

Phenomenological Modeling of Anomalous Diffusion in Polymers

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ABSTRACT: Both normal and anomalous diffusion kinetics are considered in this article. Models of the relaxation, convection, and wetting–drying-cycle kinetics and some other kinds of diffusion kinetics are evaluated. Analytically tractable solutions (when available) are presented. All cal-

culations have been performed with the new nonlinear regression software Fitter (Moscow, Russia). © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1102–1114, 2005

Key words: diffusion; modeling; composites; relaxation

INTRODUCTION

Diffusion models are widely used in the chemical physics of polymers (see refs. 1 and 2 and the literature references therein for examples). These models have a special value for the study of the behavior of glassy polymers. The sorption of moisture is the first stage and a necessary stage; it provides and appreciably determines all further effects of material aging. During this process, we can observe changes in the properties and structure of materials. These effects can be reversible (swelling and porous filling) or irreversible (chemical degradation, physical crystalline transformation, hydrolysis, etc.). However, any structural changes in the material, either reversible or irreversible, have an influence on the kinetics of sorption. Thus, diffusion in polymers deserves to be studied from two points of view: first, as a phenomenon that results in aging, and second, as a tool that allows us to investigate the structure and composition of a material.

Real-world data rarely come within conventional Fickian laws. The modeling of anomalous diffusion effects forces us to build rather complex mathematical descriptions. Often, the model can be constructed only numerically with a difference solution^{3,4} that is inconvenient for data fitting. An analytically tractable solution, when available, as a rule has the form of an infinite series.² In this article, I suggest several phenomenological models of anomalous sorption, which are presented analytically by means of finite sums combined with asymptotic formulas. Such models

have two evident advantages. First, they can be easily applied for data fitting and analysis. Second, all the models have a clear physical meaning, so they may be efficiently interpreted. This approach is used for modeling relaxation and convection diffusion kinetics and wetting–drying-cycle kinetics. In addition, I consider the popular model of diffusion with a chemical reaction. All the models are analyzed to determine how they can explain the anomalous sorption effects observed in the experiments.

In this article, I show that it is possible to apply relaxation and convection models for the fitting of anomalous sorption kinetics. The results of fitting can be interpreted and used to explain changes in the properties and structure of the materials. I also demonstrate that the model of the wetting–drying cycle has a special value in the investigation of composite materials. It describes the particular experiment, and that is very sensible for the polymer property changes. By applying this model, we can connect the mechanical properties with the reversible and irreversible effects of sorption.

I believe that modeling should always include the last, but not the least, stage, which is a computer implementation of the constructed equations. To demonstrate how the proposed formulas may be actually calculated and fitted, I present their interpretation in the form (text box) that is appropriate to the software tool Fitter (Moscow, Russia).^{6–8} This is a program (add-in type) that may be attached to the standard Microsoft Excel package. Fitter is an instrument of statistical analysis that solves multivariate nonlinear regression problems. It is used to estimate parameter values of complicated user-defined functions, which may be entered in ordinary algebraic notation as a set of explicit, implicit, and ordinary differential equations (see the appendix).

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GENERAL CONCEPTS

The main part of any model describing the process of diffusion in specimen B is the classical equation that (for a constant diffusion coefficient D) has the following form:^{2,3}

$$\frac{\partial c}{\partial t} = D\Delta c \quad (1)$$

where $c(x, t)$ is the sorbent concentration at point x at time t . In addition to eq. (1), a diffusion model should also include the initial $c(x, 0) = \phi(x)$ and boundary $c(x, t)|_{x \in \partial B} = \mu(t)$ conditions. The functions $\phi(x)$ and $\mu(t)$ are known, and ∂B is the border of body B. In experiments, the following quantity (sorption kinetics) is measured:

$$M(t) = \int_B c(x, t) dx \quad (2)$$

where $M(t)$ is the change in the specimen mass at time t .

In many cases, it is possible to ignore the influence of volumetric factors on diffusion and reduce the problem to a one-dimensional case. Then, eq. (1) turns into

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3)$$

NORMAL DIFFUSION MODEL (N MODEL)

I begin with a simple, well-studied situation of normal Fickian diffusion, which gives us a basis for further improvements. First, consider a case in which body B is a large plane-parallel plate with thickness l . Because of the large surface of the plate, we can neglect edge effects and consider only one-dimensional flow through the two face sides. The usual conditions for such a system are the following:

$$c(x, 0) = \varphi(x) \quad c(0, t) = \mu_1(t) \quad c(l, t) = \mu_2(t)$$

The solution to eq. (3) under these conditions may be presented as^{3,9}

$$c(x, t) = u(x, t) - \int_0^t \int_0^l G_1(x, \xi, t - \tau) u'_t(\xi, \tau) d\xi d\tau + \int_0^l G_1(x, \xi, t) [\varphi(\xi) - u(\xi, 0)] d\xi \quad (4)$$

where

$$G_1(x, \xi, t) = \frac{2}{l} \sum_{n=1}^{\infty} \exp\left[-\left(\frac{\pi n}{l}\right)^2 Dt\right] \sin \frac{\pi n}{l} x \times \sin \frac{\pi n}{l} \xi \quad (5)$$

is the (source) propagator function for diffusion in interval (plain) [3, 9], and

$$u(x, t) = \mu_1(t) - \frac{x}{l} [\mu_2(t) - \mu_1(t)]$$

$$u'_t(x, t) = [\partial u(x, t) / \partial t]$$

are an auxiliary function and its time derivation.

In some cases, the influence of the second plane face can also be neglected, and it is worth considering the specimen as a semi-infinite $(0, +\infty)$ medium. Formally, a solution can be obtained as the limit in eq. (4) at $Dt/l^2 \rightarrow 0$. However, it is more convenient to solve eq. (3) under the new conditions:

$$c(x, 0) = c_0 \quad \text{and} \quad c(0, t) = \mu(t) \quad (6)$$

where c_0 is the initial concentration. Its solution is given by

$$c(x, t) = c_0 \int_0^{\infty} [G_2(x, \xi, t) - G_2(x, -\xi, t)] d\xi + 2D \int_0^t \frac{\partial G_2}{\partial \xi}(x, 0, t - \tau) \mu(\tau) d\tau \quad (7)$$

where

$$G_2(x, \xi, t) = \frac{1}{2\sqrt{\pi Dt}} e^{-[(x-\xi)^2/4Dt]} \quad (8)$$

is the (source) propagator function for an axis. The first term in eq. (7) can be presented as³

$$c_1(x, t) = \frac{c_0}{2} \left[1 + \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right]$$

where $\operatorname{erf}(z) = (2/\sqrt{\pi}) \int_0^z e^{-t^2} dt$ is the error function.²⁴ For the constant boundary conditions in eq. (6), the second term in eq. (7) can be represented as

$$c_2(x, t) = \mu_0 \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right]$$

If c_0 is not zero, the initial mass of the sorbent $M(0)$ is formally equal to infinity; however, the value $M(t) - M(0)$ is finite and equal to

$$m(t) = M(t) - M(0) = (2\mu_0 - c_0) \sqrt{\frac{Dt}{\pi}} \quad (9)$$

Let us consider the sorption kinetics in eq. (2) for the conditions

$$c(x, 0) = c_0 \quad \text{and} \quad c(0, t) = c(l, t) = \mu_0 \quad (10)$$

If we use eq. (5), we get³

$$c(x, t) = \mu_0 + (c_0 - \mu_0) \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{1}{2k+1} e^{-[(2k+1)\pi/l]^2 Dt} \sin\left[\frac{(2k+1)\pi}{l} x\right] \quad (11)$$

It is obvious that for the conditions in eq. (10), the initial and limiting values of M are $M(0) = lc_0$ and $M(+\infty) = l\mu_0$. If we integrate eq. (11) with respect to x , we get the formula for the sorption kinetics:

$$M(t) = l \left\{ c_0 + (\mu_0 - c_0) \left[1 - 8 \sum_{k=0}^{\infty} \frac{1}{n_k^2} \exp\left(-\frac{n_k^2 D}{l^2} t\right) \right] \right\} \quad (12)$$

where $n_k = \pi(2k + 1)$.

It is known⁹ that the series in eq. (12) converges well only at large values of t . To calculate the sorption kinetics at the beginning of the process, it is necessary to keep plenty of terms in the series. At the same time, at a short distance from zero, it is enough to have only four to five terms to obtain an acceptable description of the process. Therefore, another formula for the calculation of $M(t)$ at a small t value should be used. It is obvious that at the beginning of the process, we can apply eq. (9) for semi-infinite medium. When the fact that there are two surfaces is considered, through which the diffusion is going, we obtain

$$M(t) = M(0) + 2(2\mu_0 - c_0) \sqrt{\frac{Dt}{\pi}} \quad (13)$$

Now, I consider when it is possible to apply the asymptotic formula presented in eq. (13) using the following notations:

$$d = Dl^{-2}, \quad M_0 = l\mu_0, \quad \text{and} \quad C_0 = lc_0 \quad (14)$$

Equations (12) and (13) can be represented in a single formula that is more convenient for practical calculations (the N model):

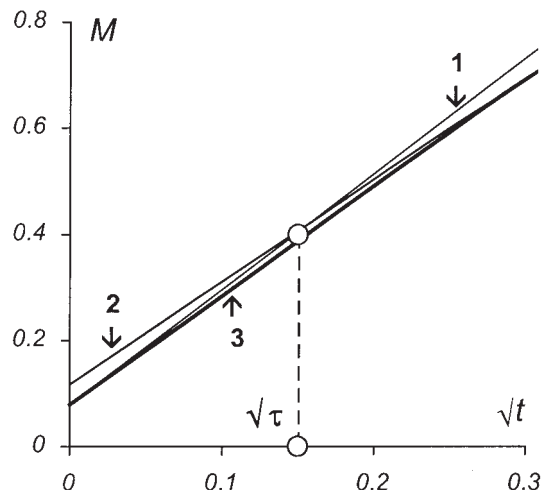


Figure 1 Initial stage of normal diffusion kinetics.

$$M(t) = \begin{cases} C_0 + 2(2M_0 - C_0) \sqrt{\frac{dt}{\pi}} & t < \tau \\ M_0 + 8(C_0 - M_0) \sum_{k=0}^{\infty} \frac{e^{-n_k^2 dt}}{n_k^2} & t \geq \tau \end{cases} \quad (15)$$

It is obvious that at the initial stage $t < \tau$, the asymptotic value in eq. (13) is smaller than any sum in eq. (12) with a finite number of terms.

In Figure 1, the initial stage of diffusion kinetics in the coordinates $[M(t), \sqrt{t}]$ is shown for the following parameter values: $d = 1$, $M_0 = 1$, and $C_0 = 0.08$. Thin curve 1 in Figure 1 corresponds to the asymptotic case in eq. (13), thin curve 2 corresponds to eq. (12) with four terms in the sum, and solid curve 3 corresponds to eq. (15). At the beginning, curve 2 in Figure 1 gives an overestimated value; at the end, curve 1 lies above curve 2. Thus, the moment of time τ in eq. (15) should be chosen for the equality of $M(t)$ in eqs. (12) and (13). However, it is not necessary to calculate the explicit τ value.

From eq. (15), it follows that in the coordinates $[M(t)/M(\infty); \sqrt{t}/l]$, the normal diffusion kinetic curves (1) are monotonic, (2) have no points of inflexion, and (3) do not depend on the specimen size (l). These formal features characterize normal diffusion,¹ and at their violation, diffusion is anomalous.

The typical kinetic curve of normal diffusion is shown in Figure 2, in which the sorption curve of the organoplastic Organite-7T is presented. This can be easily modeled with the help of the Fitter program with the N model given by eq. (15). The corresponding model in the form that is used in Fitter is presented in the appendix.

ANOMALOUS DIFFUSION

Real-world data can seldom be fitted with the normal model.¹⁰ Some examples of typical anomalous sorp-

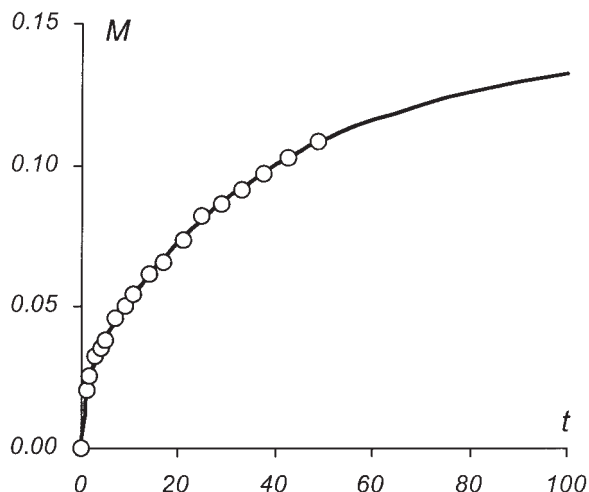


Figure 2 Real-world example of the N model.

tion curves are shown in Figure 3 (curves 1–4); the normal sorption kinetic curve (curve 0) is also shown.

Figure 3, curves 1 and 3

These are so-called pseudonormal curves. They are similar to the normal kinetics at the initial stage of the process but have a very fast (curve 1) or very slow (curve 3) state of equilibrium at the final stage. For their interpretation, either concentration dependence of D is presumed^{2,5} or the sorbent is considered a two-phase system consisting of disperse and dispersive media, which have different D values.¹¹

Figure 3, curve 2

This is anomalous sorption kinetics of the so-called extreme type. As a rule, this case occurs in systems in which the sorbent is initially in a nonequilibrium state. While the sorbent is plasticized with the sorbate molecules, the system structurally relaxes and moves to a new thermodynamically steadier state. Therefore, the excess of the sorbate that filled the sorbent during the previous stage of the process can be pushed out from the specimen.¹² Also, other reasons for the occurrence of the extreme type of sorption kinetics are possible.^{13–15,17,18}

Figure 3, curve 4

This is S-shaped kinetics of sorption. Usually, this type is observed in strongly swelling glassy polymer systems. From a formal point of view, this is connected to the processes of the relaxation of the boundary concentration on the specimen surface.¹⁶

Two complex approaches are used next to describe anomalous diffusion. They are the relaxation and convection models.

RELAXATION MODEL OF ANOMALOUS DIFFUSION (R MODEL)

In the R model, variable boundary conditions are assumed:²¹

$$\mu(t) = \mu_1 + (\mu_0 - \mu_1)e^{-rt}, \quad r \geq 0 \quad (16)$$

where μ_0 is the initial concentration, μ_1 is the limiting concentration, and r is the relaxation constant. It can be shown that this model describes all of the effects of anomalous diffusion. The physical background of eq. (16) is that it accounts for the influence of structural relaxation on the sorption in the simultaneously proceeding processes. The variable μ_1 is a characteristic of submolecular structure, and it reflects the structure reorganizations stimulated by the sorbent. These changes can be connected, for example, with the formation of additional free volume in the specimen.^{22,23}

Boundary conditions play a special role in the diffusion models. First, they are charged with the limiting, steady state of the system, which is always equal to $\lim_{t \rightarrow \infty} \mu(t)$. Therefore, if we want to describe a change in the equilibrium state in the course of sorption, it is constructive to apply variable boundary conditions [i.e., eq. (16)]. Therefore, relaxation diffusion is considered under the following conditions: $c(x, 0) = c_0$ and $c(0, t) = c(l, t) = \mu(t)$.

Using eq. (4) with the symbols in eq. (14) and denoting $M_1 = l\mu_1$, we get

$$M(t) = C_0 + (M_0 - C_0)Y_0(t) - r(M_0 - M_1) \int_0^t e^{-r(t-\tau)} Y_0(\tau) d\tau \quad (17)$$

where $Y_0(t)$ is the sorption kinetics under the constant boundary condition $\mu(t) = 1$ [see eq. (12)]. Integrating

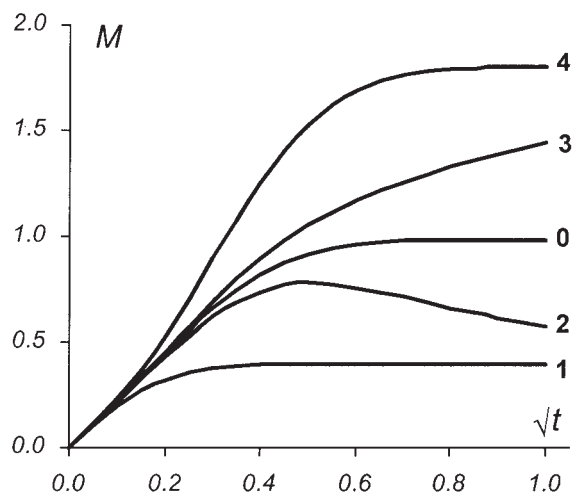


Figure 3 Typical kinetic curves of (0) normal and (1–4) anomalous diffusion.

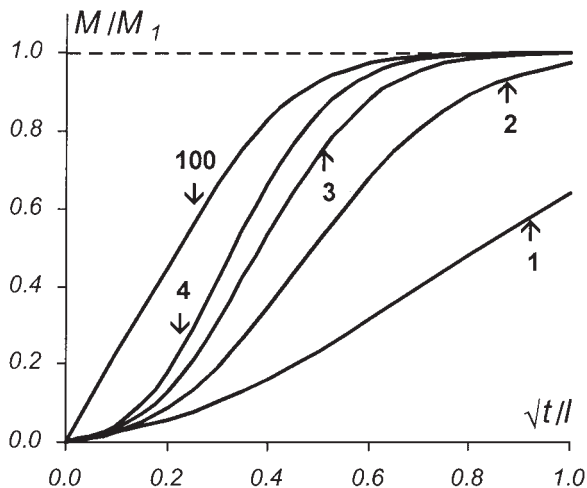


Figure 4 Relaxation diffusion curves at the coordinates $(M/M_1, \sqrt{t}/l)$ at $D = 0.05, \mu_0 = 0.1; \mu_1 = 1$, and $r = 1$ for various values of specimen l (1, 2, 3, 4, and 100).

eq. (17), we obtain the model for relaxation sorption kinetics:

$$M(t) = M_1 + (M_0 - M_1)e^{-rt} - 8 \sum_{k=0}^{\infty} S_k$$

$$S_k = \frac{(V_0 n_k^2 d - V_1 r) e^{-n_k^2 dt} + r(M_1 - M_0) e^{-rt}}{n_k^2 (n_k^2 d - r)}$$

$$V_0 = M_0 - C_0, \quad V_1 = M_1 - C_0 \tag{18}$$

As in the N model, the series in eq. (18) converges well only for large values of t . Therefore, an asymptotic solution at $dt \ll 1$ should be constructed. Using eq. (15) for $C_0 = 0$ and $M_0 = 1$, we obtain

$$M(t) \approx C_0 + 4\pi^{-(1/2)} \sqrt{dt} [M_0 - C_0 + (M_1 - M_0)\beta(rt)] \tag{19}$$

where the function $\beta(x)$ can be expressed with the confluent hypergeometrical function.²⁴ However, for practical calculation, it is more convenient to use the following approximation:

$$\beta(x) = 1 - e^{-z} \quad z = \frac{a_1 x + a_2 x^2 + a_3 x^3}{1 + b_1 x + b_2 x^2 + b_3 x^3} \tag{20}$$

where the coefficients are

$$a_1 = 0.66666448235932 \quad a_2 = -0.0845402528610$$

$$a_3 = 0.0088582230275$$

$$b_1 = -0.0601632363536 \quad b_2 = 0.0135016609125$$

$$b_3 = 0.0002360095898$$

Such an approximation gives a relative accuracy of the $\beta(x)$ calculation that is not less than 0.001. Finally, the R model can be presented as

$$M(t) = \begin{cases} C_0 + 4\pi^{-(1/2)} \sqrt{dt} [M_0 - C_0 + (M_1 - M_0)\beta(rt)] & t < \tau \\ M_1 + (M_0 - M_1)e^{-rt} - 8 \sum_{k=0}^{\infty} S_k & t \geq \tau \end{cases} \tag{21}$$

where $\beta(x)$ is defined in eq. (20) and S_k is defined in eq. (18). The asymptotic case is used until the value calculated in eq. (19) is smaller than the series solution presented in eq. (18). However, it is difficult to define the moment of time (τ) when this condition is broken.

Figure 4 presents the curves of relaxation diffusion in the coordinates $(M/M_1, \sqrt{t}/l)$ calculated for various l values (1, 2, 3, 4, and 100) of the specimen. The curves depend on the specimen size; this is a typical feature of anomalous diffusion.

When the limiting solubility in eq. (16) is less than the initial value (i.e., $\mu_1 < \mu_0$), the sorption curve passes through a maximum.²⁵ This case is shown in Figure 3 (curve 2). It is clear that this curve is related to the case in which the boundary conditions decrease slowly (in comparison with a characteristic time of diffusion $\pi^{-2}d^{-1}$), whereas curve 1 in Figure 3 corresponds to fast falling. Curves 3 and 4 represent the cases of slow and fast growth, respectively, of the boundary conditions.

Table I shows the parameter values at which the R model fits all of the curves in Figure 3. Thus, it is clear that with the help of the R model, it is possible to describe all of the features of anomalous diffusion.

The R model in Fitter style is shown in the appendix.

Formally, the R model could be considered for the case when r is less than 0. The series solution [eq. (18)]

TABLE I
Parameters of the R Model that Fit the Anomalous Diffusion Curves in Figure 3

Curve	d	M_0	r	M_1
0	1.0	1.0	0.0	1.0
1	1.0	1.0	25.0	0.4
2	1.0	1.0	2.0	0.5
3	1.0	1.0	1.5	1.6
4	1.0	1.0	10.0	1.8

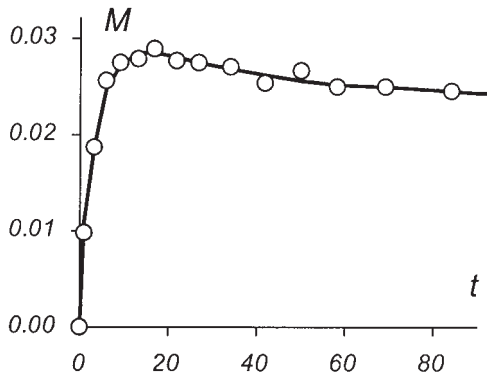


Figure 5 Real-world example of the R model.

may be applied as well as the asymptotic solution in eq. (19). However, at a negative r , the limiting sorption value M_1 [see eq. (16)] tends to infinity, which is apparently not physically possible. Nevertheless, for the model submitted in the appendix (Fig. A.1, shown later), keeping continuity and accuracy even at negative values of r is very important for the correct estimation of the model parameters.

Figure 5 shows the real-world application²⁶ of the R model. This is the sorption kinetics of a glass-fiber-reinforced polymer composite wetted at a temperature of 60°C and a relative humidity of 100%. Time is given in days. The data are fitted by the R model at the following values: $d = 0.018$, $M_0 = 0.037$, $M_1 = 0.025$, $C_0 = 0$, and $r = 0.067$.

CONVECTION MODEL OF ANOMALOUS DIFFUSION (C MODEL)

To consider the convection phenomena in strongly swelling glassy polymers, an additional term is embedded into eq. (3):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \left| \frac{\partial c}{\partial x} \right| \quad (22)$$

This term describes the flow of the sorbent as a whole at the rate v . The equation is solved under the following conditions:

$$c(x, 0) = 0 \quad \text{and} \quad c(0) = c(l, t) = \mu_0 \quad (23)$$

The study of eq. (22) begins with a steady-state case that is presented by the system

$$D \frac{\partial^2 c_\infty}{\partial x^2} - v \left| \frac{\partial c_\infty}{\partial x} \right| = 0 \quad c_\infty(0) = c_\infty(l) = \mu_0$$

It is easy to see that its solution is

$$c_\infty(x) = \mu_0 \left[\frac{1 + \exp\left(\frac{v}{D} \left| x - \frac{l}{2} \right| \right)}{1 + \exp\left(\frac{vl}{2D}\right)} \right] \quad (24)$$

After integration with respect to x on interval $[0, l]$, we get the limiting sorption at the equilibrium state:

$$M_\infty = \frac{M_0}{1 + \exp w} \left[\frac{\exp w - 1}{w} + 1 \right] \quad (25)$$

where the parameter M_0 is defined in eq. (14) and the parameter w is now defined as

$$w = 0.5vl/D \quad (26)$$

It is obvious that a solution to eq. (22) with conditions presented in eq. (23) should tend to the value in eq. (25) at large t values [i.e., $\lim_{t \rightarrow \infty} M(t) = M_\infty$].

A diagram of convection sorption equilibrium in the coordinates $(M_\infty/M_0, w)$ is shown in Figure 6. Here, there are two extreme cases. At a large positive rate of convection (i.e., $w \rightarrow \infty$), the limiting sorption tends to zero. In this case, the sorbent is taken out by convection faster than diffusion gets it in. When parameter w approaches negative infinity, this corresponds to the large negative rate of convection, and the limiting sorption tends to M_0 . In this case, the convection helps to fill the sample faster than the diffusion process alone. In intermediate cases, the limiting sorption can be smaller and larger than M_0 , depending on the direction of the convection. The maximum equilibrium sorption ($M_\infty = 1.264M_0$) is reached at $w = -2.3$.

Now, I return to the full C model [eq. (22)] and present its solution as

$$c(x, t) = c_\infty(x) - \exp(\gamma|x| - dw^2t)\rho(x, t) \quad (27)$$

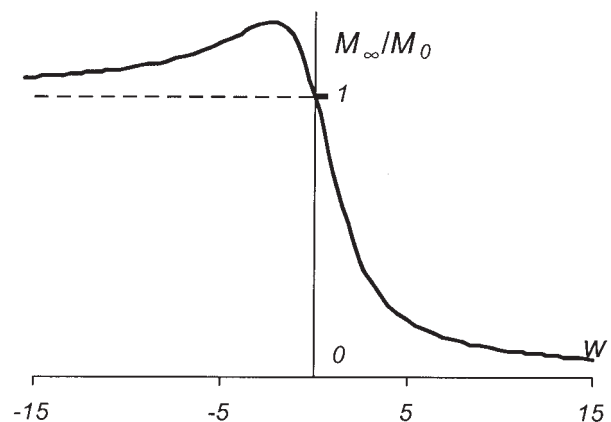


Figure 6 Limiting equilibrium sorption for the C model as dependent on the convection rate (w).

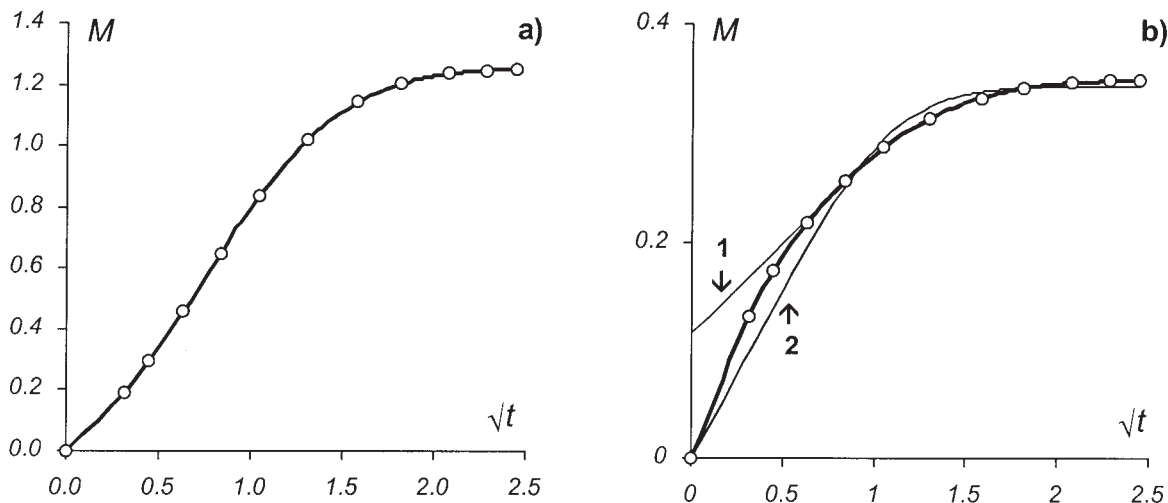


Figure 7 (—) Kinetic curves of convection diffusion versus \sqrt{t} at $d = 0.05$, $M_0 = 1$, and $w =$ (a) -3 and (b) 3 . (○) Approximation by the (a,b) the R model, curves 1, 2 (b) approximation by the N model.

where the function $c_\infty(x)$ is the equilibrium concentration [i.e., function in eq. (24)], the variable w is defined in eq. (26), and the parameter γ is now defined as

$$\gamma = 0.5\nu/D = w/l \tag{28}$$

With eq. (24), it is possible to find the kinetics of convection sorption:

$$M(t) = M_\infty - \frac{16M_0\text{ch}(0.5w)}{1 + e^w} \sum_{k=0}^{\infty} \frac{n_k[n_k e^{0.5w} + (-1)^{k+1}w]}{(w^2 + n_k^2)^2} e^{-(n_k^2 + w^2)t} \tag{29}$$

where the value M_∞ is defined in eq. (25).

To find the asymptotic case of eq. (29) at small t , the C model in semi-infinite medium, is considered:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \nu \frac{\partial c}{\partial x} \quad c(x, 0) = 0 \quad c(0, t) = \mu_0 \tag{30}$$

The variable x varies over the semiaxis $[0, \infty]$. The solution to eq. (30) can be presented as $c(x, t) = \mu_0 \exp(\gamma x - \lambda t)\rho(x, t)$, where λ is equal to $d w^2$ and the parameter γ is defined in eq. (28). From eq. (7), it follows that

$$c(x, t) = 2\mu_0 D e^{\gamma x} \int_0^t \frac{\partial G_2}{\partial \xi}(x, 0, \tau) e^{-\lambda \tau} d\tau$$

where the propagator function G_2 is defined in eq. (8). After integrating and decomposing in series with respect to the small λt , we get the C model:

$$M(t) = M_0 \begin{cases} 2|w|dt + \frac{4\sqrt{dt}}{\sqrt{\pi}} \left(1 + \frac{2}{3}w^2dt\right) & t < \tau \\ \varphi(w) - 8\psi(w) \sum_{k=0}^{\infty} S_k & t \geq \tau \end{cases} \tag{31}$$

where

$$\varphi = \frac{e^w - 1 + w}{w(e^w + 1)} \quad \psi = \frac{2\text{ch}(w)}{e^w + 1} \quad S_k = \frac{n_k[n_k e^{0.5w} + (-1)^{k+1}w]}{(w^2 + n_k^2)^2} e^{-(n_k^2 + w^2)t} \tag{32}$$

Figure 7 shows typical curves of convection sorption in the coordinates (M, \sqrt{t}) . The shape of these curves is similar to that of curves of relaxation sorption kinetics (see Fig. 4), and they actually can be approximated by the R model (the open circles in Fig. 7). The approximation accuracy is so high (the average deviation is less than 0.00002) that the corresponding curves and dots cannot be distinguished in Figure 7(a,b). At $w > 0$ (see Figure 7(b)), the convection kinetic curve has no point of inflexion, and so it could be fitted with the model of normal diffusion. In Figure 7(b), this approximation is shown by thin curves 1 and 2. The initial stage of curve 1 and the middle stage of curve 2 strongly differ from the convection diffusion curve. It shows that at $w > 0$, the main difference between the N model and the C model is the fast growth of the sorption curve at the initial stage. The C model also depends on the specimen size, like the R model. The examples of this dependence were quite similar to the curves shown in Figure 4; therefore, they

TABLE II
Parameters of the C Model that Fit Anomalous Diffusion Curves in Figure 3

Curve	d	M_0	w
0	1.0	1.0	0.0
1	1.9	0.9	2.2
2	—	—	—
3	0.4	1.8	0.8
4	0.2	0.7	-1.8

were not submitted. The Fitter form of the C model is shown in the appendix.

I return to the typical curves of anomalous sorption shown in Figure 3. Table II presents the parameter values of the C model that fit the curves. Curve 2 in Figure 3, which has a maximum, cannot be described by the C model. The other curves are fitted with a very good accuracy. Thus, the C model can explain all the phenomena of anomalous diffusion, except for curve 2 in Figure 3, which is a violation of monotonicity.

Figure 8 shows a practical application of the C model.²⁷ This kinetics curve presents the water sorption through the end faces of a metal-plastic laminate at a temperature of 60°C and a relative humidity of 100%. The time (t) is given in days. The data are fitted by the C model at the following parameter values: $d = 0.0002$, $M_0 = 0.01$, and $w = -16.65$.

WETTING-DRYING-CYCLE KINETIC MODEL (WD MODEL)

The wetting-drying experiment is a very popular approach for studying the sorption in composite materials. The idea is to keep a specimen initially in a humid environment (e.g., in water) and then dry it. For cycle modeling, it is natural to add the following conditions to eq. (3):

$$c(x, 0) = c_0 \quad c(0, t) = c(l, t) = \mu(t) \\ = \begin{cases} \mu_1 + (\mu_0 - \mu_1)e^{-rt} & t < t_1 \\ 0 & t \geq t_1 \end{cases}$$

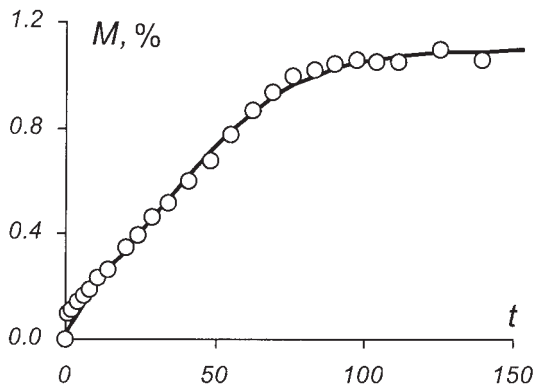


Figure 8 Real-world example of the C model.

where t_1 is the moment when wetting is changed to drying. It is obvious that at the wetting stages ($t < t_1$), the sorption curve can be described by eq. (18). To find the desorption kinetics, it is necessary to solve eq. (3) under zero boundary conditions and with the initial value of concentration, which is equal to the value achieved at the last moment of the sorption stage, that is, $c(x, t_1)$. From eq. (4), it follows that the desorption kinetics can be written as

$$M(t) = 8 \sum_{k=0}^{\infty} \frac{a_k(t_1)}{n_k^2} \exp[-n_k^2 d(t - t_1)], \quad t > t_1$$

where factor a_k depends on t_1 only. From the continuity of the kinetics, it follows that

$$a_k = M_1 + (M_0 - M_1)e^{-rt_1} - U_k(t_1)$$

where

$$U_k(t) = \frac{(V_0 n_k^2 d - V_1 r) e^{-n_k^2 d t} + r(M_1 - M_0) e^{-rt}}{n_k^2 d - r} \quad (33)$$

Therefore, we get the end formula for the WD model:

$$M(t) = \begin{cases} C_0 + 4\pi^{-(1/2)} \sqrt{dt} [M_0 - C_0 + (M_1 - M_0)\beta(rt)] & 0 \leq t < \tau \\ K(t) - 8 \sum_{k=0}^{\infty} \frac{U_k(t)}{n_k^2} & \tau \leq t < t_1 \\ K(t_1) \left[1 - \frac{4}{\sqrt{\pi}} \sqrt{d(t - t_1)} \right] - 8 \sum_{k=0}^{\infty} \frac{U_k(t_1)}{n_k^2} & t_1 \leq t < t_1 + \tau \\ 8 \sum_{k=0}^{\infty} \frac{K(t_1) - U_k(t_1)}{n_k^2} e^{-n_k^2 d(t - t_1)} & t_1 + \tau \leq t < \infty \end{cases} \quad (34)$$

where $K(t)$ is equal to $M_1 + (M_0 - M_1)e^{-rt}$, U_k is defined in eq. (33), and $\beta(x)$ is defined in eq. (20).

In the WD model, I use four asymptotic functions that are sewn together. An example is shown in Figure 9. Curves 1s and 2s present the asymptotic cases for sorption kinetics at a small t and at the end of wetting ($t = t_1 - 0$), respectively. Curves 1d and 2d show the asymptotic cases for drying kinetics in the beginning of desorption at $t = t_1 + 0$ and at a large t .

I do not present the Fitter version of the WD model as it is similar to the models shown in the appendix but takes much more space. The appropriate text box is available in ref. 30.

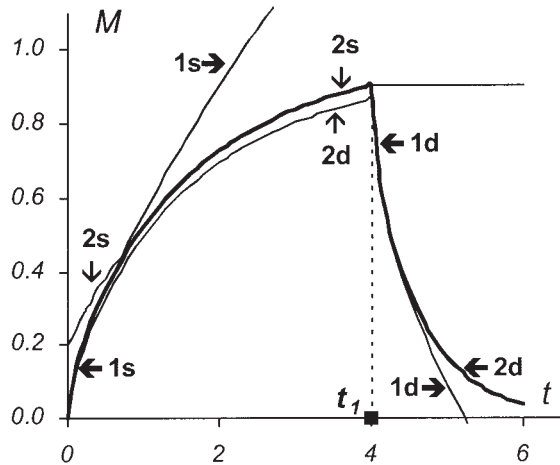


Figure 9 Asymptotic cases used in the WD model.

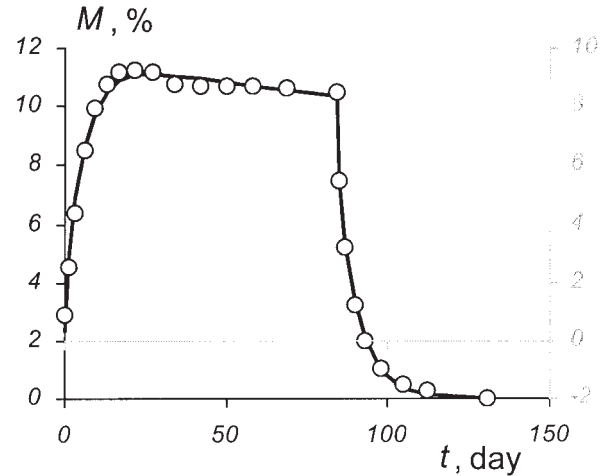


Figure 11 Real-world example of the WD model.

Figure 10 presents a real-world example for which the WD model is used. The data (open circles) are related to a composite material with a glassy matrix.²⁸ Sorption is measured in percentages, and time is measured in days. This kinetic curve corresponds to that in curve 3 in Figure 3, that is, a slow growth of boundary conditions. Solid curve 1 presents the WD model, which is fitted at the following parameter values: $d = 0.030$, $M_0 = 2.261$, $M_1 = 4.290$, $r = 0.025$, and $t_1 = 25$. Thin curve 2 shows the change of limiting sorption: $M_1 + (M_0 - M_1) \exp(-rt)$.

In addition, two kinetic curves of normal sorption [eq. (15)] are presented. Thin curve 3 is constructed with the N model for the same d and at the initial value of the equilibrium sorption, that is, for $d = 0.030$, $M_0 = 2.261$, and $C_0 = 0$, and curve 4 is calculated at the limiting value of the equilibrium sorption, that is, for $d = 0.030$, $M_0 = 4.290$, and $C_0 = 0$.

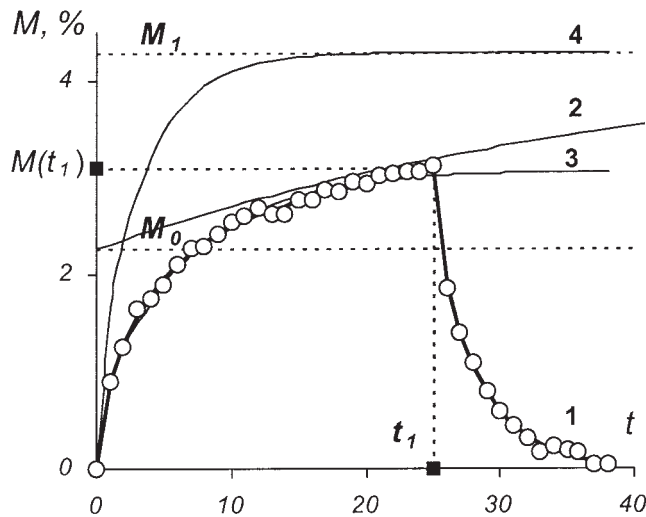


Figure 10 Kinetics of the wetting-drying cycle.

If the wetting-drying cycles are repeated with the same specimen, it is possible to study the changes of the initial M_0 and limiting M_1 sorption values, depending on the number of cycles. In ref. 28, it is shown that at the second cycle, the initial solubility is equal to the sorption achieved at the end of the first cycle, that is, $M_0 = M(t_1) = 3.12$. In addition, a good correlation between the mechanical properties and the value of M_1 has been reported. This correlation does not depend on the conditions (temperature and time) of the experiment. This study proves that the value of M_1 actually characterizes the irreversible structural changes occurring in the material.

In Figure 11, another example of the wetting-drying cycle for a hybrid composite material is shown.²⁹ These data are interesting because the kinetics start with the nonzero initial value. However, this is not related to the initial moisture that is present in the specimen at the beginning of the experiment. This is an effect of material destruction during the experiment. If one translates the beginning of the coordinates into the point appropriate to the initial condition (the right Y axis), the sorption kinetic curve will be negative after the time point that is equal to 93 days. This means that during the experiment, the original specimen loses more sorbate than it gains sorbent.

OTHER MODELS OF ANOMALOUS SORPTION (H MODEL)

Various models have been used to model anomalous diffusion. In particular, the Berens-Hopfenberg model is known.^{19,20} It assumes a linear superposition of relative weight gain by normal diffusion and by relaxation of the first order. Each mechanism has a fixed fraction in the general equilibrium sorption. Such models have a rather simple structure, which, as a rule, consists of the normal diffusion model and some

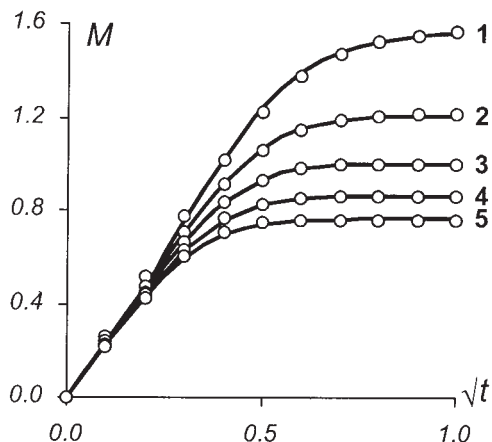


Figure 12 Kinetic curves of the H model versus \sqrt{t} at $d = 1$ and $\mu_0 = 1$ for $k = -4, -2, 0, 2,$ and 4 .

straightforward additives. Obviously, such models can be easily used in the Fitter system by the application of the N model shown in the appendix as a basis.

Often in the literature,^{1,2} the sorption model with a chemical reaction of the first order (hydrolysis of sorbent) is used:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - kc \quad k \geq 0 \quad c(x, 0) = c_0$$

$$c(0, t) = c(l, t) = \mu_0 \quad (35)$$

Apparently, the popularity of this model (the H model) comes from its simplicity. When substitution is applied, $c = ue^{-kt}$, the system can be transformed into the standard form of eq. (3). However, many researchers fail to consider that such mapping also transforms the boundary conditions. They become $u(0, t) = u(l, t) = \mu_0 e^{kt}$. Now, it is easy to see that the H model presented in eq. (35) turns into the R model [eq. (21)] at $r = -k$ and $\mu_1 = 0$. Therefore, the H model can be presented as

$$M(t) = \begin{cases} e^{-kt} \{ C_0 + 4\pi^{-(1/2)} \sqrt{dt} [M_0(1 - \beta(-kt)) - C_0] \} & t < \tau \\ M_0 - 8 \sum_{k=0}^{\infty} S_k & t \geq \tau \end{cases}$$

$$S_k = \frac{[(M_0 - C_0)n_k^2 d - kC_0]e^{-(n_k^2 d + k)t} + kM_0}{n_k^2(n_k^2 d + k)} \quad (36)$$

where the function $\beta(x)$ is determined in eq. (20).

In Figure 12, several sorption curves in the coordinates (M, \sqrt{t}) are shown. They are constructed with the H model for various values of the reaction rate constant ($k = -4, -2, 0, 2,$ and 4 ; curves 1–5). These

curves are rather similar to the curves of the N model (curve 3 in Fig. 12). This fact can be easily proven by simple calculations, the results of which are presented by the open dots in Figure 12. These values are obtained after the curves are fitted by the N model.

Parameter estimates are given in Table III. The accuracy of the fitting is very good (the average error is less than 0.01); that, however, can be easily seen in Figure 12.

Thus, we see that the use of the H model for the modeling of the anomalous sorption is not justified. This claim can be confirmed by the shapes of the kinetic curves, which are similar to those of normal diffusion kinetics and thus fit that model well.

CONCLUSIONS

Several models for anomalous diffusion modeling have been presented. It can be claimed that the R model is the most suitable among them. It allows us to describe all anomalies that are typical for non-Fickian diffusion. Moreover, this model has physical meaning that can be used for the interpretation of data. The parameters of the R model can be interpreted as some reasonable values characterizing the system behavior.

The next is the C model, which is almost as appropriate as the R model. The C model also has some theoretical meaning, but it cannot describe the diffusion kinetics with a maximum, which is a typical effect in anomalous sorption. Formally, this shortcoming comes from the lack of unknown parameters in the model. There are only three parameters versus five parameters in the R model. However, the C model may be preferred in cases in which the convection effect is presumed.

The WD model has a special value in diffusion modeling. It gives a description of a particular design experiment that is reported to be most sensible for polymer property investigations. This model combines normal and relaxation concepts, and thus it is very flexible and stable in applications. It is strongly recommended for the study of composite materials.

Other models are less suitable. In particular, the model of diffusion with a chemical reaction turns out

TABLE III
Parameters of the N Model that Fit Curves of the H Model, Shown in Figure 12

Curve	k	d	M_0
1	-4.0	0.526	1.572
2	-2.0	0.756	1.212
3	0.0	1.000	1.000
4	2.0	1.259	0.860
5	4.0	1.531	0.760

to be rather weak in the description of anomalous sorption effects.

My aim has been to present highly practical end-user models that can be adapted easily for real-world diffusion problems. All of the models have been calculated and fitted with Fitter software. Corresponding model text boxes are shown in this article. Even most complicated models can be implemented and evaluated with this program. The main advantage of the approach is that any small or large modification of the model can be done directly in the text box by the ordinary way of formula writing. The particulars of the calculations are available in ref. 30.

APPENDIX

Fitter is an instrument of statistical analysis that may solve multivariate nonlinear regression problems.⁶ It is used to estimate parameters of complicated user-defined functions, which may be entered in ordinary algebraic notation as a set of explicit, implicit, and ordinary differential equations. Fitter allows us to use prior knowledge of parameters and the accuracy of the measurements. With the help of Fitter, we can obtain statistical information concerning the input data and the quality of fitting. They are the parameter estimates, the covariance matrix, the correlation matrix, and the error variance calculated by fit and by population. Moreover, there is hypothesis testing as well as the calculation of confidence intervals.

The input information required for fitting consists of several parts. The first part is data, which are numerical values to be fitted. The second part is the model, which contains the mathematical equations. These two parts are required for fitting. The third part is prior information, which is optional. Some elements of the information are common. For example, the response name (e.g., Y) is used in the data and the model. Fitter takes all the information from open Excel workbooks. It is placed directly on a worksheet as data and parameters or written in a text box as a model. All the results are also output as tables on the worksheets. To explain which data should be used, it is necessary to register them with the help of the Fitter wizards. The amount of data and the number of predictors are limited only by the capabilities of the computer.

Every model is written into a separate text box with multiple statements complete with intermediate variables. The only requirement is that the whole model, as the composition of all input equations, should be executed to define the estimated value of the dependent variables. In Fitter, we can use a different combination of explicit and implicit functions and ordinary differential equations. An explicit function is written in the text box in its natural form as

$$y = f(x, a, I)$$

An implicit function is written with the following syntax:

$$0 = f(x, a, I, y); \quad YL < y < YR$$

where y is a dependent variable (response or intermediate variable), vector x is a set of predictors, a is a vector of unknown parameters, and I is a set of intermediate variables. It is necessary to use the dependent variable y in the right part of the implicit formula. Also, this function should have a zero in the left part of the equation. A semicolon is used as the delimiter between the implicit equation and its boundary condition. The symbol $<$ (less than) is used to separate the dependent variable y from its left and right bounds YL and YR . These bounds may be constant, predictors, or intermediate variables, but they cannot be expressions. Fitter can process the model, that is, ordinary differential equations of the type

$$\frac{dy}{dt} = f(y, x, a, I) \quad y(t_0) = y_0$$

where y is the dependent variable (response or intermediate variable) and t is some variable that may be a predictor, parameter, or intermediate variable. To enter such an equation, one needs to write the following expression in the text box:

$$D[y]/D[t] = f(y, x, a, I) \quad y(t_0) = y_0$$

A semicolon is used as the delimiter between the equation and its initial conditions. Variables t_0 and y_0 may be constants, predictors, or intermediate variables but not expressions.

I now submit the Fitter presentation of the diffusion models that are considered in the main part of the article. The N model [eq. (15)] has the form shown in Figure A.1. The first line of the model (as well as other lines starting with an apostrophe) is a comment. Actually, the model begins with the second line. Here, the standard Fitter functions $\text{hev}(x)$ and $\text{imp}(x)$ are used. They are defined in eq. (37):

$$\text{hev}(x) = \begin{cases} 0, & x \leq 0 \\ 1, & x < 0 \end{cases} \quad \text{imp}(x) = \begin{cases} 0, & x \neq 0 \\ 1, & x = 0 \end{cases} \quad (37)$$

It is clear that if USEm1 is greater than 0, M is equal to m1, and if USEm1 is greater than 0, M is equal to m2. This matches eq. (15). The variable USEm1, which sets up the condition of the asymptotic case, is calculated in the fourth line. The variables $P2 = \pi^2$ and $P12 = \pi^{-0.5}$ are constants. In the 10th line, the equation for the asymptotic case (m1) is presented, and in the 12th line, the formula for the series case (m2) can be seen. I used the sum with only four terms, as they were

```

'Normal model
M=m1*hev(USEm1)+m2*[hev(-USEm1)+imp(-USEm1)]
'condition to apply asymptotic case m1
USEm1=m2-m1
'constants and intermediates
P2=PI*PI
P12=(PI)^(-0.5)
x=d*t
'asymptotic case at t<tau
m1=C0+2*P12*(2*M0-C0)*(x)^0.5
'series case at t>tau
m2=M0+(C0-M0)*8*(S0+S1+S2+S3+S4)
n0=P2
S0=exp[-n0*x]/n0
n1=P2*9
S1=exp[-n1*x]/n1
n2=P2*25
S2=exp[-n2*x]/n2
n3=P2*49
S3=exp[-n3*x]/n3
n4=P2*81
S4=exp[-n4*x]/n4
'unknown parameters
d=?
M0=?
C0=?

```

Figure A.1 N model as it is used in Fitter.

```

'
' Relaxation model
M=m1*hev(USEm1)+m2*[hev(-USEm1)+imp(-USEm1)]
'condition to apply asymptotic case m1
USEm1=m2-m1
'constants and intermediates
P2=PI*PI
P12=(PI)^(-0.5)
x=r*t
V0=M0-C0
V1=M1-C0
'asymptotic case at t<tau
m1=C0+4*P12*(d*t)^0.5*[M0-C0+(M1-M0)*beta]
beta=1-exp(-z)
z=(a1*x+a2*x*x+a3*x*x*x)/(1+b1*x+b2*x*x+b3*x*x*x)
a1 = 0.6666644823593
b1 = -0.0601632363536
a2 = -0.0845402528610
b2 = 0.0135016609125
a3 = 0.0088582230275
b3 = 0.0002360095898
'series case at t>tau
m2=M1+(M0-M1)*exp(-x)-8*S
R=r*(M1-M0)*exp(-x)
S=S0+S1+S2+S3+S4
n0=P2
S0=[(V0*n0*d-V1*r)*exp(-n0*d*t)+R]/(n0*d-r)/n0
n1=P2*9
S1=[(V0*n1*d-V1*r)*exp(-n1*d*t)+R]/(n1*d-r)/n1
n2=P2*25
S2=[(V0*n2*d-V1*r)*exp(-n2*d*t)+R]/(n2*d-r)/n2
n3=P2*49
S3=[(V0*n3*d-V1*r)*exp(-n3*d*t)+R]/(n3*d-r)/n3
n4=P2*81
S4=[(V0*n4*d-V1*r)*exp(-n4*d*t)+R]/(n4*d-r)/n4
'unknown parameters
d=?
M0=?
M1=?
C0=?
r=?

```

Figure A.2 R model as it is used in Fitter.

enough for a reasonable evaluation. The last lines of the model explain which variables are the unknown parameters that have to be estimated.

The R model [eq. (21)] in the Fitter notation has the form shown in Figure A.2.

Its structure is similar to the N model presented previously. Only some essential details are worth mentioning. At $r = 0$, the model turns into the normal model, and parameter M_1 cannot be estimated. At $r = n_k^2 d$ and $k = 0, 1, 2, 3$, or 4 , there is a singularity of type $0/0$. This circumstance can confuse the estimation of the parameters. If beforehand it is known that, for example, $r = n_0^2 d = \pi^2 d$, the model in Figure A.1 should be modified in such a way that one of un-

```

'
' Convectonal model
M=m1*hev(USEm1)+m2*[hev(-USEm1)+imp(-USEm1)]
'condition to apply asymptotic case m1
USEm1=m2-m1
'constants and intermediates
P12=(PI)^(-0.5)
x=d*t
psi=2*CHw2/(EXw+1)
CHw2=0.5*(EXw2+1/EXw2)
EXw=exp(w)
EXw2=exp(0.5*w)
'asymptotic at t<tau
m1=2*M0*[absW*x+2*P12*(x)^0.5*(1+2/3*w*w*x)]
absW=(w*w)^0.5
'singularity 0/0 solution
ffi=ffil/ffii2
ffil=(EXw-1+w)*NOzero+imp(w)
ffii2=w*(1+EXw)*NOzero+imp(w)
NOzero=hev(w)+hev(-w)
'series case at t>tau
m2=M0*(ffi-8*psi*S)
S=S0+S1+S2+S3+S4+S5
n0=PI
nw0=n0*n0+w*w
s0=-1
S0=n0*(n0*EXw2+s0*w)*exp(-nw0*x)/(nw0*nw0)
n1=PI*3
nw1=n1*n1+w*w
s1=1
S1=n1*(n1*EXw2+s1*w)*exp(-nw1*x)/(nw1*nw1)
n2=PI*5
nw2=n2*n2+w*w
s2=-1
S2=n2*(n2*EXw2+s2*w)*exp(-nw2*x)/(nw2*nw2)
n3=PI*7
nw3=n3*n3+w*w
s3=1
S3=n3*(n3*EXw2+s3*w)*exp(-nw3*x)/(nw3*nw3)
n4=PI*9
nw4=n4*n4+w*w
s4=-1
S4=n4*(n4*EXw2+s4*w)*exp(-nw4*x)/(nw4*nw4)
n5=PI*11
nw5=n5*n5+w*w
s5=1
S5=n5*(n5*EXw2+s5*w)*exp(-nw5*x)/(nw5*nw5)
'unknown parameters
d=?
M0=?
w=?

```

Figure A.3 C model as it is used in Fitter.

known parameters, d or r , are excluded from all equations. In this case, the expression for S_0 is replaced with the expression " $S_0=(M_0-M_1)*\exp(-x)$." More details about the singularity problem in the Fitter models are presented in an examination of the C model.

The C model [eq. (31)] in the Fitter notation is shown in Figure A.3.

This is the text box appropriate for use in the Fitter program. I now consider some of its features. In the section entitled "asymptotic at $t < \tau$," the expression " $\text{abs}W=(w*w)^{0.5}$ " is used. This is just the absolute value of the parameter w . In the section titled "singularity 0/0 solution," I use an approach that should be explained in detail. Apparently, the function $\phi(w)$ in eq. (32) has a singularity at $w = 0$. This uncertainty can be easily resolved by decomposition, which gives $\phi(0) = 1$. However, the program cannot manage such a singularity, so an attempt to use the model at $w = 0$ leads to an error of calculation, a division by zero. Therefore, it is necessary to calculate function $\phi(w)$ by the following formula:

$$\varphi(w) = \varphi_1(w) / \varphi_2(w)$$

(which corresponds to the line " $\text{ffi}=\text{ffi1}/\text{ffi2}$ " in the Fitter model) where

$$\varphi_1(w) = \begin{cases} e^w - 1 + w & w \neq 0 \\ 1 & w = 0 \end{cases} \quad \varphi_2(w) = \begin{cases} w(e^w + 1) & w \neq 0 \\ 1 & w = 0 \end{cases} \quad (\text{A.1})$$

For the calculation of these functions, the following auxiliary variable is used: " $\text{NOzero}=\text{hev}(w)+\text{hev}(-w)$." It is equal to 1 everywhere, except at $w = 0$, where it is equal to 0. Therefore, the expressions " $\text{ffi1}=(EXw-1+w)*\text{NOzero}+\text{imp}(w)$ " and " $\text{ffi2}=w*(1+EXw)*\text{NOzero}+\text{imp}(w)$ " correspond to eq. (A.1). Such a trick is the standard approach within Fitter. It allows us to apply the models with resolvable singularities of type 0/0.

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