note that real-valued solid harmonics have a number of advantages over often used complex-valued ones. The choice of irregular irreducible Cartesian tensors $\boldsymbol{X}_n^-(\mathbf{r}_i)$ (A6) as a basis of functions for solutions of the exterior steady-state diffusion problems in the configuration manifold Ω^- implies a very rapid convergence of the numerical solution, as confirmed here with several examples.

In addition, contrary to the spherical solid harmonics, there are relatively simple recursion formulas to calculate analytically the irreducible Cartesian tensors. They are based on rather easy successive differentiation of generating function in Eq. (A1). Interested readers are encouraged to refer to studies, where explicit recurrent expressions for the ICT are comprehensively presented.[97,108,118–124]

Note also that from the analytical point of view, obtained in Sec. VIII, solution $u_N(P)$ keeps an explicit analytical dependence on P. In turn, from the numerical standpoint, this property allows one to truncate the resolving ISLAE at lower sizes as compared to other numerical methods such as the finite element method.[26]

Moreover, from a pure mathematical viewpoint, the spherical coordinate system has one more serious drawback. It is easy to show that in spherical coordinates $\{O_i;\ r_i, \theta_i, \phi_i\}$ axis $O_i x_3^i$ and half-plane $\{r_1^i \geq 0, r_2^i = 0\}$ should be excluded to satisfy one-to-one property in Ω_i^-.

A number of other advantages of the ICT technique are described also elsewhere.[97,108,125]

B. Description of the diffusive interaction

Let us dwell now on several particularly important points on the diffusive interaction that directly follows from our results.

If an array comprises only fully reflecting obstacles, we have no diffusive interaction between them. Meanwhile, in situation when a given array contains at least one absorbing sink, the diffusive interaction exists and we should also take into account influence of inert obstacles.

It is very important to note that here the ICT technique was applied to the diffusion problems under consideration posed in the unbounded domains, whereas the same approach is also applicable to the similar interior boundary value problems describing reactions occurring inside a spherical region (see Refs. 9, 32, and 86 for details). So, the GMSV in terms of ICT can be very useful not only in the theory of diffusion-influenced reactions, but also in biology, when reactions can take place into bounded domains.[62] We note, incidentally, that Smoluchowski's rate constant cannot describe even one-sink reaction inside a larger spherical domain since it does not consider diffusive interaction effect due to the boundary of englobed domain.

It is interesting to note that clustering of sinks was found to reduce the absorbing rate even more significantly compared with nonclustered systems.[20] The method gives us possibility to tackle trapping reactions in several clusters of obstacles and sinks in the same way as for separated sinks.

Taking into account obtained here and our previous results,[12,126] we can conclude that diffusive interaction "glues" fully absorbing sinks effectively onto a fully absorbing effective sink. Therefore, the whole N-sink array behaves like a single, isolated fully absorbing sink of some characteristic size.

For a number of applied tasks, one should use the derived microscopic solution (51) [or (52)] along with microscopic trapping rates (53) calculating appropriate configurationally averaged values to obtain effective macroscopic values associated with heterogeneous media comprising different types of sinks.[17,19,127,128]

Let us dwell on one more possible application of the approach at issue. In Ref. 112, we have established for the first time that even classical passive phoresis of microparticles (i.e., motion due to a constant gradient of some scalar field) should be treated by means of their interaction with so-called surrounding bodies, which are responsible for the external gradient. In this context, it is worth to note that the first and only attempt to apply a similar approach for studying particle interactions for thermophoresis was undertaken by Keh and Chen in Ref. 104. They used so-called polyadic tensors, but in fact, these tensors are the same as the ICT up to a constant factor. Again, the GMSV in terms of ICT can be used to investigate these quite challenging problems.

Nevertheless, it should be stressed that the ICT technique works for the case of contact reactions only. It cannot be applied to solve the relevant diffusion–reaction problems for the distance dependent reactions between reactants, which are governed by the following equation:

$$-\nabla^2 n_N = -l(\mathbf{r}) n_N, \tag{54}$$

where $l(\mathbf{r})$ stands for a noncontact reaction rate.[2,16] An exception is a particular case when in Eq. (54) $l(\mathbf{r}) \equiv l_0 = const$.

X. CONCLUSIONS AND PERSPECTIVES

Motivated through new applications in physics, chemistry, and biology, this paper deals with the generalized method of separation of variables by means of the irreducible Cartesian tensor formalism extending our previous study on the diffusion-controlled reactions to the general case of diffusion-influenced reactions. We have developed here a complete modification of the above-mentioned method, which essentially hinges on a number of useful properties of the irreducible Cartesian tensors. Formally, we reduced the steady-state diffusion problem to a set of N Laplace equations with respect to partial solution together with the prescribed N boundary conditions.

In order to determine the place and significance of our research, we have presented a rather comprehensive review of literature devoted to the theoretical methods for diffusion-influenced reactions on spherical sinks. In addition, we paid close attention to the mathematical aspects of the appropriate diffusion problem, namely: (a) rigorous statement of the problem, including terminology clarification, and (b) refining solution algorithm. The formulation of the geometric part of the diffusion boundary value problems was performed the most fully than anywhere else. We have given a proof of the irregular to regular translation addition theorem in terms of irreducible Cartesian tensors, which seems to be the simplest among previously known theorem for solid harmonics in terms of polar spherical coordinates. For the first time, the corresponding solution algorithm was divided into eight clear steps. Then, we implemented this algorithm step by step in full detail to solve the posed diffusion problem. It turns out that the method of reduction may be used to solve numerically the resolving system to any degree of accuracy even when the simple-iteration method is inapplicable, wherein the desired accuracy of the solution can be achieved just by increasing the truncation degree. Furthermore, note that the method has advantages such as shorter calculation time and more accurate results compared to purely numerical methods.

Our results fully confirm the known Hinsen–Felderhof statement that it is more preferred to work with harmonic functions using their irreducible Cartesian tensor form throughout diffusion–reaction problems even for ensembles of spherical sinks.

This research provides also a better understanding of the reactant diffusion among arrays comprising collection of arbitrary but many fully absorbing, reflecting, and partially reflecting sinks from both mathematical and physical viewpoints.

The approach developed here is applicable to a wide class of reaction–diffusion systems, providing useful tests for numerical calculations along with approximate analytical estimates of the local concentration field and reaction rates in many specific cases of practical importance.

Finally, it is important to highlight that numerical methods can handle diffusion problems for complex geometries in unbounded domains, yet they require introducing an artificial boundary, reducing the original exterior domain to a bounded domain. The generalized method of separation of variables does not have this drawback and provides simple direct numerical and analytical calculations. So, we can obtain approximations as the truncated point multipole expansions up to the monopole, dipole, quadrupole, etc., order.

It is essential to note that self-phoresis of the Janus particles moving due to a chemical reaction in the surrounding fluid is investigated by means of monopole approximation.[40] Using the approach considered here, this important problem may be under attack taking into account multipole corrections.[112]

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Sergey D. Traytak: Conceptualization (lead); Writing – original draft (lead).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX: BACKGROUND ON THE IRREDUCIBLE CARTESIAN TENSORS

To make this paper maximally self-contained and facilitate applications in diffusion-influenced reactions theory, we provide here necessary mathematical notations, definitions, and facts, required in rigorous formulation and applications of the ICT technique.

The standard notations such as $\mathbb{N}$, $\mathbb{Z}$, $\mathbb{R}$, and $\mathbb{R}_+$ representing the sets of natural, integer, real, and strictly positive real numbers, respectively, will be used in the sequel. For the three-dimensional (3D) Euclidean space, we use common $\mathbb{R}^3$.

1. Definitions and examples

It is well-known that there exist two alternative approaches to harmonic functions theory based on either Laplace's representation of solid harmonics with respect to the polar spherical coordinates or Maxwell's theory of poles given in terms of the successive derivatives of fundamental solution written for a Cartesian coordinate system.[111,129] The latter approach may be formulated with the aid of the irreducible Cartesian tensors.

Generally speaking, the irreducible tensors transform according to the irreducible representation of the special rotation group $SO(3)$. In other words, the irreducible tensors like spherical harmonics form a basis in the representation space of group $SO(3)$. To our knowledge, the ICT simple mathematical description suitable for applied physicists has been provided in Ref. 125. Moreover, for many years, there has been a significant number of publications devoting to the use of the ICT formalism in a wide variety of applications (see, e.g., Refs. 120, 130–133 and references therein). As regards adopted notations and definitions, in this paper, we basically follow known books by Hess[97] and Snider,[108] where comprehensive discussions on the various facets of irreducible Cartesian tensors are presented.

Any tensor, which cannot be reduced to a tensor of lower rank is known as an *irreducible tensor*.[97] While a generic (reducible) nth order Cartesian tensor $\boldsymbol{T}_n$ has 3^n components, the corresponding irreducible tensor besides the rank n is likewise characterized by its weight j.[125] It is common knowledge that the latter tensor has $2j+1$ independent components, which form the basis of the j weight irreducible representation of the full 3D special rotation group $SO(3)$ including mirror.[108]

Furthermore, among all ICT obtained from a given n rank tensor by means of reductions, there exists one unique irreducible tensor with the same weight and rank $n = j$. It is known in the literature as ICT *in natural form*.[125] We deal with irreducible tensors in natural form because they best suited to apply within the scope of the GMSV.

Thus, for n rank Cartesian tensors, our focus lies on their irreducible parts in natural form at that we use notations $\overline{T_n}$ and $\overline{T_{\gamma_1\dots\gamma_n}}$, where symbol $\overline{(\dots)}$ stands for the irreducible part of a Cartesian tensor $\boldsymbol{T}_n$ of rank $n \geq 2$ with respect to the special rotation group $SO(3)$.[97,108]

The irreducible tensor in natural form is appeared to be fully symmetric and traceless; therefore, this allows us to use rather simple definition of the irreducible Cartesian tensors.[98,134]

Definition X.1. A Cartesian tensor of rank $n \geq 2$ is called irreducible Cartesian tensor, if it is (i) totally symmetric under an arbitrary permutation of the indices and (ii) traceless under the contraction of any pair of indices.

An important point is that according to definition (X.1), the ICT can be expressed in terms of successive partial derivatives of the generating function $1/r$ for all points in $\mathbb{R}^3\backslash\{\mathbf{0}\}$.

Proposition X.1. An irreducible Cartesian tensors of rank n (when $n \geq 2$) may be defined as[97,111]

$$\overline{r_{\gamma_1}\dots r_{\gamma_n}} = \frac{(-1)^n}{(2n-1)!!} r^{2n+1} \partial_{r_{\gamma_1}} \dots \partial_{r_{\gamma_n}} \left(\frac{1}{r}\right). \tag{A1}$$

Here, r_{γ_ν} are Cartesian coordinates of a vector $\mathbf{r}$ ($\gamma_\nu = \overline{1,3}$) and $(2n-1)!! := 1\cdot 3\cdot \dots \cdot (2n-1)$ indicates the double factorial for odd natural numbers with the convention $(-1)!! := 1$.

Proof. Check that the tensors introduced by Eq. (A1) are symmetric for any pair of indexes and traceless.

(i) Indeed, Eq. (A1) involves directly that the introduced tensor is symmetric with respect to permutation of its indexes,

$$\overline{r_{\gamma_1}\dots r_\alpha\dots r_\beta\dots r_{\gamma_n}} = \overline{r_{\gamma_1}\dots r_\beta\dots r_\alpha\dots r_{\gamma_n}}. \tag{A2}$$

(ii) Moreover, due to harmonicity of the generating function,

$$\nabla^2\left(\frac{1}{r}\right) = \delta_{\alpha\beta}\odot^2\partial_{r_\alpha}\partial_{r_\beta}\left(\frac{1}{r}\right) = 0 \quad \text{for} \quad r>0, \tag{A3}$$

tensors (A1) are also traceless with respect to any pair of their indexes,

$$\delta_{\alpha\beta}\odot^2\overline{r_{\gamma_1}\dots r_\alpha\dots r_\beta\dots r_{\gamma_n}} = 0, \tag{A4}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. Thus, Eq. (A1) satisfies both points of definition (X.1).

□

Remark X.1. Note furthermore that traces cannot be defined for any scalars $a_0 \in \mathbb{R}$ [tensors of rank 0) or vectors (r_1, r_2, r_3) (tensors of rank 1)]. Nevertheless, they are harmonic and, therefore, irreducible by definition.[97]

Hence, in the explicit form, the first several irreducible Cartesian tensors of ranks n corresponding to the monopole $(n=0)$, dipole $(n=1)$, quadrupole $(n=2)$, and octupole $(n=3)$ potentials read as follows:

$$\overline{a_0} := a_0,\ \overline{r_{\gamma_1}} := r_{\gamma_1},\ \overline{r_{\gamma_1}r_{\gamma_2}} = r_{\gamma_1}r_{\gamma_2} - \frac{1}{3}r^2\delta_{\gamma_1\gamma_2},$$
$$\overline{r_{\gamma_1}r_{\gamma_2}r_{\gamma_3}} = r_{\gamma_1}r_{\gamma_2}r_{\gamma_3} - \frac{1}{5}r^2\left(r_{\gamma_1}\delta_{\gamma_2\gamma_3} + r_{\gamma_2}\delta_{\gamma_1\gamma_3} + r_{\gamma_3}\delta_{\gamma_1\gamma_2}\right).$$

B. Orthogonality condition

Denote by $d^2\hat{r}$ the magnitude of the surface element on the unit sphere in global coordinates: $\partial\Omega_1 \equiv \partial\Omega(\mathbf{0};1) := \{\mathbf{r}\in\mathbb{R}^3 : \hat{r}=1\}$. Then, for all $n \geq 0$, we can write the following *orthogonality condition*:[97]

$$\oint_{\partial\Omega_1}\overline{\hat{r}_{\gamma_1}\dots\hat{r}_{\gamma_n}}\cdot\overline{\hat{r}_{\mu_1}\dots\hat{r}_{\mu_k}}\,d^2\hat{r} = \frac{4\pi n!}{(2n+1)!!}\delta_{nk}\Delta^{(n)}_{\gamma_1\dots\gamma_n,\mu_1\dots\mu_n}, \tag{A5}$$

where in case of sphere, $\hat{\mathbf{n}} = \hat{\mathbf{r}}$ (in component notation $\hat{r}_\alpha = r_\alpha/r$) is a unit vector identifying a point on $\partial\Omega_1$ and $\overline{r_{\gamma_1}\dots r_{\gamma_n}}\Big|_{\partial\Omega_1} = \overline{\hat{r}_{\gamma_1}\dots\hat{r}_{\gamma_n}}$ is the restriction of the ICT to the unit sphere $\partial\Omega_1$. In Eq. (A5), $\Delta^{(n)}_{\gamma_1\dots\gamma_n,\mu_1\dots\mu_k}$ stands for the $2n$ rank projector, which projects any tensor of rank n into its irreducible part. In particular, three first projectors are[97]

$$\Delta^{(0)} = 1, \quad \Delta^{(1)} = \delta_{\alpha\beta},$$
$$\Delta^{(2)}_{\alpha\beta,\alpha'\beta'} = \frac{1}{2}\left(\delta_{\alpha\alpha'}\delta_{\beta\beta'} + \delta_{\alpha\beta'}\delta_{\beta\alpha'}\right) - \frac{1}{3}\delta_{\alpha\beta}\delta_{\alpha'\beta'}.$$

3. Connection with solid harmonics

In applications are also used the *multipole potentials* defined by $\boldsymbol{X}^{\mp}_n(\mathbf{r}) = X^{\mp}_{\gamma_1\dots\gamma_n}(\mathbf{r})$,[97] where the components read

$$X^-_{\gamma_1\dots\gamma_n}(\mathbf{r}) := (-1)^n\partial_{r_{\gamma_1}}\dots\partial_{r_{\gamma_n}}\left(\frac{1}{r}\right), \tag{A6}$$

$$X^+_{\gamma_1\dots\gamma_n}(\mathbf{r}) := (2n-1)!!\,\overline{r_{\gamma_1}\dots r_{\gamma_n}}. \tag{A7}$$

Owing to definition, they are connected by the following relation:

$$\boldsymbol{X}^+_n(\mathbf{r}) = r^{(2n+1)}\boldsymbol{X}^-_n(\mathbf{r}). \tag{A8}$$

For reasons explained below (see X C), it is quite natural to call potentials $\boldsymbol{X}^-_n$ and $\boldsymbol{X}^+_n$ *irregular* and *regular ICT*, respectively.[118] However, throughout this paper, we use ICT defined by Eq. (A1), since they are most extensively employed in applications.

As indicated in Sec. I, solid harmonics were thoroughly used previously to investigate many-sink effects during diffusion-influenced reactions. So, it is expedient to point to an intimate relationship between them and the ICT.[97,135–137]

Recall that *real solid harmonics* $\psi_{nm}(r,\theta,\phi)$, where the integer m such that $-n \leq m \leq n$ and $n = \overline{0,\infty}$, are harmonic functions in spherical coordinates $\{O;\ r,\theta,\phi\}$.[67] For brevity, we shall denote them as $\psi_n(r,\theta,\phi)$. Furthermore, according to their behavior at the origin O, two kinds of solid harmonics are distinguished:

(1) *irregular* at O solid harmonics $\psi^-_n(r,\theta,\phi)$ has a pole of order $n+1$ singularity at O;
(2) *regular* at O solid harmonics $\psi^+_n(r,\theta,\phi)$ has real-valued harmonic homogeneous polynomials of order n.

Hence, irregular solid harmonics ψ^-_n automatically satisfies the regularity condition at infinity (18) and, therefore, they are regular at infinity.

Clearly, irregular $\boldsymbol{X}^-_n$ (A6) and regular $\boldsymbol{X}^+_n$ (A7) ICT correspond to irregular and regular solid harmonics ψ^-_n and ψ^+_n.

Represent tensors $\boldsymbol{X}^{\pm}_n(\mathbf{r})$ in the form that most closely resemble classical irregular $\psi^-_n(r,\theta,\phi)$, regular $\psi^+_n(r,\theta,\phi)$, solid and real spherical $Y_n(\theta,\phi)$ harmonics,

$$X^-_{\gamma_1\dots\gamma_n}(\mathbf{r}) = r^{-(n+1)}Y_{\gamma_1\dots\gamma_n}(\hat{\mathbf{r}}), \tag{A9}$$

$$X^+_{\gamma_1\dots\gamma_n}(\mathbf{r}) = r^nY_{\gamma_1\dots\gamma_n}(\hat{\mathbf{r}}), \tag{A10}$$

$$Y_{\gamma_1\dots\gamma_n}(\hat{\mathbf{r}}) := (2n-1)!!\,\overline{\hat{r}_{\gamma_1}\dots\hat{r}_{\gamma_n}}. \tag{A11}$$

It is apparent that the ICT $Y_{\gamma_1\dots\gamma_n}(\hat{\mathbf{r}})$ like spherical harmonics depend on the direction of vector $\mathbf{r}$ only.[97]

As noted above, the ICT similar to solid harmonics form a basis in the representation space of the group $SO(3)$; therefore, there exist a non-singular linear transformation and its inverse in space $\mathbb{R}^{2n+1}$, which map these bases into each other.[111] Using known *Sylvester's theorem*,[111,137] one can find the desired connection between tensors $\boldsymbol{X}^{\pm}_n$ and classical real solid harmonics $\psi^{\pm}_n$ explicitly. We emphasize here that original Sylvester's proof is rather sophisticated;[111] therefore, interested readers are encouraged to refer to a simple proof of Sylvester's theorem proposed by Backus in Ref. 138.

Thus, it can be shown that Sylvester's theorem implies

$$\frac{1}{r^{n+1}} Y_n(\theta,\phi) = \sum_{m=0}^{n} \sum_{l=0}^{m} c_{lm} \partial_{r_1}^{l} \partial_{r_2}^{m-l} \partial_{r_3}^{n-m} \left(\frac{1}{r}\right), \tag{A12}$$

where

$$Y_n(\theta,\phi) = \sum_{m=0}^{n} Y_n^m(\theta,\phi),$$
$$Y_n^m(\theta,\phi) := \left(a_n^m \cos m\phi + b_n^m \sin m\phi\right) P_n^m(\cos\theta) \tag{A13}$$

is the real spherical harmonic of degree n and order m. In Eq. (A13), a_n^m, b_n^m, and c_{lm} are some known real coefficients and $P_n^m(\cos\theta)$ are associated Legendre functions.[139]

In particular, for the axially symmetric case ($m = 0$), taking all derivatives along the Or_3 axis, we have $r_{\gamma_1} = r_{\gamma_2} = \ldots = r_{\gamma_n} = r_3$ and formula (A12) boils down to the following well-known relation:[111]

$$\frac{1}{r^{n+1}} P_n(\cos\theta) = \frac{(-1)^n}{n!} \partial_{r_3}^{n} \left(\frac{1}{r}\right). \tag{A14}$$

REFERENCES

[1] H. J. Eyring, S. H. Lin, and S. M. Lin, *Basic Chemical Kinetics* (Wiley, New York, 1980).
[2] S. A. Rice, *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).
[3] A. V. Barzykin, K. Seki, and M. Tachiya, "Kinetics of diffusion-assisted reactions in microheterogeneous systems," Adv. Colloid Interface Sci. **89-90**, 47–140 (2001).
[4] L. Dagdug, J. Peña, and I. Pompa-García, *Diffusion Under Confinement: A Journey through Counterintuition* (Springer, New York, 2024), p. 759.
[5] S. D. Traytak, "The diffusive interaction in diffusion-limited reactions: The time-dependent case," Chem. Phys. **193**, 351–366 (1995).
[6] S. D. Traytak, "On the time-dependent diffusive interaction between stationary sinks," Chem. Phys. Lett. **453**, 212–216 (2008).
[7] S. D. Traytak, "Methods for solution of the boundary value problems in domains with disconnected boundary," J. Compos. Mech. Des. **9**, 495–522 (2003) (in Russian).
[8] S. D. Traytak and D. S. Grebenkov, "Diffusion-influenced reaction rates for active 'sphere-prolate spheroid' pairs and Janus dimers," J. Chem. Phys. **148**, 024107 (2018).
[9] D. S. Grebenkov and S. D. Traytak, "Semi-analytical computation of Laplacian Green functions in three-dimensional domains with disconnected spherical boundaries," J. Comput. Phys. **379**, 91–117 (2019).
[10] L. Rayleigh, "LVI. On the influence of obstacles arranged in rectangular order upon the properties of a medium," London, Edinburgh Dublin Philos. Mag. J. Sci. **34**, 481–502 (1892).
[11] S. D. Traytak, "Theory of recondensation of N drops," Theor. Found. Chem. Eng. **24**, 320–328 (1991).
[12] S. D. Traytak, "The diffusive interaction in diffusion-limited reactions: The steady-state case," Chem. Phys. Lett. **197**, 247–254 (1992).
[13] F. den Hollander and G. Weiss, "Aspects of trapping in transport processes," in *Contemporary Problems in Statistical Physics*, edited by G. H. Weiss (Society for Industrial and Applied Mathematics, Philadelphia, 1994), pp. 147–203.
[14] C. W. J. Beenakker and J. Ross, "Theory of Ostwald ripening for open systems," J. Chem. Phys. **83**, 4710–4714 (1985).
[15] G. H. Weiss, "Overview of theoretical models for reaction rates," J. Stat. Phys. **42**, 3–36 (1986).
[16] K. L. Ivanov, N. N. Lukzen, and A. B. Doktorov, "Non-Markovian kinetics of reactions in solutions," in *Chemical Kinetics Beyond the Textbook*, edited by K. Lindenberg, R. Metzler, and G. Oshanin (World Scientific, New Jersey, 2020), pp. 65–96.
[17] S. Torquato, *Random Heterogeneous Materials: Microstructure and Macroscopic Properties* (Springer, New York, 2002).
[18] O. Bénichou, M. Coppey, M. Moreau, and G. Oshanin, "Kinetics of diffusion-limited catalytically activated reactions: An extension of the Wilemski–Fixman approach," J. Chem. Phys. **123**, 194506 (2005).
[19] A. D. Brailsford, "Diffusion to a random array of identical spherical sinks," J. Nucl. Mater. **60**, 257–278 (1976).
[20] P. M. Richards, "Diffusion and trapping at arbitrary trap size and concentration," J. Chem. Phys. **85**, 3520–3529 (1986).
[21] H. L. Frisch and F. C. Collins, "Diffusional processes in the growth of aerosol particles," J. Chem. Phys. **20**, 1797–1803 (1952).
[22] F. S. Ham, "Theory of diffusion-limited precipitation," J. Phys. Chem. Solids **6**, 335–351 (1958).
[23] J. M. Deutch, B. U. Felderhof, and M. J. Saxton, "Competitive effects in diffusion-controlled reactions," J. Chem. Phys. **64**, 4559–4563 (1976).
[24] N. McDonald and W. Strieder, "Competitive interaction between two different spherical sinks," J. Chem. Phys. **121**, 7966–7972 (2004).
[25] V. M. Bluett and N. J. B. Green, "Competitive diffusion-influenced reaction of a reactive particle with two static sinks," J. Phys. Chem. A **110**, 4738–4752 (2006).
[26] C. Eun, P. M. Kekenes-Huskey, and J. A. McCammon, "Influence of neighboring reactive particles on diffusion-limited reactions," J. Chem. Phys. **139**, 044117 (2013).
[27] J. A. Biello and R. Samson, "Competitive effects between stationary chemical reaction centres: A theory based on off-center monopoles," J. Chem. Phys. **142**, 094109 (2015).
[28] J. C. Carstens, A. Williams, and J. T. Zung, "Theory of droplet growth in clouds: II. Diffusional interaction between two growing droplets," J. Atmos. Sci. **27**, 798–803 (1970).
[29] V. Dubinko, A. Turkin, A. Tur, and V. Yanovskiy, "Diffusion interaction of new-phase precipitates at random distances," Phys. Met. Metall. **68**, 17–25 (1989).
[30] S. P. Marsh, "Asymptotic kinetics of phase coarsening in dilute systems," Mater. Sci. Eng.: B **32**, 159–167 (1995).
[31] R. Wagner, R. Kampmann, and P. W. Voorhees, "Homogeneous second-phase precipitation," in *Phase Transformation in Materials*, edited by G. Kostorz (Wiley, Weinheim, 2001), pp. 309–407.
[32] M. Galanti, D. Fanelli, S. D. Traytak, and F. Piazza, "Diffusion to capture and the concept of diffusive interactions," in *Chemical Kinetics Beyond the Textbook*, edited by K. Lindenberg, R. Metzler, and G. Oshanin (World Scientific, New Jersey, 2020), pp. 321–352.
[33] R. Cedeno, R. Grossier, V. Tishkova, N. Candoni, A. E. Flood, and S. Veesler, "Evaporation dynamics of sessile saline microdroplets in oil," Langmuir **38**(31), 9686–9696 (2022).
[34] M. Labowsky, "A formalism for calculating the evaporation rates of rapidly evaporating interacting particles," Combust. Sci. Technol. **18**, 145–151 (1978).
[35] M. Marberry, A. K. Ray, and K. Leung, "Effect of multiple particle interactions on burning droplets," Combust. Flame **57**, 237–245 (1984).
[36] A. Z. Zinchenko, "An efficient algorithm for calculating multiparticle thermal interaction in a concentrated dispersion of spheres," J. Comput. Phys. **111**, 120–135 (1994).
[37] A. S. Sangani and G. Mo, "An $o(n)$ algorithm for Stokes and Laplace interactions of particles," Phys. Fluids **8**, 1990–2010 (1996).
[38] M. Kim, S. Lee, and J.-H. Kim, "Concentration effects on the rates of irreversible diffusion-influenced reactions," J. Chem. Phys. **141**, 084101 (2014).
[39] O. Carrier, N. Shahidzadeh-Bonn, R. Zargar, M. Aytouna, M. Habibi, J. Eggers, and D. Bonn, "Evaporation of water: Evaporation rate and collective effects," J. Fluid Mech. **798**, 774–786 (2016).
[40] H. Stark, "Artificial chemotaxis of self-phoretic active colloids: Collective behavior," Acc. Chem. Res. **51**, 2681–2688 (2018).
[41] H. Masoud, P. D. Howell, and H. A. Stone, "Evaporation of multiple droplets," J. Fluid Mech. **927**, R4 (2021).
[42] K. Lee and S. Lee, "Interplay of reactive interference and crowding effects in the diffusion-influenced reaction kinetics," J. Chem. Phys. **153**, 044129 (2020).
[43] F. G. H. Schofield, A. W. Wray, D. Pritchard, and S. K. Wilson, "The shielding effect extends the lifetimes of two-dimensional sessile droplets," J. Eng. Math. **120**, 89–110 (2020).

[44]Z. Wang, D. Orejon, Y. Takata, and K. Sefiane, "Wetting and evaporation of multicomponent droplets," Phys. Rep. **960**, 1–37 (2022).
[45]I. Baydoun and V. A. Zagrebnov, "Diffusion and Laplacian transport," Theor. Math. Phys. **168**, 1180–1191 (2011).
[46]S. Kim and S. J. Karrila, *Microhydrodynamics: Principles and Selected Applications* (Dover Publications, New York, 2013).
[47]R. A. Reck and S. Prager, "Diffusion-controlled quenching at higher quencher concentrations," J. Chem. Phys. **42**, 3027–3032 (1965).
[48]V. A. Borzilov and A. S. Stepanov, "On derivation of the equation for condensation of an array of drops," Izv. Atmos. Ocean. Phys. **7**, 164–172 (1971) (in Russian).
[49]J. J. Weins and J. W. Chan, "The effect of the size and distribution of second phase particles and voids on sintering," in *Sintering and Related Phenomena*, edited by G. C. Kuczynski (Plenum, New York, 1973), pp. 151–163.
[50]B. U. Felderhof and J. M. Deutch, "Concentration dependence of the rate of diffusion-controlled reactions," J. Chem. Phys. **64**, 4551–4558 (1976).
[51]J. A. Marqusee and J. Ross, "Theory of Ostwald ripening: Competitive growth and its dependence on volume fraction," J. Chem. Phys. **80**, 536–543 (1984).
[52]K. Mattern and B. U. Felderhof, "Rate of diffusion-controlled reactions in a random array of monopole sinks," Physica A **135**, 505–518 (1986).
[53]S. D. Traytak, "Heat and mass exchange in a spatially ordered array of drops," High Temp. **27**, 773–779 (1989).
[54]M. Strobel, S. Reiss, and K.-H. Heinig, "Evolution of nanocluster ensembles: Computer simulation of diffusion and reaction controlled Ostwald ripening," Nucl. Instrum. Methods Phys. Res., Sect. B **120**, 216–220 (1996).
[55]H. Mandyam, M. E. Glicksman, J. Helsing, and S. P. Marsh, "Statistical simulations of diffusional coarsening in finite clusters," Phys. Rev. E **58**, 2119–2130 (1998).
[56]H.-K. Tsao, S.-Y. Lu, and C.-Y. Tseng, "Rate of diffusion-limited reactions in a cluster of spherical sinks," J. Chem. Phys. **115**, 3827–3833 (2001).
[57]L. H. Zheng and Y. C. Chiew, "Computer simulation of diffusion-controlled reactions in dispersions of spherical sinks," J. Chem. Phys. **90**, 322–327 (1989).
[58]R. T. Bonnecaze and J. F. Brady, "Rate of diffusion-limited reactions in dispersions of spherical traps via multipole scattering," J. Chem. Phys. **94**, 537–540 (1991).
[59]L. Ratke and P. W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Material Processing* (Springer, Berlin, 2002).
[60]C. W. J. Beenakker and J. Ross, "Monte Carlo study of a model of diffusion-controlled reactions," J. Chem. Phys. **84**, 3857–3864 (1986).
[61]N. Akaiwa and P. W. Voorhees, "Late-stage phase separation: Dynamics, spatial correlations, and structure functions," Phys. Rev. E **49**, 3860–3880 (1994).
[62]A. Vazquez, "Optimal cytoplasmatic density and flux balance model under macromolecular crowding effects," J. Theor. Biol. **264**, 356–359 (2010).
[63]P. Bobbert, M. Wind, and J. Vlieger, "Diffusion to a slowly growing truncated sphere on a substrate," Physica A **141**, 58–72 (1987).
[64]D. F. Calef and J. M. Deutch, "Diffusion-controlled reactions," Annu. Rev. Phys. Chem. **34**, 493–524 (1983).
[65]D. L. Brown and D. Peterseim, "A multiscale method for porous microstructures," Multiscale Model. Simul. **14**, 1123–1152 (2016).
[66]S. D. Traytak, "The generalized method of separation of variables for diffusion-influenced reactions: Irreducible Cartesian tensors technique," arXiv:2404.15893 [physics.chem-ph] (2024).
[67]A. N. Tikhonov and A. A. Samarskii, *Equations of Mathematical Physics* (Pergamon Press, Oxford, 1963).
[68]P. A. Krutitskii, "A mixed problem for the Laplace equation in three-dimensional multiply connected domains," Differ. Equ. **35**, 1193–1200 (1999).
[69]S. Lee and M. Karplus, "Kinetics of diffusion-influenced bimolecular reactions in solution. I. General formalism and relaxation kinetics of fast reversible reactions," J. Chem. Phys. **86**, 1883–1903 (1987).
[70]D. Bedeaux, R. Kapral, and P. Mazur, "The effective shear viscosity of a uniform suspension of spheres," Physica A **88**, 88–121 (1977).
[71]J. R. Lebenhaft and R. Kapral, "Diffusion-controlled processes among partially absorbing stationary sinks," J. Stat. Phys. **20**, 25–56 (1979).
[72]T. Kumpulainen, B. Lang, A. Rosspeintner, and E. Vauthey, "Ultrafast elementary photochemical processes of organic molecules in liquid solution," Chem. Rev. **117**, 10826–10939 (2017).
[73]S. D. Traytak and W. S. Price, "Exact solution for anisotropic diffusion-controlled reactions with partially reflecting conditions," J. Chem. Phys. **127**, 184508 (2007).
[74]S. D. Traytak, "Convergence of a reflection method for diffusion-controlled reactions on static sinks," Physica A **362**, 240–248 (2006).
[75]G. Cossali and S. Tonini, "Analytical modelling of drop heating and evaporation in drop clouds: Effect of temperature dependent gas properties and cloud shape," Int. J. Heat Mass Transfer **162**, 120315 (2020).
[76]P. C. Bressloff, "Search processes with stochastic resetting and multiple targets," Phys. Rev. E **102**, 022115 (2020).
[77]S. G. Mikhlin, *Integral Equations and Their Applications to Certain Problems in Mechanics, Mathematical Physics, and Technology* (Pergamon Press, Oxford, 1964), p. 341.
[78]S. D. Traytak, "Boundary-value problems for the diffusion equation in domains with disconnected boundary," Diffus. Fundam. **2**, 38.1–38.2 (2005).
[79]J. C. Maxwell, *Treatise on Electricity and Magnetism* (Publishers to the University of Oxford, Oxford, 1873), Vol. I.
[80]A. B. Basset, "On the motion of two spheres in a liquid, and allied problems," Proc. London Math. Soc. **s1-18**(1), 369–377 (1886).
[81]A. G. Nikolaev and E. A. Tanchik, "Stresses in an elastic cylinder with cylindrical cavities forming a hexagonal structure," J. Appl. Mech. Tech. Phys. **57**, 1141–1149 (2016).
[82]V. Y. Miroshnikov, O. B. Savin, M. M. Hrebennikov, and O. A. Pohrebniak, "Analysis of the stress state of a layer with two cylindrical elastic inclusions and mixed boundary conditions," J. Mech. Eng. **25**, 22–29 (2022).
[83]A. N. Guz' and V. T. Golovchan, *Diffraction of the Elastic Waves in Multi-Connected Bodies* (Naukova dumka, Kiev, 1972) (in Russian).
[84]V. I. Kushch, *Micromechanics of Composites: Multipole Expansion Approach* (Elsevier, Amsterdam, 2013).
[85]E. A. Ivanov, *Diffraction of Electromagnetic Waves on Two Bodies* (Springfield, Washington, 1970).
[86]M. Galanti, D. Fanelli, S. D. Traytak, and F. Piazza, "Theory of diffusion-influenced reactions in complex geometries," Phys. Chem. Chem. Phys. **18**, 15950–15954 (2016).
[87]P. Venema and D. Bedeaux, "Reaction-diffusion on a periodic array of penetrable spherical sinks," Physica A **156**, 835–852 (1989).
[88]H.-K. Tsao, S.-Y. Lu, and C.-Y. Tseng, "Diffusion into a pair of reactive spheres with first-order reaction," J. Chem. Phys. **114**, 10247–10251 (2001).
[89]H.-K. Tsao, "Competitive diffusion into two reactive spheres of different reactivity and size," Phys. Rev. E **66**, 011108 (2002).
[90]N. McDonald and W. Strieder, "Diffusion and reaction for a spherical source and sink," J. Chem. Phys. **118**, 4598–4605 (2003).
[91]S. D. Traytak, "On the irreducible tensors method in the theory of diffusive interaction between particles," in *Mathematical Modeling: Problems, Methods*, edited by L. Uvarova and A. Latyshev (Kluwer Academic Publishers, Dordrecht, 2001), pp. 267–278.
[92]T. Erdmann, M. Kröger, and S. Hess, "Phase behavior and structure of Janus fluids," Phys. Rev. E **67**, 041209 (2003).
[93]V. E. Baranov and S. I. Martynov, "Simulation of particle dynamics in a viscous fluid near a plane wall," Comput. Math. Math. Phys. **50**, 1588–1604 (2010).
[94]M. Y. Agre, "Multipole expansions in magnetostatics," Phys. -Usp. **54**, 167–180 (2011).
[95]O. B. Gus'kov, "A self-consistent field method applied to the dynamics of viscous suspensions," J. Appl. Math. Mech. **77**, 401–411 (2013).
[96]R. Singh, S. Ghose, and R. Adhikari, "Many-body microhydrodynamics of colloidal particles with active boundary layers," J. Stat. Mech. **2015**, P06017.
[97]S. Hess, *Tensors for Physics* (Springer, Berlin, Heidelberg, 2015).
[98]S. R. Mane, "Irreducible Cartesian tensors of highest weight, for arbitrary order," Nucl. Instrum. Methods Phys. Res., Sect. A **813**, 62–67 (2016).

[99]C. Bechinger, R. Di Leonardo, H. Löwen, C. Reichhardt, G. Volpe, and G. Volpe, "Active particles in complex and crowded environments," Rev. Mod. Phys. **88**, 045006 (2016).
[100]R. K. Manna, P. B. S. Kumar, and R. Adhikari, "Colloidal transport by active filaments," J. Chem. Phys. **146**, 024901 (2017).
[101]D. L. Andrews, "Irreducible Cartesian tensor analysis of harmonic scattering from chiral fluids," Symmetry **12**, 1466 (2020).
[102]G. Turk, R. Singh, and R. Adhikari, "Stokes traction on an active particle," Phys. Rev. E **106**, 014601 (2022).
[103]R. Schmitz and B. U. Felderhof, "Creeping flow about a sphere," Physica A **92**, 423–437 (1978).
[104]H. J. Keh and S. H. Chen, "Particle interactions in thermophoresis," Chem. Eng. Sci. **50**, 3395–3407 (1995).
[105]S. Kim, "Stokes flow past three spheres: An analytic solution," Phys. Fluids **30**, 2309–2314 (1987).
[106]W. Miller, *Symmetry and Separation of Variables* (Addison-Wesley, Massachusetts, 1977).
[107]E. O. Steinborn and K. Ruedenberg, "Rotation and translation of regular and irregular solid spherical harmonics," Adv. Quantum Chem. **7**, 1–81 (1973).
[108]R. F. Snider, *Irreducible Cartesian Tensors* (De Gruyter, Berlin, 2018).
[109]M. J. Caola, "Solid harmonics and their addition theorems," J. Phys. A: Math. Gen. **11**, L23–L25 (1978).
[110]E. J. Weniger and E. O. Steinborn, "A simple derivation of the addition theorems of the irregular solid harmonics, the Helmholtz harmonics, and the modified Helmholtz harmonics," J. Math. Phys. **26**, 664–670 (1985).
[111]R. Courant and D. Hilbert, *Methods of Mathematical Physics* (John Wiley & Sons, New York, 1989), Vol. I.
[112]S. D. Traytak, "Hydrodynamic theory of phoretic propulsion: Clarifications, new concepts, and reassessment," in *Chemical Kinetics Beyond the Textbook*, edited by K. Lindenberg, R. Metzler, and G. Oshanin (World Scientific, New Jersey, 2020), pp. 565–592.
[113]L. V. Kantorovich and V. I. Krylov, *Approximate Methods of Higher Analysis* (Interscience Publishers, New York, 1964).
[114]L. V. Kantorovich and G. P. Akilov, *Functional Analysis* (Pergamon Press, Oxford, 1982).
[115]B. G. Krasovitov, "Evaporation and condensation of large size and moderate size droplets in gases with an arbitrary temperature gradients," Ph.D dissertation, Moscow Region Pedagogical Institute, 1991.
[116]R. Samson and J. M. Deutch, "Exact solution for the diffusion controlled rate into a pair of reacting sinks," J. Chem. Phys. **67**, 847 (1977).
[117]V. Mityushev and W. Nawalaniec, "Effective conductivity of a random suspension of highly conducting spherical particles," Appl. Math. Modell. **72**, 230–246 (2019).
[118]K. Hinsen and B. U. Felderhof, "Reduced description of electric multipole potential in Cartesian coordinates," J. Math. Phys. **33**, 3731–3735 (1992).
[119]S. P. Efimov, "Transition operator between multipole states and their tensor structure," Theor. Math. Phys. **39**, 425–434 (1979).
[120]J. Cipriani and B. Silvi, "Cartesian expressions for electric multipole moment operators," Mol. Phys. **45**, 259–272 (1982).
[121]B. Blaive and J. Metzger, "Explicit expressions of the *n*th gradient of $1/r$," J. Math. Phys. **25**, 1721–1724 (1984).
[122]J. Applequist, "Traceless Cartesian tensor forms for spherical harmonic functions: New theorems and applications to electrostatics of dielectric media," J. Phys. A: Math. Gen. **22**, 4303–4330 (1989).
[123]H. Ehrentraut and W. Muschik, "On symmetric irreducible tensors in *d*-dimensions," Int. J. Phys. Eng. Sci. **51**, 149–159 (1998).
[124]S. P. Efimov, "Coordinate space modification of Fock's theory. Harmonic tensors in the quantum Coulomb problem," Phys.-Usp. **65**, 952–967 (2022).
[125]J. A. R. Coope, R. F. Snider, and F. R. McCourt, "Irreducible Cartesian tensors," J. Chem. Phys. **43**, 2269–2275 (1965).
[126]S. D. Traytak, "Ligand binding in a spherical region randomly crowded by receptors," Phys. Biol. **10**, 045009 (2013).
[127]M. Loewenberg and G. R. Gavalas, "Steady-state reactant flux into a medium containing spherical sinks," Chem. Eng. Sci. **43**, 2431–2444 (1988).
[128]V. A. Borodin, "Generalized rate theory for spatially inhomogeneous systems of point defect sinks," Physica A **211**, 279–316 (1994).
[129]R. F. Snider, *Parameterization of the Earth's Gravity Field: Point and Line Singularities* (Astronomical and Geodetic Society, Lviv, 1998).
[130]H. Brenner, "The Stokes resistance of an arbitrary particle—IV Arbitrary fields of flow," Chem. Eng. Sci. **19**, 703–727 (1964).
[131]J. L. Anderson, "Relativistic Grad polynomials," J. Math. Phys. **15**, 1116–1119 (1974).
[132]S. I. Martynov, "Hydrodynamic interaction of particles," Fluid Dyn. **33**, 245–251 (1998).
[133]A. Bonvicini, "Irreducible Cartesian tensor decomposition: A computational approach," J. Chem. Phys. **160**, 224105 (2024).
[134]M. Junk, J. Budday, and T. Bohlke, "On the solvability of maximum entropy moment problems in texture analysis," Math. Models Methods Appl. Sci. **22**, 1250043 (2012).
[135]A. J. Stone, "Transformation between Cartesian and spherical tensors," Mol. Phys. **29**, 1461–1471 (1975).
[136]J.-M. Normand and J. Raynal, "Relations between Cartesian and spherical components of irreducible Cartesian tensors," J. Phys. A: Math. Gen. **15**, 1437–1461 (1982).
[137]M. R. Dennis, "Canonical representation of spherical functions: Sylvester's theorem, Maxwell's multipoles and Majorana's sphere," J. Phys. A: Math. Gen. **37**, 9487–9500 (2004).
[138]G. Backus, "A geometrical picture of anisotropic elastic tensors," Rev. Geophys. **8**, 633–671, https://doi.org/10.1029/rg008i003p00633 (1970).
[139]R. W. James, "Multipole analysis. I. Theory, and geomagnetic multipoles 1965·0," Aust. J. Phys. **21**, 455–464 (1968).
[140]H. Sano, "Solutions to the Smoluchowski equation for problems involving the anisotropic diffusion or absorption of a particle," J. Chem. Phys. **74**, 1394–1400 (1981).