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ABSTRACT

Using an approach based on the diffusion analog of the Cattaneo–Vernotte differential model, we find the exact analytical solution to the corresponding time-dependent linear hyperbolic initial boundary value problem, describing irreversible diffusion-controlled reactions under Smoluchowski's boundary condition on a spherical sink. By means of this solution, we extend exact analytical calculations for the time-dependent classical Smoluchowski rate coefficient to the case that includes the so-called inertial effects, occurring in the host media with finite relaxation times. We also present a brief survey of Smoluchowski's theory and its various subsequent refinements, including works devoted to the description of the short-time behavior of Brownian particles. In this paper, we managed to show that a known Rice's formula, commonly recognized earlier as an exact reaction rate coefficient for the case of hyperbolic diffusion, turned out to be only its approximation being a uniform upper bound of the exact value. Here, the obtained formula seems to be of great significance for bridging a known gap between an analytically estimated rate coefficient on the one hand and molecular dynamics simulations together with experimentally observed results for the short times regime on the other hand. A particular emphasis has been placed on the rigorous mathematical treatment and important properties of the relevant initial boundary value problems in parabolic and hyperbolic diffusion theories.

I. MOTIVATION

The main motivation for writing this paper is to improve a well-known approximation obtained by Rice for the hyperbolic diffusion-controlled reaction time-dependent rate coefficient (further on, "time-dependent" will be omitted for brevity), first published in his famous book,[1] which has for many years served as the standard reference for all researchers in the field of diffusion-controlled reactions (DCRs).

Recently, we have studied some mathematical aspects concerning various applications of *addition theorems* and *re-expansion formulas* to describe the *diffusion interaction* often manifested in diffusion-controlled reactions.[2,3] Diffusion of Brownian particles in three-dimensional arrays of trapping static sinks embedded in surrounding media (commonly known as *host media*[4]) was under consideration. To complete a literature review, we believed that it would be advisable to briefly highlight the main features of the behavior of the particles rate coefficient at short-times to take into account the so-called *inertial effects* (see Sec. V for details) in the host media with finite values of the relevant relaxation times for diffusive fluxes. Surprisingly, we found out that general hyperbolic theory of diffusion-controlled reactions in media with diffusion relaxation still requires significant theoretical rethinking and refinement in a number of both mathematical and physical facets. Below, in Secs. V and VIII, we will discuss known Rice's theoretical study on this topic[1,5] in full detail, so here, we only note in passing that his derivation, contrary to the expectations, led to an approximate result. It should be particularly emphasized that the formula for the rate coefficient was presented in Ref. 1 referring to unpublished results[5] without any derivation or proof. What is more important is that the application of this approximation to the analysis of some experimental data for short-times caused a few incorrect physical conclusions. Among them, one of the crucial wrong conclusions is that the hyperbolic rate coefficient highly diminishes the influence of inertial effects on kinetics of particles trapping.[1] Therefore, it seems, not by chance, the emerging interest to the application of the *linear hyperbolic diffusion equation* (HDE) in chemical kinetics, associated with several pioneering Monchik's papers, entirely faded away since 1985 just after the publication of the aforementioned fundamental book (Ref. 1). This is especially noticeable against the backdrop of multiple attempts to describe the short-time regime of diffusion-controlled reactions using various theoretical methods (see a brief survey on this subject in Sec. V). In fairness, it should be noted here that a similar approximate result was obtained in different years by a number of authors, who studied hyperbolic theory of heat and mass transfer (see discussion and the references in Ref. 6).

Our ultimate objective in this paper is to extend the parabolic diffusion-controlled reactions theory to the hyperbolic one. Herewith, we intend to bridge the gap, which was formed since 1985, in the literature on the application of the hyperbolic diffusion approach to the classical Smoluchowski theory of diffusion-controlled reactions. For this purpose, the existing literature on the above subject was brought under close critical study and rethinking. That is why, our work occupies an intermediate place between a review and a research paper by the choice of material and style of its presentation.

Before closing this short section, we would like to dwell on encouraging words from the recent paper by Löwen: "Since inertial effects will necessarily become relevant for length scales between macroscopic and mesoscopic both for artificial self-propelled objects and for living creatures, a booming future of inertial active systems is lying ahead."[7] Really, there has been a pronounced trend within recent years to investigate both theoretically and experimentally the so-called *ballistic regime* of Brownian motion and its different applications, particularly in the study of the self-propulsion for active particles (for an extended discussion of this subject, see Refs. 8–10).

The current paper is laid out as follows. In Sec. II, we consider the physical background of the problem and briefly discuss mathematical methods to solve it. Pursuing pedagogical goals and keeping in mind further refinements to include inertial effects, classical Smoluchowski's theory is described in Sec. III. Section IV contains a summary on the existing theories, which revise the Smoluchowski theory to take into account inertial effects. Next, Sec. V begins with a description of the Cattaneo–Vernotte differential model analog for diffusion. Then, we derive an appropriate HDE and general integral expression for the relevant local diffusive flux of particles. In Sec. VI, the physical and mathematical formulation of the hyperbolic Cauchy–Dirichlet initial boundary value problem and its solution were considered. Section VII comprises rigorous analytical calculations of the desired reaction rate coefficient and corresponding Rice's approximation. The discussion of the obtained results are given in Sec. VIII. Finally, Sec. IX draws the main conclusions of the present study. For the convenience of the readers, we added the Appendix, which contains some mathematical definitions, notations, and formulas used in this paper.

II. INTRODUCTION

As a consequence, we shall evaluate analytically the rate coefficient for the irreversible trapping of small Brownian particles (for brevity, we call them B particles) by spherical static sinks distributed randomly in three-dimensional (3D) host media. Throughout this paper, we study the homogeneous and isotropic host media. Under the assumption of isotropy and homogeneity of the given host media, the evolution of B particles is often characterized by some finite scalar values called *diffusion relaxation times*. This case can lead to significant inertial effects for short-time scale reaction dynamics, which should be taken into account. For simplicity's sake, we shall consider here only the field-free hyperbolic diffusion of B particles.

Here, we will clarify the physical and mathematical models underlying in the basis of the diffusion theories. Furthermore, we present Smoluchowski's diffusion theory in sufficient detail since it will be straightforwardly generalized to the required case of the hyperbolic diffusion. Moreover, the following should be emphasized from the first. Considering that one of the main objectives of this paper is to derive an exact formula for the rate coefficient, which resulted due to the use of the relevant hyperbolic initial boundary value problem, we focus our special attention on the correct mathematical definitions, statements, and solutions to the problems in the diffusion theories.

Therefore, keeping in mind the above main objective of our study, for the sake of clarity, first, we shall present here a sketch of the classical Smoluchowski theory following standard approaches.[1,11]

A. General background

Two classical Fick diffusion laws are appropriate in describing various diffusive transport phenomena, including Brownian motion for the most cases of common physical applications in nature and industry.[12]

It is common knowledge that from a mathematical point of view, the theory of diffusion transfer is the counterpart of the heat transfer theory. Very often, they both may be reduced to the study of various initial boundary value problems for the linear partial differential equations of parabolic type. At the present time, the latter problems are well elaborated in mathematical physics and form a strong mathematical background, in particular, for describing diffusion, usually called *classical theory of diffusion*.[13,14]

B. Physical model

Consider now the physical background of the problem. We shall study here Brownian motion with the subsequent reaction of non-self-interacting reactants of sort B (see, e.g., Ref. 15 for effects of interactions of particles B) in a stagnant liquid non-reactive homogeneous and isotropic host medium. B particles are small enough to treat them as point-like particles. Assume that reactants B diffuse toward much larger active non-overlapping static sinks A with very quick irreversible trapping of these reactants by the whole surface of these sinks after the contact. Thus, we treat a diffusion-controlled reaction as ultrafast, i.e., the characteristic reaction time is supposed to be negligibly short.[16] In addition, we also assume that both reactants are uncharged and spherical and the diffusion interaction (many-body effects reflecting the mutual influence of the sinks on diffusion and depletion of B particles) between sinks may be ignored.[3] Furthermore, sinks are assumed to act as traps of infinite capacity. The theory should describe the changes of B reactant local concentration due to both their Brownian motion and the subsequent ultrafast reaction events on the static sinks A.

Since the pioneering work of Smoluchowski published in 1916,[17] such kinds of processes are quite successfully described theoretically by the so-called *Smoluchowski trapping model of the irreversible bulk diffusion-controlled reactions*.[1,15,18–21] Hence, for the assumptions given above, we shall investigate the case of diffusion toward a single spherical sink of radius R, whose center, for convenience sake, we locate at the origin O. Hereafter, $R = R_A + R_B$ is the radius of the reaction sphere (or encounter radius) and R_A and R_B are the van der Waals radii of reactants A and B. Moreover, since B's assumed to be point-like particles (i.e., $R_B \ll R_A$), one can set $R \approx R_A$. In the final run, this reduction leads to a spherically symmetric diffusion problem, which allows us to derive the exact analytical expressions for the distribution of particle B around a sink.[22]

The Smoluchowski theory or, more precisely, Smoluchowski Brownian coagulation theory[17,20] gained wide acceptance due to its physical clarity, mathematical simplicity, and essential accord between theoretical calculations and experimental results on various diffusion-controlled processes for the long time characteristics.[1] Therefore, consider an irreversible bulk diffusion-controlled trapping of B particles in a nonreactive host medium of a large macroscopic size with excess suspended static sinks A, as is usually the case in many applications. These reactions occur by the simple bimolecular reaction scheme,[15,20,23]

$$A + B \xrightarrow{k(t)} A + P, \tag{1}$$

where P is a product of the reaction and, according to Smoluchowski's theory, the reaction rate coefficient $k(t)$ should be taken as a time-dependent positive function $k(t) > 0$ for all $t > 0$, being calculated by means of a solution to some initial boundary value problem for the relevant diffusion equation.

The kinetic equations and initial conditions (Cauchy problems) corresponding to scheme (1) are

$$\frac{dc_B(t)}{dt} = -k(t)c_A c_B(t), \quad \frac{dc_A}{dt} = 0, \quad t > 0, \tag{2}$$

$$c_B(t)|_{t\to 0+} \to c_B^0, \quad c_A(t) \equiv c_A^0 = const, \tag{3}$$

where $c_A(t)$ and $c_B(t)$ are the bulk concentrations of reactants A and B.

C. Mathematical model

Thus, by the required solutions to the diffusion equations in a given domain of the 4D augmented configuration space (see Fig. 1), we mean the *probability of finding* a diffusing particle B around the reaction boundary of a test sink at a position $\mathbf{x}$ and at a moment t, which will be denoted for classical and hyperbolic diffusion as $w(\mathbf{x}, t)$ and $\rho(\mathbf{x}, t)$, respectively.

Remark 1. Note that for the identical, noninteracting B particles, a desired probability function may also be treated as the local concentration of B particles.[3]

For more formalization of the classical Smoluchowski theory, we recall the known *diffusion-controlled reaction* (DCR) *postulates* to use the classical diffusion description for the diffusion-controlled reactions.[18]

(1) The physical system, comprising chemically active reagents, is in thermal equilibrium, and at times $t < 0$, no reaction occurs.
(2) The specific form of the initial (as $t \to 0+$) and boundary conditions on the reaction surfaces for the diffusion equation is completely determined by the features of chemical and physical processes under study. In other words, the specific boundary condition describes boundary inherent physical and chemical nature.
(3) The diffusion problem can be reduced to study the motion of many B particles surrounding a single static sink A.

Remark 2. Mention should be made of another alternative approach to evaluate the reaction rate. The required rate may be found with the help of the survival probability of B particles, reacting with sink A. However, discussion on this subject is not our task in the present work.

According to the second postulate, we assume here that the reaction between B and A to form a product P is very fast, and therefore, we shall pose the perfectly absorbing boundary condition on the reaction surfaces. This condition appeared to be the homogeneous Dirichlet boundary condition. Throughout this paper, for brevity sake, we shall term the initial boundary value problems with the Dirichlet boundary condition for both linear parabolic and hyperbolic diffusion equations as *Cauchy–Dirichlet problems*.

It may be shown that the third DCR postulate directly yields that the motion of particles B obeys two Fick's laws of diffusion. In particular, note that the third DCR postulate is at the heart of the classical diffusion theory, and to describe inertial effects, it will be changed in Sec. V. In this connection, we will stress that here the term classical diffusion theory will be used for the parabolic diffusion theory within Smoluchowski's trapping model for the diffusion-controlled reactions.

For pedagogical reasons, to use a straightforwardly similar mathematical approach in the case of the hyperbolic diffusion (see Sec. V), in Sec. III, we will outline the corresponding solution to the classical diffusion rather thoroughly.

Remark 3. Finally, it is pertinent to note that classical solutions for both parabolic and hyperbolic Cauchy–Dirichlet problems are well-posed in cases of interest to us even when they do not obey the known initial boundary compatibility conditions.[13]

III. SMOLUCHOWSKI'S THEORY

Thus, we use here Smoluchowski's approach, which allows us to reduce the original problem to calculating the flux of diffusing B particles' trapping by only one sink, which is suspended in a host medium with B's. Keeping in mind further refinements of the Smoluchowski theory in order to include inertial effects, we present here a slightly modified solution of the appropriate spherically symmetric linear parabolic Cauchy–Dirichlet problem outside a spherical sink. This approach is based on the reduction of the original problem to the similar one, posed in the semi-infinite slab domain.

A. Statement of the problem

As already mentioned above, it is sufficient to consider diffusion of B's toward a test 3D spherical sink of radius R placed in the origin of the global coordinates $\{O;\ \mathbf{x}\}$. Hence, we assume that given sink occupies the ball domain, $\Omega := B_R(\mathbf{0}) = \{\mathbf{x} \in \mathbb{R}^3 : \|\mathbf{x}\| < R\}$, where $\|\cdot\|$ stands for the common Euclidean norm. As is customary, let $\partial\Omega$ denote the boundary of a domain Ω such that $\overline{\Omega} = \Omega \cup \partial\Omega$, where the bar symbol denotes the closure. In addition, let $(\mathbf{x}, t) \in \mathbb{R}^{3+1} := \mathbb{R}^3 \cup \mathbb{R}_+$ such that $\mathbf{x} \in \mathbb{R}^3$ and $t \in \mathbb{R}_+ := (0, +\infty)$ (see Fig. 1).

For the both parabolic and hyperbolic Cauchy–Dirichlet problems, we need the following.

Definition 1. Cylindrical evolution domain $Q \subset \mathbb{R}^{3+1}$ *with the bottom base* $\Omega \subset \mathbb{R}^3$ *at* $t = 0$ *is the set of points* $(\mathbf{x}, t)$ *such that* $Q := \Omega \times \mathbb{R}_+$.

Thus, the *exterior of the cylindrical domain Q* is the partially bounded domain $Q^- := \mathbb{R}^{3+1}\backslash\overline{Q} = \Omega^- \times \mathbb{R}_+$, where $\Omega^- := \mathbb{R}^3\backslash\overline{\Omega}$. Diffusion of B's occurs in Ω^-, and space-time domain Q^- is often called the *augmented configuration space*.

The surface $\Gamma := \partial\Omega \times \overline{\mathbb{R}}_+$ is termed the *lateral boundary of the cylinder Q associated with* Ω. The boundary $\partial Q = \Omega \cup \Gamma$ (see Fig. 1) is often called a *glass*.

We shall treat the free Brownian diffusion of point-like particles B through a homogeneous and isotropic host medium Ω^- and their instant reaction upon the contact with the spherical reaction surface of a sink $\partial\Omega = \partial B_R(\mathbf{0})$ called *perfectly absorbing sink*. Hereafter, boundary $\partial\Omega$ does not depend on time t. Furthermore, one can see that the diffusion of B particles is radial; therefore, for the problem at issue, it is expedient to use the spherical coordinates, attached to the origin O, coinciding with the sink center (i.e., $\|\mathbf{x}\| = r$). Therefore, we are looking for the radial basis function $w(r,t)$ (*time-dependent probability function* of the form $w : Q^- \to [0,1)$). In addition, it is common to assume that initially, the diffusing particles were scattered uniformly within the whole domain Ω^- of the host medium.

According to Smoluchowski, evolution of the required particle distribution function $w(r,t)$ is governed by the classical diffusion theory. Thus, a relevant external Cauchy–Dirichlet problem for the parabolic diffusion equation reads[1]

$$\frac{\partial w}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial w}{\partial r}\right) \quad \text{in} \quad Q^-, \tag{4}$$

$$w(r,t)|_{t\to 0+} \to 1 \quad \text{in} \quad \Omega^-, \tag{5}$$

$$w(r,t)|_{r\to R+} \to 0 \quad \text{in} \quad \Gamma, \tag{6}$$

$$w(r,t) \in L^\infty(\overline{Q}^-). \tag{7}$$

Hereafter, the space $L^\infty(\overline{X})$ is defined as the set of all uniformly bounded, real functions in domain $\overline{X}$. On the reaction surface $\partial\Omega$, we imposed here the homogeneous Dirichlet boundary condition (6), which in various applications to physics, chemistry, and biology is commonly called the *Smoluchowski reaction boundary condition.*[1] It is clear that physically, this condition accords with the case of a perfectly absorbing sink. Moreover, to obtain a unique solution $w(r,t)$ of the above problem, we require its boundedness in $\overline{Q}$, i.e., condition (7). One can show that this condition corresponds to the *regularity condition at infinity*, which should be imposed for the external elliptic problems, describing the steady state diffusion.[24]

Remark 4. Note that contrary to the corresponding steady state problems, here, we do not need to impose this rather strong regularity condition at infinity.[13] *Nevertheless, many non-mathematical works persistently use this unnecessary condition in the statements of appropriate initial boundary value problems (see, e.g., Refs. 25–28). These papers usually assert that to complete the mathematical statement of the above external diffusion problem, one should also require the regularity condition at infinity,*

$$w(r,t)|_{r\to+\infty} \to 1 \quad \textit{for all} \quad t > 0. \tag{8}$$

Furthermore, they even indicate the physical meaning of condition (8), claiming that the desired function $w(r,t)$ *very far from an absorbing sink should not be perturbed by this sink.*

Finally, it is important to note that throughout this work by a solution to the Cauchy–Dirichlet problems posed for the parabolic and hyperbolic diffusion equations, we shall mean the corresponding classical solutions, irrespective to the type of these equations.[13]

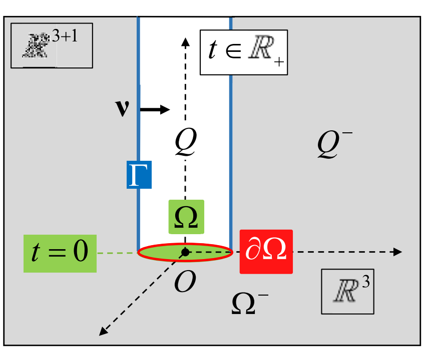

FIG. 1. Sketch of the geometrical components corresponding to the initial boundary value problem for the diffusion equations. The gray shaded region here indicates the 4D augmented configuration space $Q^- = \Omega^- \times \mathbb{R}_+ \subset \mathbb{R}^{3+1}$ for B particles.

B. Calculation of the classical rate coefficient

The main objective for the Smoluchowski theory in finite sink arrays is to calculate the total trapping rate of B particles by the reaction surface $\partial\Omega$ of a given sink,

$$k(t) = \int_{\partial\Omega} \boldsymbol{\nu}(\mathbf{x},t) \cdot \mathbf{j}(\mathbf{x},t)|_{\partial\Omega} dS. \tag{9}$$

Here, $\boldsymbol{\nu}(\mathbf{x},t)$ is the normal unit vector pointing outward of Q^- at its spatial $\mathbf{x} \in \partial\Omega$ and temporal $t > 0$ points (as shown in Fig. 1). The integration is performed over whole reaction surface $\partial\Omega$ at a fixed instant t.

Often, to study the influence of different effects (e.g., for describing diffusive interaction between sinks[3]), it is convenient to reduce the reaction rate coefficient (9) by its steady state value $k_S^0 := 4\pi DR$, which is usually called the *Smoluchowski rate constant*[1] [see Eqs. (30) and (31)]. Thus, we introduce the dimensionless *reduced rate coefficient,*

$$k^*(t) = k(t)/k_S^0. \tag{10}$$

From here on, in the present study, we shall mostly use the reduced rate coefficient (10).

Hence, the key point of the theory is how to find the exact expression for the local diffusive flux $\mathbf{j}(\mathbf{x},t)$ in general formula (9). This can be done with the aid of known solution $w(\mathbf{x},t)$ to the Cauchy–Dirichlet problem (4)–(7) and appropriate constitutive relation, which connects scalar field $w(\mathbf{x},t)$ with vector field $\mathbf{j}(\mathbf{x},t)$. The classical constitutive relation is the well-known first Fick's law of diffusion,[1]

$$\mathbf{j}(\mathbf{x},t) := -D\nabla w(\mathbf{x},t). \tag{11}$$

Using the spherical symmetry of problems (4)–(7), one can readily recast general equations [Eqs. (9) and (11)] in spherical coordinates and obtain

$$k^*(t) = R\frac{\partial}{\partial r}w(r,t)\bigg|_{r\to R+}. \tag{12}$$

C. Solution of the problem

Although the solution to the posed classical parabolic Cauchy–Dirichlet problem [(4)–(7)] is well known,[1,13,14] we will find it by a slightly modified approach, which is convenient for our later generalization to the case of the relevant hyperbolic Cauchy–Dirichlet problem.

First, let us recall known Kelvin's transformation.

Definition 2. Transformation $w \mapsto u$, $r \mapsto r^*$ is called Kelvin's one if the following relations hold:

$$u(r^*,\theta,\phi) = rw(r,\theta,\phi), \tag{13}$$

$$r = 1/r^*, \tag{14}$$

where (14) is a spatial inversion.[13]

This definition in its turn allows us to introduce the following.

Definition 3. We define the incomplete Kelvin transformation $1 - w \mapsto v$; $(r,t) \mapsto (r,t)$ as follows:[14]

$$r[1 - w(r,t)] = Rv(r,t). \tag{15}$$

Clearly, this relation is nothing but Kelvin's transform (13) if one does not perform corresponding spatial inversion (14).

Remark 5. We have to emphasize that generally, a spatial part of (15) is a 3D transform, namely, mapping of the exterior of the ball domain Ω^- to the 3D semi-space: $\Omega^- \to \mathbb{R}_+^3 := \{\mathbf{x} \in \mathbb{R}^3 : x > 0\}$. However, due to the spherical symmetry of our problem, formally, we have 1D to 1D spatial transform.

Hence, one formally reduces the posed problem to the case with 1D symmetry, with respect to an auxiliary function depending on the spatial variable x alone.

For the further consideration, it is convenient to look for the solution of problems (4)–(7) as an ansatz, written with the help of transform (15) in the form

$$w(r,t) = 1 - \frac{R}{r}v(x,\tau). \tag{16}$$

Ansatz (16) defines an auxiliary function $v : Q_x^- \to (0,1]$, where the corresponding domain transform reads $Q^- \mapsto Q_x^- := \mathbb{R}_+^2 = \mathbb{R}_+ \times \mathbb{R}_+ = \{x > 0\} \times \{\tau > 0\}$. Corresponding linear transformation to the dimensionless variables $(r,t) \mapsto (x(r),\tau(t))$ reads

$$x(r) := \frac{r}{R} - 1 \ge 0, \quad \tau(t) := \frac{t}{t_D} \ge 0. \tag{17}$$

Here, we normalized time by the *characteristic duration of the diffusional encounter on the reaction sphere of radius R*[21] or just the *diffusion time,*

$$t_D := R^2/D. \tag{18}$$

Obviously, the auxiliary function $v(x,\tau)$ in (16) is uniquely determined by the following dimensionless 1D Cauchy–Dirichlet problem:

$$\frac{\partial v}{\partial \tau} - \frac{\partial^2 v}{\partial x^2} = 0 \quad \text{in} \quad Q_x^-, \tag{19}$$

$$v(x,\tau)|_{\tau\to 0+} \to 0, \quad x \in \mathbb{R}_+, \tag{20}$$

$$v(x,\tau)|_{x\to 0+} \to 1, \quad \tau \in \mathbb{R}_+, \tag{21}$$

$$v(x,\tau) \in L^\infty\left(\overline{Q_x^-}\right). \tag{22}$$

It is clear that using this initial boundary value problem, one can describe the distribution of B particles $1 - v(x,\tau)$ outside the perfectly absorbing boundary $\{x = 0\}$ of a semi-infinite slab $\{x < 0\}$.

Simple calculations show that ansatz (16) leads to the basic formula,

$$\frac{\partial}{\partial r}w(r,\tau)\bigg|_{r\to R+} = \frac{1}{R}\left[1 - \frac{\partial}{\partial x}v(x,\tau)\bigg|_{x\to 0+}\right], \tag{23}$$

whereas the first term in the right-hand side $1/R$ describes the *curvature effects.*[29] Thus, we have the following.

Theorem 1. *Solution w(r, t), describing the spherically symmetric diffusion of B particles toward a spherical perfectly absorbing* *sink [(4)–(7)], is connected with appropriate auxiliary solution $1 - v(x,\tau)$ for diffusion of B's to a perfectly absorbing semi-infinite slab [(19)–(22)] by means of (16).*

This implies evident.

Corollary 1. Using relation (23), the formula for the reduced rate coefficient (12) may be rewritten in the most simplified form,

$$k_S^*(\tau) := \frac{k_S(\tau)}{k_S^0} = 1 + k_x^*(\tau), \tag{24}$$

$$k_x^*(\tau) := -\frac{\partial}{\partial x}v(x,\tau)\Big|_{x\to 0+} \to \frac{1}{\sqrt{\pi\tau}}. \tag{25}$$

Thus, we have obtained the reduced classical Smoluchowski rate coefficient (24), where a part responsible for the trapping rate upon the slab boundary wall $k_x^*(\tau)$ (25) was highlighted.

Remark 6. Hence, it is evident that singular behavior of the function $k^*(\tau)$ at short times is entirely caused by the slab part of this rate coefficient (25), i.e.,

$$k_x^*(\tau) = \frac{1}{\sqrt{\pi\tau}} \to +\infty \quad \text{as} \quad \tau \to 0+. \tag{26}$$

The solution to the Cauchy–Dirichlet problem [(19)–(22)] is well known, so we write down solution and its derivative with respect to x and also corresponding Laplace transforms, which are denoted by overbars,[30]

$$\begin{aligned} &\overline{v}(x;s) = \frac{1}{s}\exp(-\sqrt{s}x), && \frac{d}{dx}\overline{v}(x;s) = -\frac{1}{\sqrt{s}}\exp(-\sqrt{s}x),\\ &v(x,\tau) := \mathrm{erfc}\left(\frac{x}{2\sqrt{\tau}}\right), && \frac{\partial}{\partial x}v(x,\tau) = -\frac{1}{\sqrt{\pi\tau}}\exp\left(-\frac{x^2}{4\tau}\right). \end{aligned} \tag{27}$$

Hereafter, $\mathrm{erfc}(y)$ is the complementary error function.[31]

Hence, we readily get the important statement.

Lemma 1 (on commutativity). For the Cauchy–Dirichlet problem [(19)–(22)], the following property holds true:

$$\lim_{x\to 0+}\frac{\partial}{\partial x}\mathcal{L}^{-1}\{\overline{v}(x;s)\} = \mathcal{L}^{-1}\left\{\lim_{x\to 0+}\frac{d}{dx}\overline{v}(x;s)\right\}. \tag{28}$$

Taking into account Theorem 1 and Lemma 1, one can infer the following.

Theorem 2. *To find the trapping rate coefficient in the case of reactions described by the parabolic Cauchy–Dirichlet problem [(19)–(22)], it is sufficient to find the Laplace inverse for the derivative of the corresponding Laplace transformed solution $\overline{v}(x;s)$ with respect to x at the auxiliary slab boundary $\{x = 0\}$.*

By means of Theorem 1, we can solve Cauchy–Dirichlet problem [(4)–(7)] and obtain a well-known solution,[17]

$$w(r,t) = 1 - \frac{R}{r}\mathrm{erfc}\left(\frac{r-R}{2\sqrt{Dt}}\right) \quad \text{in} \quad Q^-. \tag{29}$$

Rewriting formula (24) in the original dimension form, we arrive at famous Smoluchowski's trapping rate coefficient,[1,17]

$$k_S^*(t) = 1 + \frac{R}{\sqrt{\pi D t}} \quad \text{for} \quad t > 0, \tag{30}$$

$$\lim_{t\to+\infty} k_S(t) = 4\pi R D. \tag{31}$$

D. Drawbacks of the classical diffusion theory

An important point is that Riemann already in the 19th century obtained a result of great importance for both heat and diffusion theories. He proved that the parabolic thermal conductivity operator corresponds to a strictly defined class of isothermal surfaces, and it is impossible to go beyond this class by any modifications of the initial and boundary conditions.[32] Unfortunately, Riemann's work[32] has not caught the attention for long time, and only by the mid-20th century, a number of authors called their attention to the serious drawbacks of the classical heat and diffusion transfer theory.[33] In summary of this brief theory survey of Smoluchowski, we have to point out a couple of important theoretical drawbacks of the classical diffusion theory, which are common to call paradoxes.[33]

Paradox 1. It has long been known that the use of the classical diffusion equation predicts an unphysical effect of an infinite propagation velocity of a diffusive perturbation, which is known in the literature as *paradox of infinite velocity* or, more precisely, *paradox of infinite speed of propagation of diffusion perturbations*.[34] Since this paradox was many times and comprehensively considered (see, e.g., Ref. 33), we shall not dwell on it here.

Paradox 2. Surprisingly, little attention had been paid, however, to another important paradox, which, as far as we know, was revealed for the first time by Planck in 1930.[35] This paradox is that classical theory leads to unphysical singular behavior of the heat local flux on a boundary as $t \to 0$. Independently, in their seminal paper of 1949, Collins and Kimball have also drawn attention to this fact, which compromise the Smoluchowski diffusion theory: "In most cases, the flux falls to a reasonable value in an extremely small time, and the total amount of reaction predicted is finite, but, nevertheless, the singular rate at $t = 0$ is a blemish on the theory"[36] [see (26)]. Thus, it is reasonable to call this unphysical local flux behavior as $t \to 0$ the *zero time paradox*.

The cause of **paradox 2** can be shown to be in violation of the so-called *compatibility condition* between initial (5) and boundary (6) conditions.[13] Really, in the case of the Cauchy–Dirichlet problem [(4)–(7)], one has the following incompatible iterated limits:

$$\lim_{t\to 0+}\left[\lim_{r\to R+} w(r,t)\right] = 0, \tag{32}$$

$$\lim_{r\to R+}\left[\lim_{t\to 0+} w(r,t)\right] = 1. \tag{33}$$

Finally, note in passing that a comprehensive discussion on the full set of now known classical diffusion theory paradoxes the interested reader can find in an informative book (Ref. 33).

Thus, the imperfection inherent in the parabolic theory of diffusion leads to a number of parabolic equation paradoxes and also the so-called *ill-posed boundary value problems*.[13] Therefore, to describe adequately diffusion transfer, one should extend the class of parabolic initial boundary value problems.

IV. EXTENSIONS OF SMOLUCHOWSKI'S THEORY

In succeeding years to improve the Smoluchowski diffusion theory, a number of its modifications appeared.

A. Collins–Kimball revisit

For the first time, a comprehensive critical analysis of the Smoluchowski theory was given by Collins and Kimball in 1949.[36] The classical Smoluchowski model was modified to the so-called Smoluchowski–Collins–Kimball (SCK) model.[37] To resolve the zero time paradox, they, particularly, proposed to replace Smoluchowski's boundary condition of a perfectly absorbing sink by the *Collins–Kimball (or radiation) boundary condition*. This condition corresponds to having a probability of reaction due to the encounter of a particle B and a sink A that is less than 1.[19] The SCK analysis lies a little apart from our study, and moreover, it was widely discussed in the literature for many years.[1,18–21] Hence, here, we do not dwell on the SCK correction any more.

B. Noyes revisit

Subsequently, in 1961, Noyes thoroughly revised Smoluchowski's theory.[38] Here, it is expedient to cite known Weiss's review paper published in 1986. "Noyes … proposed to overcome the difficulty in Smoluchowski's theory in a more phenomenological way by introducing an encounter density, $h(t)$, defined so that $h(t)dt$ is the probability that two particles separating from a nonreactive encounter at $t = 0$ will react with each other for the first time between t and $t + dt$. Noyes then writes for $k(t)$, the expression

$$k(t) = k(0)\left(1 - \int_0^t h(z)dz\right), \tag{34}$$

where $k(0)$ is the rate constant derived from equilibrium statistics."[39]

One can see that the Noyes rate coefficient (34) also resolves the zero time paradox: $k(t) \to k(0) < +\infty$ as $t \to 0$. However, with that, Noyes claimed that using Eq. (34), we cannot get an exact value for the rate coefficient at short times: $0 < t \lesssim 10$ ps.[38]

Remark 7. It should be noted that thereafter, the equivalence of the Collins–Kimball and Noyes approaches has been demonstrated by several authors (see Ref. 40 and the references therein).

C. On some subsequent generalizations

Many various refinements have subsequently been made to develop a simple Smoluchowski trapping model. Here, we just give a brief summary of some appropriate extensions only.

Generally speaking, on other theories, one should take into account DCR postulates mentioned in Sec. II. Accordingly, we agree with Torney and McConnell, who believed that all known theories that calculate a classical trapping rate coefficient are identical if they use the same initial and boundary conditions for the classical diffusion equation (4).[41] By means of the known generalized Langevin equation, Dong and Andre suggested the so-called *generalized diffusion equation* method.[42] The Dong–Andre theory easily resolves the zero time paradox; however, one can see that this approach leads to the infinite velocity paradox, and that is exactly the same lack as in the classical Smoluchowski theory case.

Worthy of mention is the *step function non-radiative lifetime model*, which assumes that the reaction occurs with a given constant probability when the distance between particles B and sink A becomes lower than some given value R.[19] It turned out that this model describes some experimental results better than the classical SCK model.[37]

In addition, subsequently, essential attempts were also performed to generalize Smoluchowski's theory in different aspects;[23,39,43–45] however, this topic requires a separate and comprehensive consideration.

V. HYPERBOLIC DIFFUSION THEORY

Although, using the SCK model, one can formally resolve the zero time paradox of the classical diffusion theory, the physical reason of this paradox stems from the fact that Fick's law neglects the inertia of B particles, i.e., this model is assumed that the distribution gradient causes the particles flux instantly. Consequently, we come to the conclusion that it is infeasible to describe theoretically required inertial effects, while remaining within the framework of the SCK model from a conceptual point of view.

A. Preliminary considerations

In addition to the above paradoxes, often, parabolic diffusion theory does not reproduce correctly even behavior of freely diffusing particles for short times and high magnitudes of the probability gradients $\nabla w(\mathbf{x}, t)$. It has been found that, from a physical point of view, this anomaly of the classical diffusion theory follows from the assumption that the particles local flux vector fields $\mathbf{j}(\mathbf{x}, t)$ and $\nabla w(\mathbf{x}, t)$ across some fixed macroscopic material volume occur at the same instant of time t. In other words, for some real host media, the diffusive flux of particles B also depends on the history of the whole relaxation process.

Thus, it is evident from the foregoing discussion that classical processes of diffusion transfer for B particles should be slow and corresponding probability gradients should be small enough in order to use Fick's approximation (11). However, these requirements are not always fulfilled in applications, and therefore, one should go beyond this approximation to take into account inertial effects at short time values.[46] Hence, we can naturally suggest the idea to treat the motion of B particles at small times as a wave like one with some damping. The latter leads to the mathematical description with the help of the hyperbolic diffusion approximation.

To study this case quantitatively, one can introduce the *characteristic diffusion relaxation time* or the *velocity correlation time* τ_D [see Eq. (35)] as the time value required to create conditions in the physical system under which the first Fick's law becomes correct. Simply speaking, τ_D is the time required for the velocity of a B

particle to randomize due to collisions with ambient solvent molecules of the host medium. One can see that the larger the τ_D, the more profound these memory effects, and obviously, values of the relaxation time τ_D depend on the physical properties of the host medium.[47]

It has been found experimentally that diffusion-controlled processes with above relaxation effects (for definiteness, in our paper, these effects are referred to as the inertial effects) are observed in a variety of engineering, physical, chemical, and biological applications, such as acoustics, combustion noise, and the melting process, which is driven by an influx of thermal energy from the environment, diffusion transfer in skin tissues, bacterial movement through a medium filled with a nutrient, turbulence diffusion transfer, etc.[1,18,47–52]

Remark 8. One has to note the lack of coordination for notions in modern diffusion theory. At the present time, many different terms: momentum relaxation, relaxation (effect), short-time, memory, non-Fickian, nonlocal, and inertial effects, are used in the literature as synonyms.

An additional important point to emphasize is that while various aspects of thermal inertial effects in the heat transfer problems have been intensively studied for many years and still are actively studied at present (see, e.g., only recent comprehensive reviews given in Refs. 53–56), the influence of inertia effects on the particles diffusion transfer has been relatively poorly investigated. Therefore, we can mention here only a few important works on the hyperbolic diffusion and its applications published over the past 50 years.[22,47,49,57,58] Works on the hyperbolic diffusion equation for the spin magnetization and relativistic Brownian motion are worthy of special attention as well.[59,60]

B. Physical background and early studies

It turns out that the above drawbacks of the classical diffusion equation can be naturally eliminated by replacing it with a hyperbolic diffusion equation, whose behavior is more satisfactory for short times $0 < t \lesssim \tau_D$ and, at the same time, has equivalent long-time properties for $\tau_D \ll t$. To resolve the paradox of infinite speed, Morse and Feshbach just postulated that the diffusion equation is hyperbolic, which depends on the finite velocity of the diffusive disturbance propagation.[61] However, discussing his failure to describe the short-times kinetics by means of classical diffusion, Noyes, nevertheless, pointed out that a hyperbolic diffusion regime "...is unimportant for currently conceivable experimental applications."[38] In this connection, the authors of the paper by Rice *et al.*[62] also concluded that "...the results given for the times less than 1 ps must be considered as having mathematical meaning only." An important point is that later progress in ultrafast laser spectroscopy at the present time allows us to study dynamics of reactions on extremely short time scales, again making this aspect of the theory an important field in current research.[16]

Nevertheless, a number of authors have repeatedly raised this question in early physics studies on hyperbolic diffusion applied to the diffusion-controlled reactions. To our knowledge, the first attempt to prove classical diffusion approximation and apply the hyperbolic diffusion equation to describe diffusion-controlled reactions was made by Monchick.[63,64]

Remark 9. In Ref. 1, Rice pointed out that there is another paper by Monchick that has also used the HDE to describe diffusion-controlled chemical kinetics. Unfortunately, this very reference is absent in the book, but it seems that most likely, Rice meant aforecited Monchick's work (Ref. 64).

Later on, independently, Doi and Kapral called attention to the fact that Smoluchowski's diffusion equation (4) is inappropriate for the description of the behavior of Brownian particles B for the short time.[43,65]

Remark 10. In turn, Tachiya showed that this behavior may be reformulated in terms of the motion of B particles within the diffusion boundary layer,[66] whose formation corresponds to the limit of very small Knudsen numbers, i.e., as $Kn := \lambda/R \to 0$, where λ is an average mean free path of a particle B.

Particularly, in his paper, Doi claimed that for the time interval $0 < t \lesssim \tau_D$, where the velocity correlation time is

$$\tau_D = m/\zeta, \quad \zeta = CR_B\eta, \tag{35}$$

the B particles behave as free particles. In Eq. (35), m represents the mass and ζ represents the friction coefficient of the B particle,[65] with η being the shear viscosity of the host medium and C being a numerical coefficient depending on the possible choices of the boundary conditions on the B particle surface (for the spherical B particle, we have the two-side bound $4\pi \le C \le 6\pi$). As seen from Eq. (35), the use of the term "inertial effects" is entirely justified by the dependence of τ_D on the mass of particle B. Note here that our definition of τ_D (35) is distinguished from that of τ_D^* given in Ref. 67 by factor 2, i.e., $\tau_D^* = 2\tau_D$.

In addition, the diffusion coefficient of a given B particle is related to its frictional coefficient by the Stokes–Einstein relation,

$$D = k_B T/\zeta, \tag{36}$$

where k_B is the Boltzmann constant and T is the absolute temperature of the host medium.

Rice derived his formula for the rate coefficient within the scope of the hyperbolic diffusion model.[1] Our principal concern will be given to the rigorous examination of this result in the present paper, so Rice's study is discussed below in all necessary details.

C. On other theories describing rates at short times

Continuing the short highlighting of works on the description of inertial effects, let us turn to the famous review on diffusion-controlled reactions by Calef and Deutch.[68] Therein, we can read as follows: "The diffusion equation is valid for timescales much larger than the momentum relaxation time of the macroparticle. Clearly, to discuss shorter times, a description that includes explicitly the particle's momentum should be adopted." Below, authors highlight the fact that to move beyond the classical Smoluchowski theory, one have to include momentum relaxation effects in the theory of diffusion-controlled reactions. Hence, here, it would be of special interest to mention briefly some attempts for extending the Smoluchowski theory by including the relaxation effects in time-dependent reaction dynamics.

In a comprehensive work of 1983, Hess and Klein have derived the memory-type transport system of the continuity equation and a modified constitutive relation. These authors also derived the corresponding hyperbolic short-time expansions for the diffusion flux $\mathbf{j}(\mathbf{x}, t)$ of B particles, but, unfortunately, they did not proceed to any applications of obtained equations.[69] Also worth noting is that rather sophisticated hyperbolic equation with respect to the deviation from the equilibrium function got Calef and Wolynes.[70] While in this paper, the authors noted the following: "…it is obvious that at such short times inertial effects are paramount," nonetheless, they have neglected the terms responsible for the inertial effects and studied the obtained parabolic diffusion approximation only. Later, in 1992, Hirata proposed a generalization of the Calef–Wolynes theory to apply it for describing the solvation dynamics, which occurs during the electron transfer reactions.[71] Noting the importance of the inertia term during short time period, nevertheless, Hirata assumed that in the general equation, this term can be ignored, and then, he considered a diffusion equation.

Starting from the classical Liouville equation, a general theory of the irreversible diffusion-influenced reactions taking into account non-Markovian effects was developed in Ref. 72. This theory substantially improved well-known Noyes and Wilemski–Fixman rate theories, providing a new effective method for calculating the rate coefficient at large and short time scales. Interested readers are encouraged to refer to the recent review by Lee, where the modified Wilemski–Fixman–Weiss approach in the theory of diffusion-influenced reactions is discussed, particularly, at short time scales.[73]

It is evident that the inertia effect in the short time region may be investigated with the help of the more simple Fokker–Planck–Kramers equation (FPKE) (see, e.g., Refs. 74–78 and the references therein). In its turn, the appropriate FPKE can also be derived from the corresponding stochastic Langevin equation.[77,79] An important point is that these theories naturally resolved both the above-mentioned paradoxes, compromising the Smoluchowski theory. However, at the present time, nontrivial initial boundary-value problems for the FPKE involving reactive boundary conditions cannot be solved analytically.[68,80]

An efficient *Brownian dynamics method* for evaluating inertial dynamic effects on diffusion-influenced reactions proposed by Lee and Karplus in 1987 was extensively employed.[80,81] "…it still fails to give an exact account of the short-time scale reaction dynamics."[80]

In a series of papers, Litniewski and Gorecki presented their results for spherical molecules by means of another widely used approach called *molecular dynamics simulations* (see Ref. 37 and the references therein). Particularly, they showed that the SCK model in the simplified version "fails completely for short times."[37,82] Moreover, Litniewski and Gorecki claimed that "within the simplified model, it is impossible to describe the initial stage of the process even qualitatively." It was nevertheless pointed out that the use of molecular dynamics simulations for a liquid of identical soft spheres at a large number of particles N (typically $N = 681\,472$[82]) allows us to obtain rather reliable quantitative results. Subsequently, Piazza and co-authors (see Ref. 83 and the list of the references therein) investigated numerically the rate coefficient for the diffusion-influenced reactions with inertia, taking into account the dependence on the volume fraction of sinks. They, particularly, showed that the standard Smoluchowski theory "… is recovered only at times greater than a characteristic time…, marking the transition from the under-damped to the over-damped regime."

Without going into detail, we shall simply note that non-Fickian diffusion in a system where mobile particles B can chemically react with static particles A according to rule (1) is also considered within a *persistent random-walk model*.[84] Furthermore, in the last few decades, great progress has been made to describe diffusion-controlled reactions of the form (1) by means of equations with both temporal and spatial fractional derivatives (see, e.g., Refs. 84–87 for lists of references).

A generalization of the Smoluchowski equation working for the case of polyatomic molecule system was derived by Kasahara and Sato.[88] Although they reported concerning drawbacks for the rate coefficient $k(t)$ in the short-time scales, even the zero time paradox has not been resolved within the scope of their approach, provided that the Smoluchowski boundary condition holds. A good agreement with the molecular dynamics simulations was found only for $k(t)$ in the long time region.[88]

D. Hyperbolic diffusion equation

Now, we can formulate the general physical problem on the free diffusion with inertia of B particles to be solved.

Numerical estimates of the characteristic physical parameters inherent to many really existing systems in nature and industry show that physical and chemical processes occur when the temperature field is already in local equilibrium.[47] If one denotes the *thermal relaxation time* as τ_T, it may be assumed that $\tau_T \ll \tau_D$ and for all points $(\mathbf{x}, t) \in \overline{Q}^-$ of the isotropic and homogeneous host medium. Indeed, according to the physical data presented by Sieniutycz,[89] in typical liquids for particles B of diameter range 10^{-7}–10^{-3} m, we have the corresponding relaxation time ranges: (a) $\tau_T = 10^{-11}$–10^{-13} s and (b) $\tau_D = 10^{-8}$–3 s. Therefore, it may be reasonably assumed that the temperature field $T(\mathbf{x}, t)$ obeys the common parabolic heat equation. Simultaneously, the diffusive flux field still remained time-dependent and establishes its equilibrium values.[18]

In addition, we suppose that the reaction occurs on a much shorter time scale as the time scales of relaxation phenomena, inherent to the given host medium. In addition, we expect that the hyperbolic theory will work well for $t \gtrsim \tau_D$ too. Indeed, the prevailing view today is that classical diffusion theory works well only for physical systems characterized by small values of the host medium diffusion relaxation time τ_D $(\tau_D \to 0)$ or for time values $t \gg \tau_D$ when the corresponding constitutive relation [see Eq. (38)] has the form of the first Fick's law (11). Moreover, it is common knowledge that hard-sphere simulations and a number of experiments showed that often the description with the help of the classical diffusion equation fails even for timescales much larger than τ_D.[90]

To describe inertial effects mathematically, we shall use the most popular approach called the *Cattaneo–Vernotte differential model*, which is based on the linear system of coupling equations.[33,47,54] Following this model for scalar $\rho(\mathbf{x}, t)$ and vector $\mathbf{j}(\mathbf{x}, t)$ fields given in the exterior of the cylindrical domain Q^-, we have the system of *continuity equation* and *constitutive relation*, respectively,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0, \tag{37}$$

$$\mathbf{j} + \tau_D \frac{\partial \mathbf{j}}{\partial t} = -D \nabla \rho. \tag{38}$$

The second term in the left-hand side of Eq. (38) is called the *diffusion-flux relaxation term*,[91] and due to this, this equation takes into account the relaxation to local equilibrium of the diffusion flux. Moreover, time derivative $\tau_D \partial \mathbf{j}/\partial t$ can also be regarded as a *diffusion inertia*, responsible for the inertial effects. It is clear that, provided that this term vanishes under condition $\tau_D = 0$, one retrieves here the classical first Fick's diffusion law. Hence, simultaneously, using Eqs. (37) and (38), we can study diffusion behavior for the time range[47]

$$\tau_T \ll t \lesssim \tau_D. \tag{39}$$

Note that continuity equation (37), being, in fact, a form of some conservation law, is an exact equation, whereas constitutive relation (38) is an approximation based on some physical assumptions. For example, constitutive relation (38) may be considered as a particular case of a general theory of heat and mass transfer with finite speeds proposed by Gurtin and Pipkin.[92] System of Eqs. (37) and (38) may be derived from more fundamental theories, e.g., from Boltzmann and Born–Green equations for rarefied gas and dilute solutions in liquid.[93] It was also shown that Eqs. (37) and (38) correspond to the first and the second moment equations under solution of the FPKE for Brownian particles.[94] Moreover, it is important to remember that the constitutive relation (38) may be treated as a differential equation, which is equivalent to introduce memory effects within the system. It is evident that constitutive relation (38) is a particular case of the so-called *dual-phase-lag models*.[56] However, one should emphasize that among other known models, resolving the paradox of infinite speeds, the Cattaneo–Vernotte differential model (38) is the most obvious and simple generalization of Fick's first law,[95] which contains the time derivative of the diffusive flux along with the flux itself.

Remark 11. Note that in hyperbolic diffusion theory, the constitutive relation (38) is most often termed Cattaneo–Vernotte equation and sometimes Maxwell–Cattaneo equation[96] following the terminology of much more elaborated hyperbolic heat theory. However, we believe that in the case of diffusion transport, it is more fair to call this constitutive relation as the Fock–Davydov equation, taking into account that for diffusion, it was derived independently and much earlier by Fock in 1926 and by Davydov in 1935, respectively (see, e.g., discussion in Ref. 97).

Combining Eqs. (37) and (38) in the domain Q^-, one can readily obtain the following HDE (or *telegrapher's equation*[98]):

$$\tau_D \frac{\partial^2 \rho}{\partial t^2} + \frac{\partial \rho}{\partial t} = D\nabla^2 \rho. \tag{40}$$

One can see that Eq. (40) as $\tau_D \to 0$ may be treated as a singular perturbed pure diffusion equation,

$$\frac{\partial w}{\partial t} = D\nabla^2 w. \tag{41}$$

In the shorthand notation, HDE (40) may be recast as follows:

$$\Box\, \rho(\mathbf{x}, t) = -\frac{1}{D}\frac{\partial}{\partial t}\rho(\mathbf{x}, t), \tag{42}$$

where the box symbol denotes the d'Alembertian operator: $\Box := \partial^2/c^2\partial t^2 - \nabla^2$. Thenceforth, c stands for the wave velocity and ∇^2 is the 3D Laplacian of a scalar field. A simple inspection of Eqs. (40) and (42) shows that $c^2 := D/\tau_D$ (see Sec. VIII for details).

Remark 12. Note in passing that Eq. (40) is a particular case of the general telegrapher's equation,[1,99–101]

$$\tau_D \frac{\partial^2 \rho}{\partial t^2} + \frac{\partial \rho}{\partial t} + b\rho = D\nabla^2 \rho, \tag{43}$$

where b is a constant.

We shall study here the diffusion problems with the reaction for the linear HDE only. For a discussion of a general nonlinear hyperbolic reaction–diffusion equation, see, e.g., Ref. 102.

Equations (40)–(43) are also known in the literature (especially in the mathematical one) as the *linear damped-wave equation*.[50] Evidently, for Eqs. (40)–(43), terms with $\partial\rho/\partial t$ are the *damping terms* that dampen the diffusive wave motion. Formally, the damping term may be removed by means of the standard substitution,[98]

$$\rho(\mathbf{x}, t) = \exp(-t/2\tau_D)\, v(\mathbf{x}, t). \tag{44}$$

Original HDE (42) is reduced to another useful form,

$$\Box\, v(\mathbf{x}, t) = \frac{1}{4c^2\tau_D^2} v(\mathbf{x}, t). \tag{45}$$

At first glance, it would seem that an approach based on the FPKE is the most preferable for the use of the HDE. However, it turns out that this statement is not always the case. First of all, the above method has the grave disadvantage described in Ref. 78: "…no exact solution has been derived for the FPKE under the boundary condition suitable for the reaction dynamics problem."

Remark 13. Most remarkably, surprisingly enough, it was found that often the HDE (40) behaves much more satisfactory than even kinetic FPKE, which is used to derive the HDE.[74]

A particular emphasis was stressed on this fact by Jou *et al.* in their famous book (Ref. 91), where a plausible explanation of this interesting behavior has also been suggested. Indeed, concerning this context, they claimed the following:[91] "The reason for the much more satisfactory behavior of the telegrapher equation is that it preserves the characteristic speed of the walker, d/t_0, in contrast to the Fokker–Planck equation, where this information is lost." In other words, the more general FPKE describes the short-time behavior of B particles as worse than its approximation HDE. This important fact is known as the *Rosenau paradox* by the name of Rosenau, who revealed it in 1993.[103]

E. Rice's formula

As stated above, another substantial revisit of Smoluchowski's theory valid for short-times was carried out by Rice in Ref. 1. It is significant that since then, it was generally agreed that the theory developed by Rice put an end to the study of relaxation effects within the framework of the HDE (40) approach. He solved the corresponding hyperbolic initial boundary value problem with respect to the time-dependent probability function $\rho(\mathbf{x},t)$ and, using it, found analytically the reaction rate coefficient. Moreover, Rice compared his result with the rate coefficient known from the classical theory of Smoluchowski (30).

In Ref. 1, Rice, referring to his unpublished results of 1978,[5] presented without any evidences the formula for the rate coefficient, which extends the classical Smoluchowski's expression (30). According to the general theory,[91] this extension should work well, including short time values, i.e., for $0 < t \lesssim \tau_D$, and therefore, it must describe the influence of the inertial effects. Concerning this formula, in page 330, he writes as follows: "Rice ... solved the field-free form of the telegrapher's equation for the Smoluchowski boundary conditions, supplemented by

$$\frac{\partial \rho(\mathbf{x},t)}{\partial t}\bigg|_{t\to 0+} \to 0, \tag{46}$$

to find the rate coefficient as

$$k_R(t) = k_S^0\left\{\left[1-\exp\left(-\frac{t}{\tau_D}\right)\right] + \left(\frac{t_D}{\tau_D}\right)^{1/2} \exp\left(-\frac{t}{2\tau_D}\right) I_0\left(-\frac{t}{2\tau_D}\right)\right\} \tag{47}$$

in which $I_0(x)$ is the first kind modified Bessel function of order zero." In addition, as we have mentioned above, to distinguish the hyperbolic diffusion model, we use here the following notation $\rho(\mathbf{x},t)$ for the time-dependent probability function.

However, it is significant to note here that expression (47) behaves in a completely different manner to the exact formula (see Fig. 2 and discussion in Sec. VIII).

We have pointed out in Sec. I that Rice's formula (47) is approximate. We also mentioned that by means of the approximate formula, erroneous conclusions were made about the applicability of the approach based on the use of the HDE, which, in its turn, brought into discredit the whole research direction for many years. The clarification of this point is very interesting by itself and besides useful as a cautionary example dealing with hyperbolic diffusion problems. Therefore, this question will be detailed and analyzed in Sec. VIII.

F. Hyperbolic local diffusive flux

In the case of hyperbolic diffusion, the local flux $\mathbf{j}(\mathbf{x},t)$ was not determined by the distribution $\rho(\mathbf{x},t)$ with the help of explicit formula (11). To find it, we should solve the relevant Cattaneo–Vernotte differential equation (38). It is evident that to obtain a unique solution, we have to supplement this equation with some physically reasonable initial condition for the local flux,

$$\mathbf{j}(\mathbf{x},t)|_{t\to 0+} \to \mathbf{j}_0(\mathbf{x}) \quad \text{in} \quad \Omega^-, \tag{48}$$

where $\mathbf{j}_0(\mathbf{x}) \in C^1(\Omega^-)$ is the initial field of the local flux. Thus, we posed the Cauchy problem [(38) and (48)], which has the general solution,[104]

$$\mathbf{j}(\mathbf{x},t) = \mathbf{j}_0(\mathbf{x})\exp\left(-\frac{t}{\tau_D}\right) - D\int_0^t K^+(t-\zeta;\tau_D)\nabla\rho(\mathbf{x},\zeta)d\zeta \quad \text{in} \quad Q^-. \tag{49}$$

Hence, it is obvious due to the non-Fickian memory term, where

$$K^+(t;\tau_D) = \frac{1}{\tau_D}\exp\left(-\frac{t}{\tau_D}\right) \tag{50}$$

is the so-called *memory kernel*.[79]

The local diffusion flux $\mathbf{j}(\mathbf{x},t)$ at a fixed space-time point $(\mathbf{x},t)$ depends on the entire history of the distribution gradient $\nabla\rho(\mathbf{x},t)$ establishing from origin time instance $t = 0$ to a given time value t.

Provided that we know the distribution $\rho(\mathbf{x},t)$ and initial local flux $\mathbf{j}_0(\mathbf{x})$, the flux field $\mathbf{j}(\mathbf{x},t)$ may be calculated with the help of Eq. (49). Thus, it is important to keep in mind that Eq. (49) is a new non-Fickian definition for the local diffusion flux, which one should use in general formula (9) to calculate the desired reaction rate coefficient $k(t)$.

In its turn, equation of continuity (37) and Eq. (49) in Q^- lead to the following inhomogeneous delayed integro-differential equation:

$$\frac{\partial\rho(\mathbf{x},t)}{\partial t} - D\int_0^t K^+(t-\zeta;\tau_D)\nabla^2\rho(\mathbf{x},\zeta)d\zeta = -\nabla\cdot\mathbf{j}_0(\mathbf{x})\exp\left(-\frac{t}{\tau_D}\right). \tag{51}$$

Again, here, we have a memory term in the left-hand side. One can see that in the limiting case as $\tau_D/t \to 0$, Eq. (51) turns into the classical second Fick's equation of diffusion.

It follows directly from Eq. (51) a significant connection

$$\frac{\partial}{\partial t}\rho(\mathbf{x},t)\bigg|_{t\to 0+} \to -\nabla\cdot\mathbf{j}_0(\mathbf{x}) \quad \text{in} \quad \Omega^-. \tag{52}$$

From a physical point of view for the trapping problem, one should set the trivial initial condition,[25,26,69,105,106]

$$\mathbf{j}_0(\mathbf{x}) \equiv \mathbf{0} \quad \text{in} \quad \Omega^-. \tag{53}$$

In this connection, e.g., Aziz and Gavino asserted the following: "An assumption of no initial flow $\mathbf{j}(0) = 0$ is consistent with our physical picture since there is no preferred direction for the initial velocity of each particle."[107] Simply speaking, we naturally assume that initially all particles B, being at the rest for early times $t < 0$, due to inertial effects when $\tau_D > 0$ as $m > 0$ [see Eq. (35)] cannot start to move at $t = 0$.

Since we study here Brownian diffusion of point-like reactants in the exterior of a spherical sink Ω^-, we should take into account the spherical symmetry of the problem under consideration. Hence, we can project the general equation [Eq. (38)] with initial condition (53) onto the radial axis,

$$\left(1+\tau_D\frac{\partial}{\partial t}\right)j_r(r,t) + D\frac{\partial\rho(r,t)}{\partial r} = 0 \quad \text{in} \quad Q^-, \tag{54}$$

$$j_r(r,t)|_{t\to 0+} \to 0 \quad \text{in} \quad \Omega^-, \tag{55}$$

where j_r is the radial component of $\mathbf{j}$. The solution to the Cauchy problem [(54) and (55)] in Q^- is given by the convolution

$$j_r(r,t) = -D\int_0^t K^+(t-\zeta;\tau_D)\frac{\partial\rho(r,\zeta)}{\partial r}d\zeta, \tag{56}$$

and (52) takes the following simplest form:

$$\frac{\partial}{\partial t}\rho(r,t)\bigg|_{t\to 0+} \to 0 \quad \text{in} \quad \Omega^-. \tag{57}$$

VI. HYPERBOLIC CAUCHY–DIRICHLET PROBLEM

Let us formulate the requirements imposed on the model used to calculate the rate coefficient.

(a) We intend to calculate analytically the rate coefficient within the scope of Smoluchowski's trapping model for the diffusion-controlled reactions occurring in stagnant, homogeneous, and isotropic media, taking into account the finite relaxation time of local diffusive fluxes.

(b) There are several approaches to attack the posed problem analytically, whereas mostly the theoretical studies concerning the problems on heat and mass transfer with inertial effects are based on the initial boundary-value problems posed for the HDE (40). Hence, in the present study, we shall follow this commonly accepted method.

A. Statement of the problem

The statement of the relevant external Cauchy–Dirichlet problem for the HDE is quite similar to the classical case. Inasmuch as the HDE is of second order in t, two initial conditions for $\rho(r,t)$ have to be imposed. Expression (57) is evidently one of these two conditions. Again, using spherical coordinates, we write the HDE (40) with corresponding initial and boundary conditions as follows:

$$\tau_D \frac{\partial^2 \rho}{\partial t^2} + \frac{\partial \rho}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \rho}{\partial r} \right) \quad \text{in} \quad Q^-, \tag{58}$$

$$\rho(r,t)|_{t\to 0+} \to 1 \quad \text{in} \quad \Omega^-, \tag{59}$$

$$\left.\frac{\partial \rho(r,t)}{\partial t}\right|_{t\to 0+} \to 0 \quad \text{in} \quad \Omega^-, \tag{60}$$

$$\rho(r,t)|_{r\to R+} \to 0 \quad \text{in} \quad \mathbb{R}_+, \tag{61}$$

$$\rho(r,t) \in L^\infty\left(\overline{Q}^-\right). \tag{62}$$

An important point is that for the problem under consideration, initial functions in initial conditions (59) and (60) cannot be chosen independently. In addition, on the reaction surface, as in the classical diffusion case, we imposed the Smoluchowski ideal trapping boundary condition (61).

One can see that in the singular limit $\tau_D \to 0$, the posed external hyperbolic Cauchy–Dirichlet problem [(58)–(62)] goes to the corresponding parabolic problem [(4)–(7)].[98]

B. Solution to the problem

It is common knowledge that hyperbolic diffusion problems are more complicated than their counterpart classical diffusion problems. In this context, it is pertinent to cite here the article by Kartashov,[6] which directly aimed at the analytical solutions of the similar hyperbolic heat-conduction problems. "Generalized transfer problems differ significantly from classical ones . . . being more complicated . . . Hence quite modest progress was made in finding exact analytical solutions of boundary value problems for Eq. (40) and mainly for the semi-infinite domain $\{x > 0\} \times \{t > 0\}$ at constant boundary functions and zero boundary conditions.[33] At the same time, in some cases the solutions found contain errors . . . ." Kartashov was echoed by Masoliver,[100] who wrote about the determination of the fundamental solution to the HDE (40) as follows: "Although this solution has been known since a very long time ago, its derivation remains quite obscure."

Here, we just briefly review known in literature mathematical methods used to solve the spherically symmetric Dirichlet initial boundary value problem for the HDE. We should observe that, by means of the deep mathematical analogy between thermal and diffusion processes, some fruitful theoretical ideas may be directly borrowed from the much more advanced hyperbolic theory of the heat transfer.[106]

Our mathematical approach is analytical and based on a straightforward reduction of the external hyperbolic diffusion problem with Laplacian possessing spherical symmetry to, formally, the case of the relevant diffusion problem with semi-infinite slab geometry carried out by means of the well-known transform (15) (see, e.g., Ref. 14). We used this reduction method because the analytical solutions for both finite and semi-infinite slabs are currently thoroughly elaborated in the literature (see Sec. VI).

The use of 3D potentials for the solution of the general hyperbolic initial boundary value problems is worthy of special attention.[108] Another powerful approach to tackle these problems is based on some probabilistic representations of the desired solutions and uses the exact solutions of the wave equation by the Monte Carlo method.[109] However, as in previous classical diffusion case, it is expedient to transform the posed Cauchy–Dirichlet problem [(58)–(62)] to some simple dimensionless problem, changing the independent variables according to Eq. (17). Then, we again look for the required solution in the form of the ansatz similar to (16). This allows us to recast the original Cauchy–Dirichlet problem [(58)–(62)] in a more convenient form of an auxiliary problem, describing, formally, the trapping of B's by a plane wall boundary in a semi-infinite slab,

$$\epsilon \frac{\partial^2 u}{\partial \tau^2} + \frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial x^2} \quad \text{in} \quad Q_x^-, \tag{63}$$

$$u(x,\tau)|_{\tau\to 0+} \to 0, \quad x \in \mathbb{R}_+, \tag{64}$$

$$\left.\frac{\partial u(x,\tau)}{\partial \tau}\right|_{\tau\to 0+} \to 0, \quad x \in \mathbb{R}_+, \tag{65}$$

$$u(x,\tau)|_{x\to 0+} \to 1, \quad \tau \in \mathbb{R}_+, \tag{66}$$

$$u(x,\tau) \in L^\infty\left(\overline{Q}_x^-\right). \tag{67}$$

Here, we introduced an important small dimensionless parameter ϵ, which is equal to the ratio of characteristic velocity correlation (35) and diffusion (18) times,

$$\epsilon := \tau_D / t_D \ll 1. \tag{68}$$

Thus, the above auxiliary hyperbolic problem [(63)–(67)] is a singular perturbed one, and

$$u(x,\tau) \to v(x,\tau) \quad \text{as} \quad \epsilon \to 0. \tag{69}$$

Several approaches to obtain the analytical solution of the Cauchy–Dirichlet problem [(63)–(67)] for the finite and semi-infinite slab geometry were presented by many authors (see, e.g., Refs. 6, 25–27, 55, and 110–115 and the references therein). Nevertheless, one can infer that the standard operational method is most commonly performed to find the analytical solution of this problem.[30]

Remark 14. It is worth noting here that the reader should bear in mind the complete inconsistency in the notations used by different authors.

Hyperbolic initial boundary value problems for diffusion in non-rectangular coordinates are investigated much less.[6] "For domains of the canonic type (an infinite plate, a continuous or hollow cylinder, a continuous or hollow sphere, etc.), exact solutions of hyperbolic models of transfer are still unknown, and this problem essentially remains open, including the correct statement of boundary value problems for the hyperbolic equations."[115]

The hyperbolic Cauchy–Dirichlet problem was solved for infinite, cylindrical, and spherical host media using the method of *relativistic transformation of variables* by Sharma in 2007.[27,53] Nevertheless, attention should be drawn to the fact that, as far as we know, in the previous works, a similar spherically symmetric Cauchy–Dirichlet problem, which takes into account inertial effects, was solved mostly numerically (see, e.g., Refs. 29 and 96).

The inner Cauchy–Dirichlet problem for hyperbolic diffusion was treated inside a sphere with the help of the separation of variable method (see, e.g., Refs. 52 and 116). An external hyperbolic diffusion problem for 3D space outside a sphere with spherically symmetric Laplacian was studied analytically by means of the Laplace transform approach.[117] However, the boundary condition imposed on the sphere is rather sophisticated, and therefore, the obtained result is too far from our present interest.

In this regard, it is worth mentioning Ref. 118 where the corresponding 3D inner problem in spherical coordinates was solved.

Applying Laplace's transform (A12) to the hyperbolic Cauchy–Dirichlet problem [(63)–(67)], one can easily arrive at

$$\frac{d^2}{dx^2}\overline{u}(x;s) - s(1+\epsilon s)\overline{u}(x;s) = 0, \quad x \in \mathbb{R}_+, \tag{70}$$

$$\overline{u}(x;s)|_{x\to 0+} \to 1/s \in \mathbb{C}, \tag{71}$$

$$\overline{u}(x;s)|_{x\to +\infty} \rightrightarrows 0, \quad x \in \mathbb{R}_+. \tag{72}$$

It is clear that the solution to the boundary value problem [(70)–(72)] reads

$$\overline{u}(x;s) = \frac{1}{s}\exp\left[-\sqrt{s(1+\epsilon s)}\,x\right], \quad x \in \overline{\mathbb{R}}_+. \tag{73}$$

Hence, one can see that the condition of small wave effect is $\epsilon|s| \ll 1$, and therefore, in this case, classical diffusion solution (27) works well.

Taking inverse Laplace transform in (73), we obtain the desired solution $u(x,\tau) = \mathcal{L}^{-1}\{\overline{u}\}(\tau)$. Thus, the solution of the auxiliary Cauchy–Dirichlet problem [(63)–(67)] in $\overline{Q}_x$ may be written as[110]

$$u(x,\tau) = H\left(\tau - x\sqrt{\epsilon}\right)\left[\exp\left(-\frac{x}{2\sqrt{\epsilon}}\right) + \frac{x}{2\sqrt{\epsilon}}\int_{x\sqrt{\epsilon}}^{\tau} I_1\left(\frac{1}{2\epsilon}\sqrt{\zeta^2 - \epsilon x^2}\right)\frac{\exp(-\zeta/2\epsilon)}{\sqrt{\zeta^2 - \epsilon x^2}}\,d\zeta\right] \tag{74}$$

or, using an evident property of Heaviside's step function $H(x)$ (A1), in another equivalent form,

$$u(x,\tau) = H\left(\tau - x\sqrt{\epsilon}\right)\exp\left(-\frac{x}{2\sqrt{\epsilon}}\right) + \frac{x}{2\sqrt{\epsilon}}\int_0^{\tau} I_1\left(\frac{1}{2\epsilon}\sqrt{\zeta^2 - \epsilon x^2}\right)\left(\zeta^2 - \epsilon x^2\right)^{-1/2} \times \exp\left(-\frac{\zeta}{2\epsilon}\right)H\left(\zeta - x\sqrt{\epsilon}\right)d\zeta. \tag{75}$$

Rewriting ansatz (16) with the help of solution $u(x,\tau)$ (74) and taking into account connection (17), one obtains the explicit form of the solution $\rho(r,t)$ to the original Cauchy–Dirichlet problem (58)–(62). In this way, the following proposition holds true.

Theorem 3. *Solution $\rho(r,t)$, describing the hyperbolic diffusion of B particles toward a spherical perfectly absorbing sink [(58)–(62)], is connected with appropriate auxiliary solution $u(x,\tau)$ for hyperbolic diffusion of B's to a perfectly absorbing semi-infinite slab [(63)–(67)] by means of ansatz*

$$\rho(r,t) = 1 - \frac{R}{r}u(x,\tau), \tag{76}$$

where variables x and τ are given in (17).

Direct inspection shows that general formula (23) holds for the hyperbolic Cauchy–Dirichlet problem (58)–(62) as well.

VII. ESTIMATION OF THE REACTION RATE COEFFICIENT

Knowing exact B particle distribution function (76), one embarked on the accurate analytical calculation of the desired reaction rate coefficient for the diffusion-controlled reactions due to hyperbolic diffusion.

A. General formula for the rate coefficient

Let us derive an important corollary to Theorem 3. Plainly, the general expression (9) is $k(t) = -4\pi R^2 j_r(r,t)$, and with the aid of known local flux (56), the required reduced rate coefficient $k^*(t)$ in the case of hyperbolic diffusion reads

$$k^*(t) = \frac{R}{\tau_D}\exp\left(-\frac{t}{\tau_D}\right)\int_0^t \exp\left(\frac{\xi}{\tau_D}\right)\frac{\partial\rho(r,\xi)}{\partial r}\bigg|_{r\to R+} d\xi. \tag{77}$$

Utilizing ansatz (76), we can easily recast Eq. (77) in a more convenient form,

$$k^*(t) = \frac{1}{\tau_D}\exp\left(-\frac{t}{\tau_D}\right)\int_0^t \exp\left(\frac{\xi}{\tau_D}\right)\left[1 - \frac{\partial u(x,\xi)}{\partial x}\bigg|_{x\to 0+}\right]d\xi, \quad (78)$$

whereas it is clear that the first integral in the right-hand side, which we denote as $k_c^*(t)$, describes curvature effects due to the sphericity of the sink reaction surface. One can see that

$$k_c^*(t) = \left[\exp\left(\frac{t}{\tau_D}\right) - 1\right]\exp\left(-\frac{t}{\tau_D}\right). \quad (79)$$

Hence, we have the following.

Corollary 2. For spherically symmetric hyperbolic diffusion transfer, the formula for the reduced rate coefficient (77) yields

$$k^*(t) = k_c^*(t) + k_x^*(t), \quad (80)$$

where $k_x^*(t)$ is a part, corresponding to the total rate coefficient upon the wall of the semi-infinite slab,

$$k_x^*(t) = -\frac{1}{\tau_D}\exp\left(-\frac{t}{\tau_D}\right)\int_0^t \exp\left(\frac{\zeta}{\tau_D}\right)\frac{\partial u(x,\zeta)}{\partial x}\bigg|_{x\to 0+} d\zeta. \quad (81)$$

We emphasize that (78) and (81) directly imply an important property,

$$\lim_{t\to 0+} k^*(t) = \lim_{t\to 0+} k_x^*(t) = 0. \quad (82)$$

This property is an evident consequence of the initial condition for the local flux (53), and they are rather reasonable since at $t = 0$ Brownian particles cannot be trapped by the absorbing surfaces due to inertial effects.

B. Simplified derivation of the rate coefficient on the wall

At first glance, it would seem that the reduced reaction rate coefficient for the semi-infinite slab $k_x^*(t)$ can be very easy calculated directly, without knowing the explicit expression for the function $u(x,t)$ in the physical space (74). Applying the Laplace transform to the general expression at issue (81) by means of convolution theorem and formula (A15), we readily obtain Laplace's transform of the desired rate coefficient,

$$\bar{k}_x^*(s) = -\frac{1}{1+\epsilon s}\frac{\partial}{\partial x}\bar{u}(x;s)\bigg|_{x\to 0+}. \quad (83)$$

In other words, it seems reasonable to simplify significantly the calculations required to derive the expression for the rate coefficient from general formula (81) by taking the limit as $x \to 0+$ in the right-hand side derivative of Eq. (83) before Laplace's transform inverse. It is pertinent to note here that in the classical diffusion case, this procedure leads to correct expression for the rate coefficient [see formulas (25) and (27)]. Unfortunately, this way appeared to be incorrect for the case of hyperbolic diffusion, leading to an inexactness in the required formula for the reaction rate coefficient. Let us show this.

Introducing the function

$$\bar{K}(x;s) := -\frac{1}{1+\epsilon s}\frac{\partial}{\partial x}\bar{u}(x;s),$$

we, obviously, get

$$\bar{K}(x;s) = \frac{1}{\sqrt{s(1+\epsilon s)}}\exp\left[-\sqrt{s(1+\epsilon s)}x\right], \quad (84)$$

$$\bar{k}_{xR}^*(s) := \bar{K}(0+;s) = \frac{1}{\sqrt{s(1+\epsilon s)}}. \quad (85)$$

Applying here the Tauberian theorem for Laplace's transform, one obtains

$$\lim_{s\to\infty} s\bar{K}(0+;s) = \frac{1}{\sqrt{\epsilon}} \neq 0, \quad (86)$$

$$k_{xR}^*(t) = \mathcal{L}^{-1}\{\bar{K}(0+;s)\} = \frac{R}{\sqrt{\tau_D D}}\exp\left(-\frac{t}{2\tau_D}\right)I_0\left(\frac{t}{2\tau_D}\right). \quad (87)$$

Moreover, it follows from property (A8) that in physical space,

$$\lim_{t\to 0+} k_{xR}^*(t) = 1/\sqrt{\epsilon} = R/\sqrt{\tau_D D} \neq 0. \quad (88)$$

One can see that result (86) [or (88)] is in contradiction with trivial initial condition (82).

Using general representation (80) and formula (85), one arrives at the relation in Laplace's domain,

$$\bar{k}_R^*(s) = \frac{1}{s(1+\epsilon s)} + \frac{1}{\sqrt{s(1+\epsilon s)}}. \quad (89)$$

Hence, inverting here the Laplace transform by means of formulas (A16) and (A17), we reproduce the known Rice formula (47) in the physical space.

C. Straightforward calculation of the rate coefficient

Now, let us give a thorough derivation of the reduced rate coefficient $k^*(t)$ with the help of an explicit solution in the physical space $\rho(r,t)$. According to Corollary 2, our task is simplified and reduced to the calculation of the trapping rate on a semi-infinite slab surface $k_x^*(t)$ (81).

With the aid of auxiliary solution (74) and recalling result (A4), we can easily find the required limit,

$$-\frac{\partial}{\partial x}u(x,\tau)\bigg|_{x\to 0+} = \frac{1}{2\sqrt{\epsilon}} - \frac{1}{2\sqrt{\epsilon}}\int_0^\tau \zeta^{-1}I_1\left(\frac{\zeta}{2\epsilon}\right)\exp\left(-\frac{\zeta}{2\epsilon}\right)d\zeta. \quad (90)$$

One can calculate the integral here by means of the change of variable $z = \xi/2\epsilon$ and using known quadrature (A10) at $\nu = 1$. To easily compare our result with the Rice formula (47), here, we will carry out calculations of the rate coefficient for the real time value t. Returning the obtained result to the original variables (r,t) and substituting it into (76), we have

$$-\frac{\partial}{\partial x}u(x,t)\bigg|_{x\to 0+} = \frac{R}{2\sqrt{\tau_D D}}\exp\left(-\frac{t}{2\tau_D}\right)\left[I_0\left(\frac{t}{2\tau_D}\right) + I_1\left(\frac{t}{2\tau_D}\right)\right]. \quad (91)$$

Finally, one can obtain the explicit form of integral in Eq. (81). Using Eq. (91) with the help of auxiliary relation (A9), one arrives at

$$\int_0^t \exp\left(\frac{\zeta}{2\tau_D}\right)\left[I_0\left(\frac{\zeta}{2\tau_D}\right)+I_1\left(\frac{\zeta}{2\tau_D}\right)\right]d\zeta = 2\tau_D\left[\exp\left(\frac{t}{2\tau_D}\right)I_0\left(\frac{t}{2\tau_D}\right)-1\right]. \quad (92)$$

Note in passing that taking into account connection (76), the reduced rate of particles trapping by a plane wall $\{x = 0\}$ reads

$$k_x^*(t) = \exp\left(-\frac{t}{\tau_D}\right)\left\{\frac{R}{\sqrt{\tau_D D}}\left[\exp\left(\frac{t}{2\tau_D}\right)I_0\left(\frac{t}{2\tau_D}\right)-1\right]\right\}. \quad (93)$$

Substituting this result into (80), one finds the required formula for the reduced rate coefficient,

$$k^*(t) = \exp\left(-\frac{t}{\tau_D}\right)\left\{\left[\exp\left(\frac{t}{\tau_D}\right)-1\right] + \frac{R}{\sqrt{\tau_D D}}\left[\exp\left(\frac{t}{2\tau_D}\right)I_0\left(\frac{t}{2\tau_D}\right)-1\right]\right\}. \quad (94)$$

One can see that in contrast to Eqs. (87) and (47), the derived formulas [(93) and (94)] possess (82) as should be.

Taking (87) and (93) into consideration, it is clear that the error in the rate coefficient $k_R^*(t)$ (47) arose because of the apparent fact that Lemma 1 on commutativity (28) is not valid for the hyperbolic diffusion case, i.e.,

$$\lim_{x\to 0+}\frac{\partial}{\partial x}\mathcal{L}^{-1}\{\overline{u}(x;s)\} \neq \mathcal{L}^{-1}\left\{\lim_{x\to 0+}\frac{d}{dx}\overline{u}(x;s)\right\}. \quad (95)$$

Obviously, the basic reason for this property is that $s_0 = -1/\epsilon$ is a singular branch point of the function $\overline{K}(x;s)$ in Eq. (84). Note also that operations in relation (95) become commutative in the particular case of Fickian kinetics (28), i.e., when $s_0 \to -\infty$.

VIII. DISCUSSION

A. Wave properties of the solution

It follows directly from Theorem 3 that the time evolution of the diffusive field in the vicinity of a spherical sink is the same as that around a flat ideally absorbing wall. Thus, for both the obtained solutions around the wall $u(x,\tau)$ (74) and around the sink $\rho(r,t)$ (76), there is a sharp *propagating diffusive front*, spreading in space with a constant finite velocity,

$$c = \sqrt{\frac{D}{\tau_D}} = v_D\sqrt{\frac{t_D}{\tau_D}} = v_D\epsilon^{-1/2}, \quad v_D = \frac{D}{R}, \quad (96)$$

where v_D is a characteristic diffusion velocity, sometimes used in the theory of the pure diffusion transfer.[24] Mathematically, the diffusive front is a jump discontinuity of the function $\rho(r,t)$ [or $u(x,\tau)$] (76). What is more, taking into account that usually $t_D \gg \tau_D$, an interesting relation between velocities $c \gg v_D$ follows from (96). Velocity c is a constant for fixed intrinsic parameters of the given host medium: D and τ_D, so the diffusive front kinematics is determined by the relation

$$r(t) = R + ct, \quad (97)$$

i.e., diffusive wave spreads to the right, away from the sink surface. It is also clear from Eq. (63) that pure parabolic diffusion case means $\epsilon \to 0$, and therefore, we get the infinite speed paradox $c \to \infty$. In terms of diffusion wave motion, τ_D is the time over which the B particle recalls in which direction it was originally traveling.[1]

Moreover, taking into consideration relations (96) and (97), one can see that for all $t > 0$, there exists the front of the solution $\rho(r,t)$ amplitude, which in course of time decays exponentially accordingly to the law $\propto \exp(-t/2\tau_D)$. Hence, from this point of view, the relaxation time τ_D may be treated as a *characteristic time of the diffusive wave damping*. Thus, in course of time (mathematically as $t \to +\infty$), HDE (58) turns into the classical parabolic diffusion equation (4); at that, both solution $\rho(r,t)$ (76) and reaction rate coefficient $k^*(t)$ (94) tend to the corresponding Smoluchowski solution $\rho_S(r,t)$ (29) and rate coefficient $k_R^*(t)$ (30). It is worth noting that this important property is a direct consequence of known in mathematical physics the so-called *diffusion phenomenon*.

Let us take a brief look at the diffusion phenomenon. First of all, note that it seems to us that the term "diffusion phenomenon" is not quite successful. Indeed, very often, in physical literature, the concept diffusion phenomenon is understood just as a set of problems relating to diffusion (see, e.g., Refs. 119 and 120).

Definition 4. The function $\rho(r,t)$ possesses diffusion phenomenon if $\rho(r,t) \sim w(r,t)$ uniformly as $t \to +\infty$ and parameter τ_D is a finite number.

Simply stated, the diffusion phenomenon is an asymptotical relation between hyperbolic and parabolic diffusion models. We emphasize that this is not so evident mathematical concept as it seems at a glance. Particularly, one can prove that $u(x,\tau) \to v(x,\tau)$ as $\tau \to +\infty$ [compare this with Eq. (69)] such that for the initial conditions, the following relation holds true:

$$v(x,\tau)|_{\tau\to 0+} = \left[u(x,\tau) + \frac{\partial u(x,\tau)}{\partial \tau}\right]\Bigg|_{\tau\to 0+}.$$

In our opinion, the most simple treatment of the diffusion phenomenon was given with the aid of a Tauberian theorem for Laplace transforms.[121] We suggest the readers who are interested in the detailed mathematical study of the diffusion phenomenon to refer the 2018 book by Ebert and Reissig.[34]

On the other hand, one can show that, at least for time values $0 < t \ll \tau_D$, the HDE (58) may be approximated by the standard wave equation, and therefore, its solution $\rho(r,t)$ (76) describes the ballistic regime of the Brownian motion of particles B mentioned in Sec. I. Thus, ballistic and diffusion regimes are naturally included in the hyperbolic diffusion model as its particular cases as $t \to 0$ and as $t \to \infty$, respectively. An additional point to emphasize here is that sometimes "based on the stochastic approach using Langevin equations, the active particle motion is split into a diffusive part and a ballistic part."[10]

B. Some remarks on Rice's approximation

The above thorough analytical calculation of the rate coefficient leads to Eq. (94). Using this formula and asymptotic expansion for the modified Bessel functions of the first kind (A11), one can obtain Smoluchowski's rate coefficient for any fixed time t (30) when the relaxation time vanishes, i.e., as $\tau_D \to 0$. Moreover, we have found out that the exact value of the reduced rate coefficient (94) differs from the known Rice approximation $k_R^*(t)$ (47) [1] by the last term,

$$k^*(t) = k_R^*(t) - \frac{R}{\sqrt{\tau_D D}} \exp\left(-\frac{t}{\tau_D}\right). \quad (98)$$

Hence, it is evident that we have a uniform estimate

$$k(t) < k_R(t) \quad \text{for all} \quad t > 0. \quad (99)$$

In this way, Rice's approximation $k_R(t)$ is a uniform upper bound for the exact rate coefficient.

One can see that basic property (82) does not hold for Rice's rate coefficient (47), but for $\tau_D > 0$, it possesses property (88), i.e.,

$$0 < \lim_{t\to 0+} k_R^*(t) = \frac{R}{\sqrt{\tau_D D}} < +\infty. \quad (100)$$

Therefore, the Rice approximation (47), while successfully resolving the zero time paradox, nevertheless, does not satisfy the correct initial condition (82). Hence, formula (47) is not an exact expression for the rate coefficient.

Then, the natural question arises as to: "Why the latter fact was not detected until now?" It was really hard to detect an inexactness in formula (47) because it gives correct limiting cases as $t/\tau_D \to +\infty$, i.e., when (a) for all fixed $t > 0$ as $\tau_D \to 0$ and (b) for all fixed $\tau_D > 0$ as $t \to +\infty$ (diffusion phenomenon). Thus, in these two cases, Rice's expression (47) is reduced to the correct classical Smoluchowski result (30). It is rather important that Rice's approach also resolves the paradox of infinite speed. Moreover, provided that one deals with finite values of diffusive relaxation time τ_D, relation (100) shows that the Rice approximation, at least formally, also resolves the zero time paradox.

Another important question is as follows: "Why this inexactness appeared?" It seems that the most plausible answer is as follows. Rice applied a well-elaborated method for the derivation of the rate coefficient in the case of classical diffusion theory, which fails in the case of Cauchy–Dirichlet problems for the HDE. Really, we showed in Sec. VII that Lemma 1 on commutativity (28) does not hold for the hyperbolic diffusion [see(95)].

C. Comparison of rate coefficients for short times

To compare the behavior of the curves, which represent the reduced rate coefficients for the different theories on the plot, it is convenient to use the dimensionless form of the reduced rate coefficient (94) written as a function of variable τ and one parameter ϵ (68),

$$k^*(\tau) = \exp\left(-\frac{\tau}{\epsilon}\right)\left\{\left[\exp\left(\frac{\tau}{\epsilon}\right) - 1\right] + \frac{1}{\sqrt{\epsilon}}\left[\exp\left(\frac{\tau}{2\epsilon}\right) I_0\left(\frac{\tau}{2\epsilon}\right) - 1\right]\right\}, \quad (101)$$

$$k_R^*(\tau) = k^*(\tau) + \frac{1}{\sqrt{\epsilon}} \exp\left(-\frac{\tau}{\epsilon}\right). \quad (102)$$

For the illustrative plots, we chose most of the parameters as in the paper by Rice *et al.*[62] who considered particular examples of diffusion-controlled reactions for the following physical magnitudes of the diffusing B particles: $D = 10^{-8}$ m^2 s^{-1}, $T = 300$ K, $m = 5 \cdot 10^{-26}$ kg, and friction coefficient $\zeta \approx 7.14 \cdot 10^{-14}$ kg s^{-1}. Hence, these values give for the relaxation time $\tau_D = 0.7$ ps [see formula (35)]. In addition, it follows from Eqs. (35) and (36) that the explicit relation for the dimensionless parameter ϵ (68) reads

$$\epsilon = mk_B T/R^2\zeta^2. \quad (103)$$

For definiteness sake, we assume here that the reaction radius is $R = 1.32$ nm such that Eq. (103) gives $\epsilon \approx 0.004$. Note that for another value $R = 0.5$ nm used in Ref. 62, we get sufficiently larger value of the parameter $\epsilon \approx 0.028$, and therefore, inertial effects seem to be even more pronounced.

Figure 2 depicts a comparison of different approximations of the reduced time-dependent reaction rate coefficients $k_A^*(\tau)$ for short time values. We plotted here the corresponding curves for the classical Smoluchowski $k_S^*(\tau)$ (24) and known Rice rate coefficients $k_R^*(\tau)$ (102) together with the rate coefficient $k^*(\tau)$ calculated in the present paper (101) as functions of the dimensionless time τ. In Fig. 2, one can see that the rate coefficient $k^*(\tau)$ first rises sharply from the zero value at $\tau = 0$, attaining its local maximum. Then, on decreasing, it intersects the curve for the classical Smoluchowski rate at some point τ_c, which is determined by $k^*(\tau_c) = k_S^*(\tau_c)$. When $\tau > \tau_c$, rate coefficient $k^*(\tau)$ rapidly approaches Rice's approximation $k_R^*(\tau)$ from below due to the fast decreasing of the correction term $\epsilon^{-1/2}\exp(-\tau/\epsilon)$ for $\tau > \epsilon$. Moreover, in course of time, both these approximations, because of the diffusion phenomenon, approach the classical Smoluchowski rate coefficient $k_S^*(\tau)$ from above, and what is more, for $\tau > \tau_c$, the two-sided estimate $k_S^*(\tau) < k^*(\tau) < k_R^*(\tau)$ holds true. We also emphasize that obtained reaction rate $k^*(\tau)$ behavior differs essentially from that of the Rice formula $k_R^*(\tau)$ for $0 \le \tau \lesssim 0.02 \gg \epsilon$.

One can see that the course of the curves for the rate coefficients $k^*(\tau)$ and $k_S^*(\tau)$ in Fig. 2 qualitatively agrees with the conclusion drawn by the authors of Ref. 122 that the standard SCK model overestimates the reaction rate coefficient for very short times $\tau < \tau_c$.

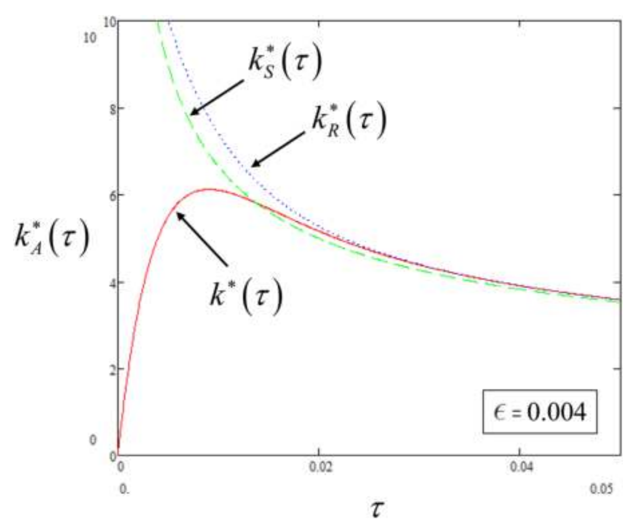

FIG. 2. Comparison of different approximations for the reduced rate coefficient $k_A^*(\tau)$ at $\epsilon = 0.004$: $k_S^*(\tau)$ is Smoluchowski's rate coefficient (green dashed line), $k_R^*(\tau)$ is Rice's approximation (blue dotted line), and $k^*(\tau)$ is the result of the present work (red solid line).

In addition, an important point is that some experimental results support this conclusion. Really, Langhoff *et al.* were the first who investigated picosecond recombination kinetics of laser-dissociated iodine atoms in solution experimentally. To describe their results, they applied classical diffusion theory[67] and came to a conclusion that Smoluchowski's theory for the short times $t < 200$ ps predicts a faster recombination rate than is actually measured (see, e.g., Refs. 1 and 123). Note in passing that the so-called *cage effect* was used to explain the observed slow rate of recombination for iodine atoms; however, this explanation seems to be rather questionable.[1]

IX. CONCLUDING REMARKS

A brief survey of the literature on the short-time behavior of the diffusion-controlled rate coefficient, performed here, has made it clear that the appropriate theory is not yet sufficiently advanced. In this connection, we fully share the opinion of a number of researchers that the hyperbolic Brownian diffusion model appeared to be a reasonable generalization of the corresponding classical parabolic diffusion model at least for a short time scale. Furthermore, we focused here our attention on two important theoretical facts concerning the hyperbolic diffusion model. First, this model reproduces the correct behavior of diffusing particles, including the ballistic regime stage. Second, regardless of the diffusion relaxation time magnitude τ_D, due to the diffusion phenomenon, both models lead to the same results at long enough time values. It is important to note that the deep results obtained in the mathematical literature on the diffusion phenomenon still remain unknown for most researchers in physics and, particularly, in chemical physics.

Thus, the ultimate objective of this paper has been the development of 3D hyperbolic diffusion theory for the irreversible bulk diffusion-controlled reactions between small Brownian particles and uniformly distributed perfectly absorbing spherical sinks. We have shown that in many respects, this approach may be treated as a natural generalization of the classical Smoluchowski diffusion theory. In passing, we revealed here that the violation of the compatibility condition between initial and boundary conditions resulted in the known zero time paradox of the Smoluchowski diffusion theory.

Contrary to the simple classical diffusion case, in this work, we deal with the coupled system of the Cauchy problem [(54) and (55)] for the local diffusion flux and the hyperbolic initial boundary value problem under Smoluchowski's boundary condition [(58)–(62)] for the particle distribution function.

We showed that the posed 3D spherically symmetric hyperbolic diffusion problem, similar to the corresponding classical parabolic diffusion problem, may be reduced to an appropriate auxiliary 1D problem, which, in turn, can be straightforwardly solved by means of Laplace's transform.

The performed analysis of the literature clearly brings out that the existing theory of hyperbolic diffusion transfer often uses not established yet terminology and, what is the most disagreeably it contains, many misunderstandings and even various mathematical errors, whereas we paid a special attention to the inconsistency in terminology, some misunderstandings, and a few mathematical errors of the existing theory. Therefore, in this paper, we treated different mathematical aspects of the posed hyperbolic problem in some detail. However, a comprehensive critical analysis of the published results on the topic under consideration is not included in the tasks set in this article and will be considered in our subsequent works.

The obtained exact hyperbolic particle distribution function (76) predicts that the diffusion disturbance due to the sink presence propagates as an attenuating wave with a constant speed (96). It has been shown that the Smoluchowski theory is inappropriate for the description of the inertial effects, which are significant for Brownian particles at short times. Furthermore, known Rice's formula (47) for the time-dependent hyperbolic reaction rate coefficient was investigated in full detail. Using solution (76), we obtained exact reaction rate coefficient (94) and proved that rate coefficient (47), commonly recognized earlier as an exact, turned out to be the only uniform upper bound of the exact one. We also showed that Rice's formula does not obey the physically reasonable initial condition for the local diffusive flux (53). In this connection, note that initial condition (53) should be a key point for any reasonable physical theory of diffusion-controlled reactions, describing inertial effects. Moreover, we have proved that Rice's formula, being a good approximation at large enough times, does not work well for short time values. It has been shown that this is due to the fact that Lemma 1 on commutativity does not hold in the hyperbolic diffusion case.

We think that the existing gap between both computer simulations and experimental results on the one hand and theoretical results on the other hand for the rate coefficients at short values of time will be overcome by the use of the hyperbolic diffusion model under appropriate boundary conditions, posed on the reaction surfaces. We also believe that the potentialities of various applications of the hyperbolic diffusion model in chemical physics problems (e.g., to describe ultrafast elementary photochemical processes in liquid solution[16]) have far not been yet exhausted. That is why, we hope that our study will encourage the ulterior beneficial use of the hyperbolic diffusion model in theory of diffusion-controlled reactions, while looking more closely at subtle mathematical pitfalls to be avoided.

It is worth noting that in the present paper, we have considered only the case of reactions with the complete diffusion control. A generalization to the case of Collins–Kimball boundary conditions can be carried out straightforwardly, provided that they are modified according to the hyperbolic diffusion model.[6]

We would like to finish our paper citing p. 335 of Rice's book:[1] "There is a strong indication that a model which better mimics the velocity autocorrelation would give very interesting results." and below "Further developments are eagerly awaited."

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Sergey D. Traytak: Conceptualization (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX: SOME AUXILIARY MATHEMATICAL FACTS AND CALCULATIONS

In this appendix, for readers' convenience, we recall some important mathematical notations, definitions, formulas, and perform auxiliary calculations which we used in this paper.

1. Some properties of Heaviside's step function

The Heaviside step function usually denoted by $H(x)$ is a piecewise function given on $\mathbb{R}$, whose values are

$$H(x) := \begin{cases} 1 & \text{for} \quad x \geq 0, \\ 0 & \text{for} \quad x < 0. \end{cases} \tag{A1}$$

Consider a sequence of the real-valued differentiable functions $\{h_n\}_{n=1}^{\infty}$ on $\mathbb{R}$ such that for each $n \in \mathbb{N}$, we have a function $h_n : \mathbb{R} \to \mathbb{R}$ of the form

$$h_n(x) := [1 + \exp(-nx)]^{-1}. \tag{A2}$$

One can see that a (a) sequence of functions $\{h_n\}_{n=1}^{\infty}$ is uniformly bounded by unity $|h_n(x)| \leq 1$ for all $n \in \mathbb{N}$ and $x \in \mathbb{R}$ and (b) $\{h_n\}_{n=1}^{\infty}$ converges uniformly $h_n(x) \rightrightarrows H(x)$ as $n \to \infty$ almost everywhere on $\mathbb{R}$. Hence, $\{h_n\}_{n=1}^{\infty}$ is a fundamental sequence.[124] It is well-known that the equivalence class of fundamental sequences $\{h_n\}_{n=1}^{\infty}$ (A2) is determined by the distribution called Heaviside's step function $H(x)$.[124]

Thus, for any real-valued function $g \in C^1(\mathbb{R}_+)$ and for all $t > 0$, consider the product

$$u(x,t) := h_n(t-x)g(x,t). \tag{A3}$$

Hence, one readily gets

$$\left.\frac{\partial u(x,t)}{\partial x}\right|_{x\to 0+} = -\lim_{n\to\infty} h_n'(t)g(0,t) + H(t)\left.\frac{\partial g(x,t)}{\partial x}\right|_{x\to 0+}.$$

Using here the evident limit $\lim_{n\to\infty} h_n'(t) = 0$, we arrive at the important relation,

$$\left.\frac{\partial}{\partial x}H(t-x)g(x,t)\right|_{x\to 0+} = \left.\frac{\partial g(x,t)}{\partial x}\right|_{x\to 0+}. \tag{A4}$$

2. Some results for the Bessel function

Recall that the Bessel function of the first kind of order ν may be defined by its series expansion around $y = 0$, i.e.,[31]

$$J_\nu(y) := \sum_{k=0}^{\infty} \frac{(-1)^k}{k!\Gamma(\nu+k+1)}\left(\frac{1}{2}y\right)^{2k+\nu}. \tag{A5}$$

Function $I_\nu(y) = e^{\nu\pi i}J_\nu(iy)$, which are calling the modified Bessel function of the first kind of order ν, is defined by the expansion around $y = 0$ for any $\nu \in \overline{\mathbb{Z}}_+$,

$$I_\nu(y) := \sum_{k=0}^{\infty} \frac{1}{k!\Gamma(\nu+k+1)}\left(\frac{1}{2}y\right)^{2k+\nu}. \tag{A6}$$

By means of expansion (A6), it may be readily shown that

$$I_0'(y) = I_1(y), \tag{A7}$$

$$I_\nu(0) = \begin{cases} 1 & \text{for} \quad \nu = 0, \\ 0 & \text{for} \quad \nu \in \mathbb{N}. \end{cases} \tag{A8}$$

Using integration by parts and relation (A7), one can readily find

$$\int_0^y \exp(z)[I_0(z) + I_1(z)]dz = \exp(y)I_0(y) - 1. \tag{A9}$$

According to Ref. 125 for $\nu \neq \frac{1}{2}$, the following quadrature holds:

$$\int_0^y \xi^{-\nu}\exp(-\xi)I_\nu(\xi)d\xi = \frac{1}{2^{\nu-1}(2\nu-1)\Gamma(\nu)} - \frac{y^{1-\nu}\exp(-y)}{2\nu-1}[I_{\nu-1}(y) + I_\nu(y)]. \tag{A10}$$

Consider the asymptotic expansion of the modified Bessel functions of the first kind for large values of argument as $|y| \to +\infty$,[31]

$$I_\nu(y) \sim \frac{1}{\sqrt{2\pi y}}\exp(y)\left(1 - \frac{4\nu^2-1}{8y} + \cdots\right). \tag{A11}$$

3. Some inverse Laplace transform formulae

The Laplace transform of a local integrable on $\overline{\mathbb{R}}_+ := [0,+\infty)$ real-valued function $g(x,t)$ with respect to time $t \in \overline{\mathbb{R}}_+$ $\mathcal{L}\{g\}(s) := \overline{g}(x;s)$ is defined as

$$\overline{g}(x;s) = \int_0^\infty g(x,t)\exp(-st)dt. \tag{A12}$$

Here, $s \in \mathbb{C}$ is termed the Laplace transform variable and $\overline{g}(x;s)$ is an analytical function in the complex domain $\Omega_C := \{s \in \mathbb{C} : \mathrm{Re}\, s > 0\}$. Symbol $\mathcal{L}^{-1}$ denotes the inverse Laplace transform, i.e., $\mathcal{L}^{-1}\{\overline{g}\}(t) := g(x,t)$; at that, it is given by the Bromwich inversion integral,[126]

$$g(x,t) = \frac{1}{2\pi i}\lim_{\omega\to+\infty}\int_{c-i\omega}^{c+i\omega}\exp(st)\overline{g}(x;s), \tag{A13}$$

where $c \in \mathbb{R}$ is a vertical contour in the plane $\mathbb{C}$ chosen so that all singularities of the function $\overline{g}(x;s)$ are to the left of it.

For easy reference, we present here a few selected formulas for the inverse Laplace transforms, which are used in this paper,[12,30,53,126]

$$\mathcal{L}^{-1}\left\{\frac{1}{s}\exp(-\alpha s)\right\} = H(t-\alpha), \tag{A14}$$

$$\mathcal{L}^{-1}\left\{\frac{1}{(1+\alpha s)}\right\} = \frac{1}{\alpha}\exp\left(-\frac{t}{\alpha}\right) \quad (\alpha \neq 0), \tag{A15}$$

$$\mathcal{L}^{-1}\left\{\frac{\alpha}{s(s+\alpha)}\right\} = 1-\exp(-\alpha t) \quad (\alpha \neq 0), \tag{A16}$$

$$\mathcal{L}^{-1}\left\{\frac{1}{\sqrt{s+\alpha}\sqrt{s+\beta}}\right\} = \exp\left(-\frac{\gamma t}{2}\right) I_0\left(\frac{\sigma t}{2}\right), \tag{A17}$$

$$\mathcal{L}^{-1}\left\{\exp\left[-\chi\sqrt{(s+2\alpha)(s+2\beta)}\right]\right\} = \exp(-\chi\gamma)\delta(t-\chi) + \sigma\chi\exp(-\gamma t)\frac{I_1\left(\sigma\sqrt{t^2-\chi^2}\right)}{\sqrt{t^2-\chi^2}}H(t-\chi), \tag{A18}$$

$$\mathcal{L}^{-1}\left\{\frac{1}{s}\exp\left[-\chi\sqrt{(s+2\alpha)(s+2\beta)}\right]\right\} = \left[\exp(-\chi\gamma) + \sigma\chi\int_{\chi}^{t} d\xi \exp(-\gamma\xi)\frac{I_1\left(\sigma\sqrt{\xi^2-\chi^2}\right)}{\sqrt{\xi^2-\chi^2}}\right] H(t-\chi). \tag{A19}$$

Here, α, β, and χ are real parameters such that $\gamma = \alpha + \beta$, $\sigma = \alpha - \beta$.

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