Fractional differentiation method: Some applications to the theory of subdiffusion-controlled reactions

Sergey D. Traytak *

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

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The fractional differentiation method's broad possibilities are demonstrated with rather simple but important examples of the anomalous diffusion trapping problems. In particular we evaluate the reaction rate coefficients for the subdiffusion-controlled reactions and for reactions describing by a diffusion equation with a half-order time derivative as a damping term. The distinctive feature of this aproach is that the reaction rate coefficient may be obtained by means of some factorization procedure immediately, without a preliminary solution to the corresponding initial boundary value diffusion problem. The explanations given in the paper are detailed enough to provide the mathematical background for the fractional differentiation method needed to apply it to a wide range of reaction-diffusion problems with time-fractional derivatives in the Riemann-Liouville sense.

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I. INTRODUCTION

Diffusion processes with reactions are finding ever-widening applications in biology, chemistry, neuroscience, and physics including optics and astrophysics to name just a few. Among them of particular importance are subdiffusion-controlled reactions, which are attracting increasing attention in recent decades. Often the reaction-subdiffusion systems are modeled within the continuous-time random walk approach and its modifications. On the other hand, the alternative theoretical approach which we are going to treat here may be formulated in terms of initial boundary value problems for equations with fractional derivatives [1]. This is a significant point since the calculus of fractional order derivatives has gained impressive developments. From the very beginning we would like to stress that it is not our intention here to enter into even a brief survey of multiple and rather complex physical aspects of this problem. Readers can find good insights into this vast subject in Refs. [1–13] and in other works cited below.

Specifically speaking, we focus our treatment on the application of the fractional differentiation method (or Babenko's symbolic calculus method) [14–17] to study the theory of diffusion (subdiffusion)-controlled reactions.

As far as we know, the basic idea of application of a half order time derivative to find a boundary gradient for the classical parabolic initial boundary value problems of mathematical physics was conceived first by Courant and Hilbert [18].

Next, in 1969 Oldham proposed to use a fractional derivative of order $1/2$ (called the "semidifferentiation operator") to solve some electrochemical problems involving diffusion in the semi-infinite space [19]. This approach was significantly developed for the cases of diffusion in media with cylindrical and spherical geometry by Oldham and Spanier [20,21]. It has been shown there that the original initial boundary value diffusion problem may be reduced to a single equation which involves only a first-order spatial derivative and a half-order time-fractional derivative.

We highly emphasize that the above attempts to use a half-order time-fractional derivative to solve some problems of heat and normal diffusion transfer may be treated only as a germ of the idea for the method under consideration. In a proper sense the *fractional differentiation method* (FDM) for heat transfer problems (counterparts to the diffusion ones) was originally suggested later by Babenko [14]. In 1996 Babenko published a landmark book *Heat and Mass Transfer: Calculating of Heat and Diffusion Fluxes* [15], where he described the general concept of the FDM and also gave a number of examples of its implementation in the heat and mass transfer theories. Subsequently, further development of the FDM was presented in his other considerably revised and enlarged book [16]. It is appropriate to note that the above books are available only in Russian, and apparently, therefore, the FDM has not received due attention worldwide. We underline, however, that Sec. 6.3 of the book by Podlubny describes briefly the FDM and a few its applications [17]. In this paper we detail enough to provide the necessary mathematical background for the FDM.

An additional point to emphasize is that applicability of the FDM is much wider than the known classical Laplace transform method. Problems for partial differential equations including time-fractional derivatives and integral equations may be effectively tackled even when coefficients depend on both spatial and temporal variables. Moreover, some problems of nonlinear differential equations are amenable to theoretical treatment by the FDM.

The FDM proved to be useful to solve integral equations [22] and even for pure mathematical problems concerning the existence and uniqueness of solutions for the time-fractional nonlinear partial integro-differential equation with Caputo derivatives (see, e.g., Ref. [23] and references therein). Here

*Contact author: sergtray@mail.ru

it is expedient to cite the recent paper by Li and Beaudin: "Babenko's approach is a very useful method in solving differential and integral equations by treating integral operators as variables and derives convergent infinite series as solutions in spaces under consideration" [24].

Thus, it turned out that Babenko's approach is an efficient tool used to solve analytically partial differential equations (including time-fractional differential equations) with initial conditions or initial boundary value problems describing diffusion. Moreover, note that the FDM allows us to find desired boundary gradients of the local concentration immediately in a rather simple and elegant manner. Nevertheless, it has been known that application of the FDM in a general case leads to some functional series which are valid mostly at small time values [15,16]. However, it is significant that even within the scope of the FDM there are several ways to extend the covergence of these series to the case of large times [16]. In particular, to obtain long-time expansions, Babenko proposed to seek the boundary gradient as a series in positive powers of the fractional-order derivatives (see also Sec. IX below). A number of mathematical aspects concerning substantiations for the method were presented in Ref. [16]. However, the comprehensive investigation of convergence conditions for the FDM series is a quite difficult task, and final results have not yet been obtained. So here we focus our attention mainly on the FDM application algorithm (see details in Sec. VI), putting aside fairly subtle questions on its mathematical justifications.

The present paper stems from our previous works devoted to different applications of the FDM to the theory of trapping reactions in which reactants undergo normal diffusion [25–29]. Note in passing that in those works on the FDM we used term the *method of fractional-order differential operators,* and, moreover, it is also known as *Babenko's symbolic calculus method* [17]. However, we think that the term "fractional differentiation method" originally proposed by Babenko should be put to better use.

We proved that for the general one-dimensional normal diffusion problem with coefficients depending only on spatial variables the use of the FDM is equvalent to application of the known Wentzel-Kramers-Brillouin method performed in the Laplace transform space with respect to time [25]. The use of singular perturbations theory allowed us to sum up the leading terms of the relevant asymptotic functional series obtained by means of the FDM for the rate coefficient of the normal diffusion-controlled reactions with Coulomb interaction potential [26,27]. This procedure helped us to go beyond the short-time restriction imposed by the direct utilization of the standard FDM algolothm. Taking advantage of the FDM we manage to establish the exact connection between the rate coefficient in the case of the perfect absorption and the corresponding rate for the partially reflecting condition in a very simple fashion [28]. With the aid of the FDM we also investigated mobility effects of the phase transition boundary on capture of aerosol particles by a droplet [25]. It is worth also noting that in one specific case of a series with respect to fractional derivatives their radius of convergence has been establised [29]. Finally, in the recent Ref. [30] we considered different aspects of the FDM applications to study kinetics of reactions for both Fickian and non-Fickian normal diffusion of reactants within the scope of Smoluchowski's trapping model. In particular the known Rice formula for the hyperbolic rate coefficient was derived there by means of the FDM.

We conclude this survey noting that the operator factorization is not new in physics and can be traced back to Dirac, who, to our knowledge, pioneered the application of the square root of the wave operator to derive his relativistic wave equation, which is the first-order in both space and time. Note also that the operator factorization, being an important feature of the FDM, is not an exhaustive point (see Sec. VI).

Since this article focuses on the description of a mathematical method we mainly have to deal with mathematical concepts rather than the physical ones. That is why, for readers' convenience, the most important mathematical notations, definitions, and formulas are given (see the Appendix), and, moreover, all necessary calculations are provided in some detail.

This paper is structured as follows. The following Sec. II contains basic physical assumptions on the trapping model for reactions due to anomalous diffusion. Section III elucidates the operators factorization idea. In Sec. IV we formulate the general external initial boundary value problems for the time-fractional diffusion equations. Discussion of the trapping rate coefficient is also considered here. Next Sec. V is devoted to a description of an important case of the subdiffusion problems with spherical symmetry. In the short Sec. VI we represent the FDM as an algorithm comprising seven main steps. Application of the FDM to the normal diffusion-controlled reactions is presented in Sec. VII. In Sec. VIII we apply the FDM to the subdiffusion-controlled reactions and compare obtained results with the known Wyss solution. In Sec. IX we investigate in detail an important special case of the problem for the time-fractional telegraph equation. Finally, we give brief concluding remarks in Sec. X. We provided some important mathematical background technical details of the method in the Appendix.

II. PHYSICAL BACKGROUND

Consider an unconfined, quiescent, homogeneous, and isotropic inert host medium containing spherical particles A and B. Hence, we can neglect anisotropy and dependence on spatial and temporal coordinates of physical quantities inherent in this host medium. We focus here on the irreversible bulk diffusion-controlled reactions between A and B particles that occur in the host medium with the elementary reaction scheme [31]

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

We assume that B particles moves toward static A's by diffusion and, furthermore, that the reaction between reactants A and B to form a product P is much faster than the diffusion time. Moreover, let reaction (1) be heterogeneous, i.e., it takes place at the encounter distance, $R = R_A + R_B$, where R_A and R_B are radii of particles A and B, respectively. In this way we can formally treat an immobile particle A as an absorbing sink of radius R but then B becomes a pointlike particle. According to the classical Smoluchowski trapping model, the reaction rate coefficient $k(t)$ in (1) should be taken as a time-dependent positive function $k(t) > 0$ for all times $t > 0$, calculated by means of a solution to some initial boundary value problem for a relevant diffusion equation [31]. Here, for simplicity's sake, we shall consider the force-free reaction-diffusion processes, occurring in three-dimensional (3D) host media.

It has been observed that the behavior of the *mean-square displacement* for a diffusing B reactant often reveals a power-like asymptotic law [1,32–34]:

$$\langle \mathbf{r}^2(t)\rangle \sim K_\alpha t^\alpha \quad \text{as} \quad t \gg \tau_D\,, \tag{2}$$

where $\langle\cdots\rangle$ represents an ensemble average, K_α is a positive constant, α is some nonnegative number, and τ_D is the diffusion relaxation time inherent the host medium [35].

The mean-square displacement (2) is the fundamental relation, which depends on the host medium structure. Provided $0 < \alpha < 1$ the diffusion transport of B particles is slower than the *normal diffusion* one ($\alpha = 1$) and known as *anomalous subdiffusion*. The corresponding number α is called the *anomalous subdiffusion exponent* [33,34], and in turn the particles B and host medium are referred to as the subdiffusive particles and subdiffusive medium, respectively [32].

Numerous reactions of the type (1) appear to be subdiffusion-controlled, and for this reason they have attracted the close attention of many researchers (see references in Sec. IV).

III. THE OPERATOR FACTORIZATION

In general terms the FDM is one in which initial boundary value problems for the second-order or higher partial differential equations are reduced to the corresponding systems of equations of a lower order (see Sec. VI). Without going into subtle mathematical details, we shall elucidate the key idea of the operator factorization by means of simple equations without the boundary conditions.

A. The 1D normal wave equation

Consider the 1D wave equation

$$\Box_c\varphi := \left(\partial_t^2 - c^2\partial_x^2\right)\varphi(x,t) = 0 \quad x\in\mathbb{R}\,,\ \ t\in\mathbb{R}_+\,, \tag{3}$$

where $\Box_c$ is the d'Alembert operator with the wave velocity $c > 0$. For brevity, henceforth ∂_ς stands for the partial derivative $\partial/\partial\varsigma$ with respect to the independent variable ς. Taking into account that $\partial_t\partial_x = \partial_x\partial_t$ one can carry out factorization of the d'Alembert operator as follows:

$$\Box_c = \mathcal{L}^-\mathcal{L}^+\,, \tag{4}$$

$$\mathcal{L}^- := (\partial_t - c\partial_x)\,,\quad \mathcal{L}^- := (\partial_t + c\partial_x)\,. \tag{5}$$

Thus, the second-order partial differential equation (3) leads to a system of two equations of the first order:

$$\mathcal{L}^-\varphi^+ = 0\,,\quad \mathcal{L}^+\varphi^- = 0\,. \tag{6}$$

It may be proved that $\ker(\mathcal{L}^\mp) \subset \ker(\Box_c)$ and general solution to the wave equation (3) reads $\varphi(x,t) = \varphi^+(x,t) + \varphi^-(x,t)$, where function $\varphi^+(x,t)$ [$\varphi^-(x,t)$] describes a wave moving to the left (right) at the speed c, respectively.

B. The 1D time-fractional diffusion wave equation

In Ref. [36] Gorenflo and Mainardi considered the fundamental solution $u(x,t)$ of the time-fractional drift equation

$$\begin{aligned} {}^C\mathcal{D}_t^\beta u(x,t) &= -\partial_x u(x,t), \quad 0 < \beta \leqslant 1,\\ u(x,0+) &= \delta(x), \qquad\quad x\in\mathbb{R},\ \ t\in\mathbb{R}_+ \end{aligned} \tag{7}$$

with $\delta(x)$ the Dirac delta function and ${}^C\mathcal{D}_t^\beta$ the fractional derivative of order β in the Caputo sense (A3). There they noted that Eq. (7) is simply related to that of the *time-fractional diffusion wave equation*

$$\left({}^C\mathcal{D}_t^{2\beta} - \partial_x^2\right)u(x,t) = 0\,,\quad x\in\mathbb{R}\,,\ \ t\in\mathbb{R}_+ \tag{8}$$

under initial conditions

$$u(x,0+) = \delta(x) \quad \text{if} \quad 0 < \beta \leqslant 1\,, \tag{9}$$

$$\partial_t u(x,0+) = 0 \qquad \text{if} \quad 1/2 < \beta \leqslant 1\,. \tag{10}$$

By factorizing Eq. (8) we get [36]

$$\left({}^C\mathcal{D}_t^{2\beta} - \partial_x^2\right)u = \left({}^C\mathcal{D}_t^{\beta} - \partial_x\right)\left({}^C\mathcal{D}_t^{\beta} + \partial_x\right)u\,. \tag{11}$$

Hence one can see that to find the fundamental solution of the time-fractional drift equation (7) we must treat the solution of Eq. (8) for the right factor in the representation (11). In Ref. [36] Eq. (8) has been solved by using the Laplace transform, and then the required fundamental solution was found.

C. The subdiffusion of cosmic rays

The subdiffusion model at $\alpha = 1/2$ has been widely used also to solve the problem of the diffusion motion of particles in a weakly inhomogeneous magnetic field occuring for cosmic radiation, which has been defined as extraterrestrial charged particle radiation (see Ref. [37] and the bibliography therein).

In 1977, studing the cross-field transport of cosmic rays, Urch concluded that their diffusion differs from the normal first Fick law by the presence of the third derivative instead of the first one: $j_x := -D_U\,\partial_x^3 u$. Hereafter $u(x,t)$ is the isotropic distribution for the particles, averaged over all particle momentum directions, and D_U stands for the relevant transport constant. Then, with the help of the continuity relation, Urch derived his transport equation

$$\left(\partial_t - D_U\,\partial_x^4\right)u(x,t) = 0\,,\quad x\in\mathbb{R}\,,\ \ t\in\mathbb{R}_+\,. \tag{12}$$

Webb *et al.* pointed out that Urch's solution exhibited the anomalous subdiffusion property (2) at $\alpha = 1/2$ [37]. In its turn they used an alternative model and derived the time-fractional diffusive equation

$$\left(\mathcal{D}_t^{1/2} - \sqrt{D_U}\,\partial_x^2\right)u = 0, \quad x\in\mathbb{R}\,,\ \ t\in\mathbb{R}_+. \tag{13}$$

To establish connection between Eqs. (12) and (13) Urch's Eq. (12) was factorized as follows [37]:

$$\left(\partial_t - D_U\,\partial_x^4\right)u = \left(\mathcal{D}_t^{1/2} - \sqrt{D_U}\,\partial_x^2\right)\left(\mathcal{D}_t^{1/2} + \sqrt{D_U}\,\partial_x^2\right)u\,. \tag{14}$$

Thus, in this section we have demonstrated how the operator factorization is used to find the time-fractional drift equation (7) and the time-fractional diffusive equation (13). However, it should be emphasized that although the operator factorization is an important component of the FDM we wll not apply it here to derive any new physical relations to describe anomalous diffusion phenomena.

IV. STATEMENT OF THE PROBLEM

It is known that memory influence can change the rate of the particle reaction-diffusion transport, and as this takes place, the original partial differential equations of normal diffusion naturally turn into the integro-differential, which often appear to be some form of time-fractional diffusion equations [1,38].

Reactions in subdiffusive media and associated fractional diffusion equations have been intensively investigated [32,33,38–43]. Futher fractional diffusion equations were generalized to the corresponding fractional Kramers equation [44] and fractional telegraph equation [45–47]. Therefore, here we formulate the problems omitting technical details, which readers can find in the above cited references.

A. General time-fractional telegraph equation

We shall study subdiffusion of a subdiffusive particle B in terms of the probability of finding it at space-time point $(\mathbf{r}, t)$, denoting it as $\rho(\mathbf{r}, t)$. For the identical, noninteracting B particles this function also may be treated as the so-called complementary normalized local concentration [31], which, for brevity, we shall call just local concentration. Obviously, concentration is a real-valued nonnegative function $\rho : \overline{Q}^- \to [0, 1]$. Hereafter $\overline{Q}^- = \overline{\Omega}^- \times \overline{\mathbb{R}}_+$, where we assume that a given test sink occupies a 3D ball domain Ω called a *subdiffusive sink* [32].

Assume that similar to the normal diffusion case the subdiffusion may be mathematically descibed by a linear system of coupling conservation law and nonlocal (generalized Cattaneo) constitutive relation given in the 4D augmented configuration space Q^- with respect to $\rho(\mathbf{r}, t)$ and its flux [39,45–47].

Thus, suppose that the evolution of the desired function $\rho(\mathbf{r}, t)$ in Q^- is governed by the *fractional diffusive Cattaneo system*

$$\partial_t \rho = -\nabla \cdot \mathbf{j}\,, \tag{15}$$

$$\mathcal{C}_t^{(\alpha)} \mathbf{j} = -D_\alpha \mathcal{D}_t^{1-\alpha} \nabla \rho\,. \tag{16}$$

Here and elsewhere we use the simplest generalization of normal relaxation operator

$$\mathcal{C}_t^{(\alpha)} := 1 + \tau_D^\alpha \mathcal{D}_t^\alpha, \tag{17}$$

which describes memory (inertial) effects on particles' B subdiffusion (see, e.g., Refs. [35,48,49] and references therein) and is called the *fractional relaxation operator*. In addition vector $\mathbf{j}(\mathbf{r}, t)$ is a nonlocal flux of subdiffusive B particles, ∇ stands for the gradient operator, and $\mathcal{D}_t^\nu\{\cdot\}$ is the Riemann-Liouville fractional derivative of νth order (see Definition A.3), and we assume that the subdiffusion exponent α is fixed such that $0 \leqslant 1 - \alpha < 1$. The positive constant D_α denotes the subdiffusion coefficient connected with the constant K_α in relation (2), and it differs from that of a normal diffusivity [32], having physical dimension $[D_\alpha] = L^2 T^{-\alpha}$. Fractional time τ_D^α ($[\tau_D^\alpha] = T^\alpha$) is an important parameter of the subdiffusive medium [39]. It generalizes the known relaxation time of the normal diffusive wave damping [35].

By the known Kac's trick $(\rho, \mathbf{j}) \to (\rho, \partial_t \rho)$ the fractional system (15), (16) may be reduced to so-called *time-fractional telegraph equation* (TFTE) [39]

$$\left(\tau_D^\alpha \mathcal{D}_t^{2\alpha} + \mathcal{D}_t^\alpha - D_\alpha \nabla^2\right)\rho = 0 \quad \text{in} \quad Q^-\,, \tag{18}$$

where ∇^2 is the Laplace operator.

Thus, the constitutive equation (16) suggested by Compte and Metzler [39] allows us to generalize the subdiffusion equation (22), taking the relaxation effects into account. Note in passing that another choice of the fractional constitutive equation leads naturally to another TFTE [50].

The investigation of the general TFTE (18) when the subdiffusion exponent $0 < \alpha \leqslant 1$ needs some modification of the FDM we will discuss elsewhere.

B. Special and limiting cases of the time-fractional telegraph equation

If it does not cause confusion to denote the desired solution regardless of their physical meaning the same notation will be used throughout the text. Hence, at $\alpha = 1$ in Q^- we have normal relaxation operator $\mathcal{C}_t^{(1)} = 1 + \tau_D \partial_t$ with the normal telegraph equation and, further, as $\tau_D \to 0$ the normal diffusion equation, respectively,

$$\left(\tau_D \partial_t^2 + \partial_t - D_1 \nabla^2\right)\rho = 0\,, \tag{19}$$

$$(\partial_t - D_1 \nabla^2)\rho = 0\,. \tag{20}$$

Note that reactions of scheme (1) for the subdiffusive regime including inertial effects was treated in Ref. [51]. From a mathematical viewpoint Eq. (18) is a time-fractional hyperbolic diffusion equation [35].

The magnitude of fractional time τ_D^α characterizes the transport of subdiffusive particles and, e.g., as $\tau_D^\alpha \to 0$ constitutive equation (16) yields nothing more than a fractional generalization of the first Fick law [32,41]

$$\mathbf{j} = -D_\alpha \mathcal{D}_t^{1-\alpha} \nabla \rho\,. \tag{21}$$

In this case the fractional diffusive Cattaneo system (15) and (16) leads to the *time-fractional subdiffusion equation* (TFDE) [32,41]

$$\left(\partial_t - D_\alpha \mathcal{D}_t^{1-\alpha} \nabla^2\right)\rho = 0 \quad \text{in} \quad Q^-. \tag{22}$$

An important point is that the same limit for the model proposed in Ref. [50] simplifies the fractional constitutive equation to the normal Fick's law. Moreover, note that the convolution term in Eq. (22) (due to the fractional derivative $\mathcal{D}_t^{1-\alpha}$) still retains memory effects on the diffusion.

It is important to bear in mind that to find concentration ρ for $0 < \alpha \leqslant 1/2$, the only condition on its initial value should be imposed, while, for $1/2 < \alpha \leqslant 1$, we need to pose an initial condition for $\partial_t \rho$ as well [52,53]. So, to avoid prescribing that extra initial condition, we shall treat here the limiting case of the anomalous subdiffusion exponent $\alpha = 1/2$ only [54,55]. This case is especially noteworthy since it corresponds the well-known 3D comb model, describing anomalous diffusion in numerous comblike structures, particularly in a disordered nanostructure [16,55–59]. Therefore, considering the above, in the sequel (see Sec. IX) we shall study this limiting case for general TFTE (18), i.e., an equation of the form

$$\left(\sqrt{\tau_D}\partial_t + \mathcal{D}_t^{1/2} - D_{1/2}\nabla^2\right)\rho = 0 \quad \text{in} \quad Q^- . \tag{23}$$

One can see that the TFTE (23) may be physically interpreted as a diffusion equation subject to a damping effect, represented by the $1/2$-order time derivative [52].

C. Initial and boundary conditions

For both TFDE (22) and TFTE (23) we impose the initial condition

$$\rho|_{t=0+} = 0 \quad \text{in} \quad \Omega^- . \tag{24}$$

It should be stressed that very often time-fractional derivatives in the Caputo sense are used in the theoretical works on TFDE [43,54,60]. So the zero initial condition (24) plays an important role in view of discussions of Eqs. (A2) and (A13).

Let us also impose the Dirichlet condition on the boundary $\partial\Omega$ of subdiffusive sink

$$\rho|_{\partial\Omega+} = \rho_s(t) \quad \text{in} \quad \mathbb{R}_+ , \tag{25}$$

where we assume boundary function $\rho_s \in L^1_{\text{loc}}(\mathbb{R}_+)$ such that $0 < \rho_s(t) \leqslant 1$ for all $t \in \mathbb{R}_+$. It is significant that one should not require the *consistency relation* between initial and boundary conditions [61], i.e., stipulate

$$\lim_{t\to 0+} \rho_s(t) = \lim_{\mathbf{r}\to\partial\Omega+} \lim_{t\to 0+} \rho(\mathbf{r}, t) \tag{26}$$

to apply the FDM. For instance, the absorbing boundary condition corresponds to the case when $\rho_s(t) \equiv 1$, and, plainly, this condition is not consistent in sense of relation (26). The case of the arbitrary boundary function $\rho_s(t)$ will be retained hereafter since it describes many important physical phenomena, particularly the so-called signaling problem [53,62].

To complete the formulation of the external time-dependent diffusion problem and then obtain its unique solution one should prescribe a condition at infinity

$$\rho(\mathbf{r}, t) \to 0 \quad \text{as} \quad \|\mathbf{r}\| \to \infty \quad \text{for all} \quad t \in \mathbb{R}_+ . \tag{27}$$

Condition (27) is called the *regularity condition at infinity* (or *Fujita condition* in the context of the time-fractional equations [52]).

Throughout the paper, for brevity sake, the external initial boundary value problems for the TFDE (22) and TFTE (23) under the initial condition (24) and Dirichlet boundary condition (25) which satisfy the regularity condition at infinity (27) we will term *Cauchy-Dirichlet problems*.

To apply the FDM to the posed Cauchy-Dirichlet problems, first, they should be reduced to an appropriate form.

D. Canonical Cauchy-Dirichlet problems

Let $\mathcal{L}(x, t)$ be a linear time-fractional operator with variable coefficients

$$\mathcal{L}(x, t) := \mathcal{D}_t^{2\nu} + \beta(x, t)\mathcal{D}_t^{\nu} - \alpha_2(x, t)\partial_x^2 - \alpha_1(x, t)\partial_x + \alpha_0(x, t) \quad \text{in } \mathbb{R}^2_+ . \tag{28}$$

Here $0 < \nu \leqslant 1$ and coefficients $\beta(x, t)$, $\alpha_i(x, t)$ $(i = 0, 1, 2)$ are smooth real-valued functions in $\mathbb{R}^2_+$; moreover, we suppose that $\alpha_0(x, t) \geqslant 0$, $\alpha_2(x, t) > 0$.

Definition IV.1. For the operator $\mathcal{L}(x, t)$ (28) acting on a function $u : \mathbb{R}^2_+ \to (0, 1)$ we define the external Cauchy-Dirichlet problem of the *canonical form* as follows:

$$\mathcal{L}(x, t)u = 0 \quad \text{in} \quad \mathbb{R}^2_+, \tag{29}$$

$$u|_{t=0+} = 0\,, \quad u|_{x=0+} = u_s(t)\,, \quad u|_{x\to+\infty} \to 0\,, \tag{30}$$

where $u_s(t) \in L^1_{\text{loc}}(\mathbb{R}_+)$ such that $0 < u_s(t) \leqslant 1$.

Canonical problems with both classical and time-fractional operators often arise in diffusion theory. For example, in Ref. [63] the corresponding initial boundary value problem (20)–(23) was formulated with respect to the spherically symmetric survival probability $P_S(r, t)$, but if we introduce the trapping probability $u(r, t) = 1 - P_S(r, t)$ that problem is transformed into a canonical one.

These kinds of problems are important since the FDM is the most well elaborated for the canonical Cauchy-Dirichlet problems [15,16]. Therefore, to apply the FDM it is expedient first to reduce the problem under consideration to some form of the canonical problem (29), (30). At the same time we should particularly emphasize that the class of problems resolved via the FDM is much wider than proper canonical problems. It includes, e.g., some multidimensional problems, problems under Neumann and Robin boundary conditions, nonlinear problems, etc. [15,16].

E. The trapping rate coefficient

The main objective for the reaction kinetics theory is to calculate the total trapping rate of subdiffusive particles by the reaction surface $\partial\Omega$ of a given subdiffusive sink

$$k(t) = \oint_{\partial\Omega} \boldsymbol{\nu}(\mathbf{r}_s) \cdot \mathbf{j}(\mathbf{r}_s, t) dS\,. \tag{31}$$

Here $\boldsymbol{\nu}(\mathbf{r}_s)$ is the normal unit vector pointing outward of Ω^- at its spatial boundary point $\mathbf{r}_s \in \partial\Omega$. Clearly, the reaction (1) is pseudo-monomolecular, and the corresponding chemical kinetics equations along with initial conditions read

$$\frac{dc_B(t)}{dt} = -k(t)c_A c_B(t), \quad \frac{dc_A}{dt} = 0, \quad t > 0, \tag{32}$$

$$c_B(t)|_{t\to 0+} \to c_B^0, \quad c_A(t) \equiv c_A = \text{const}, \tag{33}$$

where c_A and $c_B(t)$ are the bulk concentrations of reactants A and B. Hence, provided rate coefficient (31) is known, the decay of reactants B due to subdiffusion-controlled reactions on the nonevanescent sinks governs the formula [42,64]

$$c_B(t) = c_B^0 \exp\left[-c_A \Phi(t)\right] , \tag{34}$$

$$\Phi(t) := \int_0^t k(\varsigma) d\varsigma\,. \tag{35}$$

Using the definition (A6) at $\nu = -1$ this integral may be rewritten in the operator form as follows:

$$\Phi(t) = \mathcal{D}_t^{-1} k(t)\,. \tag{36}$$

With the help of this representation the FDM allows us to find function $\Phi(t)$ directly without evaluation of the field $\rho(\mathbf{r}, t)$.

V. SPHERICALLY SYMMETRIC CASE

One can see that if B particles' subdiffusion has spherical symmetry, it is expedient to use the spherical coordinates, attached to the origin O, coinciding with the subdiffusive sink center. So we are looking for the radial-dependent concentration field $\rho(r,t)$ of the form $\rho : Q_r^- \to (0,1)$, where $Q_r^- := (r > R) \times \mathbb{R}_+$. The spherically symmetric diffusion problems have a wide variety of applications; therefore, we consider here subdiffusive trapping problems under spherical symmetry.

A. Spherically symmetric Cauchy-Dirichlet problems

Spherical symmetry greatly simplifies the problems since only the radial part of the Laplacian $\nabla_r^2 := 2r^{-1}\partial_r + \partial_r{}^2$ is nonzero. Using this we may rewrite above posed Cauchy-Dirichlet problems.

(a) For the spherically symmetric case the TFDE (22) and diffusive flux (21) may be recast as

$$\left(\partial_t - D_\alpha \mathcal{D}_t^{1-\alpha}\nabla_r^2\right)\rho = 0 \quad \text{in} \quad Q_r^-, \tag{37}$$

$$j_r = -D_\alpha \mathcal{D}_t^{1-\alpha}\partial_r\rho\,. \tag{38}$$

(b) Similarly the spherically symmetric TFTE (23) and corresponding fractional constitutive relation (16) are reduced to

$$\left(\sqrt{\tau_D}\partial_t + \mathcal{D}_t^{1/2} - D_{1/2}\nabla_r^2\right)\rho = 0 \quad \text{in} \quad Q_r^-, \tag{39}$$

$$\mathcal{C}_t j_r = -D_{1/2}\mathcal{D}_t^{1/2}\partial_r\rho\,. \tag{40}$$

Here and below we use simplified notation for the relaxation operator at $\alpha = 1/2$: $\mathcal{C}_t := \mathcal{C}_t^{(1/2)}$. Both Eqs. (37) and (39) should be solved under the following Cauchy-Dirichlet conditions:

$$\rho|_{t=0+} = 0\,, \qquad \rho|_{r=R+} = \rho_s(t)\,. \tag{41}$$

Note that acting in Eq. (39) from left by operator $\mathcal{D}_t^{1/2}$ we obtain

$$\left(\sqrt{\tau_D}\mathcal{D}_t^{3/2} + \partial_t - D_{1/2}\mathcal{D}_t^{1/2}\nabla_r^2\right)\rho = 0\,.$$

As $\tau_D \to 0$ we have an equation with a small parameter at a high-order (3/2) time derivative, and, rigorously speaking, this asymptotic should be investigated by means of singular perturbation theory. Formally the Cauchy-Dirichlet problem for the TFTE (39), (41) turns to the specific case of the problem (37), (41) at $\alpha = 1/2$.

Although the FDM is directly applicable to the problems with spherical symmetry it is more convenient to use it after elimination of the curvature effects. Therefore, first the above Cauchy-Dirichlet problems should be transformed to formally 1D in space problems with respect to an auxiliary functions $u(x(r),t)$, taking into account the well-known relation $r\nabla_r^2(r^{-1}u) = \partial_r{}^2 u$. This may be performed by means of incomplete Kelvin transformation: $\Omega^- \to \mathbb{R}_+^3$ [35] such that $Q_r^- \to \mathbb{R}_+^2$. The corresponding field $\rho(r,t)$ and its gradient $\partial_r\rho(r,t)$ read, respectively

$$\rho(r,t) = \frac{R}{r}u(x,t)\,, \tag{42}$$

$$\partial_r\rho(r,t) = -\frac{R}{r^2}u(x,t) + \frac{R}{r}\partial_x u(x,t)\,,$$
$$(x,t) \in \mathbb{R}_+^2\,, \quad x := r - R \geqslant 0\,. \tag{43}$$

Thus, one formally reduces the posed above Cauchy-Dirichlet problems to the corresponding 1D canonical ones, with respect to the auxiliary functions $u(x,t)$ depending on the spatial variable x and temporal t. This has particular importance in simplifying the spherically symmetric problems [20,34].

B. Spherically symmetric rate coefficients

Henceforward we always suppose that function is "good enough" in order that the following property holds true:

$$\lim_{r\to R+}\partial_r\mathcal{D}_t^{\nu}\{\rho(r,t)\} = \mathcal{D}_t^{\nu}\Big\{\lim_{r\to R+}\partial_r\rho(r,t)\Big\}\,, \tag{44}$$

where $0 < \nu \leqslant 1$ and $t \in \mathbb{R}_+$. Note here that property (44) turns out to be correct for many various diffusion problems [16]; however, in a general case it must be proved.

For the spherical symmetry general formula the rate coefficient (31) is simplified to

$$k(t) = 4\pi R^2\, j_r(r,t)|_{r=R+}\,. \tag{45}$$

In case (a), taking into account constitutive relation (38), we arrive at the explicit formula for the boundary flux

$$j_r|_{r=R+} = -D_\alpha \mathcal{D}_t^{1-\alpha}\,\partial_r\rho|_{r=R+}\,. \tag{46}$$

Since constitutive relation (40) is an ordinary time-fractional differential equation with respect to the flux, case (b) becomes more complicated. Applying the FDM to Eq. (40) similar to Refs. [16,22] we can plainly obtain the operator expression

$$j_r|_{r=R+} = -D_{1/2}\mathcal{C}_t^{-1}\mathcal{D}_t^{1/2}\,\partial_r\rho|_{r=R+}\,, \tag{47}$$

where $\mathcal{C}_t^{-1}$ is the inverse operator to the relaxation one. Formally it may be written in the following fashion:

$$\mathcal{C}_t^{-1} = \frac{1}{1 + \sqrt{\tau_D}\mathcal{D}_t^{1/2}}\,. \tag{48}$$

Specific calculations for the boundary flux (47) depend on the operator (48) realizations and will be considered in Sec. IX.

Thus, the main objective for the theory of subdiffusion-controlled physical processes is to calculate the surface gradient of the auxiliary function $\partial_x u(x,t)|_{x=0+}$ since Eq. (43) yields the relationship

$$\partial_r\rho(r,t)|_{r=R+} = -\frac{1}{R}u_s(t) + \partial_x u(x,t)|_{x=0+}\,. \tag{49}$$

It is obvious that the first term in the right-hand side of Eq. (49) describes curvature effects due to sphericity of the subdiffusive sink reaction surface.

VI. OUTLINE OF THE FDM

Before proceeding to specific applications of the FDM to evaluate the desired reaction rate coefficients corresponding to the posed above Cauchy-Dirichlet diffusion problems, we express this method as an algorithm.

The FDM may be formulated as the algorithm comprising the following seven main steps:

(1) Reduce the original Cauchy-Dirichlet diffusion problem to its canonical form.

(2) Factorize the relevant partial (fractional) differential equation to a system of partial (fractional) differential equations, containing the space partial (fractional) derivatives of lower orders.

(3) Extract an equation with a particular solution satisfying the original initial condition and condition at infinity.

(4) Express the boundary gradient of the desired solution through the prescribed boundary function.

(5) Represent the reaction rate coefficient as an infinite (finite) series with respect to fractional derivatives by means of the given constitutive relation for the flux.

(6) Investigate the convergence of the obtained functional series for short-time values.

(7) Extend the result to the case of large values of time.

It is important to keep in mind that performing the last two steps one can face highly difficult mathematical problems, which is far from its being resolved up to now.

Lastly, we would like to emphasize again that derivation of any equations to describe subdiffusion processes is not the purpose of the method under consideration.

VII. NORMAL DIFFUSION-CONTROLLED REACTIONS

Although the main emphasis of the paper is placed on application of the FDM to problems posed for the TFDE and TFTE we start our treatment from the normal diffusion case when $\alpha = 1$. This allows us to clarify the essence of the method in a more complicated anomalous subdiffusion case.

A. Auxiliary 1D normal diffusion

In the normal diffusion case the Cauchy-Dirichlet problem for the TFDE (37), (41), (27) and flux (38) under transform (42) take the canonical 1D form:

$$\left(\partial_t - D_1\partial_x^2\right)u = 0 \quad \text{in} \quad \mathbb{R}_+^2, \tag{50}$$

$$u|_{t=0+} = 0\,, \quad u|_{x=0+} = u_s(t)\,, \quad u|_{x\to+\infty} \to 0, \tag{51}$$

$$j_x(x,t) = -D_1\partial_x u, \tag{52}$$

where $u_s(t) \equiv \rho_s(t)$ and D_1 is the common normal diffusion coefficient.

Factorization of Eq. (50) yields the relation

$$\left(\mathcal{D}_t^{1/2} - \sqrt{D_1}\partial_x\right)\left(\mathcal{D}_t^{1/2} + \sqrt{D_1}\partial_x\right)u = 0\,. \tag{53}$$

It is proved that a nontrivial solution to Eq. (50) $u(x,t)$ satisfies the time-fractional partial differential equation [65]

$$-\sqrt{D_1}\partial_x u = \mathcal{D}_t^{1/2} u \quad \text{in} \quad \mathbb{R}_+^2\,. \tag{54}$$

Moreover it may be shown that solution to Eq. (54) satisfies initial condition and condition at infinity (51) automatically [16]. In its turn the use of the boundary condition (51) in Eq. (54) directly leads to the expression for the auxiliary flux at the boundary

$$-D_1\,\partial_x u|_{x=0+} = \sqrt{D_1}\lim_{x\to 0+}\mathcal{D}_t^{1/2}u = \sqrt{D_1}\mathcal{D}_t^{1/2}u_s(t) \tag{55}$$

or with the help of Definition A.3 in the explicit form

$$-D_1\,\partial_x u|_{x=0+} = \sqrt{D_1}\frac{1}{\sqrt{\pi}}\partial_t\int_0^t \frac{1}{\sqrt{t-\varsigma}}u_s(\varsigma)d\varsigma\,. \tag{56}$$

It is significant that for the normal diffusion formula (A21) allows us to obtain the exact solution $u(x,t)$ as well:

$$\begin{aligned} u(x,t) &= \exp\left(x\mathcal{D}_t^{1/2}\right)u_s(t) \\ &= \partial_t\int_0^t \operatorname{erfc}\left(\frac{x}{2\sqrt{t-\varsigma}}\right)u_s(\varsigma)d\varsigma\,. \end{aligned} \tag{57}$$

Hereafter we use known complementary error function defined by

$$\operatorname{erfc}(z) := \frac{2}{\sqrt{\pi}}\int_z^\infty \exp\left(-\xi^2\right)d\xi\,. \tag{58}$$

Thus, the FDM directly gives the well-known textbook result for the desired flux on the boundary (56) and even for the field $u(x,t)$ (57) in an elegant and simple way.

Particularly, using expressions (56) and (57) for the absorbing boundary condition $u_s(t) \equiv 1$ and formula (A18), one arrives at

$$-D_1\,\partial_x u|_{x=0+} = \sqrt{D_1}\mathcal{D}_t^{1/2}1 = \sqrt{\frac{D_1}{\pi t}}\,, \tag{59}$$

$$u(x,t) = \exp\left(x\mathcal{D}_t^{1/2}\right)1 = \operatorname{erfc}\left(\frac{x}{2\sqrt{t}}\right). \tag{60}$$

B. Spherically symmetric normal diffusion-controlled reactions

Substituting expression (46) at $\alpha = 1$ and (49) into Eq. (45) by means of the auxiliary doundary flux (55) one can immediately derive for the rate coefficient a compact formula

$$k(t) = k_1\left(1 + R{D_1}^{-1/2}\mathcal{D}_t^{1/2}\right)u_s(t)\,, \tag{61}$$

where $k_1 := 4\pi RD_1$ is the steady-state Smoluchowsi rate constant.

For the case of normal diffusion we can also find formula (61) in another, more common way. With the aid of Eqs. (42) and (60) we obtain a general representation for the concentration field:

$$\rho(r,t) = \frac{R}{r}\exp\left[(r-R)\mathcal{D}_t^{1/2}\right]u_s(t)\,. \tag{62}$$

Using this representation one can find formula (61) for the rate coefficient.

In particular, setting in Eqs. (61) and (62) $u_s(t) \equiv 1$ we can reproduce classical Smoluchowsi's concentration field and rate coefficient [31]:

$$\rho(r,t) = \frac{R}{r}\operatorname{erfc}\left(\frac{r-R}{2\sqrt{t}}\right), \tag{63}$$

$$k(t) = k_1\left(1 + \frac{R}{\sqrt{\pi D_1 t}}\right). \tag{64}$$

It should be stressed that, as we have mentioned above, the FDM does not allow us to find concentration field in general case. However, often one is not interested in the concentration field, looking for the values connected with the relevant boundary flux only, and the FDM works well leading directly to the desired result. An additional point to emphasize is that nowadays the general mathematical theory of the FDM is not as advanced as for the normal diffusion [16]. Readers are referred to Ref. [65], where corresponding theorems have been proved.

VIII. SUBDIFFUSION-CONTROLLED REACTIONS

Let us now generalize the above formulas for the rate coefficients (61) and (64) to the case of reactions occuring in subdiffusive media when $0 < \alpha < 1$.

A. Auxiliary problem with the FDM

Clearly, the auxiliary subdiffusive Cauchy-Dirichlet problem to a spherically symmetric one (37), (41) with respect to the auxiliary regular at infinity function $u(x,t)$ takes the canonical form

$$\left(\partial_t - D_\alpha \mathcal{D}_t^{1-\alpha}\partial_x^2\right)u = 0 \quad \text{in} \quad \mathbb{R}_+^2, \tag{65}$$

$$u|_{t=0+} = 0\,, \quad u|_{x=0+} = u_s(t)\,, \quad u|_{x\to+\infty} \to 0, \tag{66}$$

$$j_x(x,t) = -D_\alpha \mathcal{D}_t^{1-\alpha}\partial_x u\,. \tag{67}$$

In view of the above our main task is to find the auxiliary flux (67) at the boundary, i.e., $j_x(x,t)|_{x=0+}$.

According to the FDM using the commutation relation (A15) at $\nu = 1/2$ one can factorize the diffusion operator in (65) in the following fashion:

$$\left(\partial_t - D_\alpha \mathcal{D}_t^{1-\alpha}\partial_x^2\right) = \left(\mathcal{D}_t^{1/2} - \sqrt{D_\alpha}\mathcal{D}_t^{(1-\alpha)/2}\partial_x\right) \times \left(\mathcal{D}_t^{1/2} + \sqrt{D_\alpha}\mathcal{D}_t^{(1-\alpha)/2}\partial_x\right) \tag{68}$$

in the sense of operator algebra [16].

It may be shown that to obey the regularity condition (27) we should treat the equation with the right factor in (68). Hence, equating this equation to zero, similar to Eq. (54) one readily obtains

$$-\sqrt{D_\alpha}\mathcal{D}_t^{(1-\alpha)/2}\partial_x u(x,t) = \mathcal{D}_t^{1/2}u(x,t)\,. \tag{69}$$

Multiplication of this equation by operator $\mathcal{D}_t^{(\alpha-1)/2}$ from the left yields

$$-\sqrt{D_\alpha}\partial_x u(x,t) = \mathcal{D}_t^{\alpha/2}u(x,t)\,. \tag{70}$$

Taking here the limit as $x \to 0+$ we finally find

$$-\sqrt{D_\alpha}\,\partial_x u|_{x=0+} = \mathcal{D}_t^{\alpha/2}u_s(t)\,. \tag{71}$$

In the particular case of the absorbing boundary condition expression (71) according to formula (A18) gives

$$-\sqrt{D_\alpha}\,\partial_x u|_{x=0+} = \mathcal{D}_t^{\alpha/2}1 = \frac{t^{-\alpha/2}}{\Gamma(1-\alpha/2)}\,, \tag{72}$$

where function $\Gamma(1-\alpha/2)$ may be calculated with the help of the integral

$$\Gamma\left(1-\frac{\alpha}{2}\right) = 2\int_0^{+\infty} \xi^{1-\alpha}\exp(-\xi^2)d\xi\,.$$

Thus, the FDM algorithm again allows us to find immediately the desired boundary gradient (71) [(72)] in the easiest way.

B. Wyss's solution

It is common knowledge that 1D B's subdiffusion towards an absorbing boundary may be descibed exactly in terms of Fox's H function.

Applying operator $\mathcal{D}_t^{\alpha-1}$ to Eq. (65) from the left by means of the semigroup property (A11) we get FTDE in the form used by Wyss [66]

$$\left(\mathcal{D}_t^{\alpha} - D_\alpha\partial_x^2\right)u = 0\,. \tag{73}$$

With the aid of Laplace's transform method he obtained solution in the form corresponding to Cauchy-Dirichlet conditions (66) under an absorbing boundary condition [66]

$$u(x,t) = 1 - \pi^{-1/2} \times H_{23}^{21}\left(\frac{1}{2\sqrt{D_\alpha}}t^{-\alpha/2}x\,\middle|\,\begin{matrix}(1,1);(1,\alpha/2)\\ \left(\frac{1}{2},\frac{1}{2}\right),\left(1,\frac{1}{2}\right);(0,1)\end{matrix}\right), \tag{74}$$

where $H_{pq}^{mn}(\zeta)$ is the so-called Fox's H function. An explicit form of the Fox's H function is not given here because of its cumbersomeness (it can be found, e.g., in Refs. [1,43,67]).

By means of the exact solution (74) in a right neighborhood of the point $x = 0$ Wyss also derived an asymptotic formula [see Eq. (5.3) in Ref. [66]], which in our notation reads

$$u(x,t) \sim 1 - \frac{xt^{-\alpha/2}}{\sqrt{D_\alpha}\Gamma(1-\alpha/2)} \quad \text{as} \quad x \to 0+\,. \tag{75}$$

Wyss claimed that formula (75) describes the "long-time behavior" of the exact solution (74); however, one can see that it leads to the same result as Babenko's approach (72) for the boundary gradient of the solution $\partial_x u|_{x=0+}$ in the whole domain of this function $\mathbb{R}_+$.

C. Spherically symmetric subdiffusive rate

Combining formula (45) and relation (49) for the spherically symmetric subdiffusive rate coefficient we can readily obtain a convenient representation

$$k(t) = k_R(t) + k_x(t)\,. \tag{76}$$

Hereinafter $k_R(t)$ is the correction of the rate to curvature effects, and $k_x(t)$ is 1D auxiliary rate coefficient given by

$$k_x(t) = 4\pi R^2\, j_x|_{x=0+}\,. \tag{77}$$

In the case under study we evidently have

$$k_R(t) = 4\pi D_\alpha R \mathcal{D}_t^{1-\alpha}u_s(t)\,, \tag{78}$$

$$k_x(t) = 4\pi R^2\sqrt{D_\alpha}\mathcal{D}_t^{1-\alpha/2}u_s(t)\,. \tag{79}$$

For the absorbing boundary condition with the help of the formula (A18) the above expressions lead to

$$k_R(t) = 4\pi D_\alpha R\,\frac{t^{-1+\alpha}}{\Gamma(\alpha)}\,, \tag{80}$$

$$k_x(t) = 4\pi R^2\sqrt{D_\alpha}\,\frac{t^{\alpha/2-1}}{\Gamma(\alpha/2)}\,. \tag{81}$$

Clearly, formulas (78)–(81) work for the whole range of time $t \in \mathbb{R}_+$ and the subdiffusion exponent $0 < \alpha \leqslant 1$.

IX. TIME-FRACTIONAL REACTION–TELEGRAPH MODEL AT $\alpha = 1/2$

Now consider the case of the spherically symmetric TFTE at $\alpha = 1/2$ (39) under initial and boundary conditions (41).

The corresponding reaction rate coefficient $k(t)$ is determined by formulas (45), (47), and (49). This shows that, to calculate the rate coefficient, one should first find the boundary gradient of the auxiliary solution $u(x,t)$, which may be estimated by means of the FDM.

Thus, let us reduce the problem (39), (41), and (27) to the auxiliary Cauchy-Dirichlet problem of canonical form

$$\left(\partial_t + \sigma_0 \mathcal{D}_t^{1/2} - D_0 \partial_x^2\right) u = 0 \quad \text{in} \quad \mathbb{R}_+^2, \tag{82}$$

$$u|_{t=0+} = 0\,, \quad u|_{x=0+} = u_s(t)\,, \quad u|_{x\to+\infty} \to 0, \tag{83}$$

$$\sigma_0 \mathcal{C}_t\, j_x = \left(\sigma_0 + \mathcal{D}_t^{1/2}\right) j_x = -D_0 \mathcal{D}_t^{1/2} \partial_x u, \tag{84}$$

where for convenience sake we introduced the notation $\sigma_0^{-1} := \sqrt{\tau_D}$ and $D_0 := \sigma_0 D_{1/2}$. Recall that term $\sigma_0 \mathcal{D}_t^{1/2} u$ describes here the damping effects [52].

We have already noted in Sec. IV that, contrary to the general Eq. (18), we deal with a parabolic time-fractional diffusion equation and, therefore, do not need to specify an initial condition for the time derivative of the solution [52]. Moreover, note in passing that the case at issue $\alpha = 1/2$ is important from the theoretical viewpoint as well. In this connection, e.g., Masoliver wrote the following: "When $0 < \alpha < 1/2$ there is a transition from two different subdiffusive regimes, while if $1/2 < \alpha < 1$ the transition is from superdiffusion to subdiffusion" [68].

A. General expression for the rate coefficient

It is important to keep in mind that there are exist two modifications of the FDM depending on the way in which the original diffusive operator can be factorized [15,16]. In the first way factorization is performed directly by means of infinite series with respect to the fractional derivatives (see also Ref. [27]). The second modification of the method used factorization with the aid of some auxiliary operators and in this way needs formal calculations within the scope of the operator algebra. For the canonical problem (82), (83) it is convenient to use the second modification of the FDM.

Owing to commutation relation (A15) at $\nu = 1/2$ one can factorize the diffusion operator in Eq. (82) as follows [16]:

$$\left(\partial_t + \sigma_0 \mathcal{D}_t^{1/2} - D_0 \partial_x^2\right) = \left(\sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}} - \sqrt{D_0}\partial_x\right) \times \left(\sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}} + \sqrt{D_0}\partial_x\right), \tag{85}$$

where the operator root is defined by the relation (A19).

It is straightforward to show that to obey the regularity condition in (83) we should seek a solution corresponding to the equation formed by the right operator factor in Eq. (85),

$$\left(\sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}} + \sqrt{D_0}\partial_x\right) u(x,t) = 0\,, \tag{86}$$

which can be rewritten as

$$-\sqrt{D_0}\partial_x u = \sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}}\, u\,. \tag{87}$$

In its turn, similar to Eq. (47) we arrive at the formula

$$j_x = -\frac{1}{\sigma_0 + \mathcal{D}_t^{1/2}} \mathcal{D}_t^{1/2} D_0 \partial_x u\,, \tag{88}$$

where the inverse relaxation operator is defined by the relation

$$\left(1 + \sigma_0 \mathcal{D}_t^{1/2}\right) \frac{1}{1 + \sigma_0 \mathcal{D}_t^{1/2}} = 1\,. \tag{89}$$

Combining Eqs. (87) and (88) we derive the general expression for the auxiliary boundary flux of B particles:

$$j_x|_{x=0+} = \frac{1}{\sigma_0 + \mathcal{D}_t^{1/2}} \mathcal{D}_t^{1/2} F_0(t)\,. \tag{90}$$

Henceforth, for short we introduced an auxiliary "Fick-like" boundary flux:

$$F_0(t) := -D_0\, \partial_x u|_{x=0+} = \sqrt{D_0}\sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}}\, u_s(t)\,. \tag{91}$$

Quite apparently, two extreme regimes of the problem (82), (83) may be naturally distinguished [68]: (a) small times when $\sigma_0\sqrt{t} \ll 1$ and (b) large times when $\sigma_0\sqrt{t} \gg 1$.

In its turn to obtain the corresponding auxiliary boundary fluxes by means of formula (90) explicitly one should distinguish two steps of calculations. One has to find the appropriate realization of the root operator $\sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}}$ in Eq. (91) and also appropriate realization of the inverse relaxation operator $\mathcal{C}_t^{-1}$ in Eq. (48) (see *Definition A.1*). Below we shall find these realizations of the root operator in Eq. (91) and the inverse operator (48) for regimes (a) and (b) separately.

B. Expansion for small times

Here we shall obtain the auxiliary boundary flux of subdiffusive particles for short times: $\sigma_0\sqrt{t} \ll 1$ (or $\sqrt{t} \ll \sqrt{\tau_D}$).

Step 1. First, find an appropriate realization of the root operator in Eq. (91). Taking into account the operator identity

$$\sqrt{\mathcal{D}_t + \sigma_0 \mathcal{D}_t^{1/2}} = \mathcal{D}_t^{1/2}\sqrt{1 + \sigma_0 \mathcal{D}_t^{-1/2}}$$

Eq. (91) may be recast as

$$F_0(t) = \sqrt{D_0}\mathcal{D}_t^{1/2}\sqrt{1 + \sigma_0 \mathcal{D}_t^{-1/2}}\, u_s(t)\,. \tag{92}$$

We further can formally expand the operator root here in powers of $\mathcal{D}_t^{-1/2}$ by means of the binomial operator series (A20)

$$F_0(t) = \sqrt{D_0}\mathcal{D}_t^{1/2} \sum_{m=0}^{\infty} \binom{1/2}{m} {\sigma_0}^m \mathcal{D}_t^{-m/2} u_s(t) = \sqrt{D_0}\left(\mathcal{D}_t^{1/2} + \frac{1}{2}\sigma_0 - \frac{1}{8}{\sigma_0}^2 \mathcal{D}_t^{-1/2} + \frac{1}{16}{\sigma_0}^3 \mathcal{D}_t^{-1} - \frac{5}{128}{\sigma_0}^4 \mathcal{D}_t^{-3/2} + \cdots\right) u_s(t)\,. \tag{93}$$

Step 2. Now let us find a realization of the inverse relaxation operator to perform calculations at small times. One can see that

$$\frac{1}{\sigma_0+\mathcal{D}_t^{1/2}}=\mathcal{D}_t^{-1/2}\frac{1}{1+\sigma_0\mathcal{D}_t^{-1/2}}\,. \tag{94}$$

This representation allows us to utilizes here the series with respect to powers of $\mathcal{D}_t^{-1/2}$. Identity similar to (89) yields the expansion

$$\frac{1}{1+\sigma_0\mathcal{D}_t^{-1/2}}=1-\sigma_0\mathcal{D}_t^{-1/2}+\sigma_0^2\mathcal{D}_t^{-1}-\sigma_0^3\mathcal{D}_t^{-3/2}+\sigma_0^4\mathcal{D}_t^{-2}-\cdots\,. \tag{95}$$

At any finite t, using in Eq. (90), realization (94), and corresponding expansion (95), we can express the desired auxiliary boundary flux in the form

$$j_x|_{x=0+}=\left[1-\sigma_0\mathcal{D}_t^{-1/2}+\sigma_0^2\mathcal{D}_t^{-1}-\sigma_0^3\mathcal{D}_t^{-3/2}+O(\sigma_0^4)\right]F_0\quad\text{as}\quad\sigma_0\to0. \tag{96}$$

Substitution of the expansion (93) into Eq. (96) gives

$$j_x|_{x=0+}=\sqrt{D_0}\left[\mathcal{D}_t^{1/2}-\tfrac{1}{2}\sigma_0+\tfrac{3}{8}\sigma_0^2\mathcal{D}_t^{-1/2}-\tfrac{5}{16}\sigma_0^3\mathcal{D}_t^{-1}+O(\sigma_0^4)\right]u_s(t)\quad\text{as}\quad\sigma_0\to0\,, \tag{97}$$

which in case of the absorbing condition acquires the form

$$j_x|_{x=0+}=\frac{\sqrt{D_0}}{\sqrt{\pi t}}\left[1-\frac{\sqrt{\pi}}{2}\sigma_0\sqrt{t}+\frac{3}{4}\sigma_0^2t-\frac{5\sqrt{\pi}}{16}\sigma_0^3t\sqrt{t}+O(\sigma_0^4)\right]\quad\text{as}\quad\sigma_0\sqrt{t}\ll1. \tag{98}$$

C. Expansion for large times

It is worth noting that there is no standard procedure to find the boundary flux for the general external canonical Cauchy-Dirichlet problem (29), (30) [15,16]. Each specific case requires careful mathematical consideration. Particularly in the case at issue one should investigate a possibility to perform expansion in positive orders of operator $\mathcal{D}_t^{1/2}$. This may be carried out by redefining the fractional derivatives according to the extensions given in the Appendix (see Sec. A 4). However, to keep the derivation from becoming too involved, we will limit ourselves to determination of the leading term of the rate coefficient asymptotic expansion as $\sigma_0\sqrt{t}\to\infty$. It is significant that in a forthcoming paper by means of the numerical calculations we will show that for the long time values the FDM procedure leads to the expansion correct at least to the order $O(\sigma_0^{-4})$.

To calculate the auxiliary boundary flux of B particles for large times $\sigma_0\sqrt{t}\gg1$ (or $\sqrt{t}\gg\sqrt{\tau_D}$) we have to use another realization of the root and inverse relaxation operators.

Step 1. Let us transform the root operator in Eq. (91) in another way, suitable for large times. With the help of the operator identity

$$\sqrt{\mathcal{D}_t+\sigma_0\mathcal{D}_t^{1/2}}=\sqrt{\sigma_0}\mathcal{D}_t^{1/4}\sqrt{1+\sigma_0{}^{-1}\mathcal{D}_t^{1/2}} \tag{99}$$

we have

$$F_0(t)=\sqrt{D_0\sigma_0}\mathcal{D}_t^{1/4}\sqrt{1+\sigma_0{}^{-1}\mathcal{D}_t^{1/2}}u_s(t)\,. \tag{100}$$

This time, using the binomial series (A20), we can formally expand the operator root (100) in powers of $\mathcal{D}_t^{1/2}$:

$$F_0(t)=\sqrt{D_0\sigma_0}\mathcal{D}_t^{1/4}\sum_{m=0}^{\infty}\binom{1/2}{m}\sigma_0{}^{-m}\mathcal{D}_t^{m/2}u_s(t)\,. \tag{101}$$

Hence, one can see that starting from the third term fractional derivatives have the form $\mathcal{D}_t^{\nu}$, where $\nu>1$. Leaving in this expansion only terms with $\nu<1$ we arrive at

$$\frac{F_0(t)}{\sigma_0}=\sqrt{D_{1/2}}\left(\mathcal{D}_t^{1/4}+\frac{1}{2\sigma_0}\mathcal{D}_t^{3/4}-\cdots\right)u_s(t)\,. \tag{102}$$

Step 2. Similarly to Eq. (95) for the inverse relaxation operator one has an expansion useful at large times

$$\mathcal{C}_t^{-1}=\frac{1}{1+\sigma_0^{-1}\mathcal{D}_t^{1/2}}=1-\frac{1}{\sigma_0}\mathcal{D}_t^{1/2}+\frac{1}{\sigma_0^2}\mathcal{D}_t-\cdots\,. \tag{103}$$

Taking (102) and (103) into account, general formula (90) at any finite t as $\sigma_0\to\infty$ leads to the leading-term asymptotics

$$j_x|_{x=0+}=\sqrt{D_{1/2}}\mathcal{D}_t^{3/4}u_s(t)+O(\sigma_0^{-1})\,. \tag{104}$$

For the absorbing boundary condition asymptotics (104) as $\sigma_0\to\infty$ is simplified to

$$j_x|_{x=0+}=\sqrt{D_{1/2}}\frac{t^{-3/4}}{\Gamma(1/4)}\left[1+O(\sigma_0^{-1})\right]. \tag{105}$$

The auxiliary boundary fluxes (97) for small times and (104) for large times are also of independent interest since they correspond to the 1D TFTE at $\alpha=1/2$ (23). Moreover, it is clear that the leading terms in Eqs. (104) and (105) correspond to the subdiffusion case at $\alpha=1/2$.

D. Spherically symmetric rate coefficient

In representation (76) for the spherically symmetric reaction rate coefficient under consideration the correction to the rate due to curvature effects reads

$$k_R(t)=4\pi D_{1/2}R\mathcal{C}_t^{-1}\mathcal{D}_t^{1/2}u_s(t)\,. \tag{106}$$

It turns out that the FDM allows us to represent function $k_R(t)$ explicitly in quadrature with the help of a general formula (A22). So, according to formula (76) to calculate the desired rate coefficient $k(t)$ it is sufficient to know the 1D auxiliary rate coefficient $k_x(t)$, or, in view of Eq.(77), auxiliary boundary flux $j_x|_{x=0+}$ of subdiffusive particles.

Thus, formula (106) together with expansions of the 1D auxiliary boundary fluxes for small times (97) and for large times (104) completes the determination of the required rate coefficient in the case of arbitrary boundary function $u_s(t)$. To be specific, let us write here the 1D auxiliary rate coefficient $k_x(t)$ in the case of the absorbing boundary condition. Clearly, for small (when $\sqrt{t/\tau_D}\ll1$) and large times (when $\sqrt{t/\tau_D}\gg1$) formulas (98) and (105) can be recast, respectively,

$$k_x(t) = 4\pi R^2 \sqrt{\frac{D_{1/2}}{\sqrt{\tau_D}}} \frac{1}{\sqrt{\pi t}} \left\{ 1 - \frac{\sqrt{\pi}}{2}\left(\frac{t}{\tau_D}\right)^{1/2} + \frac{3}{4}\frac{t}{\tau_D} - \frac{5\sqrt{\pi}}{16}\left(\frac{t}{\tau_D}\right)^{3/2} + O\left[\left(\frac{t}{\tau_D}\right)^2\right]\right\}, \tag{107}$$

$$k_x(t) = 4\pi R^2 \sqrt{D_{1/2}} \frac{t^{-3/4}}{\Gamma(1/4)}\left[1 + O\left(\sqrt{\frac{\tau_D}{t}}\right)\right]. \tag{108}$$

X. CONCLUDING REMARKS

The fractional differentiation method belongs to the class of methods reducing partial (fractional) differential equations to some systems of (fractional) differential equations of lower orders. This circumstance makes it possible to calculate the desired reaction rate coefficient directly, without a preliminary solution to the corresponding initial boundary value diffusion problem.

We introduced the concept of the "canonical Cauchy-Dirichlet problem" and formulated the fractional differentiation method as the algorithm involving seven main steps.

To outline the fractional differentiation method technique in detail several important examples were considered. We applied this method to obtain trapping rate coefficients for reactions due to normal diffusion and anomalous diffusion including subdiffusion and also an important particular case of the time-fractional telegraph diffusion. It is established that the fractional differentiation method leads to the correct short-time asymptotics for the boundary flux, whereas its expansion at large times often should be treated as heuristic one.

With the help of the fractional differentiation method we reproduced known results for normal and pure subdiffusive-controlled reactions in rather simple and elegant manner. Along with those corresponding results in case of reactions which are described by the time-fractional telegraph diffusion equation seem to be new.

Thus, we clearly showed that the fractional differentiation method is quite promising in relation to numerous initial boundary value problems involving kinetics of diffusion-influenced reactions in condensed matter.

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APPENDIX: SOME MATHEMATICAL AIDS

To make this work maximally self-contained and facilitate understanding of rigorous formulation and applications of the fractional differentiation method, we present here the basic notation, definitions, and some mathematical facts which are used throughout the paper.

1. Basic mathematical definitions and notations

Recall common symbols: $\mathbb{R}$ denotes the reals, $\mathbb{R}_+$ the strictly positive reals, and $\mathbb{R}^3$ the 3D vector space associated with 3D Euclidean space comprising points $\mathbf{r} := (x_1, x_2, x_3)$ with respect to an origin O. The subdiffusive medium is naturally modeled by $\mathbb{R}^3$. As is customary, let $\partial\Omega$ denote the boundary of a domain $\Omega \subset \mathbb{R}^3$ such that $\overline{\Omega} = \Omega \cup \partial\Omega$, where the bar symbol denotes the closure. If $\Omega \subset \mathbb{R}^3$ is a bounded domain we denote its unbounded compliment as $\Omega^- := \mathbb{R}^3 \backslash \overline{\Omega}$. For example, the ball domain of radius R is $\Omega := \{\mathbf{r} \in \mathbb{R}^3 : \|\mathbf{r}\| < R\}$ while $\Omega^- = \{\mathbf{r} \in \mathbb{R}^3 : \|\mathbf{r}\| > R\}$, where $\|\cdot\|$ stands for the common Euclidean norm. The cylindrical evolution 4D domain $Q \subset \mathbb{R}^{3+1}$ with the bottom base $\Omega \subset \mathbb{R}^3$ at $t = 0$ is the set of points $(\mathbf{r}, t)$ such that $Q := \Omega \times \mathbb{R}_+$.

Thus, the *exterior of the cylindrical domain* Q is the partially bounded domain $Q^- := \mathbb{R}^{3+1} \backslash \overline{Q}$. Clearly, if the diffusion of B's occurs in the configuration space Ω^- and space-time domain Q^- is often called the *augmented configuration space*. In particular for the set of points on a positive spacial semiaxis $(x, t) \in Q^- = \mathbb{R}_+ \times \mathbb{R}_+ = \mathbb{R}_+^2$.

The 3D semispace we denote as $\mathbb{R}_+^3 := \{\mathbf{r} \in \mathbb{R}^3 : x_1 \in \mathbb{R}_+\} \subset \mathbb{R}^3$, and in particular 1D space $\{x : x \in \mathbb{R}_+\}$ is known as the *semi-infinite domain*.

Let X and Y be some functional spaces. For a real-valued function $f \in X$ consider an operator $\mathcal{A} : f \to Y$.

Definition A.1. Any transformation of the operator $\mathcal{A}$, which allows us to carry out calculations of its action $\mathcal{A}f(t)$ is termed a *realization of the operator* $\mathcal{A}$ on space X [16].

Clearly, the operator $\mathcal{A}$ realization is not unique (see Sec. IX).

2. Definitions on fractional derivatives

It seems worthwhile to present briefly some important mathematical definitions for the fractional calculus, which are often used in diffusion theory [1,16,17].

First, recall the following definition.

Definition A.2. A real-valued function $f : \mathbb{R}_+ \to \mathbb{R}$ is said to be absolutely locally integrable on $\mathbb{R}_+$ if, for every point $t_0 \in \mathbb{R}_+$, there is an interval $(a, b) \subset \mathbb{R}_+$ such that $t_0 \in (a, b)$ and the following integral exists:

$$\int_a^b |f(t)|dt < +\infty .$$

We designate the class of these functions as $L^1_{\text{loc}}(\mathbb{R}_+)$.

Example A.1. Commonly used in applications is function $f(t) \equiv 1 \in L^1_{\text{loc}}(\mathbb{R}_+)$ but it is not integrable on $\mathbb{R}_+$.

Throughout this paper we shall consider real-valued functions $f \in L^1_{\text{loc}}(\mathbb{R}_+)$.

Definition A.3. The *left-sided Riemann-Liouville fractional derivative operator* of ν-th order with respect to the variable $t \in \mathbb{R}_+$ is defined by the convolution

$$\mathcal{D}_t^\nu f(t) := \frac{1}{\Gamma(1-\nu)} \partial_t \int_0^t (t - \varsigma)^{-\nu} f(\varsigma) d\varsigma , \tag{A1}$$

where $\nu < 1$.

Strictly speaking, clarification "at the zero base point" should be added to this definition [17]. Hereafter we use the short-hand notation $\mathcal{D}_t^\nu$ instead of common notation ${}_0\mathcal{D}_t^\nu$ and $\Gamma(y)$ denotes the Euler gamma function. Besides, for the notation unification, symbols ∂_t and $\mathcal{D}_t = \mathcal{D}_t^1$ are alternatively used. In the ensuing, for brevity's sake, we shall call operator $\mathcal{D}_t^\nu$ just a *fractional derivative*.

Remember, fractional derivatives are defined in an ambiguous way [17]. In particular integration Eq. (A1) by parts leads to the so-called regularized fractional derivative

$$ {}^{C}\mathcal{D}_t^{\nu} f(t) = \mathcal{D}_t^{\nu} f(t) - \frac{t^{-\nu}}{\Gamma(1-\nu)} f(0+)\,, \tag{A2} $$

which is called the *left-sided Caputo fractional derivative of order* ν and given explicitly as [17]

$$ {}^{C}\mathcal{D}_t^{\nu} f(t) := \frac{1}{\Gamma(-\nu)} \int_0^t (t-\varsigma)^{-\nu} \partial_\varsigma f(\varsigma) d\varsigma\,. \tag{A3} $$

We emphasize that often the fractional Cattaneo equation (16) is involved with the Caputo derivatives, and, broadly speaking, these fractional derivatives are used extensively in research, particularly to study subdiffusion [51].

The above Eq. (A2) implies that both fractional derivatives $\mathcal{D}_t^{\nu}$ and ${}^{C}\mathcal{D}_t^{\nu}$ coincide for functions $f : \mathbb{R}_+ \to \mathbb{R}$ with a nullvalue from the right at the zero. This is a reason why we shall treat these functions only [for another reason see also the discussion on formula (A13)]. It may be shown that for both fractional derivatives (A1) and (A3) the correspondence principle holds true [16]:

$$ \lim_{\nu \to 1-} \mathcal{D}_t^{\nu} f(t) = \lim_{\nu \to 1-} {}^{C}\mathcal{D}_t^{\nu} f(t) = \partial_t f(t)\,. $$

For orders $-\nu \in \mathbb{R}_-$ integration in Eq. (A2) by parts once again, and with the aid of the known relation $\Gamma(1-\nu) = -\nu\Gamma(-\nu)$, yields another very compact and useful expression [16].

Definition A.4. When $\nu \in \mathbb{R}_+$ the *left-sided Riemann-Liouville fractional integral operator* is

$$ \mathcal{D}_t^{-\nu} f(t) := \frac{1}{\Gamma(\nu)} \int_0^t (t-\varsigma)^{\nu-1} f(\varsigma) d\varsigma\,. \tag{A4} $$

Plainly the left-sided Riemann-Liouville fractional derivative (A1) is the left inverse to the fractional integral (A4) with the same order, i.e., for all $\nu \in \mathbb{R}_-$ and $t \in \mathbb{R}_+$ the following relation holds:

$$ \mathcal{D}_t^{-\nu} \mathcal{D}_t^{\nu} f(t) = f(t)\,. \tag{A5} $$

The fractional integral (A4) leads to the expression for the classical integral operator, i.e., when order $\nu = -n$ and $\Gamma(n) = (n-1)!$:

$$ \mathcal{D}_t^{-n} f(t) = \frac{1}{(n-1)!} \int_0^t (t-\varsigma)^{n-1} f(\varsigma) d\varsigma, \quad n \in \mathbb{N}\,. \tag{A6} $$

Note that in applications for an important specific case of $\nu = 1/2$ the designations $\mathcal{D}_t^{1/2}$ and $\sqrt{\mathcal{D}_t}$ are alternatively used.

Frequently the FDM implementations deal with operators $\mathcal{D}_t^{\nu}$, when $\nu > 1$. For simple cases one can easily reduce them to the lower order operators, e.g., $\mathcal{D}_t^{1+\alpha} = \mathcal{D}_t \mathcal{D}_t^{\alpha}$ when $0 < \alpha < 1$ (see the discussion in Sec. IX).

Recall the following.

Definition A.5. If for a given equation an unknown function is contained under the operation of the fractional order derivatives it is called a *differential equation of fractional order*.

3. Some properties of fractional derivatives

Let us dwell on some noteworthy properties of the fractional derivatives which are used in the paper.

Given Definition A.3 preserves the well-known properties of the ordinary derivative of integer order. For complementation sake let us define the *identity operator* $\mathcal{I} := \mathcal{D}_t^0$ (*zero rule*); i.e., we mean [17]

$$ \mathcal{D}_t^0 f(t) = \mathcal{I} f(t) = f(t), \tag{A7} $$

$$ \partial_t^n f(t) \equiv \mathcal{D}_t^n f(t) \quad \text{if} \quad n \in \mathbb{N}\,. \tag{A8} $$

Throughout the text, we use the simplified notation $\mathcal{I} = 1$, if this does not cause confusion. Clearly $\mathcal{D}_t^{\nu}$ is a linear operator; i.e., for any functions $f(t)$ and $g(t)$ from $L^1_{\text{loc}}(\mathbb{R}_+)$ and all real constants a and b we can write

$$ \mathcal{D}_t^{\nu}\{af(t) + bg(t)\} = a\mathcal{D}_t^{\nu}\{f(t)\} + b\mathcal{D}_t^{\nu}\{g(t)\}\,. \tag{A9} $$

To avoid discussion of rather subtle mathematical questions we consider functions with a null value from the right at the zero, i.e., we assume that the following limit holds true:

$$ \lim_{t \to 0+} f(t) = 0\,. \tag{A10} $$

Then Definition A.3 implies the basic *semigroup property* of the fractional derivative operator $\mathcal{D}_t^{\nu}$:

$$ \mathcal{D}_t^{\nu} \mathcal{D}_t^{\mu} f(t) = \mathcal{D}_t^{\nu+\mu} f(t), \quad \nu + \mu \leqslant 1, \tag{A11} $$

which in turn leads to the operator *commutative property*:

$$ \mathcal{D}_t^{\nu} \mathcal{D}_t^{\mu} = \mathcal{D}_t^{\mu} \mathcal{D}_t^{\nu}\,. \tag{A12} $$

Property (A11) may be readily proved for $\nu + \mu < 1$, and in the case when $\nu + \mu = 1$ its proof is more difficult and requires a separate consideration (see, e.g., Ref. [16]). Note that condition (A10) is important for the FDM. Indeed, in a general case $\mathcal{D}_t^{-1/2}\mathcal{D}_t \neq \mathcal{D}_t \mathcal{D}_t^{-1/2}$ since, for an arbitrary smooth function $f(t)$, one can show that

$$ \mathcal{D}_t^{-1/2} \mathcal{D}_t f(t) = \mathcal{D}_t \mathcal{D}_t^{-1/2} f(t) - f(0+)(\pi t)^{-1/2}\,. \tag{A13} $$

Similarly the law of exponents for integration holds:

$$ \mathcal{D}_t^{-\nu} \mathcal{D}_t^{-\mu} = \mathcal{D}_t^{-\nu-\mu} $$

and Eq. (A5) in the operator form reads

$$ \mathcal{D}_t^{-\nu} \mathcal{D}_t^{\nu} = 1\,. \tag{A14} $$

Moreover, for all smooth functions on $\mathbb{R}_+^2$ the following commutation relation holds true:

$$ \mathcal{D}_t^{\nu} \partial_x = \partial_x \mathcal{D}_t^{\nu}\,, \quad \nu < 1\,. \tag{A15} $$

Consider also some useful formulas for fractional derivatives. The known classical Leibniz rule can be extended to fractional derivatives. For any two smooth functions $f(t)$ and $g(t)$ the fractional derivative operator of their product is given by the *general Leibniz rule* [15,54]:

$$\mathcal{D}_t^\nu\{f(t)g(t)\} = \sum_{n=0}^{\infty}\binom{\nu}{n}\mathcal{D}_t^n f(t)\mathcal{D}_t^{\nu-n}g(t)\,. \tag{A16}$$

Here the generalized binomial function defined for all $\nu \in \mathbb{R}$ and given by formulas

$$\binom{\nu}{0} := 1\,,$$
$$\binom{\nu}{n} := \frac{1}{n!}\nu(\nu-1)\cdots(\nu-n+1)\,, \quad n \in \mathbb{N}\,. \tag{A17}$$

The action of operators $\mathcal{D}_t^\nu$ on the power functions t^μ, playing an important role for many applications, is [16,21]

$$\mathcal{D}_t^\nu t^\mu = \frac{\Gamma(\mu+1)}{\Gamma(\mu+1-\nu)}t^{\mu-\nu}, \quad \mu > -1\,, \quad \nu < 1\,. \tag{A18}$$

Note in passing that property (A18) resembles those for the classical differential operator, i.e., when $\nu \in \overline{\mathbb{N}}$.

For any $b \in \mathbb{R}$ the operator root $\sqrt{\mathcal{D}_t + b}$ is defined as [15,17]

$$\sqrt{\mathcal{D}_t + b}\sqrt{\mathcal{D}_t + b} = \mathcal{D}_t + b\,. \tag{A19}$$

Moreover, the following formal binomial series expansion of the operator root is frequently used in applications [15]:

$$\sqrt{1 + b\mathcal{B}_t} = \sum_{m=0}^{\infty}\binom{1/2}{m}b^m\mathcal{B}_t^m\,, \tag{A20}$$

where $\mathcal{B}_t$ is a time-dependent operator.

For all points $(x,t) \in \overline{\mathbb{R}}_+ \times \mathbb{R}_+$ we can define the *exponent operator* as follows [16]:

$$\exp\left[x\mathcal{D}_t^{1/2}\right]f(t) := \partial_t\int_0^t \operatorname{erfc}\left(\frac{x}{2\sqrt{t-\varsigma}}\right)f(\varsigma)d\varsigma\,. \tag{A21}$$

In the table of fractional derivatives of Ref. [16] one can find a useful formula

$$\frac{1}{a + \mathcal{D}_t^{1/2}}g(t) = \int_0^t \frac{g(\varsigma)}{\sqrt{\pi(t-\varsigma)}}d\varsigma - a\int_0^t \times \exp[a^2(t-\varsigma)]\operatorname{erfc}(a\sqrt{t-\varsigma})g(\varsigma)d\varsigma\,, \tag{A22}$$

where a is a nonnegative real parameter.

Finally note that Ref. [16] contains rather comprehensive tables of fractional derivatives and operators action on appropriate functions.

4. An extension of the fractional derivatives

Strictly speaking the semigroup property (A11) does not work at $\nu + \mu > 1$. In order to avoid this difficulty the definition of the fractional derivative (A1) may be extended to the following [16]:

$$_{-\infty}\mathcal{D}_t^\gamma f(t) := \frac{1}{\Gamma(1-\gamma)}\partial_t\int_{-\infty}^t (t-\varsigma)^{-\gamma}f(\varsigma)d\varsigma \tag{A23}$$

when $\gamma < 1$ and

$$_{-\infty}\mathcal{D}_t^\gamma f(t) := \frac{1}{\Gamma(2-\gamma)}\partial_t^2\int_{-\infty}^t (t-\varsigma)^{1-\gamma}f(\varsigma)d\varsigma \tag{A24}$$

if $1 \leqslant \gamma < 2$. In Eqs. (A23) and (A24) for arguments of the fractional derivatives $_{-\infty}\mathcal{D}_t^\gamma$ one should use real-valued causal functions of time $f(t) = g(t)\mathbf{1}_+(t)$ such that $\lim_{t\to 0-}|f(t)| < +\infty$ and $g \in L^1_{\text{loc}}(\mathbb{R}_+)$. Here we defined the unit step function $\mathbf{1}_+ : \mathbb{R}\backslash\{0\} \to \mathbb{R}$ as a piecewise function, which values are $\mathbf{1}_+(t) = 1$ if $t \in \mathbb{R}_+$ and zero otherwise.

Example A.2. Consider the semigroup property for the case $\nu = 1$ and $\mu = 1/2$ when $t > 0$:

$$\mathcal{D}_t\mathcal{D}_t^{1/2}1 = \mathcal{D}_t(\pi t)^{-1/2} = -\frac{1}{2\sqrt{\pi}}t^{-3/2} \neq \mathcal{D}_t^{1/2}\mathcal{D}_t 1 = 0\,.$$

On the other hand one can see that in this case

$$\mathcal{D}_{t\,-\infty}\mathcal{D}_t^{1/2}1 = -\frac{1}{2\sqrt{\pi}}t^{-3/2} =_{-\infty}\mathcal{D}_t^{1/2}\mathcal{D}_t 1$$
$$= {}_{-\infty}\mathcal{D}_t^{1/2}\delta(t) = \frac{1}{\sqrt{\pi}}\partial_t\int_{-\infty}^t \frac{\delta(\varsigma)}{\sqrt{t-\varsigma}}d\varsigma$$

as it should be.

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