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BOUNDARY VALUE PROBLEMS FOR SUBDIFFUSION UNDER DEGRADATION*

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We consider boundary value problems for a subdiffusion-degradation problem within an approach based on reaction-subdiffusion equations derived earlier. Thus, boundary value problems for subdiffusion with degradation can be solved within the Green functions approach, where the new Green functions have the structure of a product of the Green functions for mere subdiffusion with an exponential. Although the equations with non-decoupling reaction and transport appear complicated at first glance, it turns out that the methods for the solution of the corresponding linear reaction-diffusion equations can easily be adopted to the anomalous case. In particular, the solutions can be expressed in terms of solutions to the problem without degradation.

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1. Introduction

Anomalous diffusion is characterized by a mean square displacement that goes as $\langle r^2 \rangle \propto t^\alpha$, with $\alpha > 1$ corresponding to the superdiffusive case and $0 < \alpha < 1$ to the subdiffusive case. In many situations, subdiffusion can be modelled within the continuous time random walks (CTRW) scheme. The probability density function (pdf) of the waiting times between successive jumps of a particle lacks its mean and obeys a power law, $\psi(t) \propto t^{-(1+\alpha)}$, which involves time-fractional operators in the deduced transport equations [1].

Boundary value problems (BVP) for the fractional diffusion equation can be solved using *e.g.* the standard Laplace technique already known from BVP under normal diffusion [2–5], although nontrivial higher transcendental functions may appear as solutions.

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For normal reaction-diffusion equations in general, it is impossible to express the solutions analytically. However, there are some special cases which allow for a fully analytical representation of the solution to special BVPs. One of them is the Dirichlet BVP for degrading particles, *i.e.* the simple reaction $A \to 0$. We will focus on this special case in order to generalize it to subdiffusion.

There have been different proposals for setting up reaction-subdiffusion equations, mostly on a phenomenological basis [6]. Analogous to normal reaction-diffusion, a reaction term, either without or with a fractional derivative acting upon it, was added to the fractional transport term. The latter version holds for subdiffusion controlled reactions on microscopic scales [7–9], so that within the CTRW scheme reactions are only possible when the particle performs a step, *i.e.* at the beginning or end of a waiting time period.

In this paper we apply a third type of reaction-subdiffusion equations put forward *e.g.* in [10,11], where the transport term is affected by reaction. The equation used here was derived in [12], corresponding to the situation in which the reaction (here degradation) is diffusion controlled on a microscopic scale so that classical reaction rate kinetics remains valid, while subdiffusive transport emerges at a mesoscopic scale due to trapping *e.g.* in the cavities of a porous medium.

For normal diffusion, it was shown that in order to obtain the solution to the Dirichlet BVP for degrading particles, one has to subject the solution to the same BVP without degradation to a transformation [13]. As will turn out, this holds true as well for the subdiffusion-reaction equations under consideration, moreover, this transformation is the same as the one in the normal diffusive case.

2. Reaction-subdiffusion equations

In order to model our subdiffusion process with degradation of particles, we are going to use the CTRW scheme as put forward in [12]. A particle arriving at site i stays there for a sojourn time t drawn from a pdf $\psi(t)$. In a one-dimensional situation, the particles leaving a site make a step to the left or to the right, where for an unbiased random walk the probabilities for either direction are equal to 1/2. Accounting for the local balance of probability gain and loss at site i on the one hand and continuity of the probability flux (particle conservation during jumps) on the other, the balance equation for the occupation number of A-particles at each site reads:

$$\begin{aligned} \dot{A}_i(t) &= j_i^+(t) - j_i^-(t) - \kappa A_i && (1)\\ &= \tfrac{1}{2}\, j_{i-1}^-(t) + \tfrac{1}{2}\, j_{i+1}^-(t) - j_i^-(t) - \kappa A_i\,, && (2)\end{aligned}$$

where $j_i^-(t)$ and $j_i^+(t)$ are the loss- and gain flux of A-particles at site i, respectively, and κA_i is the reaction term, describing loss of particles due to degradation $A \to 0$. The loss flux at site i is determined by the gain flux at the site at all previous times and by the survival probability and is given by

$$j_i^-(t) = \psi(t) P_i(t,0) A_i(0) + \int_0^t \psi(t-t') P_i(t,t') j_i^+(t')\, dt' , \tag{3}$$

that means the particles leaving site i at time t either were there from the very beginning and did not degrade until t, or arrived there at some later time $t' < t$ and did neither jump nor degrade until t. Here, the probability density to make a step at t having arrived at t' is given by the waiting time pdf $\psi(t-t')$, and the probability not to degrade is given by the classical kinetic rate equation

$$\frac{d}{dt} P_i(t) = -\kappa P_i(t) \tag{4}$$

so that

$$P_i(t,t_0) = \exp\left(-\kappa(t-t_0)\right) . \tag{5}$$

Substituting the gain flux by means of Eq. (1), we find

$$\begin{aligned} j_i^-(t) &= \psi(t) P_i(t,0) A_i(0) + \int_0^t \psi(t-t') \exp\big(-\kappa(t-t')\big) \\ &\quad \times \Big[\dot{A}_i(t') + j_i^-(t') + \kappa A_i(t')\Big]\, dt' . \end{aligned} \tag{6}$$

Since both the survival probability P_i and the waiting time pdf ψ in the integrand are functions of $(t-t')$, we are able to write explicitly an expression for the loss flux,

$$j_i^-(t) = \int_0^t M(t-t') \exp\left[-\kappa(t-t')\right] A(x,t')\, dt' , \tag{7}$$

where we made use of the shift theorem of Laplace Transform:

$$\mathcal{L}\left\{\exp\left[-\kappa t\right] f(t)\right\} = \tilde{f}(u+\kappa) \tag{8}$$

and the convolution theorem. The emerging new kernel M is defined by the waiting time pdf in Laplace domain, $\tilde{M}(u) = u\tilde{\psi}/(1-\tilde{\psi})$.

Since the relative change in concentration between neighboring sites is considered to be small, we change to the continuous coordinate $x = ai$ and insert (7) into (2), so that

$$\frac{\partial A(x,t)}{\partial t} = \frac{a^2}{2}\Delta \int_0^t M(t-t') \exp\left[-\kappa(t-t')\right] A(x,t')\, dt' - \kappa A(x,t)\,. \quad (9)$$

For $\kappa \to 0$ and $\tilde{\psi}(u) \simeq 1-(u\tau)^\alpha$ this reduces to a subdiffusion equation, the convolution with the memory M corresponding to the Riemann–Liouville fractional derivative.

We find the modified Green function, *i.e.* the response to a δ-peak at $x = 0$ and $t = 0$ for (9) in Laplace domain:

$$\tilde{G}(x,u) = \frac{1}{\sqrt{K_\alpha}\,(u+\kappa)^{1-\alpha/2}} \exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}\,|x|\right] \quad (10)$$

which is exactly the Green function of the subdiffusion equation without reaction, with u changed to $u+\kappa$. $K_\alpha = a^2/(2\tau^\alpha)$ is the generalized diffusion constant.

3. The Dirichlet boundary value problem

In BVP in general and the Dirichlet BVP in particular, particles are permanently introduced into (or moved out of) the domain of interest. In subdiffusion, this might lead to difficulties due the non-Markovian nature of transport, *i.e.* to the fact that each of the particles will memorize the time it was inserted, and the question is whether there can be an integral description of all the particles. Let us for now omit the degradation of particles in the discussion of the problems that may arise due to the different ages of particles in the system. The results will be applicable to the case with degradation included as well.

We label the particles according to the time t_0 they were introduced into the system, so that *e.g.* $A(x,t|t_0)dt_0$ is the partial concentration at x at time t of A-particles that were introduced between t_0 and $t_0 + dt_0$. Each partial concentration will behave according to the Green function G of subdiffusion. The boundary value will be maintained by a source at the boundary that compensates for losses, so that we can write

$$A(x,t|t_0)dt_0 = G(x,t-t_0)q(t_0)\, dt_0\,, \quad (11)$$

where $q(t_0)dt_0$ is the amount of particles inserted between t_0 and t_0+dt_0. For simplicity we assumed only one boundary, and the location of it is already included in G (*i.e.* the spatial integration over the point source is already carried out). The initial particle concentration in the interior of the system is taken to be zero. The overall concentration is the integral of (11) with respect to t_0 from 0 to t, which is a temporal convolution, in Laplace domain:

$$\tilde{G}(x,u)\tilde{q}(u) \;=\; \frac{1}{\sqrt{K_\alpha}u^{1-\alpha/2}}\exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}|x-x_{\text{bound}}|\right]\tilde{q}(u)\,. \tag{12}$$

With the boundary condition $\tilde{A}(x_{\text{bound}},u) = A_0/u$ we find the source needed to compensate for the losses:

$$\tilde{q}(u) \;=\; A_0\sqrt{\frac{K_\alpha}{u^\alpha}}\,, \tag{13}$$

so that in the end

$$\tilde{A}(u) \;=\; \frac{A_0}{u}\exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}|x-x_{\text{bound}}|\right]\,, \tag{14}$$

a result not differing from the one we obtain by fitting the boundary. The Laplace variable u is related to the residence time of the particles in the system (which will be cut off in the case of degradation), and it is justified to perform the standard fitting procedures in Laplace domain, where a constant boundary value A_0 in time corresponds to A_0/u. Moreover, the lower integration limit in Eq.(7), or in the Riemann–Liouville fractional derivative in the fractional diffusion equation, has actually to be interpreted as the time the respective particles were inserted into the system, and not as the time that has passed since the initial preparation of the system (those two are of course the same if no particles are inserted in the course of time).

We know that the solutions to the subdiffusive Dirichlet BVP with degradation will be, generally speaking, linear combinations of temporal convolutions of functions of the type (10). As constant boundary values lead to the prefactor $1/u$ in Laplace space, we can express the solution with degradation in terms of the solution without degradation, but for the same boundary conditions. Let for now A^* be the solution to the problem without degradation. The solution with degradation included is then in Laplace domain:

$$\tilde{A}(x,u) \;=\; \frac{\kappa+u}{u}\tilde{A}^*(x,\kappa+u) \tag{15}$$

and in original domain (again using the shift theorem):

$$A(x,t) \;=\; \kappa\int\limits_0^t A^*(x,t')\exp\left[-\kappa t'\right]\,dt' + A^*(x,t)\exp\left[-\kappa t\right] \tag{16}$$

a result already found for the construction of the solution for normal diffusion with degradation [13], corresponding to $\alpha = 1$.

In the following, we examine a one-dimensional system with given boundary concentrations. We account for two cases: one fixed boundary value in a semi-infinite domain, and two fixed boundary values at a finite interval. In all these considerations we assume that initially, the interior of the region of interest is completely empty, $A(x, t = 0) = 0$, and its boundaries are determined by the aforementioned Dirichlet boundary conditions.

3.1. Semi-infinite domain

We put $A(0, t) = A_0$. Without reaction, the solution to the BVP is found by going to Laplace domain and fitting the Green function to the boundary $\tilde{A}(x = 0, u) = A_0/u$, so that

$$\tilde{A}(x, u) = \tilde{A}(x, u) = \frac{A_0}{u} \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}\,|x|\right] . \tag{17}$$

In the limiting case of $\alpha = 1$, this corresponds to the well known result $A(x, t) = A_0 \operatorname{erfc}\left[x/\sqrt{4K_\alpha t}\right]$ for normal diffusion with a boundary kept constant [14]. Figure 1 shows the particle profiles under subdiffusion for different times.

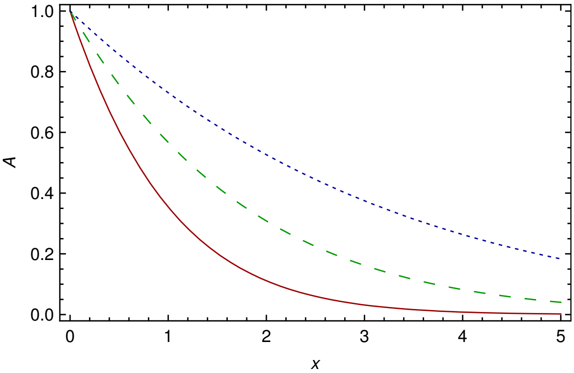

Fig. 1. Reaction free case: Particle profiles under subdiffusion, $\alpha = 0.5$ for $t = 0.5$ (solid/red), $t = 5$ (dashed/green) and $t = 50$ (dotted/blue); $K_\alpha = 1$.

Implying degradation, we repeat the same procedure as above, but this time the modified Green function (10) constitutes the basic structure of the solution. We find

$$\tilde{A}(x, u) = \frac{A_0}{u} \exp\left[-\sqrt{\frac{(u + \kappa)^\alpha}{K_\alpha}}\,|x|\right] \tag{18}$$

which gives us immediately the stationary profile in the limit $u \to 0$:

$$A(x, t \to \infty) = A_0 \exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}|x|\right], \tag{19}$$

an exponential just as in the normal diffusive case $\alpha = 1$, differing only by the exponent α in the rate coefficient which increases the profile's steepness (if $\kappa < 1$). Figure 2 shows the profiles under reaction-subdiffusion. Here and in the preceding figure we used a series expansion and term-by-term inversion of the corresponding expressions in Laplace domain.

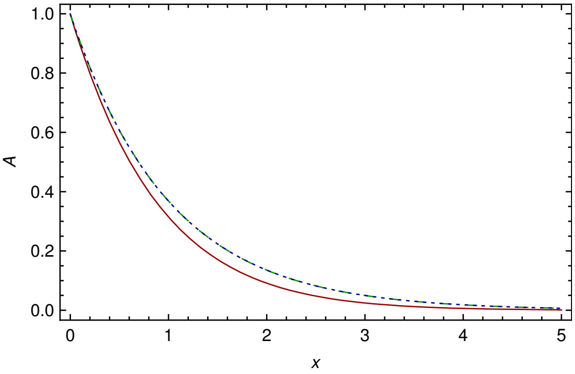

Fig. 2. Particle profiles under reaction-subdiffusion, $\alpha = 0.5$ for $t = 0.5$ (solid/red), $t = 5$ (dashed/green) and $t = 50$ (dotted/blue); $K_\alpha = 1$, $\kappa = 1$.

4. Finite interval $(0, L)$

On a finite interval with two boundary conditions, the solutions to (9) will in general be a linear combination of two convolutions of functions of the type (10) (for mere subdiffusion let $\kappa \to 0$), which have to be fitted to the boundaries.

We are first going to investigate the case where the concentration at one boundary is constant and the other is zero, $A(0, t) = A_0$, $A(L, t) = 0$. In this case the solution to the subdiffusion (or reaction-subdiffusion) can be described in terms of a (temporal) convolution of a function that takes the value 0 at L, so that only the value at $x = 0$ has to be fitted. In the following, we will call this construction G^*, with $G^*(L, t) = 0$.

The new Green function G^* of the subdiffusion equation corresponding to an absorbing boundary at $x = L$ can be obtained via the method of images [2], *i.e.* we construct an odd continuation of our function to the interval of double length (Fig. 3):

$$G^*(x, t) = G(x, t) - G(2L - x, t), \tag{20}$$

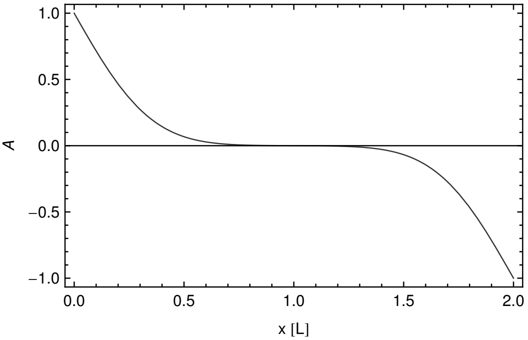

Fig. 3. Sketch of the construction of Ansatz (20).

where $G(x,t)$ is the Green function of the free problem, so that the solution of the BVP can be found by fitting the boundary:

$$\tilde{A}(x,u) = \frac{A_0}{u}\frac{\exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}x\right] - \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}(2L-x)\right]}{1-\exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}\,2L\right]}\,. \tag{21}$$

Expanding this expression around $u=0$ and keeping only the leading orders we find the stationary solution

$$\begin{aligned}\tilde{A}(x,u\to 0) &= \frac{A_0}{u}\frac{L-x}{L}\,,\\ A(x,t\to\infty) &= A_0\left(1-\frac{x}{L}\right)\,,\end{aligned}$$

and the lowest order u-correction:

$$\frac{2A_0}{3K_\alpha}\left[Lx-L^2\right]u^{\alpha-1}\,, \tag{22}$$

which in time domain behaves as

$$\frac{2A_0}{3K_\alpha}\left[Lx-L^2\right]\frac{t^{-\alpha}}{\Gamma[1-\alpha]}\,.$$

For subdiffusion with degradation we again modify our Green function (20) according to (10) and finally find the solution in Laplace domain:

$$\tilde{A}(x,u) = \frac{A_0}{u}\frac{\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}\,x\right] - \exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}\,(2L-x)\right]}{1-\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}\,2L\right]}\,. \tag{23}$$

The stationary profile is obtained in the limit $u \to 0$,

$$A(x, t \to \infty) = A_0 \frac{\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}\,x\right] - \exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}\,(2L - x)\right]}{1 - \exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}\,2L\right]}\,, \tag{24}$$

shown in Fig. 4. The relaxation behaviour is governed by the exponential survival probability (essentially the rate coefficient κ governs time scale of relaxation as seen from Eq. (16)).

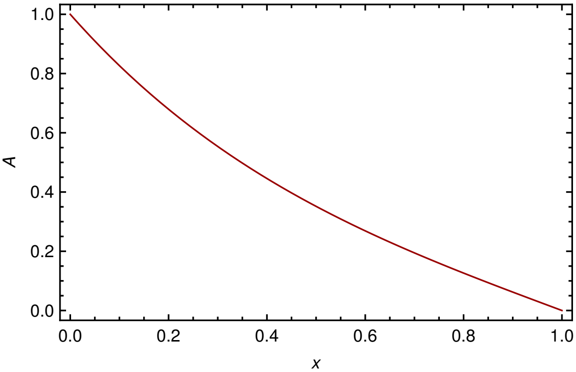

Fig. 4. Stationary particle profile under reaction-subdiffusion, $\alpha = 0.5$, $K_\alpha = 1$, $k = 10$, $L = 1$, $A_0 = 1$.

Let us now turn to the case where both boundaries have non-zero constant values, $A(0, t) = A_0$, $A(L, t) = A_L$. The solution takes the form of a linear combination of convolutions of functions of the type (10), we choose as an Ansatz in Laplace domain:

$$\tilde{A}(x, u) = A_0 \tilde{q}_0(u)\, \tilde{G}(x, u) + A_L \tilde{q}_L(u)\, \tilde{G}(x - L, u)\,. \tag{25}$$

with $x \in (0, L)$.

The fitting procedure gives us for mere subdiffusion:

$$\begin{aligned} \tilde{A}(x, u) \;=\; \frac{1}{u} \Bigg[& A_0 \left(1 - \frac{A_L}{A_0} \frac{\exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}} L\right] - \frac{A_0}{A_L} \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}} 2L\right]}{1 - \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}} 2L\right]} \right) \\ & \times \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}} x\right] \\ & + A_L \left(\frac{1 - \frac{A_0}{A_L} \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}} L\right]}{1 - \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}} 2L\right]} \right) \exp\left[-\sqrt{\frac{u^\alpha}{K_\alpha}}\,(L - x)\right] \Bigg]\,. \end{aligned} \tag{26}$$

We find the stationary solution

$$\begin{aligned}\tilde{A}(x,u\to 0) &= \frac{1}{u}\left[\frac{A_L-A_0}{L}x+A_0\right],\\ A(x,t\to\infty) &= \frac{A_L-A_0}{L}x+A_0\end{aligned}$$

and the relaxation term

$$\frac{A_Lx\,(-5L+3x)+A_0(6L^2-Lx+3x^2)}{12K_\alpha}\,u^{\alpha-1}\,, \tag{27}$$

corresponding to

$$\frac{A_Lx(-5L+3x)+A_0(6L^2-Lx+3x^2)}{12K_\alpha\Gamma[1-\alpha]}\,t^{-\alpha}$$

in time domain.

Proceeding as above we find the solution for the reaction-subdiffusion equation

$$\begin{aligned}\tilde{A}(x,u) = \frac{1}{u}\Bigg[&A_0\left(1-\frac{A_L}{A_0}\frac{\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}L\right]-\frac{A_0}{A_L}\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}2L\right]}{1-\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}2L\right]}\right)\\ &\times\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}x\right]\\ &+A_L\left(\frac{1-\frac{A_0}{A_L}\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}L\right]}{1-\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}2L\right]}\right)\exp\left[-\sqrt{\frac{(u+\kappa)^\alpha}{K_\alpha}}(L-x)\right]\Bigg]\,,\end{aligned} \tag{28}$$

and the stationary solution for degrading particles (Fig. 5):

$$\begin{aligned}A(x,t\to\infty) = A_0&\left(1-\frac{A_L}{A_0}\frac{\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}L\right]-\frac{A_0}{A_L}\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}2L\right]}{1-\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}2L\right]}\right)\\ \times\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}x\right]&+A_L\left(\frac{1-\frac{A_0}{A_L}\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}L\right]}{1-\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}2L\right]}\right)\exp\left[-\sqrt{\frac{\kappa^\alpha}{K_\alpha}}(L-x)\right].\end{aligned}$$

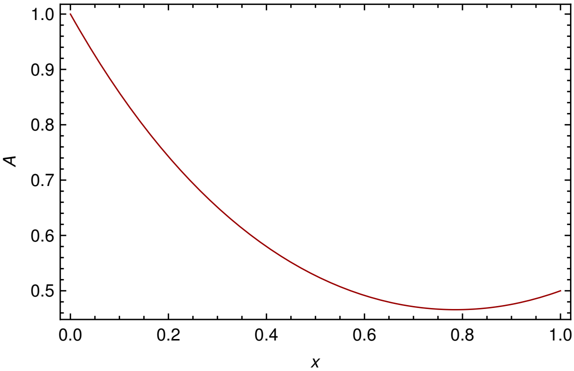

Fig. 5. Stationary particle profile under reaction-subdiffusion, $\alpha = 0.5$, $K_\alpha = 1$, $k = 10$, $L = 1$, $A_0 = 1$, $A_L = 0.5$.

5. Conclusions

We examined the solutions to the equations that describe degradation of subdiffusing particles, $A \to 0$, under Dirichlet boundary conditions. The type of reaction-subdiffusion equations we use here is based on a CTRW approach and takes into account the fact that particles that react during their waiting times do not contribute to transport anymore, which leads to an exponential (reaction-dependent) cutoff of the long-ranged kernel in the transport term. For such kind of equations we have shown that the problem of the Dirichlet BVP with degradation in subdiffusion can be reduced to the Dirichlet BVP without degradation, just as in normal diffusion. We note again that for this treatment of the reaction-subdiffusion equation with degradation the exponential cutoff of the transport kernel due to reaction is essential.

REFERENCES

[1] R. Metzler, J. Klafter, *Phys. Rep.* **339**, 1 (2000).

[2] R. Metzler, J. Klafter, *Physica A* **278**, 107 (2000).

[3] J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London 1956.

[4] H.S. Carslaw, J.C. Jaeger, *Conduction of Heat in Solids*, 2nd Ed., Oxford University Press, London 1959.

[5] T. Kosztolowicz, *J. Phys.* **A37**, 10779 (2004).

[6] B.J. Henry, S.L. Wearne, *Physica A* **276**, 448 (2000); *SIAM J. Appl. Math.* **62**, 870 (2002); B.I. Henry, T.A.M. Langlands, S.L. Wearne, *Phys. Rev.* **E72**, 026101 (2005).

[7] T. Kosztolowicz, K.D. Levandowska, *Acta Phys. Pol. B* **37**, 1571 (2006).

[8] K. Seki, M. Wojcik, M. Tachiya, *J. Chem. Phys.* **119**, 2165 (2003).

[9] J.Y. Sung, R.J. Silbey, *Phys. Rev. Lett.* **91**, 160601 (2003).

[10] M.O. Vlad, J. Ross, *Phys. Rev.* **E66**, 061908 (2002).

[11] A. Yadav, W. Horsthemke, *Phys. Rev.* **E74**, 066118 (2006).

[12] I.M. Sokolov, M.G.W. Schmidt, F. Sagués, *Phys. Rev.* **E73**, 031102 (2006).

[13] P.V. Danckwerts, *Trans. Faraday Soc.* **47**, 1014 (1951).

[14] *Tables of Integral Transforms*, Ed. A. Erdelyi, Vol. 1, McGraw-Hill, New York 1954.