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TIME EVOLUTION OF THE REACTION FRONT IN THE SYSTEM WITH ONE STATIC AND ONE SUBDIFFUSIVE REACTANT[*]

Tadeusz Kosztołowicz

Institute of Physics, Świętokrzyska Academy
Świętokrzyska 15, 25-406 Kielce, Poland
`tkoszt@pu.kielce.pl`

Katarzyna D. Lewandowska

Department of Physics and Biophysics, Medical University of Gdańsk
Dębinki 1, 80-211 Gdańsk, Poland
`kale@amg.gda.pl`

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We study a subdiffusion-reaction system with initially separated reactants in the case where one of the reactants is static. Using the scaling method we show that the reaction front $x_{\rm f}$ evolves in time according to the power law $x_{\rm f} \sim t^{\alpha/2}$ where α is the subdiffusion parameter. Comparing the theoretical formula with the experimental data we find that the transport of acids molecules inside the tooth enamel during the caries progress is of subdiffusive character.

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1. Introduction

Subdiffusion is a process where the transport of particles is significantly hindered due to internal structure of the medium. It occurs among others in gels, porous media or amorphous semiconductors [1, 2]. The subdiffusion is defined by the time dependence of the mean-square displacement $\langle \Delta x^2 \rangle$ of a transported particle. In a one-dimensional system this dependence takes the form [1]

$$\langle \Delta x^2 \rangle = \frac{2D_\alpha}{\Gamma(1+\alpha)}\, t^\alpha\,,$$

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where D_α is a subdiffusion coefficient measured in units of $\mathrm{m}^2/\mathrm{s}^\alpha$ and α is a subdiffusion parameter which obeys $0 < \alpha < 1$. For $\alpha = 1$ one deals with the normal diffusion. In the absence of chemical reactions the subdiffusion can be described by the following equation (here C denotes the concentration of the particles)

$$\frac{\partial C(x,t)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 C(x,t)}{\partial x^2} \,,$$

with the Riemann–Liouville fractional time derivative defined for $\alpha > 0$ as

$$\frac{\partial^\alpha f(t)}{\partial t^\alpha} = \frac{1}{\Gamma(n-\alpha)} \frac{\partial^n}{\partial t^n} \int_0^t dt' \frac{f(t')}{(t-t')^{1+\alpha-n}} \,,$$

where n is the smallest natural number which fulfills the equation $n - \alpha > 0$.

Let us consider a subdiffusion-reaction system where subdiffusively transported particles of spice A react with static reactant B according to the chemical formula $A + B \to P(inert)$. The equations describing this process are

$$\frac{\partial C_A(x,t)}{\partial t} = D_{\alpha A} \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 C_A(x,t)}{\partial x^2} - R_\alpha(x,t) \,, \tag{1}$$

$$\frac{\partial C_B(x,)}{\partial t} = -R_\alpha(x,t) \,, \tag{2}$$

where the reaction term $R_\alpha(x,t)$ takes the form [3]:

$$R(x,t) = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left[k C_A(x,t) C_B(x,t) \right] \,,$$

k is the reaction rate constant. In the following we consider the system where the particles A and B are separated at the initial moment $t = 0$. An important function characterizing such a system is a time evolution of the reaction front $x_\mathrm{f}(t)$. The reaction front $x_\mathrm{f}(t)$ is defined as a point where the reaction term reaches its maximum (see Fig. 1) $R_\alpha(x_\mathrm{f}, t) = \mathrm{max}$. A progress of the reaction front for the normal diffusion-reaction system is given as $x_\mathrm{f} \sim t^{1/2}$ [4, 5]. As shown in the paper [3], in the subdiffusion-reaction system where the subdiffusion coefficients of the reactants are equal to each other ($D_{\alpha A} = D_{\alpha B}$), there is

$$x_\mathrm{f} \sim t^{\alpha/2} \,, \quad \text{with} \quad \alpha < 1 \,. \tag{3}$$

We study here the subdiffusion-reaction system with one mobile A and one static substrate B. We derive the time evolution of the reaction front by means of the scaling method in the long time limit. The situation of

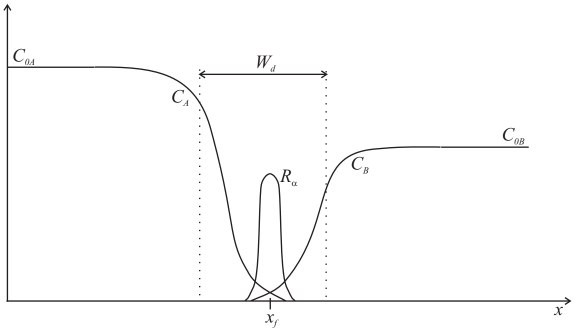

Fig. 1. The concentration profiles of the reactants $C_{A,B}$ and reaction term R_α. The W_d denotes the depletion zone, x_f is the reaction front.

one mobile and one static reactant occurs in the formation of carious lesion in the tooth enamel. By comparison of our theoretical result with the experimental data we show that the limit of caries (that is identified with the reaction front x_f) evolves in time according to Eq. (3). Thus, we find that the transport of acid molecules inside the enamel is subdiffusive.

The main difficulty occurring in the study of subdiffusion-reaction is that the equations describing this process (1) and (2) are non-linear partial differential ones with the fractional derivatives. Even the normal diffusion-reaction equations are difficult to solve and one uses several assumptions to simplify the calculations, such as the quasistationary approximation [5–7], the scaling method [4, 6, 8, 9], and the perturbation one [10]. Using these methods, some characteristics of the system were derived. They include the time evolutions of the reaction front, the width of the reaction or depletion zone *etc.* Although the methods seem to oversimplify the problem, the results obtained by means of these methods were confirmed by numerical calculations and simulations [5, 8, 9]. In this paper we adopt the scaling method to study the subdiffusion-reaction system with one mobile and one static reactant.

2. The method

According to the assumptions, the initial and boundary conditions of that system are as follows:

$$\begin{aligned} C_A(x,0) &= C_{0A}\Theta(-x)\,, \quad && C_B(x,0) = C_{0B}\Theta(x)\,,\\ C_A(-\infty,t) &= C_{0A}\,, && C_A(\infty,t) = 0\,,\\ C_B(-\infty,t) &= 0\,, && C_B(\infty,t) = C_{0B}\,, \end{aligned}$$

where $\Theta(x)$ is the Heaviside function.

In the first step of the scaling method, the Eqs. (1) and (2) are transformed to the dimensionless form. By means of the substitutions $x = \rho x_s$, $t = \tau t_s$, $a(\rho,\tau) = C_A(\rho,\tau)/C_{A0}$ and $b(\rho,\tau) = C_B(\rho,\tau)/C_{B0}$, where $x_s = \sqrt{D_{\alpha A}\tau_s^\alpha} = \sqrt{D_{\alpha A}/(kC_{B0})}$ and $\tau_s = 1/(kC_{B0})^{1/\alpha}$, we obtain

$$\begin{aligned}\frac{\partial^\alpha}{\partial\tau^\alpha}a(\rho,\tau) &= \frac{\partial^2}{\partial\rho^2}a(\rho,\tau) - a(\rho,\tau)b(\rho,\tau)\,,\\ \frac{\partial^\alpha}{\partial\tau^\alpha}b(\rho,\tau) &= -qa(\rho,\tau)b(\rho,\tau)\,,\end{aligned} \tag{4}$$

where ρ and τ are the dimensionless space and time variables, a and b denote the dimensionless concentrations and $q = C_{A0}/C_{B0}$. Next, one assumes the following form of the concentration profiles inside the reaction zone:

$$a(\rho,\tau) = \frac{1}{\tau^\gamma}\,\tilde{a}(\eta)\,, \qquad b(\rho,\tau) = \frac{1}{\tau^\lambda}\,\tilde{b}(\eta)\,, \tag{5}$$

where $\eta = (\rho + \nu\tau^\sigma)/\tau^\beta = (\rho - \rho_{\mathrm{f}})/\tau^\beta$ with $\rho_{\mathrm{f}} \equiv x_{\mathrm{f}}/x_s = -\nu\tau^\sigma$. Let us note that the minus sign in the last formula is caused by the fact that substrate B, which occupies the region $x < 0$, does not diffuse. The equations (5) play a crucial role in the following considerations. Their usefulness is supported by the analytical [4,6] and numerical [8,9] considerations. For the normal diffusion-reaction system, where both reactants have the same diffusion coefficients, it was shown [6,8,9] that $\beta = 1/6$, $\sigma = 1/2$, $\gamma = \lambda = 1/3$, and for the system with one static reactant [4,5] it was found that $\beta = 0$, $\sigma = 1/2$, $\gamma = 1/2$, $\lambda = 0$. We assume that the scaling functions (5) can be also used for the subdiffusive system with one static reactant.

We are interested in calculating the exponent σ which can be obtained from the Eq. (4) only. Substituting the Eqs. (5) into the Eq. (4), we find the parameter σ comparing the terms with the same order of the derivative on the left and right sides of the equation. This procedure is relatively simple in the case of normal diffusion but it appears to be rather complicated for the subdiffusion because of specific properties of the fractional derivative. The Leibnitz rule of the fractional derivative is significantly changed compared to the case of natural order derivative. Namely [11],

$$\frac{d^\alpha(f\,g)}{d\tau^\alpha} = \sum_{j=0}^{\infty}\frac{\Gamma(\alpha+1)}{\Gamma(\alpha-j+1)\Gamma(j+1)}\,\frac{d^{\alpha-j}(f)}{d\tau^{\alpha-j}}\frac{d^j(g)}{d\tau^j}\,. \tag{6}$$

Substituting (5) into (6) we obtain

$$\frac{\partial^\alpha a(\rho,\tau)}{\partial\tau^\alpha} = \sum_{j=0}^{\infty}\frac{\Gamma(\alpha+1)}{\Gamma(\alpha-j+1)\Gamma(j+1)}\,\frac{\partial^{\alpha-j}(\tau^{-\gamma})}{\partial\tau^{\alpha-j}}\frac{\partial^j\tilde{a}(\eta)}{\partial\tau^j}\,. \tag{7}$$

To calculate the derivative of j^{th} order we use the formula of Faa' di Bruno [11]

$$\frac{\partial^j \tilde{a}(\eta)}{\partial \tau^j} = j! \sum_{m=1}^{j} \frac{d^m \tilde{a}(\eta)}{d\eta^m} \sum_{P_k} \prod_{k=1}^{j} \frac{1}{P_k} \left[\frac{1}{k!} \frac{\partial^k \eta}{\partial \tau^k} \right]^{P_k} , \tag{8}$$

where the second sum is taken over all natural numbers P_k defined for each natural j and m by the equations $\sum_{k=1}^{j} kP_k = j$ and $\sum_{k=1}^{j} P_k = m$. It is easy to see that in a long time limit we get

$$\frac{d^j \eta}{d\tau^j} \approx E_j \tau^{\sigma-\beta-j} ,$$

where

$$E_j = \nu(\sigma-\beta) \ldots (\sigma-\beta-j+1) .$$

Using the formula

$$\frac{d^\alpha \tau^{-\gamma}}{d\tau^\alpha} = \frac{\mathit{\Gamma}(-\gamma+1)}{\mathit{\Gamma}(-\gamma-\alpha+1)} \tau^{-\gamma-\alpha}$$

for $\gamma < 1$ and substituting equations (5)–(8) into (4), after simple calculations we obtain

$$\begin{aligned} & C_0 \tau^{-\gamma-\beta} \tilde{a} + C_1 \tau^{\sigma-\gamma-\beta-\alpha} \frac{\partial \tilde{a}}{\partial \eta} + C_2 \tau^{2(\sigma-\beta)-\gamma-\alpha} \frac{\partial^2 \tilde{a}}{\partial \eta^2} \\ & + C_3 \tau^{3(\sigma-\beta)-\gamma-\alpha} \frac{\partial^3 \tilde{a}}{\partial \eta^3} + \ldots = \tau^{-\gamma-2\beta} \frac{\partial^2 \tilde{a}}{\partial \eta^2} - \tau^{-\gamma-\lambda} \tilde{a}(\eta) \tilde{b}(\eta) . \end{aligned} \tag{9}$$

Comparing the terms with $\partial^2 \tilde{a}/\partial \eta^2$ in the left- and right-hand side of Eq. (9), one finds the relation $\sigma = \alpha/2$ which gives $\rho_{\mathrm{f}} \sim t^{\alpha/2}$. So, we finally get

$$x_{\mathrm{f}} \sim t^{\alpha/2} . \tag{10}$$

This relation was earlier obtained for the case of two mobile reactants with the same subdiffusion coefficients [3]. However, the complete series (6) was not considered, but only the first two terms was taken into account. We also give up here a detailed analysis of the remaining terms on the left- and right-hand side of Eq. (9) which must be mutually balanced or vanish in the long time limit (a similar analysis for the normal diffusion is presented in [4]).

3. Carious lesion

The formation of carious lesion of the enamel starts when concentration of organic acids in the dental plaque reaches sufficient value and pH of the dental plaque lowers below an appropriate point. Then the organic acids are transported inward the enamel and react with the mineral to form soluble calcium ions and phosphate ions (or complexes) [12–15].

It is commonly accepted that the products of the reaction, which do not react with ions and minerals, are transported outwards the enamel [14]. The organic acids (*e.g.* acetic or lactic) are produced in the dental plaque by oral microorganisms that metabolize the simple sugars coming from diet [14]. The enamel is composed of crystal of hydroxyapatie. These crystals are organized in larger forms called prisms. The intercrystalline and interprismatic spaces of enamel are filled with water [14]. Hence, an internal structure of the enamel is rather complex and it can be treated as a porous medium.

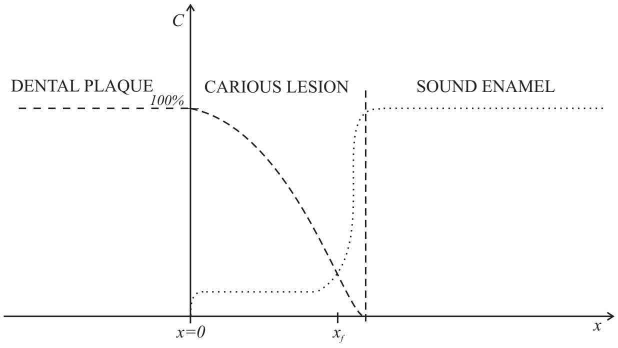

Fig. 2. The schematic view of the tooth enamel. The dotted line and dashed one represent the concentration of the hydroxyapatite and the organic acid, respectively.

We are interested in identification of the process which is responsible for the transport of organic acids inward the enamel. It seems to be subdiffusive. The reaction front x_{f} is identified by the depth of the carious lesion (see Fig. 2), so we use (10) to extract the parameter α from the experimental data which are taken from [13]. In [13] the depth of the carious lesion was measured by means of the scanning electron microscopy and the artificial caries was produced in lactate buffers containing disodium-methane-hydroxy-diphosphonate. In Fig. 3 we present the experimental data (squares) and the power function (solid line)

$$x_{\mathrm{f}} = 0.93\, t^{0.32}\,, \tag{11}$$

which is the best fit to the experimental data obtained by means of the least squares method. Comparing the functions (10) and (11) we find $\alpha = 0.64$

(here we omit the calculation of the error of the parameter). Since the obtained value of the subdiffusion parameter is significantly smaller than 1, we conclude that the subdiffusion occurs in the enamel.

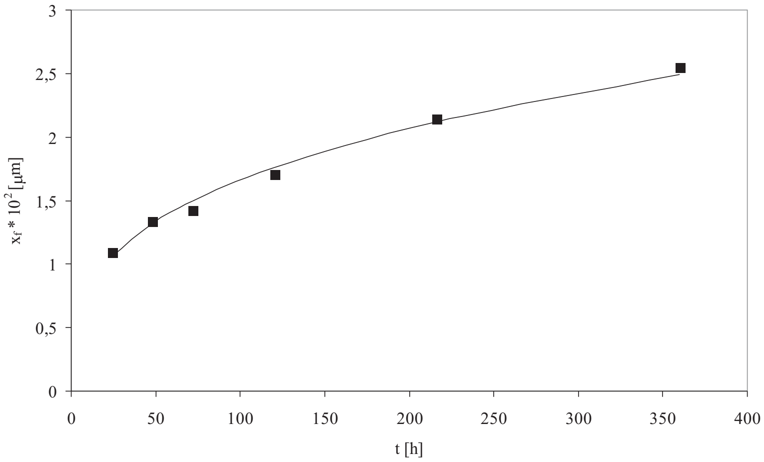

Fig. 3. Lesion depth *versus* time; the squares represent experimental data, the solid line is the plot of the power function (11).

4. Concluding remarks

The time evolution of the reaction front (10) does not depend on the reaction term, so it appears to be a general property of the subdiffusion-reaction process. Our result coincides with the one presented in [3] for the system where $D_{\alpha A} = D_{\alpha B}$. The equation (10) can be used to extract the subdiffusion parameter α from experimental data. In this way we find that the progress of caries is subdiffusive. This result is not surprising as the tooth enamel is of rather complex structure and it can be treated as a porous medium. Therefore, the transport of large undissociated acid molecules can be subdiffusive because of strongly limited mobility of the molecules.

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