THEORY OF TRACER EXCHANGE IN SINGLE-FILE SYSTEMS*

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Tracer exchange in single-file systems (one-dimensional diffusional systems where the particles are not able to pass each other) shows peculiar and interesting features which differ considerably from that of transport diffusion or from the behaviour known from ordinary diffusional systems. A formalism relating the tracer exchange curve (as the observable of the tracer exchange experiment) to the residence time distribution (describing the intracrystalline diffusional mechanism) and the boundary condition (describing the situation outside) is introduced. The formalism is quite general and valid for any diffusional regime. Typical examples of the residence time distribution of a single-file system can be inferred from the tracer exchange curves obtained in a previous study by numerical simulations. Based on these examples, the tracer exchange curves for the single-file system subject to different boundary conditions (corresponding to a variety of experimental set-ups) are plotted and discussed.

Key words: Single-file systems; Tracer exchange; Residence time distribution; Zeolites.

Let us consider diffusion of particles through a narrow channel-like pore. If the diameter of the particles exceeds the radius of the pore, the particles are not able to pass each other within the pore. The stochastic motion arising from this strong mutual hindrance of the particles is known as *single-file diffusion*. Systems of this type, *e.g.*, occur in superionic conductors[1] or in ion channels through biological membranes[2]. Recently, the existence of single-file diffusion in various zeolites with one-dimensional channel system has been confirmed by the Pulsed Field Gradient (PFG) NMR measurements[3].

As long as we are interested only in transport or collective diffusion (*e.g.*, adsorption or desorption processes), there is no difference between the single-file and normal one-dimensional diffusion: Both the concentration profile and the mass current are insensitive whether the particles may change their order or not[4]. Today, the behaviour of

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systems undergoing the normal or Fickian diffusion is well understood. As an example, Crank[5] considers the Fickian diffusion is a plane sheet (of a certain thickness in the x-direction but infinite in the y- and z-directions) being in contact with a surrounding well-stirred solution or gas phase. Since the sheet is infinite, only the one-dimensional diffusion in the x-direction has to be taken into account. Crank[5] gives, among many other results, the time dependence of the amount of particles adsorbed by the sheet in accordance with the time dependence of the particle concentration outside the sheet which plays the role of a *boundary condition*.

A completely different situation, however, arises in case of the *tracer diffusion* where the relative amount of distinguishable species of particles is considered. While in a system behaving according to the Fickian diffusion (*e.g.*, two- or three-dimensional pore networks or matrices, as well as one-dimensional channels wide enough to allow mutual passage of the molecules), the concentration of any of the species can be described by the well-known results of the transport diffusion, single-file systems show particular features.

In this paper, we present a formalism capable of describing the tracer exchange in single-file systems. The system considered is the single-file analogue of the plane sheet given in ref.[5]: an array of parallel identical single-file channels directed along the x-axis. Since any particle exchange between adjacent channels is excluded, there is, *a priori*, no diffusion along the y- or z-directions so that we do not need to assume that the sheet is infinite. From now on, this array of channels will be referred to as *crystal*, irrespective whether it is in fact a single crystal, a heap or bed of crystallites, a membrane, or any other non-crystalline structure, as long as it contains identical channels. It is surrounded by a well-stirred solution or gas phase in such a way that both ends of each of the channels have contact to this surrounding space. The system is assumed to be in macroscopic *sorption equilibrium*, *i.e.*, the mean total amount of particles within the crystal does not change, but the *relative* amount of the two distinguishable species varies with time according to the given initial and boundary conditions. In analogy to ref.[5], the scope of our study is the determination of the *tracer exchange curve* $\gamma(t)$ under different experimental conditions. The formalism used is quite general and remains valid if surface resistances or additional particle interactions are introduced.

In chapter Theoretical, the basic equation is established. The first five sections of chapter Results and Discussion consider several experimental set-ups, give the corresponding boundary conditions, and show their influence on the time dependence of the tracer exchange. Finally, in the sixth section the results are generalized to arrays of unequal channels.

THEORETICAL

Consider an individual diffusional channel of finite length with particle exchange at the margins. Let there be two species of particles in the system, labelled A and B, which do not differ in their transport behaviour.

To begin with, assume that the channel consists of N discrete sites. As in ref.[6], we define the following variables describing the state and the system dynamics:

$$\Sigma_i = \begin{Bmatrix} 1 \\ 0 \end{Bmatrix} \text{ if site } i \text{ is } \begin{Bmatrix} \text{occupied} \\ \text{vacant} \end{Bmatrix} , \tag{1}$$

$$\tau_i = \text{ time (duration) which the particle occupying site } i \tag{2}$$
$$\text{has already spent within the channel,}$$

$$\Lambda_i = \begin{Bmatrix} \lambda_A \\ \lambda_B \end{Bmatrix} \text{ if site } i \text{ is occupied by the } \begin{Bmatrix} A \\ B \end{Bmatrix} \text{ particle} . \tag{3}$$

At a given time t, the stochastic variable Σ_i gives the *occupation* of site i, while τ_i and Λ_i give, provided site i is occupied by a particle ($\Sigma_i = 1$), the *residence time* and the *kind* of this particle. The probability distributions of these stochastic variables are given by the quantities

$$\Theta_i = P(\Sigma_i = 1) , \tag{4}$$

$$\varphi_i^*(\tau) \, d\tau = P(\Sigma_i = 1, \tau \le \tau_i < \tau + d\tau) , \tag{5}$$

$$\rho_i^* = P(\Sigma_i = 1, \Lambda_i = \lambda_A) . \tag{6}$$

From these probabilities describing the situation at the individual sites, one gets quantities referring to the whole channel:

$$\varphi(\tau)\, d\tau = \frac{\displaystyle\sum_{i=1}^{N} \varphi_i^*(\tau)\, d\tau}{\displaystyle\sum_{i=1}^{N} \Theta_i} \ , \tag{7}$$

the mean total relative amount of particles having spent a time between τ and $\tau + d\tau$ within the channel, where $\varphi(\tau)$ will be referred to as *residence time distribution*; and

$$\rho = \frac{\displaystyle\sum_{i=1}^{N} \rho_i^*}{\displaystyle\sum_{i=1}^{N} \Theta_i} \ , \tag{8}$$

the *mean relative amount of* A *particles in the channel.*

It is understood that the *sorption equilibrium* has already maintained a time longer than the residence time of any of the present particles. This implies that $\varphi(\tau)$ is a *stationary* distribution not varying with time. Moreover, this quantity is a sole property of the diffusion mechanism in the channel (including the mechanism of the particle exchange between the channel and the surrounding space). In contrast, ρ may change with time and depends both on the intracrystalline diffusion and on the development of the ratio of the two species outside the channel. The connection between these functions $\rho(t)$ and $\varphi(\tau)$ can be established as follows.

If, at any time t, a particle is newly adsorbed from outside into the channel, the stochastic variable Λ_0 shall tell whether the particle is of A or B type, and we define the probability

$$\rho_0 = P(\Lambda_0 = \lambda_A) \tag{9}$$

that this new particle belongs to the A species. Since $\varphi_i^*(\tau)\, d\tau$ is the probability that site i is occupied by a particle having been adsorbed a time between τ and $\tau + d\tau$ ago, and $\rho_0(t - \tau)$ is the probability that a particle having been adsorbed a time τ ago is of A type, one gets for the individual sites

$$\rho_i^*(t) = \int_0^\infty \rho_0(t - \tau)\, \varphi_i^*(\tau)\, d\tau, \quad \forall i = 1,\dots N \ . \tag{10}$$

According to Eqs (7) and (8) we have for the whole channel

$$\rho(t) = \int_0^\infty \rho_0(t - \tau)\, \varphi(\tau)\, d\tau \,. \qquad (11)$$

This is our basic equation relating the relative amount ρ of A particles in the channel at time t to the past development of the boundary condition, $\rho_0(t)$, and the properties of the diffusional mechanism, represented by the intracrystalline residence time distribution $\varphi(\tau)$. All subsequent results follow thereof by special choices of the boundary condition.

We stress that Eq. (*11*) does not refer to individual sites any more and is, therefore, equally valid for discrete or continuous models of diffusion. Moreover, we did not have to consider whether or not the diffusion proceeds according to single-file behaviour. This means that Eq. (*11*) holds for any diffusional regime. The particularities of the intracrystalline behaviour of the system are exclusively contained in the residence time distribution $\varphi(\tau)$.

So far, we considered an individual channel. Nevertheless, Eq. (*11*) is valid for an array of identical channels as well, because both ρ and φ are relative quantities, and the boundary condition ρ_0 is common to all channels (provided the phase surrounding the crystal is well-stirred).

In the following, the general relation, Eq. (*11*), is applied to tracer exchange processes. All these processes follow a common scheme: Before the starting time, $t = 0$, there are only B particles in the system, *i.e.*, $\rho(t) = 0$ for $t < 0$. This is ensured by the condition

$$\rho_0(t) = 0 \quad \text{for } t < 0 \,. \qquad (12)$$

At $t = 0$, the particle species in the surrounding phase is switched, where the particular development of the boundary condition $\rho_0(t)$ depends on the experimental set-up. Since the quantity $\rho(t)$ monitors the progress of the exchange of the two particle species its time dependence will be referred to as *unnormalized tracer exchange curve*. It starts at $\rho(0) = 0$ and ultimately reaches the final value

$$\rho(\infty) = \rho_0(\infty) =: g \qquad (13)$$

when the equilibrium of the species is attained. Following the usual convention, in all figures of this paper, we give the *(normalized) tracer exchange curve*

$$\gamma(t) := \frac{\rho(t)}{g} \tag{14}$$

which differs from $\rho(t)$ by a simple normalization ensuring

$$\gamma(\infty) = 1 . \tag{15}$$

On calculating $\rho(t)$, we will use its Laplace transform which simply is

$$\rho(s) = \rho_0(s) \, \varphi(s) . \tag{16}$$

(Both the Laplace transforms on the right-hand side surely exist because $0 \le \rho_0 \le 1$, Eq. (12), and $\int_0^\infty \varphi(\tau) \, d\tau = 1$.) We will use Eq. (16) in two opposite ways. If the residence time distribution φ of the diffusional system is known, one can compute the tracer exchange curve for an arbitrary experimental condition. If, on the other hand, the tracer exchange curve for special experimental conditions is known, one can infer the residence time distribution of the crystal which, in turn, gives the tracer exchange curves for all other cases. (Beyond the scope of this paper, the knowledge of φ is the key to other quantities as well, e.g., the effectiveness factor of catalytic reactions[6].)

RESULTS AND DISCUSSION

Constant Boundary Conditions

In the simplest tracer exchange experiment, the particle species in the surrounding phase is, at the initial time $t = 0$, suddenly switched to pure A. Hereafter, it is kept pure, e.g., by immediately removing all desorbing B particles. In our notation,

$$\overline{\rho}_0(t) = \begin{cases} 0, & t < 0, \\ 1, & t \ge 0. \end{cases} \tag{17}$$

(The bar always indicates quantities referring to constant boundary conditions defined in this way.) From Eqs (13) and (17) we have

$$\overline{g} = 1 \tag{18}$$

which implies that, for constant boundary conditions, normalized and unnormalized tracer exchange curves coincide. Inserting Eq. (*17*) into Eq. (*11*) yields

$$\overline{\rho}(t) = \overline{\gamma}(t) = \int_0^t \varphi(\tau)\, d\tau, \quad t \geq 0. \tag{19}$$

If the residence time distribution $\varphi(\tau)$ is known, we can now compute the tracer exchange curve according to Eq. (*19*). Since $\varphi(\tau)$ depends on all the peculiarities of the system there is, of course, no general expression comprising all single-file systems one could think of. In ref.[6] we gave an exact derivation of $\varphi(\tau)$ which allows an analytical solution for a discrete model of a single-file channel with the variable surface resistance and the attractive particle–particle interactions. Unfortunately, the procedure is numerically very expensive in real applications. Since, however, the scope of this paper is only to illustrate the principal situation, we might restrict ourselves to a typical example. To do this, we go the other way round and start with curves of $\overline{\gamma}(t)$ which we had obtained previously by Monte-Carlo simulations[7]. These simulations revealed that the tracer exchange curves subject to constant boundary conditions can, depending on the particular choice of the system parameters, be approximated by one of the following analytical expressions:

$$\overline{\gamma}_{sf}(t) = 1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp\left(-\frac{\pi^2}{15} i^2 \frac{t}{\tau_{intra}}\right), \tag{20}$$

$$\overline{\gamma}_{nd}(t) = 1 - \frac{8}{\pi^2} \sum_{\substack{i=1 \\ odd}}^{\infty} \frac{1}{i^2} \exp\left(-\frac{\pi^2}{12} i^2 \frac{t}{\tau_{intra}}\right), \tag{21}$$

$$\overline{\gamma}_{exp}(t) = 1 - \exp\left(-\frac{t}{\tau_{intra}}\right). \tag{22}$$

(Though the index "sf" stands for single-file diffusion, the index "nd" for normal diffusion, and the index "exp" for exponential, these indices are, first of all, solely mean as labels for the respective analytical expressions.) Here we used the *intracrystalline mean lifetime* τ_{intra} defined as[8]

$$\tau_{intra} = \int_0^{\infty} (1 - \overline{\gamma}(t))\, dt; \tag{23}$$

inserting Eq. (*19*) into this definition gives, after some rearrangement of the integration[6], the expected identity

$$\tau_{\text{intra}} = \int_0^\infty \tau \, \varphi(\tau) \, d\tau \ . \tag{24}$$

The quantity τ_{intra} is a property of the diffusional mechanism: It is determined by the channel length, the rate of the intracrystalline motion, the interactions of the particles, possible surface resistances, *etc.*[6,7]. According to the simulations, the quantity τ_{intra} already represents the main dependence of the tracer exchange curve on these parameters; if the time axis is scaled by τ_{intra}, the remaining differences between the curves are rather small (see Fig. 1). Single-file systems with strong surface resistances are best approximated by $\overline{\gamma}_{\text{exp}}(t)$, $\overline{\gamma}_{\text{nd}}(t)$ is, among other cases, the low-concentration limit, and $\overline{\gamma}_{\text{sf}}(t)$ approximates cases where the mutual hindrance of the particles is pronounced[7]. Thus, we might refer to $\overline{\gamma}_{\text{sf}}(t)$ as the *prototype* of the tracer exchange curve of single-file systems subject to constant boundary conditions.

By the way, $\overline{\gamma}_{\text{nd}}(t)$ is exactly the expression for the Fickian diffusion system[5]. However, this does not mean that there is only little difference between normal and single-file tracer exchange: The intracrystalline mean lifetime of single-file systems is, in general, orders of magnitude larger than that of Fickian systems. It merely means that the *shape* of the tracer exchange curve is not very sensitive to the differences in the diffusional regime[7]. We again stress, however, that the expression $\overline{\gamma}_{\text{nd}}(t)$ applies not only to Fickian processes but approximates some single-file processes as well.

With $\overline{\gamma}(t)$ chosen, we can now determine the residence time distribution by differentiation of Eq. (*19*),

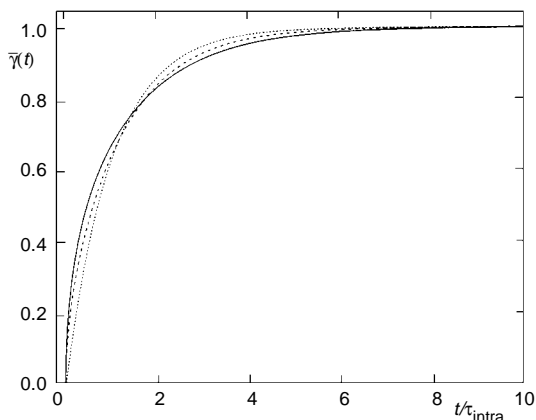$$\varphi(t) = \frac{d}{dt}\overline{\gamma}(t) \ . \tag{25}$$

Fig. 1
Analytical curves approximating the tracer exchange curve of a single-file system subject to constant boundary conditions: —— $\overline{\gamma}_{\text{sf}}$, – – – $\overline{\gamma}_{\text{nd}}$, · · · · $\overline{\gamma}_{\text{exp}}$

Figure 2 shows, in a semi-log plot, the results corresponding to the three examples of Fig. 1. In the long-time region, all curves are simple exponentials $\alpha \exp(-at/\tau_{intra})$ (only the first terms of the sums survive); the respective factor a in the exponent (*i.e.* the slope in the semi-log representation) differs by the ratio $\pi^2/15 : \pi^2/12 : 1 \approx 0.66 : 0.82 : 1$ according to which of the curves is used.

While many tracer exchange experiments observe the tracer exchange curve $\gamma(t)$, Eic and Ruthven[9] developed an experimental technique for the measurement of intracrystalline diffusivity (the so-called zero length column technique, ZLC) which is based on the determination of the *time derivative* of the desorption[9] or tracer exchange[10] curve. Since the experimental set-up ensures constant boundary conditions, it turns out that this technique measures the residence time distribution $\varphi(t)$ directly.

For further reference we give the Laplace transform of Eq. (25):

$$\varphi(s) = s\,\overline{\gamma}(s) . \tag{26}$$

This is true only because $\overline{\gamma}$ obeys, per definition, the initial condition $\overline{\gamma}(t = 0) = 0$.

Exponentially Varying Boundary Conditions

As pointed out by Crank[5], in real experiments, it is often impossible to switch the particle species outside the channel *instantaneously* from pure B to pure A. Instead, one might assume an *exponential transition*. Moreover, one should allow for the case that the transition switches to an experimentally given ratio g between the two species instead of pure A. Thus we get

$$\rho_0(t) = \begin{cases} 0, & t < 0, \\ g(1 - \exp(-\beta t)), & t \geq 0. \end{cases} \tag{27}$$

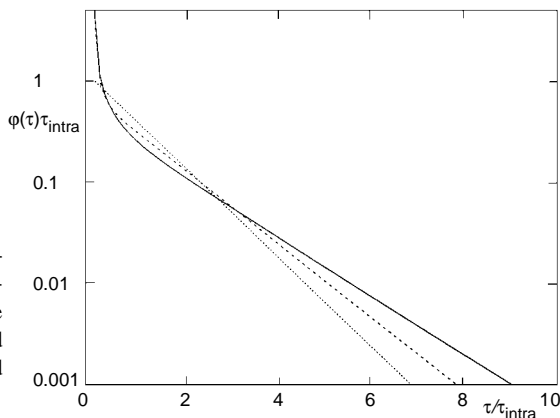Fig. 2

Intracrystalline residence time distribution $\varphi(\tau)$ of a single-file system as obtained in terms of Eq. (25) from the choices of $\overline{\gamma}$ shown in Fig. 1: —— based on $\overline{\gamma}_{sf}$, – – – – based on $\overline{\gamma}_{nd}$, · · · · based on $\overline{\gamma}_{exp}$

Inserting the Laplace transform $\rho_0(s)$ of this boundary condition into Eq. (*16*) gives

$$\rho(s) = g \left(\frac{1}{s} - \frac{1}{s + \beta} \right) \varphi(s) \,. \tag{28}$$

Once the tracer exchange curve subject to constant boundary conditions is known we obtain by combining Eqs (*26*) and (*28*)

$$\rho(s) = g \left(1 - \frac{s}{s + \beta} \right) \overline{\gamma}(s) \,. \tag{29}$$

According to the considerations in the previous section, we assume that $\overline{\gamma}(t)$ is given by $\overline{\gamma}_{sf}(t)$ due to Eq. (*20*). Figure 3 shows the time dependence $\gamma(t) = \rho(t)/g$ for various values of the transition rate β (in units of τ_{intra}^{-1}). The curves have been obtained by the numerical Laplace and inverse Laplace transformation according to Eq. (*29*). The value g cancels by the normalization. The case of an infinite transition rate, $\beta = \infty$, recovers constant boundary conditions.

Linearly Increasing Boundary Conditions

Exponential boundary conditions are not the only possibility to describe the switching processes starting at $t = 0$. Instead, one might assume a linearly increasing relative amount of A particles outside the crystal as it was observed in some sorption experiments[11]. If $\rho_0(t)$ increases linearly during the time interval $0 \ldots t_\delta$ up to a given fraction g and then remains constant, one can write
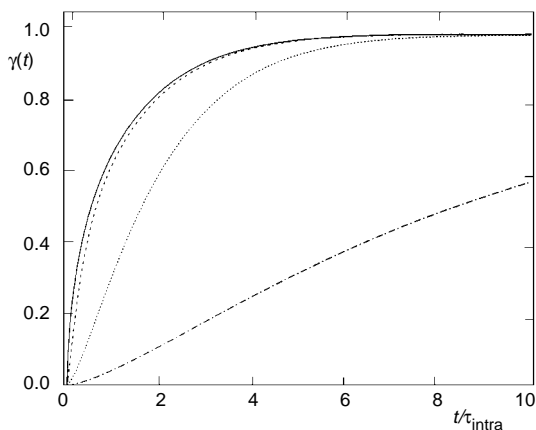

Fig. 3

Tracer exchange curve of a single-file system subject to exponentially varying boundary conditions (Eq. (*27*)) for different values of the transition rate coefficient β. The parameter of the representation is the scaled rate $B = (\beta\tau_{intra})$: ——— $B \to \infty$, – – – – $B = 10$, $\cdots\cdots B = 1$, $-\cdot-\cdot-\cdot$ $B = 0.1$

$$\rho_0(t) = \begin{cases} 0, & t < 0, \\ g\, t/t_\delta, & 0 \le t < t_\delta, \\ g, & t \ge t_\delta. \end{cases} \tag{30}$$

The Laplace transformation of $\rho_0(t)$ and Eq. (16) yields

$$\rho(s) = \frac{g}{t_\delta} \frac{1 - \exp(-st_\delta)}{s^2} \varphi(s) . \tag{31}$$

As before, we use Eq. (26) to relate the considered process to that with constant boundary conditions,

$$\rho(s) = g \frac{1 - \exp(-st_\delta)}{st_\delta} \overline{\gamma}(s) , \tag{32}$$

and set $\overline{\gamma} = \overline{\gamma}_{sf}$. The (normalized) tracer exchange curve $\gamma(t) = \rho(t)/g$ for different values of the transition time t_δ (in units of τ_{intra}) is plotted in Fig. 4. For $t_\delta = 0.01\ \tau_{intra}$ or less, the curves already coincide with that of $t_\delta = 0$ (constant boundary conditions).

Tracer Exchange from a Finite Reservoir

Constant boundary conditions could be maintained if the crystal is connected to an infinite particle reservoir, which, at time $t = 0$, is filled with A particles. Now we reduce the mean total number of particles in the reservoir to a finite value R. Let the mean total number of particles in the crystal be C. The value of $\rho_0(t)$, unknown for $t \ge 0$, can be obtained from the particle balance equation
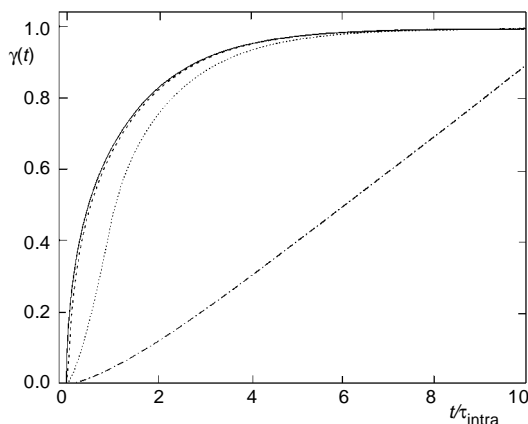

FIG. 4
Tracer exchange curve of a single-file system subject to linearly increasing boundary conditions (Eq. (30)) for different values of the transition time t_δ. The parameter of the representation is the scaled transition time $T = (t_\delta/\tau_{intra})$: —— $T = 0$, – – – $T = 0.1$, · · · · $T = 1$, – · – · – · $T = 10$

$$R\rho_0(t) + C\rho(t) = R = \text{const.} \quad (t \geq 0) . \tag{33}$$

Equation (*33*) expresses the fact that the total number of A particles in the system, *i.e.*, the sum of the numbers of A particles in the reservoir, $R\rho_0(t)$, and in the crystal, $C\rho(t)$, is constant for all times *t*. This constant is given by the initial value at time $t = 0$, namely the capacity *R* of the reservoir. Writing $R\rho_0(t)$ we assume that the reservoir is well-stirred so that any particle in it has equal probability to be adsorbed into the crystal. This gives

$$\rho_0(t) = \begin{cases} 0, & t < 0, \\ 1 - \dfrac{C}{R}\,\rho(t), & t \geq 0, \end{cases} \tag{34}$$

or, by the Laplace transformation,

$$\rho_0(s) = \frac{1}{s} - \frac{C}{R}\,\rho(s) . \tag{35}$$

If we introduce the *relative reservoir capacity*

$$\nu = \frac{R}{C} \tag{36}$$

we obtain, on combining Eqs (*16*) and (*35*), the final result

$$\rho(s) = \frac{1}{s}\,\frac{\varphi(s)}{1 + \varphi(s)/\nu} . \tag{37}$$

In the limit $t \to \infty$, the system reaches equilibrium of the ratio of the particle species between crystal and reservoir, *cf*. Eq. (*13*). From the balance Eq. (*33*), we easily compute

$$g = \frac{1}{1 + 1/\nu} . \tag{38}$$

As before, we get from Eqs (*26*) and (*37*)

$$\rho(s) = \frac{\overline{\gamma}(s)}{1 + s\overline{\gamma}(s)/\nu} . \tag{39}$$

This equation relates, though in Laplace language, the unnormalized tracer exchange curve of the system with arbitrary reservoir capacity to that of the system with infinite reservoir (constant boundary conditions). It can again be evaluated numerically. Figure 5 shows the resulting curves $\gamma(t) = \rho(t)/g$. Their validity was checked by the comparison with Monte-Carlo simulations similar to that reported in ref.[7].

The question remains whether the finite reservoir enhances the sensitivity of the shape of the exchange curve to the diffusional mechanism. Figure 6 compares the curves for the case $\nu = 0.1$ when $\overline{\gamma}(t)$ is chosen to be either $\overline{\gamma}_{exp}(t)$, $\overline{\gamma}_{nd}(t)$, or $\overline{\gamma}_{sf}(t)$. Compared with Fig. 1, the differences between the curves are indeed much more pronounced. This confirms the expected behaviour: The smaller the capacity of the reservoir, the greater the influence of the intracrystalline processes on the reservoir and, consequently, on ρ_0, which, in turn, influences the tracer exchange curve.

Tracer Exchange Between Two Different Diffusional Systems

In the previous section, the reservoir was assumed to be represented by the well-stirred surrounding space, *i.e.*, the diffusional processes within the reservoir are assumed to be much faster than those within the crystal. Now we consider a more general process involving tracer exchange between two different crystals being in contact *via* a well-stirred solution or gas phase. The experimental set-up is assumed as follows:

At $t < 0$, the two crystals, each surrounded by a certain space, are separated from each other. As before, both crystals are in sorption equilibrium with their respective surroundings. Moreover, the total particle concentrations in the two surrounding spaces are identical. The *investigated crystal* and its surrounding space are purely filled with B particles; let there be an amount C of particles in the crystal and S_C outside. Similarly, the second crystal, which will be referred to as *reservoir crystal*, contains an amount R of particles and its space S_R, all of A type.
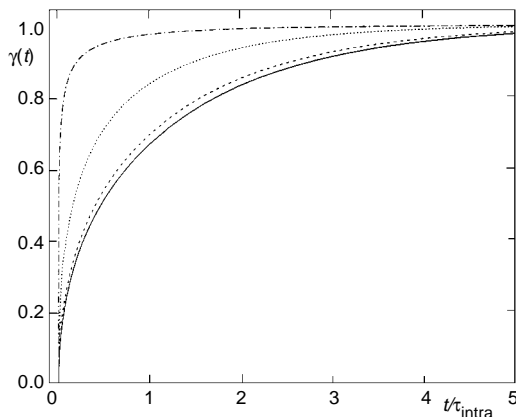

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Tracer exchange curve of a single-file system coupled with a well-stirred particle reservoir of different capacity. The parameter of the representation is the relative reservoir capacity $\nu = R/C$: —— $\nu \rightarrow \infty$, – – – – $\nu = 10$, $\cdots$ $\nu = 1$, – $\cdot$ – $\cdot$ – $\cdot$ $\nu = 0.1$

At $t = 0$, the separation wall between the two spaces is removed so that now both crystals are surrounded by a common, again well-stirred, space providing a particle exchange. The changes of the ratio of the particle species within the investigated crystal are observed.

Let us assume that the quantities φ, ρ, and ρ_0 refer, as before, to the investigated crystal while the correponding quantities referring to the reservoir crystal will be denoted by a tilde, $\tilde{\varphi}$, $\tilde{\rho}$ and $\tilde{\rho}_0$. For mathematical reasons, we have to define $\tilde{\rho}$ and $\tilde{\rho}_0$ as the relative amounts of B particles (rather than A particles) in the reservoir crystal or its surrounding space, respectively, because only in this way we have $\tilde{\rho}(t) = \tilde{\rho}_0(t) = 0$ for $t < 0$ which is the necessary condition for the existence of their Laplace transforms. Then we can write an additional equation corresponding to Eq. (*16*) valid for the reservoir crystal:

$$\tilde{\rho}(s) = \tilde{\rho}_0(s)\, \tilde{\varphi}(s) \, . \tag{40}$$

After removing the separation wall, there is a homogeneous ratio of the particle species throughout the unified space, thus

$$\tilde{\rho}_0(t) = \begin{cases} 0, & t < 0, \\ [1 - \rho_0(t)], & t \geq 0. \end{cases} \tag{41}$$

Further, the system has to obey a particle balance (constant number of A particles),

$$R\,[1 - \tilde{\rho}(t)] + (S_R + S_C)\,\rho_0(t) + C\rho(t) = R + S_R = \text{const.} \quad (t \geq 0) \, , \tag{42}$$
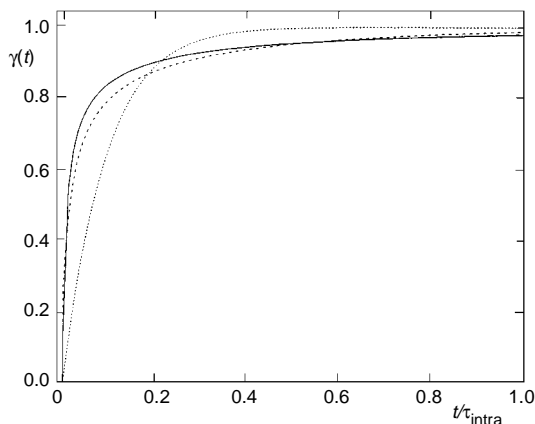

Fig. 6

Tracer exchange curve of a single-file system coupled with a particle reservoir of relative capacity $\nu = 0.1$. The different curves correspond to the three different approximations considered in Fig. 1: —— based on $\overline{\gamma}_{sf}$, – – – based on $\overline{\gamma}_{nd}$, ... based on $\overline{\gamma}_{exp}$

which yields

$$\rho_0(t) = \begin{cases} 0, & t < 0, \\ \dfrac{R\tilde{\rho}(t) + S_R - C\rho(t)}{S_R + S_C}, & t \geq 0. \end{cases} \tag{43}$$

The Laplace transforms of the boundary conditions are

$$\tilde{\rho}_0(s) = \frac{1}{s} - \rho_0(s) \tag{44}$$

and

$$(S_R + S_C)\,\rho_0(s) = R\,\tilde{\rho}(s) + S_R\frac{1}{s} - C\,\rho(s)\,. \tag{45}$$

Combining Eqs (16), (40), (44), and (45) gives

$$\rho(s) = \frac{1}{s}\,\frac{(R\,\tilde{\varphi}(s) + S_R)\,\varphi(s)}{R\,\tilde{\varphi}(s) + S_R + S_C + C\,\varphi(s)}\,. \tag{46}$$

The long-time behaviour is obtained from the balance equation (42) and the equilibrium $[1 - \tilde{\rho}(\infty)] = [1 - \tilde{\rho}_0(\infty)] = \rho_0(\infty) = \rho(\infty) = g$ (generalization of Eq. (13)) to yield

$$g = \frac{R + S_R}{R + S_R + S_C + C}\,. \tag{47}$$

In order to reduce the variety of parameters in Eq. (46), we assume that the number of particles in the surrounding phase is negligible in comparison with that in the crystals, $S_R + S_C \ll R + C$, and set $S_R = S_C = 0$. On using the definition equation (36), we get

$$\rho(s) = \frac{1}{s}\,\frac{\tilde{\varphi}(s)\,\varphi(s)}{\tilde{\varphi}(s) + \varphi(s)/\nu}\,. \tag{48}$$

Moreover, both crystals shall be of equal capacity, $R = C$ or $\nu = 1$. Equation (48) is still rather general: One may choose arbitrary functions for the residence time distributions of the two crystals. As an example, we here assume that the investigated crystal shows single-file behaviour which could be described by $\varphi(s) = s\bar{\gamma}_{sf}(s,\tau_{intra})$ (cf. Eq. (26)), while the reservoir crystal is assumed to behave due to normal diffusion which implies

$\widetilde{\varphi}(s) = s\overline{\gamma}_{\mathrm{nd}}(s,\widetilde{\tau}_{\mathrm{intra}})$ with $\widetilde{\tau}_{\mathrm{intra}} \ll \tau_{\mathrm{intra}}$. The unnormalized tracer exchange curve for this special case is thus given as

$$\rho(s) = \frac{\overline{\gamma}_{\mathrm{nd}}(s,\widetilde{\tau}_{\mathrm{intra}})\,\overline{\gamma}_{\mathrm{sf}}(s,\tau_{\mathrm{intra}})}{\overline{\gamma}_{\mathrm{nd}}(s,\widetilde{\tau}_{\mathrm{intra}}) + \overline{\gamma}_{\mathrm{sf}}(s,\tau_{\mathrm{intra}})} \ . \tag{49}$$

This decision done, the only free parameters are the two mean residence times, and we define their ratio as

$$\psi = \frac{\widetilde{\tau}_{\mathrm{intra}}}{\tau_{\mathrm{intra}}} \ . \tag{50}$$

Numerical results according to this example for different values of the ratio ψ are given in Fig. 7. The curve for $\psi = 0.01$ already coincides with that of the well-stirred reservoir (*cf.* Fig. 5, $\nu = 1$), *i.e.*, in this case the diffusional processes within the reservoir are fast enough that their influence is negligible. In contrast, in the case $\psi = 10$, the behaviour is mostly determined by the reservoir rather than by the investigated crystal. For $\psi = 1$, *i.e.*, for equal mean residence times of reservoir and crystal, the resulting curve is sort of an average between $\overline{\gamma}_{\mathrm{sf}}(t)$ and $\overline{\gamma}_{\mathrm{nd}}(t)$.

Note two further consequences of the more general relation Eq. (*48*). First, the well-stirred reservoir could be described by $\widetilde{\varphi}(t) = \delta(t)$ with the Laplace transform $\widetilde{\varphi}(s) = 1$. Inserting this into Eq. (*48*) indeed recovers Eq. (*37*). Second, in the limit $\nu \to \infty$, Eq. (*48*) approaches

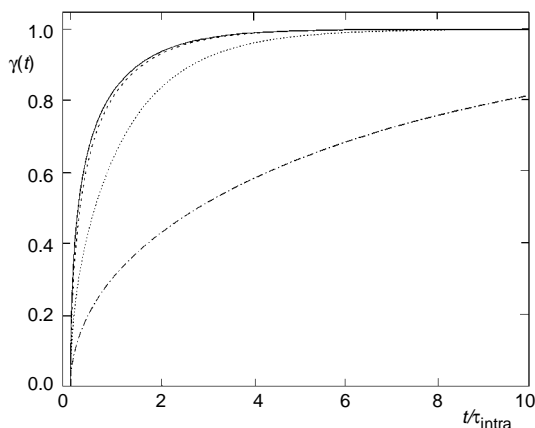$$\rho(s) = \frac{1}{s}\,\varphi(s) \tag{51}$$

Fig. 7
Tracer exchange curve of a single-file crystal coupled with a crystal reservoir undergoing normal diffusion. The graphs correspond to different ratios ψ between the mean residence times of the two crystals: —— $\psi = 0.01$, – – – – $\psi = 0.1$, · · · · $\psi = 1$, – · – · – · $\psi = 10$

which is the Laplace transform of the tracer exchange curve $\overline{\rho}(t)$ for constant boundary conditions (see Eq. (*19*)). This means that in case of an infinite reservoir (ensuring constant boundary conditions), the tracer exchange curve is independent of the diffusional properties of the reservoir.

Channels that are not Identical

The basic equation (*11*), derived for an individual channel, could also be applied to an array of arbitrarily many, but *identical*, channels. Many real systems already mentioned in the introduction, *e.g.*, a crystal with parallel faces or a membrane of constant thickness, can be assumed to represent such an array. Other examples, however, such as a bed of crystallites of different sizes, a membrane of varying thickness, or an irregularly shaped crystal, violate the condition of identity of the channels. In the following, we give the generalization of the results of this paper allowing for channels that are *not identical*.

For simplicity, we assume that the length L of the individual channels of the array is the only parameter describing their dissimilarity. Let $f(L)$ be the distribution of L, *i.e.*, if the crystal consists of M channels, $M f(L)\, dL$ of them have a length between L and $L + dL$. Let $F(L)$ be the mean total number of particles in an individual channel of length L. Then we might define the concentration

$$c(L) = \frac{F(L)}{L}\,. \tag{52}$$

In the general case, this concentration depends on the channel length L, *e.g.*, in a single-file system with attractive particle–particle interaction[6]. Let the relative amount of A particles in a channel of length L be $\rho(t,L)$ while $\rho(t)$ is understood to refer to the crystal as a whole. With these quantites defined, we have

$$C = \int_0^\infty L c(L)\, M f(L)\, dL \tag{53}$$

for the mean total number of particles in the whole crystal while the mean number of A particles is

$$C\rho(t) = \int_0^\infty \rho(t,L)\, L c(L)\, M f(L)\, dL\,. \tag{54}$$

Further, we write Eq. (*11*) with explicit dependence on the length L of the channel considered

$$\rho(t,L) = \int_0^\infty \rho_0(t - \tau) \, \varphi(\tau,L) \, d\tau \, . \tag{55}$$

By dividing Eq. (54) by Eq. (53) and inserting Eq. (55) we obtain

$$\rho(t) = \int_0^\infty \rho_0(t - \tau) \, \frac{\displaystyle\int_0^\infty \varphi(\tau,L) \, Lc(L) \, f(L) \, dL}{\displaystyle\int_0^\infty Lc(L) \, f(L) \, dL} \, d\tau \, . \tag{56}$$

This suggests the definition of the *residence time distribution of the crystal*

$$\varphi(t) = \frac{\displaystyle\int_0^\infty \varphi(\tau,L) \, Lc(L) \, f(L) \, dL}{\displaystyle\int_0^\infty Lc(L) \, f(L) \, dL} \tag{57}$$

as the weighted average of the residence time distributions of the individual channels. This result confirms that the introduced residence time distribution is a well-defined quantity for arbitrary arrays of channels, too. As before, it may be inferred from the tracer exchange curve obtained under known experimental conditions or, if all necessary information is available, calculated in terms of Eq. (57). Then all the results presented in this paper may be used in their unchanged form.

SYMBOLS

B	scaled transition rate ($\beta \, \tau_{intra}$)
C	capacity (*i.e.*, mean number of guest particles in sorption equilibrium) of crystal investigated
$c(L)$	concentration in channel of length L, m^{-1}
$F(L)$	mean total number of particles in channel of length L
$f(L)$	distribution (probability distribution) of L in crystal, m^{-1}
g	equilibrium value of the ratio of two particle species in tracer exchange experiment after infinite time, see Eq. (13)
L	channel length, m
M	number of channels in crystal
N	number of sites per channel in discrete model
R	reservoir capacity
S_C	capacity of space surrounding crystal investigated
S_R	capacity of space surrounding reservoir crystal
s	independent variable of Laplace transforms, s^{-1}
T	scaled transition time (t_δ / τ_{intra})
t	time, s
t_δ	time interval during which linearly increasing boundary condition varies, s
β	transition rate of exponentially varying boundary conditions, s^{-1}
$\gamma(t)$	(normalized) tracer exchange curve, see Eq. (14)

$\bar{\gamma}(t)$	tracer exchange curve under constant boundary conditions, see Eq. (*19*)
$\bar{\gamma}_{sf}(t)$	analytical expression, see Eq. (*20*), approximating $\bar{\gamma}(t)$ for certain single-file systems where mutual hindrance of particles is pronounced; in this paper chosen as prototype for single-file system
$\bar{\gamma}_{nd}(t)$	analytical expression, see Eq. (*21*), approximating $\bar{\gamma}(t)$ for certain single-file systems (*e.g.*, with low particle density) as well as for systems undergoing normal diffusion
$\bar{\gamma}_{exp}(t)$	analytical expression, see Eq. (*22*), approximating $\bar{\gamma}(t)$ for systems with strong surface resistances
Θ_i	probability distribution of Σ_i, see Eq. (*4*)
Λ_i	kind of particle occupying site i, see Eq. (*3*), $\{\lambda_A, \lambda_B\}$
Λ_0	kind of newly adsorbed particle, $\{\lambda_A, \lambda_B\}$
λ_A	realization of Λ_i or Λ_0 in case of type A particle
λ_B	realization of Λ_i or Λ_0 in case of type B particle
ν	relative reservoir capacity, see Eq. (*36*)
$\rho(t)$	mean relative amount of A particles in crystal, see Eq. (*8*); its time dependence gives unnormalized tracer exchange curve
$\tilde{\rho}(t)$	mean relative amount of B particles in reservoir crystal
ρ_i	probability distribution of Λ_i, see Eq. (*6*)
ρ_0	probability distribution of Λ_0, see Eq. (*9*), acting as boundary condition
$\bar{\rho}_0$	constant boundary condition, see Eq. (*17*)
$\tilde{\rho}_0$	probability that particle newly adsorbed into reservoir crystal is of type B.
Σ_i	occupation of site i, see Eq. (*1*)
τ	residence time, s
τ_i	residence time of particle occupying site i, see Eq. (*2*), s
τ_{intra}	intracrystalline mean lifetime, see Eq. (*23*), s
$\tilde{\tau}_{intra}$	intracrystalline mean lifetime of reservoir crystal, s
$\varphi(t)$	residence time distribution, see Eq. (*7*), s^{-1}
$\tilde{\varphi}(\tau)$	residence time distribution of reservoir crystal, s^{-1}
$\varphi_t^*(\tau)$	probability distribution of τ_i, see Eq. (*5*), s^{-1}
ψ	ratio between mean residence times of investigated and reservoir crystals, see Eq. (*50*)

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