

Modelling linear reactions in inhomogeneous catalytic systems

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Received: 16 October 2012 / Accepted: 30 November 2012 / Published online: 13 December 2012
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Abstract The kinetics of linear chemical reactions in an inhomogeneous medium is modeled as an evolutionary system characterized by a fractional derivative. The corresponding mathematical model depending on one nonlocal parameter $0 < \alpha < 1$ is proposed. Reactions with one degree of freedom are analyzed. Solutions of the corresponding kinetic equations are shown to depend on the nonlocality parameter α . The concept of the critical moment of time is introduced, and the dependence of its value on the value of the relaxation coefficient is determined.

Keywords Catalysis · Reaction kinetics · Dynamical system · Mathematical modeling

1 Introduction

From chemical kinetics, it is known that a homogeneous reacting chemical system with the concentration C_i of its components is described by a system of first-order differential equations [1–3]:

$$\frac{dC_i}{dt} = F_i(C_1, C_2, \dots, C_f), \quad i = 1, 2, \dots, f. \quad (1)$$

The definite kind of functions F_i depends on the reaction; it is a well-known fact that even the simplest reactions result in non-linear functions F_i . Therefore, in chemical kinetics, non-linearity is of decisive importance. In mechanics and

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electrical engineering we deal with quite definite types of non-linearity, whereas in chemical reactions, because of their immense diversity, the scope of non-linearity types is much broader. In 1967, Korzukhin proved a theorem that in the case when F_i in Eq. (1) is an arbitrary polynomial with non-negative integer exponents of a non-negative whole number, it is always possible to construct at least one asymptotically equivalent chemical reacting system [4]. It is not always possible exactly, e.g., there is no reaction leading to $x' = y, y' = -x$, since no negative cross-effect should be present [5]. From this theorem, it follows that in chemical kinetics any, even most complex, types of non-linearity are possible [6].

In case of an inhomogeneous chemical system, the mathematical modelling of a kinetic equation is a result of the further complication of the functions F_i , i.e. of the right side of Eq. (1). On the other hand, as our recent study has shown [7], inhomogeneity may be stated as a result of generalizing the very concept of a dynamical system, i.e. the left side of Eq. (1).

In the physical sense, such a generalization is based on experimental facts showing a slower so-called subdiffusion ($(\Delta x)^2 \sim t^{1-\alpha}$) and a faster superdiffusion ($(\Delta x)^2 \sim t^{1+\alpha}$) [8,9]. The physical processes in these cases qualitatively agree with the results of the computer modelling of diffusion on fractal polynomials [10,11].

In the mathematical sense, the generalization of the concept of a dynamical system means transition from the concept of the classical derivative to its integro-differential generalization [12]. Numerous examples of physical and technical applications of the fractional calculus are mentioned in the monographs [13,14].

The present study is an attempt to apply the generalized concepts of a dynamical system, proposed by the author, to the description of linear catalytical reactions in inhomogeneous chemical systems. Instead of a system of Eq. (1), we propose to consider a system of integro-differential equations:

$$\frac{d^{(\alpha_i)}C}{dt^{(\alpha_i)}} = F_i(C_1, C_2, \dots, C_f), \quad \alpha_i > 0, \quad i = 1, 2, \dots, f, \quad (2)$$

where d^α/dt^α is the so-called fractional derivative (see “Appendix” and, e.g., [12,14]) and $d^{(\alpha)}/dt^{(\alpha)} = \tau^{\alpha-1}d^\alpha/dt^\alpha - \delta_{\alpha,0}$ is the evolutionary operator. To escape the problems related to dimensions, we have used the operator $d^{(\alpha)}/dt^{(\alpha)}$ with parameter τ , which is the characteristic time scale of reaction (2).

2 Autocatalytical reactions

Autocatalysis takes place when the reaction products catalytically accelerate the reaction itself, i.e. when the rate of the reaction increases with increasing the concentration of its products. Autocatalytic reactions are reactions of propagation or growth. A substance exhibiting an autocatalytic action is capable of self-reproduction at the expense of the initial substances A, B, \dots , which are either consumed in the course of the reaction or are changed into structurally and energetically poorer end products

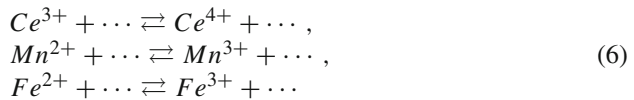
F, G, \dots as a rule, the reactions proceed through the formation of catalytical complexes with a lower energy of activation, for example:



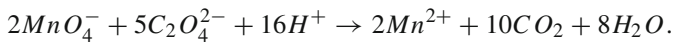
The kinetic equation of this reaction is typical of autocatalysis:

$$\frac{d}{dt}C_X = kC_A C_X. \quad (5)$$

A known example of autocatalytic reaction is oxidation–reduction reactions:

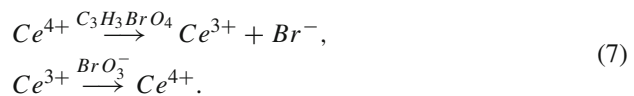


in the presence of Br^- , BrO_3^- ions and organic reductants such as malonic, bromomalonic, acetoacetic, oxalic, apple or citric acids. One of the best-known examples of autocatalysis among oxidation–reduction reactions is the oxidation of oxalic acid by potassium permanganate:



Mn^{2+} ions serve as the catalysers of this reaction.

While studying these oxidation–reduction reactions, Bray [15], Belousov [16], Zhabotinsky [4, 17] and numerous other investigators observed the periodical course of a special type of such reactions [18, 19]. The light absorption variation curve shows the presence of typical relaxation oscillations, their shape greatly differing from sinusoidal. Relaxation oscillations are typical of strongly nonlinear systems [20]. Light absorption was measured in the violet and close-to-violet regions of the spectrum; it is determined mainly by the concentration of Ce^{4+} , Mn^{3+} and Fe^{3+} ions. Zhabotinsky in [17], observed 10 to 50 oscillations of absorption, with the frequency and amplitude instability not exceeding 1%. The reaction took place in a strongly acidic medium ($3nH_2SO_4$) in the presence of $KBrO_3$. The frequency of oscillations depends on the concentration of reductants (about 0.25 gmol/l) and potassium bromide (about 0.07 gmol/l) and varies within 0.01 to 0.2 s. According to Zhabotinsky, the course of this reaction in the presence of bromomalonic acid may be presented by the following scheme:



Autocatalytic as well as cross-catalytical (mutually catalytical) and fermentative reactions are interesting as dynamical systems, as the evolutionary systems exhibiting

considerable nonlinearities. Nonlinear dynamical systems have the kinetic equation solutions which describe unstable stationary states, periodical processes or processes in trigger systems. Solutions with such properties (as was shown by Jost and Meixner) are in principle impossible in linear systems [21,22]. However, the possible nonlocality in an evolutionary Eq. (2) even more complicates the behavior of its solution.

Employing the methodological principle of R. Descartes (“from simple to complex”), let us consider the general properties of a nonlinear, one-dimensional evolutionary system and the difference in the local and nonlocal evolutionary behavior of a chemical reaction.

3 Nonlocal reactions with one degree of freedom

For a reaction in which the concentration $C(t)$ of one component changes, instead of a system of Eq. (2) let us consider a kinetic equation of the type

$$\frac{d^{(\alpha)}C}{dt^{(\alpha)}} = f(C; \lambda), \quad C(t_0) = C_0, \quad (0 < \alpha \leq 1), \tag{8}$$

where $\lambda = \{\lambda_1, \dots, \lambda_s\}$ is a set of parameters. In the dimensionless variables $X = C/C_0, \tau = t/t_0$, where C_0 is the initial concentration and t_0 is the initial or characteristic time-scale. Considering that the fractional derivative is a linear operator, Eq. (8) may be expressed in a dimensionless form:

$$\frac{d^{(\alpha)}X}{d\tau^{(\alpha)}} = \frac{t_0}{C_0} F(XC_0, \lambda) = f(X; \lambda). \tag{9}$$

Like in the classical case, a happy selection of the units of concentration C_0 and time t_0 frequently allows a significant simplification of the function $f(C, \lambda)$.

The stationary solutions of Eq. (9) coincide with the roots of the algebraic equation:

$$f(X; \lambda) = 0. \tag{10}$$

Since X is the concentration, only the positive roots have a physical sense; we shall denote them as $X^{(0)}, X^{(1)}, X^{(2)}$, etc. The number of positive roots depends mainly on the values of parameter $\lambda = \{\lambda_1, \dots, \lambda_s\}$, as will be shown on examples. The stability of each of the states $X^{(s)}$ will be investigated by the method of perturbed solutions [23]. Inasmuch as $X^{(s)}$ does not depend on time, the magnitude

$$x(\tau) = X(\tau) - X^{(s)} \tag{11}$$

in the linear approximation is described by the equation

$$\frac{d^{(\alpha)}x(\tau)}{d\tau^{(\alpha)}} = px(\tau); \quad p = f'(X^{(s)}), \tag{12}$$

its solution having the form of

$$x(\tau) = x_0 E_{\alpha,1}(p\tau^\alpha), \quad x_0 = x(0), \quad (13)$$

where $E_{\alpha,\beta}(z)$ is the Mittag-Leffler function (see, e.g., [24]):

$$E_{\alpha,\beta}(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(\alpha n + \beta)}, \quad (\alpha > 0, \beta > 0), \quad (13a)$$

and $\Gamma(z)$ is Euler's gamma function.

It is possible to show, as follows from the general properties of the Mittag-Leffler function [24], that when p is a real number and α and β are not integer, solution (13) does not oscillate. Depending on the sign of the exponent, two regimes are possible. At $f'(X^{(s)}) < 0$, slight deviations from the stationary concentration $X^{(s)}$ monotonously decrease and at $f'(X^{(s)}) > 0$ monotonously increase. Thus, the stability of a stationary concentration depends on the value of the first derivative function $f(X)$ at a concentration equal to the stationary value. The case when the derivative at this point turns into zero requires separate consideration.

A typical behavior of autocatalytic systems is blow-up, i.e. the fact that the solution is not defined on the whole real time axis (see, e.g., [25]). According to this behavior of the autocatalytic systems, the time of a chemical reaction $t \geq t_0 > -\infty$, i.e. we consider the dynamical systems determined on the half-axis $t \in [t_0; +\infty)$.

Note that in the classical case when $\alpha = 1$, Eq. (9) can always be integrated in elementary or special functions:

$$\int_{X_1}^X \frac{dX}{f(X, \lambda)} = \tau - \tau_1. \quad (14)$$

In the general case when $\alpha \neq 1$, Eq. (9) can be integrated only numerically.

4 Linear nonlocal reactions

Let us consider definite reactions and some systems in the increasing order of their complexity and strictly keeping to the established scheme. Upon writing down a reaction, we will derive the rule of its change in time, employing stoichiometric coefficients. The variable components will be designated through X and their concentrations at the moment t through $C(t)$; hence, $C_0 \equiv C(t_0)$ is the initial concentration. The initial and final products of a reaction will be designated through A and F , respectively, and their concentration through C_A and C_F . We will analyze the behavior of an open system under condition of the constant concentration C_A (the system is open for component A) and the constant or changing in time influx of component X (the system is open with respect to component X , connection with the reservoir is established) and compare it with the behavior of a closed system. The stationary states of the reactions will be classified as follows:

- A. Equilibrium: stable stationary to a complete thermodynamical balance with the environment;
- B. Mobile equilibrium: stable stationary reactions with entropy production non-equal to zero, supported by a constant exchange of substance with the environment;
- C. Unstable stationary states: stationary reactions that at weak perturbations spontaneously deviate from the initial state.

Let us start the discussion from the simplest types of reactions.

4.1 Generation and destruction of component X



$$\frac{d^{(\alpha)}C}{dt^{(\alpha)}} = k_1 C_A - k_{-1} C + \dot{C}_e \tag{16}$$

A. Stable concentration of component A

$$\text{Condition : } \dot{C}_e = 0 \tag{17a}$$

$$\text{Equilibrium : } \bar{C} = \left(\frac{k_1}{k_{-1}}\right) C_A \tag{17b}$$

$$\text{Solution : } C(t) = \bar{C} + [C_0 - \bar{C}]E_{\alpha,1}(-k_{-1} |t - t_0|^\alpha) \tag{17c}$$

B. Constant influx.

$$\text{Condition : } \dot{C}_e = \Phi \tag{18a}$$

$$\text{Mobile equilibrium : } \tilde{C} = \frac{1}{k_{-1}}(\Phi + k_1 C_A) \tag{18b}$$

$$\text{Solution : } C(t) = \tilde{C} + [C_0 - \tilde{C}]E_{\alpha,1}(-k_{-1} |t - t_0|^\alpha) \tag{18c}$$

C. Closed system, concentration $C_A + C$ is set.

$$\text{Condition : } C^{(0)} = C_A + C \tag{19a}$$

$$\text{Equilibrium : } \bar{\bar{C}} = \frac{k_1}{k_1 + k_{-1}} C^{(0)} \tag{19b}$$

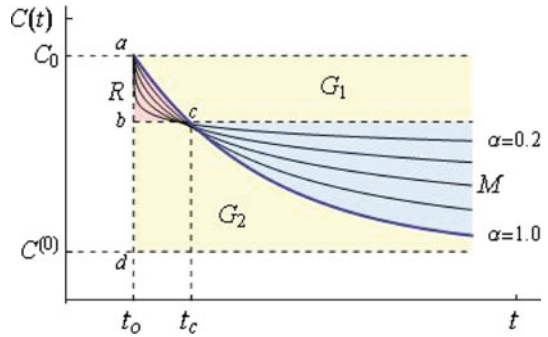
$$\text{Solution : } C(t) = \bar{\bar{C}} + [C_0 - \bar{\bar{C}}]E_{\alpha,1}(-(k_1 + k_{-1}) |t - t_0|^\alpha) \tag{19c}$$

4.2 Catalytical generation and destruction



$$\frac{d^{(\alpha)}C}{dt^{(\alpha)}} = k_1 C_Y C_A - k_{-1} C_Y C + \dot{C}_e = k'_1 C_A - k'_{-1} C + \dot{C}_e \tag{21}$$

Fig. 1 Changes of the initial concentration C_0 depending on the solution (17c) of kinetic equation (16), where $k_{-1} = 0.5$ and $\alpha = 0.2, 0.4, 0.6, 0.8, 1.0$ (Color figure online)



Equilibrium: as in reaction 1.

Mobile equilibrium for a system open with respect to X :

$$\tilde{C} = \frac{1}{k'_{-1}} (\Phi + k'_1 C_A). \quad (22)$$

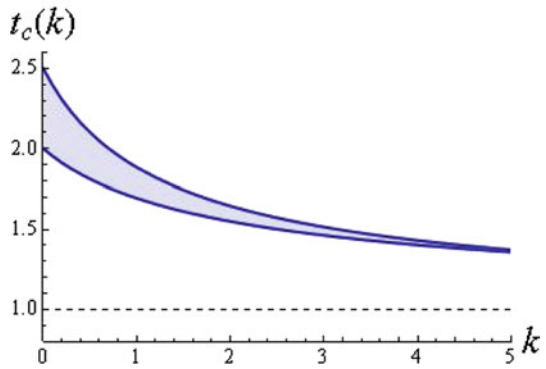
Solutions: as in reaction 1 for $k_1 \rightarrow k'_1, k_{-1} \rightarrow k'_{-1}$.

5 Properties of linear reactions

First of all, let us note that the limit conditions, i.e. whether a system is open or closed, exert a significant influence on the position and type of stationary state. Inasmuch as the above reactions are linear, they are characterized by only one stationary state which is always stable and corresponds to simple or mobile equilibrium. Introduction of a catalyzer does not disturb the equilibrium, although it replaces the position of mobile equilibrium.

Now, let us focus attention on the difference between the classical ($\alpha = 1$) and the non-classical fractional cases ($\alpha \neq 1$). We will differentiate between two types of velocity—the classical integer $\dot{C}(t)$ and the fractional $\dot{C}^{(\alpha)}(t)$. Note that the fractional velocity of the reaction is determined by the same coefficients k_1 and k_{-1} , but its quantitative behavior will change. Introduction of the new parameter α , in principle, allows obtaining any kind of degenerative behavior from the asymptotic value $C^{(0)} = \text{const}$ for $\alpha = 0$ up to the classical exponential degeneration for $\alpha = 1$. Moreover, by continuously changing the parameter α we obtain a continuous deformation of the solution $C(t) = \bar{C} + [C_0 - \bar{C}] \exp(-k_{-1} |t - t_0|^\alpha)$ into solution (17c). In Fig. 1 we have two areas R and M , which appear due to varying the parameter $0 < \alpha < 1$, and two areas G_1 and G_2 , which in contrast with the classical exponential decrease, is never filled while varying of the parameter α . Note here, that the rate of the chemical reaction in the area R is faster and in the area M slower than in the usual classical case. The point c corresponds to the critical value of time t_c , when the concentration $C^{(\alpha)}(t)$ of the chemical reaction according to the kinetic equation (16) becomes equal to concentration $C(t)$ of the classical kinetic equation ($\alpha = 1$):

Fig. 2 The behavior of the value of parameter t_c depending on the coefficient k . Variation of the parameter $0 < \alpha < 1$ corresponds to the blue area of the plot (Color figure online)



$$E_{\alpha,1}(-k|t - t_0|^\alpha) = \exp(-k|t - t_0|). \tag{23}$$

In this equation, the parameter k corresponds to the parameter k_{-1} . The solution of Eq. (23) depends on the values of the parameters α and k :

$$t_c = t_c(k, \alpha). \tag{24}$$

Taking into account the range of the parameters $\alpha(0 < \alpha < 1)$ and $k(0 < k < \infty)$, it is more informative to consider the plot of $t_c = t_c(k)$ where variations of the parameter α correspond to the filling area (see Fig. 2).

An important difference between fractional generalization and formula (16) used in classical modeling is the possibility to vary the rate of the process. If in the classical model the deceleration velocity is k_{-1} , than for $0 < \alpha < 1$ the deceleration velocity is

$$k_{-1}^{(\alpha)} = \frac{k_{-1}}{\tau^{\alpha-1}}, \tag{25}$$

where τ is the characteristic timescale.

It is well known that linear evolutionary systems have no characteristic timescale value; such values occur in nonlinear systems. In the nonlocal case, we have no characteristic timescale value, either, but a comparison of two different kinetic processes—fractional and classical (exponential)—allows us obtaining such kind of value. The critical time t_c (24) is such a value and could be used as a characteristic timescale τ (25) in reaction (16).

The phase portrait of fractional velocity in $(C, \dot{C}^{(\alpha)})$ coordinates, like in the classical case $\alpha \equiv 1$, is a set of straight lines crossing the origin of the coordinates. However, in coordinates (C, \dot{C}) we have a phase portrait only for $\alpha = 1$, since \dot{C} of solution (17c) or (19c) for $0 < \alpha < 1$ does not exist, we have to turn to the area of the parameter $1 < \alpha < 2$. As follows from direct calculations, the function $\dot{C}(t)$ in case $C(t)$ is the solution (17c) or (19c), is not continuous at the point t_0 ; therefore, the function $\dot{C}(t)$ has no chemical sense. From the mathematical point of view, this is no surprise: an α times continuous differential function must not be an $1 + \alpha$ times continuous

differential function, the same as one time differentiated function must not be two times continuously differentiated.

A standard mathematical model of chemical reactions, based on the reaction-diffusion equation, see, e.g., in [5,26]. The reaction-diffusion equation, in its turn, is based on the mathematical description of the standard diffusion process. In the case of non-standard diffusion, we have to use the generalization of the reaction-diffusion equation. Theoretical investigations of diffusion on fractal polynomials [10,11] mean that at least fractal inhomogeneity could be described by the new mathematical instruments. Indeed, let us have the fractional generalization of the diffusion in the form

$$\frac{\partial^\beta C}{\partial t^\beta} = D \frac{\partial^\alpha C}{\partial x^\alpha}, \quad (26)$$

where $C = C(x, t)$, $\partial^\beta / \partial z^\beta$ is the fractional derivative (see below and Appendix) and D is the diffusion coefficient. The important remark concerning the orthant invariance in respect to the space inverse operator implies a special form of the fractional reaction-diffusion model in which the order of the space fractional derivative is 2α . The parity of the space fractional derivative preserves the orthant as an invariant set.

Let $\langle |x|^\alpha \rangle = \int |x|^\alpha C(x, t) dx$ be the statistical (central) moment of $C(x, t)$. In the classical case, $\alpha = 1, 2, 3$ is an integer, but now let α be arbitrarily positive. Then, the evolution of the moments of $|x|^\alpha$ is

$$\frac{\partial^\beta \langle |x|^\alpha \rangle}{\partial t^\beta} = D \int |x|^\alpha \frac{\partial C(x, t)}{\partial |x|^\alpha} dx = D \int C(x, t) \frac{\partial}{\partial |x|^\alpha} |x|^\alpha dx = D \Gamma(1 + \alpha), \quad (27)$$

where we use the formulas from “Appendix” of integration by parts. After fractional integration (27) over t^β we obtain:

$$\langle |x|^\alpha \rangle = D \frac{\Gamma(1 + \alpha)}{\Gamma(1 + \beta)} t^\beta \quad (28)$$

From (28) it follows that at $\alpha = 2$ we have

$$\langle |x|^2 \rangle = \frac{2D}{\Gamma(1 + \beta)} t^{\beta/2} \quad (29)$$

Thus, this expression generalizes the classical mean square displacement formula.

6 Conclusions and discussion

Note that in this paper, only linear catalytical reactions are presented; however, even in this—simplest—case, the inhomogeneous behavior of the reaction, accounted for by the parameter α , reveals an interesting qualitative diversity of dynamical behavior. The method proposed in the paper does not deny the classical method but is more

efficient in cases of small gradients of concentrations and allows explaining the non-traditional dynamics without employing nonlinear terms. Of particular interest are nonlinear reactions: they are much more complicated, but also much more diverse.

The limits of change of the parameter $0 < \alpha \leq 1$ are closely related to the dimensionality of a dynamical system. If $1 < \alpha \leq 2$, the evolutionary equation $\dot{C}^{(\alpha)} = f(C)$, as a result of introducing a new variable, $C_1(t)$, is equivalent to the system

$$\begin{cases} \dot{C}_1^{(\alpha-1)} = f(C), \\ C_1 = \dot{C}. \end{cases}$$

In this paper, we consider only one-dimensional systems. Multidimensional inhomogeneous reactions need special consideration.

An important thesis of physics, referred to as such in cybernetics by N. Wiener, says that the isomorphism of differential evolutionary equations describing heterogeneous phenomena testifies to the structural isomorphism of these phenomena (see, e.g., [27]). Therefore, under certain conditions, differential equations of chemical kinetics are isomorphous to differential equations of nonlocal dynamics, electrical engineering, population regulation and dynamics theory. In other words, it is possible to find chemical systems whose behavior is similar to the behavior of a mechanical perturbation spreading in an inhomogeneous viscoelastic medium, or to the reduction of a biological population in an ecological system. This observation implies that the results presented in this study may be of interest to wide circles of researchers.

7 Appendix

The left Riemann–Liouville fractional derivative

$${}^RL D_{t+}^{\alpha} f(t) = \frac{1}{\Gamma(n-\alpha)} \left(\frac{d}{dt}\right)^n \int_a^t \frac{f(\tau) d\tau}{(t-\tau)^{1+\alpha-n}}. \quad (30)$$

The right fractional derivative

$${}^RL D_{t-}^{\alpha} f(t) = \frac{1}{\Gamma(n-\alpha)} \left(-\frac{d}{dt}\right)^n \int_t^b \frac{f(\tau) d\tau}{(\tau-t)^{1+\alpha-n}}, \quad (31)$$

where $n = |\alpha| + 1$ and $\alpha > 0$.

Unfortunately, the Riemann–Liouville fractional derivative of the constant function is non-zero. This is not convenient when analysing, e.g., the asymptotic and other states. To escape this inconvenience, the corresponding Caputo fractional derivatives are defined as follows:

- the left Caputo fractional derivative

$${}_a D_{t+}^\alpha f(t) = \frac{1}{\Gamma(n - \alpha)} \int_a^t \frac{d\tau}{(t - \tau)^{1+\alpha-n}} \left(\frac{df(\tau)}{d\tau} \right)^n \tag{32}$$

- the right Caputo fractional derivative

$${}_b D_{t-}^\alpha f(t) = \frac{1}{\Gamma(n - \alpha)} \int_t^b \frac{d\tau}{(\tau - t)^{1+\alpha-n}} \left(\frac{df(\tau)}{d\tau} \right)^n, \tag{33}$$

where α represents the order of the derivative: $n - 1 < \alpha < n$ and $\alpha > 0$.

The relationship between the Riemann–Liouville and the Caputo fractional derivatives is ($0 < \alpha < 1$):

$${}_a D_{t+}^\alpha f(t) = {}_a^{RL} D_{t+}^\alpha f(t) - \frac{1}{\Gamma(1 - \alpha)} \frac{f(a)}{(t - a)^\alpha}, \tag{34}$$

$${}_b D_{t-}^\alpha f(t) = {}_b^{RL} D_{t-}^\alpha f(t) - \frac{1}{\Gamma(1 - \alpha)} \frac{f(b)}{(b - t)^\alpha}. \tag{35}$$

Thus, e.g., the left Riemann–Liouville fractional derivative of the constant function C equals $C / |\Gamma(1 - \alpha)(t - a)^\alpha|$, whereas the left Caputo fractional derivative is equal to zero. On the other hand, many properties of the Caputo fractional derivatives are the same as those of the Riemann–Liouville fractional derivative when $f(a) = f(b) = 0$:

$${}_a D_{t+}^{-\alpha} f(t) = {}_a I_{t+}^\alpha f(t), \quad {}_b D_{t-}^{-\alpha} f(t) = {}_b I_{t-}^\alpha f(t), \quad \alpha > 0 \tag{36}$$

$${}_a I_{t+}^\alpha f(t) = \frac{1}{\Gamma(\alpha)} \int_a^t \frac{f(\tau) d\tau}{(t - \tau)^{1-\alpha}}, \quad t > a, \tag{37}$$

$${}_b I_{t-}^\alpha f(t) = \frac{1}{\Gamma(\alpha)} \int_t^b \frac{f(\tau) d\tau}{(\tau - t)^{1-\alpha}}, \quad t < b, \tag{38}$$

$${}_a D_{t+}^\alpha f(t) = {}_a I_{t+}^{-\alpha} f(t), \quad {}_b D_{t-}^\alpha f(t) = {}_b I_{t-}^{-\alpha} f(t), \quad \alpha > 0 \tag{39}$$

$${}_a D_{t+a}^\alpha D_{t+}^\beta f(t) = {}_a D_{t+a}^\beta D_{t+}^\alpha f(t) = {}_a D_{t+}^{\alpha+\beta} f(t), \tag{40}$$

$${}_a I_{t+a}^\alpha I_{t+}^\beta f(t) = {}_a I_{t+a}^\beta I_{t+}^\alpha f(t) = {}_a I_{t+}^{\alpha+\beta} f(t), \tag{41}$$

The analogue of the Taylor expansion is valid here:

$$f(t) = \sum_{i=0}^{n-1} \frac{{}_a D_{t+}^{\alpha+j} f(0)}{\Gamma(1 + \alpha + j)} t^{\alpha+j} + R_n(t), \quad n = [\text{Re } \alpha] + 1, \tag{42}$$

where $R_n(t) = {}_a I_{t+}^{\alpha+j} {}_a D_{t+}^{\alpha+j} f(t)$.

As an example, let us consider the derivatives of some functions:

$${}_{-\infty}D_{t+}^{\alpha} \sin \lambda t = \lambda^{\alpha} \sin \left(\lambda t + \frac{\pi \alpha}{2} \right), \quad (43)$$

$${}_{-\infty}D_{t+}^{\alpha} \cos \lambda t = \lambda^{\alpha} \cos \left(\lambda t + \frac{\pi \alpha}{2} \right), \quad (44)$$

where $\lambda > 0$, $\alpha > -1$. When $\alpha \leq -1$, we have to use the property (39):

$${}_{-\infty}D_{t+}^{\alpha} e^{\lambda t + \mu} = \lambda^{\alpha} e^{\lambda t + \mu}, \quad \operatorname{Re} \lambda > 0. \quad (45)$$

Some special functions, e.g., the Mittag-Leffler function

$$E_{\alpha, \beta}(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(\alpha n + \beta)} \quad (46)$$

and the generalized exponential function

$$1 + E_{\alpha}^z = 1 + \sum_{n=0}^{\infty} \frac{z^{n+\alpha}}{\Gamma(1 + \alpha + n)}, \quad (47)$$

naturally appear and are widely used in fractional calculus.

In this paper, the fractional Caputo derivative ${}_{t_0}D_{t+}^{\alpha} = \frac{d^{\alpha}}{dt^{\alpha}}$ is used.

References

1. R.D. Levine, *Molecular Reaction Dynamics* (Cambridge University Press, Cambridge, 2005)
2. H. Gutfreund, *Kinetics for the Life Sciences: Receptors, Transmitters and Catalysts* (Cambridge University Press, Cambridge, 1998)
3. A.N. Gorban, I.V. Karlin, *Invariant Manifolds for Physical and Chemical Kinetics* (Springer, Berlin, Heidelberg, 2010)
4. A.M. Zhabotinsky, *Concentrated Auto-Oscillations* (Nauka, Moscow, 1974, in Russian)
5. P. Érdi, J. Tóth, *Mathematical Models of Chemical Reactions* (Princeton University Press, Princeton, 1989)
6. A.N. Gorban, V.I. Bykov, G.S. Yablonsky, *Story about Chemical Relaxation* (Nauka, Novosibirsk, 1986, in Russian)
7. P. Miškinis, *Math. Model. Anal.* **15**(2), 235 (2010)
8. F. Amblard, A.C. Maggs, B. Yurke, A.N. Pargellis, S. Leibler, *Phys. Rev. Lett.* **77**, 4470 (1996)
9. J.-P. Bouchaud, A. Georges, J. Koplik, A. Provata, S. Redner, *Phys. Rev. Lett.* **64**, 2503 (1990)
10. M. Barlow, E. Perkins, *Prob. Theory Relat. Fields* **79**, 543 (1988)
11. M.T. Barlow, R.F. Bass, *J. Funct. Anal.* **175**, 214 (2000)
12. S.G. Samko, A.A. Kilbas, O.I. Marichev, *Fractional Integrals and Derivatives. Theory and Applications* (Gordon and Breach, Yverdon, 1993)
13. I. Podlubny, *Fractional Differential Equations* (Academic Press, San Diego, 1999)
14. P. Miškinis, *Nonlinear and nonlocal integrable models* (Technika, Vilnius, 2003)
15. W.C. Bray, *J. Am. Chem. Soc.* **43**(6), 1262 (1921)
16. B.P. Belousov, *Collect. Abstr. Radiat. Med.* **147**, 145 (1959). (in Russian)
17. A.M. Zhabotinsky, *Biofizika* **9**, 306 (1964). (in Russian)
18. J. Higgins, *Ind. Eng. Chem.* **59**, 19 (1967)
19. R.M. Noyes, R.J. Field, E. Körös, *J. Am. Chem. Soc.* **94**, 1394 (1972)

20. A.A. Andronov, A.A. Vitt, S.E. Khaikin, *Theory of Oscillators* (Dover Publications, New York, 1987)
21. W. Jost, *Z. Phys. Chem.* **105**, 317 (1950)
22. J. Meixner, *Phys. Blätter* **16**, 506 (1960)
23. A.A. Kilbas, H.M. Srivastava, J.J. Trujillo, *Theory and Applications of Fractional Differential Equations* (Elsevier, Amsterdam, Netherlands, 2006)
24. H.J. Haubold, A.M. Mathai, R.K. Saxena, Mittag-Leffler functions and their applications [<http://arxiv.org/abs/0909.0230v2>]
25. R. Csikja, J. Tóth, *Enformatika. Int. J. Appl. Math. Comput. Sci.* **4**(2), 728 (2007)
26. P. Grindrod, *Patterns and Waves: The Theory and Applications of Reaction-Diffusion Equations* (Clarendon Press, Oxford, 1991)
27. *Selected Papers of Norbert Wiener* (MIT Press & SIAM, Cambridge, MA, 1964)