Diffusion Analysis in Pore Hierarchies by the Two-Region Model

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Mass transfer in hierarchically porous materials is a function of various parameters, notably including the diffusivities in the various pore spaces, their relative populations and the exchange rates. Their interplay is shown to be quantified in the two-region model of diffusion which in magnetic resonance imaging is in common use under the name Kärger equations. After manifold applications in NMR diffusometry with compartmented systems, the underlying formalism is now demonstrated to offer an excellent tool for assessing mass transfer in hierarchically porous materials. The potentials include a comprehensive description of mass transfer, in parallel with the specification of the various limiting cases and their reflection by experimental measurement. Information provided by application of microscopic techniques of measurement such as microimaging and pulsed field gradient NMR is shown to notably exceed the message of, e.g., macroscopic uptake measurement of diffusion in hierarchically porous media. This includes, in particular, experimental insight into the dominating mechanisms of mass transfer, which is crucial for the development of optimal strategies of performance enhancement for the technological exploitation of such materials. Depending on the microstructural and microdynamic situation, elucidated in such studies, very different and even mutually opposing strategies for performance enhancement are shown to result.

1. Introduction

Nanoporous solids are in the very heart of numerous processes of matter upgrading, including mass purification, separation, and conversion. Their application is based on the intimate contact of the guest molecules with the internal surface of these materials. It is, however, the interaction which, notably in narrow (micro-)pores with dramatically reduced guest mobilities, poses a limit on the performance of such processes since the gain in value-added products can never be faster than allowed by the exchange rate between the intraparticle pore space and the surroundings. This conflict, inherent to the application of nanoporous materials quite in general, has been mitigated with the advent of hierarchically structured porous material. Such materials are distinguished by the existence of a network of meso- or macro pores (quite generally referred to as transport pores), permeating the microporous bulk phase. While the space of micropores enables guest separation and/or transformation as the aspired process of matter upgrading, transport pores ensure sufficiently fast mass transfer between the origin of matter upgrading and the surroundings.

Quantification of mass transfer in nanoporous materials has proven to be a demanding task. This is an immediate consequence of the fact that the real structure of nanoporous materials may significantly deviate from their “simple” textbook structure, including the existence of additional transport resistances on either the external surface of the individual particles/crystals or the internal barriers. The situation is additionally aggravated by the fact that nanoporous materials tend to be unstable. Their textural properties and, hence, the intrinsic guest mobilities in one and the same nanoporous material must therefore be expected to vary with the mode of sample synthesis, storage, and preparation before measurement. As a consequence of this instability, different crystals within one and the same sample must be implied to, possibly, greatly differ in their transport properties. In diffusion measurements with individual crystals via microimaging such broad distributions, notably in the surface resistances, were indeed recorded and shown to lead to additional complications in assessing the relevant mechanisms of mass transfer control.

Investigations of guest diffusion in hierarchically porous materials are still in the stage of their very beginning. Given their textural complexity, variability in the real structure of hierarchically porous materials is expected to even exceed that observed with the purely microporous ones. One must therefore expect to be...
confronted with similar problems. In this context it is important to mention that, for purely microporous materials, there exists a clear understanding of the underlying diffusion equations and their solutions, provided in, e.g., the comprehensive textbooks by Crank[7] and Carslaw and Jaeger[8] and many subsequent ones based on, essentially, the formalism there presented.[10,11] These solutions are largely employed as a standard for analyzing the diffusion data obtained with, possibly more complicated systems.

To the best of our knowledge, such a standard does not yet exist for diffusion studies with hierarchically porous materials. As a consequence, measurements are often related to those with the purely microporous counterpart. This makes clearly sense with reference to an evaluation of the benefits of the interpenetrating transport pores for transport enhancement, but says little about the underlying mechanisms.

The problem with the quantification of mass transfer in hierarchical materials is a result of the complexity of the system which, as a rule, requires the introduction of a whole set of parameters. They do, notably, include the molecular diffusivities in the pore spaces involved, the respective populations of the guest molecules and their exchange rate. In the present communication, we introduce a formalism allowing a combination of the influences of all these parameters on the overall diffusion. To do so, we adopt the model of “two-region” diffusion which, in magnetic resonance imaging,[9] is in common use under the name Kärger equation.[10] It has originally been introduced as an approach for simplifying the analysis of pulsed field gradient (PFG) NMR diffusion data in beds of zeolite crystallites.[10]

So far, however, this application of zeolite has remained limited since, in its original use, it did in fact only serve as a first approximation. We are now going to show that the “two-region model,” as introduced half a century ago in a different context, does indeed offer most promising prospects for serving as a standard and, hence, a starting point for analyzing and classifying mass transfer in hierarchically porous materials. The only specification needed, within this model, is the existence of two (or more) interpenetrating pore spaces so that, at least in principle, guest molecules may cover infinitely extended diffusion pathways in each of the involved pore spaces, without interchanging between various of them. Overall diffusion appears in the combination of the diffusion paths of the individual guest molecules, composed of segments of displacements in the various pore spaces.

We begin with an overview of the experimental techniques applicable for diffusion studies in hierarchically porous materials in Section 2. Section 3 introduces the mathematical formalism of the two-region model (the “Kärger equations”), followed by Section 4 showing the solution of the relevant equations under the conditions as provided by the various types of measurement. A summarizing discussion of the existing options of measurement and the challenges in translating them into reality, including their application to systems with extended interfaces,[45] concludes our presentations in Section 5.

2. Diffusion Measurement of Guest Molecules in Nanoporous Materials

Depending the spatial dimensions over which diffusion phenomena in nanoporous materials are recorded, one commonly distinguishes between microscopic and macroscopic measurement. In microscopic measurements, the movement of the molecules themselves or the diffusion-induced evolution of their concentration is monitored. Macroscopic measurements are based on recording the diffusion-induced variation of “macroscopic” objects, such as the total weight of the host–guest system, i.e., the integral over all local guest concentrations, in uptake or release experiments. Detailed representations of the various techniques with explications of their potentials and limitations may be found in the literature.[1b,2c,13] In the present context, we confine ourselves to a brief presentation of the measuring principles and the primary data attainable in the respective experiments.

2.1. Microimaging

Up to date, the probably most direct and, hence, most informative view on the process of diffusion in the interior of nanoporous particles is provided by microimaging via infrared (IR) and interference microscopy.[5a] Within a wider spectrum of—mainly spectroscopic—techniques[14] (see Section 12.1 in ref. [1b] for further details), these techniques are distinguished by their capability to record the evolution of intracrystalline concentration during molecular uptake and release[5b] and/or catalytic reactions.[5c] Both IR and interference microscopy record, by their very nature, 2D maps of the integral of the local guest concentration along the observation direction. This, in turn, means no restriction on the applicability for 1D and 2D pore systems with the observation direction being perpendicular to the channel direction(s) since, in such systems, the concentration is only a function of the coordinates on the observation plain. The same situation may be achieved for 3D pore systems if the nanoporous particles are available as thin plates (see, e.g., ref. [16a]), with the top and bottom surfaces being impermeable to the molecules under study, but effectively transparent for the light beam used for observation.

2.2. PFG NMR

Within the given context it is sufficient to introduce the principle of diffusion measurement via PFG NMR by adopting the classical view on the nuclei (in many cases protons, the nuclei of hydrogen) as a nuclear “spin,” i.e., as an elementary particle combining the properties of a magnetic dipole and a (mechanic) gyroscope. For a more detailed introduction to this subject we refer to the many textbooks available elsewhere.[1b,11a,17] Within our model considerations, under the influence of a magnetic field the individual spins perform a rotational motion (“precession”) around the direction of the magnetic field—like a gyroscope under the influence of gravity around the direction of the gravity. The frequency of the rotation is proportional to the field intensity. In an ensemble of spins, the vector sum of each individual magnetic moment yields a net magnetization which, as each individual spin, rotates around the direction of the magnetic field. Rotating magnetization induces a voltage in a suitably arranged coil, which is recorded as the NMR signal.
In PFG NMR diffusion measurement, over two small time intervals the constant magnetic field is superimposed by two inhomogeneous fields, the “field gradient pulses.” Because of the first one, the NMR signal is immediately extinguished since, as a consequence of the field inhomogeneity during the pulses, and hence the different rotational frequencies of the spins within the sample, the individual spins have lost their coherence. They point to all directions and their vector sum, i.e., the NMR signal, has therefore dropped to zero. The second field gradient pulse (of identical duration and intensity) is thought to compensate this effect. This, however, is obviously only completely true, if the molecules (and hence the nuclear spins) have remained on one and the same position. Any movement of a molecule during the time interval \( t \) between the two field gradient pulses will affect the overall magnetization in such a way that the molecule contributes to the re-established NMR signal only with the cosine of the angle between the direction of this particular spin and the average of all spins. PFG NMR signal attenuation may, therefore, immediately be noted as

\[
\psi (q, t) = \int \cos(qx) P(x, t) \, dx
\]  

(1)

where \( q \) has been introduced as a measure of the intensity of the field gradient pulses (being proportional to their duration and amplitude). \( P(x, t) \) is referred to as the mean propagator\(^{18}\) and denotes the probability (density) that a molecule, arbitrarily selected within the sample, has been shifted over a distance \( x \) in direction of the field inhomogeneity during time \( t \), i.e., in the time span between the two field gradient pulses.

In a homogeneous, infinitely extended medium for molecules undergoing “normal” diffusion, the propagator\(^{15d,c,2c,9,11a}\) is known to be

\[
P(x, t) = (4 \pi D t)^{-1/2} \exp \left( -\frac{x^2}{4D t} \right)
\]  

(2)

with \( D \) denoting the diffusivity (more accurately: the self-diffusivity or, equivalently, the coefficient of self-diffusion). Inserting Equation (2) into Equation (1) yields the commonly quoted PFG NMR attenuation

\[
\psi (q, t) = \exp(-q^2 D t)
\]  

(3)

yielding, in a semilogarithmic plot as a function of the squared field gradient intensity \( q^2 \), a straight line whose slope is proportional to the self-diffusivity. With Equation (1), the mean propagator is seen to follow from the primary data of measurement, namely, the PFG NMR signal attenuation, as their Fourier transform.\(^{18a}\)

2.3. Measurement of Transient Uptake and Release

The conventional way of determining diffusion coefficients in nanoporous materials has been based on measuring the rate of molecular uptake or release following pressure variation in the surrounding atmosphere. Then, the diffusivities result as the best fit between the measured uptake and release curves, i.e., of relative uptake or release \( F(t) = \Delta m(t) / \Delta m(\infty) \) as a function of time, with the solution of the diffusion equation, i.e., Fick’s 2nd law

\[
c(\vec{r}, t) = D \text{div} \ n(\vec{r}, t)
\]  

(4)

for the initial and boundary conditions relevant for the given experimental procedure. With the notation of Equation (4), isotropic space as well as sufficiently small pressure (or concentration) steps is implied, so that the diffusivity (being, in general, a function of concentration) can be assumed to be constant. Then, molecular uptake and release follows as the integral of the concentration over the particle under study, \( \Delta m(t) = \int c(\vec{r}, t) \, d\vec{r} \).

There are manifold options for the measurement of molecular uptake and release, notably including measurement of the variation in mass. Details of the procedure of measurement and a survey about its various modifications may be found in the relevant textbooks, including refs. [1b,13a–d], and [19].

It is important to note that, conventionally, transient measurements of uptake and release\(^{200}\) have been performed with the implicit understanding that guest concentration close to the outer surface of the nanoporous particles under study essentially instantaneously reaches its equilibrium value as determined by the external pressure. It was notably due to the application of the microscopic techniques of diffusion measurement, in particular by PFG NMR and microimaging, that today this assumption is known to be not generally fulfilled since, besides the intracrystalline diffusion, equilibration may as well be retarded by the existence of resistances on the external particle surfaces,\(^{3b,22}\) including the formation of boundary layers as a general phenomenon occurring in solid–liquid processes.\(^{22}\) In addition to the application of the techniques of microscopic diffusion measurement, direct information about the existence of surface barriers may be attained in “partial” loading measurements.\(^{23} 23\) In this type of measurement, uptake or release experiments are started before attainment of equilibrium, giving rise to a variation in the time constants, with characteristic differences between diffusion and barrier limitations.

3. Starting Equations of Diffusion in Pore Hierarchies

Hierarchically organized pore spaces may appear in manifold structural variants.\(^{6d,13,14,24}\) Similarly diverse are mathematical formulae which are needed for an accurate reflection of diffusion in such systems. In the formalism introduced and applied in this communication, we confine ourselves to pore space hierarchies exhibiting certain patterns, which are typical for many hierarchically porous materials. The formalism may thus serve as a first-order approach for diffusion in hierarchically porous materials quite in general and, most importantly, it allows quantification of mass transfer in the various special cases that might become relevant in such complex systems.

The system is implied to consist of mutually interpenetrating pore spaces. Guest molecules undergo normal diffusion (i.e., following Fick’s laws) in each of these subspaces and are able to diffuse there over essentially infinitely long distances, with the diffusivities as relevant for each of the given pore spaces. There is, in addition, the option that, at any location and at any
instant of time, guest molecules may switch from one sub-
space to another, resulting in a corresponding variation of their
diffusivity.

As a typical example, we consider diffusion in mesoporous
zeolites (or, quite generally, in a system with a network of meso/
macro pores permeating a microporous bulk phase), with the
indices 1 and 2 referring, respectively, to the meso/macropores
(to which, quite generally, we refer as transport pores) and the
micropores. The unit volume, to which the concentrations \( c_{1(2)} \)
in the transport (micro-) pores are referred, comprises both
types of pores and are sufficiently large in comparison with
the (transport pore) diameters, so that their topology may be
implied to be uniform all over the sample. This requirement
has to be fulfilled already with diffusion analysis in materials
of monodisperse porosity\(^{[15c]}\) and has to be, correspondingly,
extended for topologies that are more complicated. In all cases,
it has to be implied that the unit volume is notably exceeded
by the particle sizes. With all these conditions fulfilled, the dif-
fasivities (sometimes referred to as the "effective" diffusivities)
may indeed be considered as genuine ones, irrespective of the
numerous elementary mechanisms involved.

Within the thus described model, variation in the local con-
centrations in the transport pores \( (c_1) \) and the micropores \( (c_2) \)
may be represented by the relations

\[
\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} - \frac{1}{\tau_1} c_1 + \frac{1}{\tau_2} c_2 \tag{5}
\]

\[
\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} - \frac{1}{\tau_2} c_2 + \frac{1}{\tau_1} c_1 \tag{6}
\]

with the diffusivity \( D_{1(2)} \) in the transport (micro-) pores and the
mean lifetime \( \tau_{1(2)} \) of a molecule in the transport (micro-) pores. They combine the options that the change of the local con-
centration (left-hand side) in one pore system with time is due to
i) diffusion within the pore system (first term on the right-hand
side), ii) escape into the other pore system (second term), and
iii) access from the other pore system (third term).

We, further on, introduce the relative populations of the
compounds in the transport (micro-) pores \( p_{1(2)} \) at equilibrium with
the external atmosphere

\[
p_1 = \frac{c_{1,eq}}{c_{1,eq} + c_{2,eq}} = 1 - p_2 \tag{7}
\]

Mean lifetimes and relative populations are correlated via the
detailed-balance equation

\[
\frac{p_1}{p_2} = \frac{\tau_1}{\tau_2} \tag{8}
\]

We note that, different from materials of monodisperse
porosity where overall diffusion is generally perfect reflected by a
single (in general concentration dependent) diffusivity,\(^{[15c]}\) for the
hierarchically porous materials knowledge of four parameters
is required, namely, the diffusivities in the two pore spaces,
their relative populations, and the exchange rate between them,
correlated by Equation (8). All of these parameters, as a matter
of course, must be implied to be a function of both loading and
temperature.

For meso/macro–microporous hierarchical systems one
might, typically, presume the two following relations

\[
p_1 \ll p_2 \approx 1 \tag{9}
\]

and

\[
D_1 \gg D_2 \tag{10}
\]

We refer to them in more detail in Section 4.1. Although we
confine ourselves to the following, to materials of only
bimodal porosity, the extension of the presented formalism to
three pore spaces interpenetrating each other is straightforward. Synthesis of such materials, for instance, macroporous–
mesoporous MFI-type zeolites, has indeed been shown to be possible.\(^{[25]}\)

Let us conclude this section with discussing the options
of an independent estimate of the parameters appearing in
the two-region model. Taking care of possible complications
during capillary condensation in the mesopores\(^{[26]}\) knowledge
of the adsorption isotherm in the purely microporous specimen and of the respective pore sizes in the hierarchical
material is, as a rule, sufficient for a reasonable approach of the
equilibrium values of concentration in the two pore spaces and,
therefore, of also \( p_1 \). Knowledge of the transport pore size
and the concentrations does, in addition, allow an estimate of the
diffusivities in the transport pores by adopting the standard
relations of molecular or Knudsen diffusion.\(^{[1a-c,9c]}\) Diffusivi-
ties in purely microporous specimens may be considered as a
first-order estimate of \( D_2 \), notably as its upper limit. This
has been demonstrated in PFG NMR diffusion studies with
mesoporous zeolite NaCaA, where increasing blockage of the
mesopores has been found to give rise to a (modest) reduction
of \( D_2 \) in comparison with diffusion in the purely microporous
zeolites.\(^{[6i]}\)

With Equations (5) and (6), molecular exchange between the
micro- and transport pores is approached by exponent-
entials, with the respective time constants \( \tau_1 \) and \( \tau_2 \). Under dif-
fusion limitation, exchange of a microporous body with its
surroundings—i.e., in the hierarchical materials here under
consideration, with the transport pores—is known to follow a
more complicated time dependence. Its approach by an ex-
ponential, however, is a commonly applied procedure, referred
to as the linear driving force approximation.\(^{[1b]}\) Within this
approach, the time constant corresponds to the first statistical
moment of the time dependence \( F(t) \) of the process under
consideration

\[
M = \int_0^\infty t \, dF = \int_0^1 [1 - F(t)] \, dt \tag{11}
\]

In the given context, \( F(t) \) is the fraction of molecules which
were initially located in the microporous space, but have
traveled to the transport pores, at least once during time \( t \).
For spherical microporous particles of radius \( R \), for diffusion-
limited exchange with the surroundings, the time constant of exchange (i.e., the first statistical moment)\(^{[10b,13a]}\) is given by the
relation

\[
M_{\text{diff}} = R^2/(15D) \tag{12}
\]
Equation (12) serves, moreover, as a reasonable approach even for any non-spherical particles if $R$ is understood as the radius of the equivalent sphere with the same surface-to-volume ratio ($A/V$) as the particle under consideration, i.e.,

$$R = 3V/A$$ (13)

Thus, with reference to exchange between the space of micropores (region 2) and that of the transport pores (region 1), combination of Equations (12) and (13) ends up with the relation

$$\tau_2 = \frac{(R_2)^2}{15D_2}$$ (14)

where

$$R_2 = \frac{3V_2}{A_1} = \frac{3(V_{\text{cryst}} - V_1)}{A_1}$$ (15)

appears as a measure of the “thickness” of the space of micropores upon uptake from (or release into) the transport pores. $V_{\text{cryst}}$ and $V_1$ are, respectively, the volume of the crystal (particle) and the region 1 (i.e., the transport pores). $A_1$ denotes the surface of the region 1, i.e., the interfacial area between the transport pores and the space occupied by the micropores.

Similarly as with the exchange between purely microporous particles and their surroundings,\cite{3} the mean exchange time may be additionally enhanced by the influence of surface resistances (surface “barriers”), referred to in already Section 2.3. As a consequence, Equation (14) has to be considered as a lower limit. Under such conditions, the first statistical moment simply corresponds to the sum of the statistical moments of the contributing resistances which, in the case of surface barriers, would be given by the relation

$$M_{\text{surf}} = R_2/(3\alpha)$$ (16)

with $\alpha$ referred to as the surface permeability (or permeance), defined as the factor of proportionality between the flux through the surface and the difference between the actual guest concentration close to the surface of the particle and its equilibrium value as determined by the surrounding atmosphere.

Being linearly proportional to $R_2$, the contribution of surface barriers to the transport resistances, in relation to that of diffusion, increases with increasing miniaturization. The prediction of surface barriers by molecular dynamic simulation is therefore of particular relevance to the study of molecular uptake and release with nanoporous nanoparticles.\cite{27} Correspondingly, barriers along the interface between transport pores and the microporous bulk phase are anticipated to represent the main factor in determining the magnitude of $\tau_2$. Thus it makes sense indeed to consider the exchange time as an independent parameter. We note in conclusion that the exponential dependence of uptake and release becomes an increasingly better approach of exchange dynamic with increasing relevance of the surface resistances.

4. Case-Dependent Solutions of the Diffusion Equation for Pore Hierarchies

4.1. Microimaging with Pore Hierarchies

4.1.1. Solution for Microimaging and Overview of the Attainable Patterns

As a prerequisite for the optimum application of microimaging, the hierarchically porous material under study is required to be available as a thin plate with sealed (top and bottom) surfaces, so that molecular uptake and release is only possible through the edges. The uptake and release is, moreover, assumed to occur in 1D, corresponding with the 1D representation of diffusion by Equations (5) and (6). Under such conditions, namely with crystals as extended plates and mass transfer mainly in the plane perpendicular to the observation direction, microimaging studies have been performed with, e.g., (purely microporous) zeolites of type ferrierite.\cite{26c,28}

In the previous section, an entity of four parameters had been introduced to quantify mass transfer in pore hierarchies. We are now going to investigate the influence of these parameters on the experimental evidence expected to become available by microimaging. We notably consider the situation typical for uptake experiments (which may be easily transformed into the situation relevant for desorption). The corresponding initial and boundary conditions, for which Equations (5) and (6) must be solved, are

$$c_i(x, t = 0) = 0; \ 0 < x < L; \ i = 1, 2$$ (17)

and

$$c_i(x = 0, t) = c_i(x = L, t) = c_{i, eq} = (c_{1, eq} + c_{2, eq})p; \ 0 \leq t \leq \infty; \ i = 1, 2$$ (18)

where $L$ has been introduced as the extension of the system in diffusion direction. The system is initially evacuated, i.e., free of guest molecules. At time $t = 0$ it has been brought into contact with an atmosphere of the guest molecules to be investigated. The pressure in the surrounding atmosphere is kept constant throughout the whole experiment, and $c_{i, eq}$ is the equilibrium concentration in the region $i$ (either micro- or macroporous space), as introduced in Section 3. Over the concentration ranges $0 \leq c_i \leq c_{i, eq}$ covered during the uptake experiment, the diffusivities $D_i$ are assumed to be constant.

For facilitating the subsequent discussion, Equations (5) and (6) are nondimensionalized and rewritten using new dimensionless variables ($C_i, X, and T$)

$$\frac{\partial C_i}{\partial T} = \frac{\alpha}{12} \frac{\partial^2 C_i}{\partial X^2} - \frac{1}{\beta \gamma} C_i + \frac{1}{\gamma} C_2$$ (19)

$$\frac{\partial C_2}{\partial T} = \frac{1}{12} \frac{\partial^2 C_2}{\partial X^2} + \frac{1}{\beta \gamma} C_1 - \frac{1}{\gamma} C_2$$ (20)

where

$$\alpha = \frac{D_1}{D_2}$$ (21)
\[
\beta = \frac{\tau_1}{\tau_2} = \frac{p_1}{p_2} = \frac{p_1}{(1 - p_1)} 
\] (22)

and

\[
\gamma = \frac{\tau_2}{T_{\text{micro}}} 
\] (23)

\[
T_{\text{micro}} = \frac{l^2}{12D_2} 
\] (24)

is the time constant (the first statistical moment) of diffusion-limited uptake for a purely microporous slab of thickness \(L\) and diffusivity \(D_2\). \(^{[1b,13a]}\)

Full steps of the nondimensionalization, along with the information on the characteristic units (or scaling factors), are given in the Supporting Information. The initial and boundary conditions given by Equations (17) and (18) are accordingly changed to

\[
C_i(X, T = 0) = 0; \quad 0 < X < 1; \quad i = 1, 2 
\] (25)

and

\[
C_i(X = 0, T) = C_i(X = 1, T) = p_i; \quad 0 \leq T < \infty; \quad i = 1, 2 
\] (26)

Overall mass transfer is now seen to be affected by three mutually independent parameters, namely, \(\alpha, \beta, \) and \(\gamma\). The influence of the parameters \(\alpha \) and \(\beta\) on overall mass transfer is easy to follow since both contribute to an enhancement of mass transfer, due to either an enhancement of the rate of mass transfer in the transport pores (\(\alpha\)) or an enhancement of the relative amount of fast-diffusing molecules (\(\beta\)). Depending on the host materials, with the given micro-, meso-, and macropore spaces, and the guest molecules under consideration, the parameters \(\alpha\) and \(\beta\) may exhibit a broad range of magnitudes. Examples of such estimates may be found in the literature, in particular in comparative studies with the results of PFG NMR diffusion measurements.\(^{[26d,29]}\)

With \(\alpha = D_1/D_2 = 10 \, 000\) and \(\beta = p_1/p_2 = 0.01\) as typical values, we are now going to explore the influence of \(\gamma\), i.e., the ratio of the mean lifetime in the region 2 (space of micropores in the hierarchically porous material) to the time constant of molecular uptake and release for a purely microporous material of the same size. We do so by considering the solutions of Equations (19) and (20) with various specifications of the exchange parameter \(\gamma\). Variation of the exchange parameter \(\gamma\) may be imagined in a straightforward way to be accomplished by varying the magnitude of the transport resistance (the “surface barrier”) at the interface between the micro- and transport pores. A first inspection of the resulting profiles and their evolution in Figure 1 reveals the following features:

i) With increasing \(\gamma\), i.e., with decreasing rate of exchange between the two pore spaces, uptake is observed to be slowed down.

ii) There is a characteristic change in the shape of the concentration profiles. For both (sufficiently) fast and slow exchange between the two pore spaces, molecular uptake is seen to mainly occur by the progression of diffusion fronts from the surface (at \(X = 0\) and 1) into the interior. In between, there is a range (in the chosen example, visible for \(\gamma = 0.03\) and \(\gamma = 0.1\)) where molecular uptake occurs essentially simultaneously spread over the whole system.

iii) In the extreme limits of slow and fast exchange (here for \(\gamma \leq 0.001\) and \(\gamma \geq 10\)) the profiles become unaffected by the exchange rate between the two pore spaces.

4.1.2. Special Cases

Extra-Slow Exchange: We start our data analysis with considering the limiting case of extremely slow exchange, choosing \(\gamma = 100\) as displayed in Figure 1a. As a consequence of this low exchange rate, the amount of molecules moving from the transport pores to the space of micropores has, obviously, remained negligibly small, in comparison with the amount of molecules diffusing only through the micropores. This is even true in the very middle of the system, so that overall uptake occurs via diffusion through, essentially, the space of micropores, starting from the outer surface of the particle under study, i.e., at \(X = 0\) and \(X = 1\). The profiles coincide, accordingly, with those calculated for a purely microporous particle with diffusivity \(D_2\) as indicated by the broken lines. The same situation holds, as a matter of course, with also larger values of \(\gamma\). The time constant of molecular uptake (first statistical moment) is, accordingly, that of a slab of thickness \(L\) with diffusivity \(D_2\).

\[
T_{\text{extra-slow exchange}} = T_{\text{micro}} = \frac{l^2}{12D_2} 
\] (27)

We shall employ this time constant as an approach of the time constant for molecular uptake and release of the purely microporous sample and, thus, as a reference value for our further discussion. Enhancement of the exchange rate between the two pore spaces in Figure 1b with \(\gamma = 10\) is seen to leave the profiles still essentially unaffected. Progressively more pronounced changes, however, are observed with further decreasing \(\gamma\).

Slow Exchange: In Figure 1d, with \(\gamma = 0.1\) the rate of exchange from the transport pores into the micropores is seen to be still slow enough so that, with the given values of \(D_1\) and \(p_1\), the transport pores may be completely filled before the guest molecules start to escape into the micropores. Hence the guest concentration, essentially anywhere in the network of the transport pores, may assume its equilibrium value. On the other hand, exchange with the micropores is now fast enough, so that molecular uptake in the micropores through the interface with the transport pores is much faster than uptake via the micropores through the external particle surface at \(X = 0\) and \(X = 1\), which was the dominating one in the limiting case of extra-slow exchange with \(\gamma = 100\) and 10 in Figure 1a,b.

Reconsidering Equations (19) and (20) we note that, under these conditions, the first one, Equation (19), may be disregarded since the concentration in the transport pores is assumed to be at, essentially, equilibrium. Concentration enhancement in the micropores is, moreover, implied to be due to exchange with the transport pores rather than by diffusive flux through the micropores, so that the diffusion term on the right-hand side in the second equation, Equation (20), may be omitted, yielding
The equilibrium values of $C_1$ and $C_2$ (namely, $p_1$ and $p_2$) are correlated via the detailed balance condition, Equation (8),

$$\frac{\partial C_2}{\partial T} = \frac{1}{\beta \gamma} C_{1,eq} - \frac{1}{\gamma} C_2$$  \hspace{1cm} (28) \hspace{1cm} \frac{C_{1,eq}}{C_{2,eq}} = \frac{C_1}{C_2} = \beta.$$ 

Insertion into Equation (28) finally yields the simple relation

$$\frac{\partial C_2}{\partial T} = -\frac{1}{\gamma}(C_2 - C_{2,eq})$$  \hspace{1cm} (29)

Figure 1. a–h) The evolution of the profiles of the normalized guest concentration $C$ (after nondimensionalization with an appropriate scaling factor) as a function of, again, the normalized coordinate $X$ during molecular uptake in a hierarchically porous 1D system, characterized by the ratios $\alpha = \frac{D_1}{D_2} = 10,000$ between the diffusivities and $\beta = \frac{p_1}{p_2} = 0.01/0.99$ between the relative populations in the two pore spaces. The ratio between the mean lifetime of the guest molecules within the space of micropores and the mean uptake time by exclusively the space of micropores $\gamma = \frac{\tau}{T_{micro}}$ is varied between 100 and 0.0001, as indicated in the individual representations. Times are given as nondimensionalized variable $T = t/T_{micro}$. The broken lines in (a) and (h) are the concentration profiles during molecular uptake by a (uniformly) nanoporous system of the same size with, respectively, the diffusivities $D_2$ and $p_1 D_1 + p_2 D_2$. The broken lines in (e) are the concentration profiles resulting from Equation (30). In Section 4.3 we shall, once again, refer to these broken lines.
With

\[ C_2(T) = 1 - \exp(-T/\gamma) \]  

as the solution of Equation (29) and the definition of the non-dimensionalized variable \( T \) (Equation (55), Supporting Information), we finally obtain the exponential dependence of molecular uptake as known for the linear driving force

\[ C_2(t) = 1 - \exp(-t/(\gamma T_{\text{micro}})) = 1 - \exp(-t/\tau_2) \]  

This can be recognized as an immediate consequence of the incorporation of the exchange terms in Equations (5) and (6).

With Equation (31), the time constant of molecular uptake in the range of “slow exchange” is thus seen, somehow expectedly, to be nothing else than the molecular mean lifetime \( \tau_2 \) within the region 2 (space of the micropores)

\[ T_{\text{slow exchange}} = \tau_2 = \left( \frac{R_2}{15D_2} \right)^2 = \gamma T_{\text{micro}} = 0.03 \times T_{\text{micro}} \]  

where, with the second equality, we have made use of Equation (14). The last equality refers to the special case of \( \gamma = 0.03 \) as considered in Figure 1e. The broken straight lines in Figure 1e show the time dependence as following from Equation (31), in reasonable agreement with the results obtained by solving the complete set of diffusion equations, Equations (19) and (20), for diffusion in the hierarchically porous system.

The message provided by Equation (31) may be further elaborated by inserting, into the defining equation \( \gamma = \frac{\tau_2}{T_{\text{micro}}} \) (Equation (23)), the expressions \( \tau_2 = \frac{(R_2)^2}{15D_2} \) and \( T_{\text{micro}} = \frac{1}{12D_2} \), as given by Equations (14) and (24), yielding

\[ T_{\text{slow exchange}} = \frac{4}{5} \left( \frac{R_2}{L} \right)^2 T_{\text{micro}} \]  

With Equation (15), \( R_2 = \frac{W_{\text{micro}} - W_{\text{lum}}}{} \) has been introduced as a measure of the extension of the space of micropores to be filled by molecular uptake through the interface with the transport pores. For providing a quantitative estimate of \( R_2 \), we assume that the microporous bulk phase is uniformly permeated by cylindrical transport pores of diameter \( d \). Each cubic unit cell of the microporous phase may thus be implied to contain a single cylindrical transport pore, resulting in

\[ R_2 = \frac{3d}{4} \left( \frac{1}{e} - 1 \right) \]  

where \( e \) is the porosity, i.e., the volume fraction of region 1 (space of transport pores) within the total volume. By inserting Equation (34) into Equation (33), uptake (and release) in hierarchical pore systems under slow-exchange conditions is seen to accelerate either with increasing transport porosity when the pore diameter is kept constant or with decreasing pore diameters when the porosity is kept constant. This is the expected behavior since in both cases the extension of the microporous space, which has to be “supplied” through the transport pores, is reduced and, hence, also the time needed for filling. Making use of the common condition \( e \ll 1 \), the factor of uptake acceleration is found to be of the order of \( (eL/d)^2 \).

**Fast Exchange**: With further increasing exchange, i.e., decreasing values of \( \gamma \), the populations of the two pore spaces get finally into mutual equilibrium. Like with the largest values of \( \gamma \), uptake must be expected to proceed with a diffusion front, starting from the particle boundaries at \( X = 0 \) and \( X = 1 \). However, now it occurs, with fluxes in both pore spaces weighted with the relative occupation numbers in equilibrium, at a resulting overall diffusivity given by the two diffusivities

\[ D_{\text{mean}} = p_1D_1 + p_2D_2 = p_1D_1 = 100 \times D_2 \]  

The last equations are a consequence of the conditions \( p_1/p_2 = 0.01 \) and \( D_1/D_2 = 10,000 \) chosen for the considered example. The broken lines in Figure 1h have been determined for uptake by a purely microporous particle with the diffusivity 100 \( \times \) \( D_2 \). Their agreement with the solutions of the complete set of diffusion equations for hierarchically porous systems as provided by Equations (5) and (6) or Equations (19) and (20) with \( \gamma = 0.0001 \), confirms the validity of our reasoning. We note that the profiles for \( \gamma = 0.001 \) shown in Figure 1g exhibit quite similar patterns, in accordance with our understanding that, under fast-exchange conditions, transient concentration profiles during uptake and release are not affected by a variation of the exchange rates.

Once again, for determining the time constant of molecular uptake (the first statistical moment), we may use that of a slab of thickness \( L_{\text{micro}}^{(1h,1s)} \) now, however, with the diffusivity \( p_1D_1 + p_2D_2 \) rather than \( D_2 \), yielding

\[ T_{\text{fast exchange}} = L^2 / \left[ 12(p_1D_1 + p_2D_2) \right] = T_{\text{micro}} \frac{D_2}{p_1D_1 + p_2D_2} \approx 0.01 \times T_{\text{micro}} \]  

The letter equality has been attained by inserting the ratio between the various diffusivities considered in the given example (Equation (35)).

**Case Correlations**: Transport enhancement in a hierarchically porous material in comparison with its purely microporous counterpart has been shown to be achieved along two essentially different routes. Both are based on the prerequisite that the contribution \( p_iD_i \) of diffusion within the transport pores to overall mass transfer significantly exceeds the contribution \( p_2D_2 \) by the micropores.

In one limiting case, referred to as “slow exchange,” transport enhancement (i.e., a reduction of the time constant of molecular uptake or release—see Equation (33)) is brought about by a reduction of the “effective” particle size, which is not anymore the particle diameter but some smaller value brought about by the incorporation of the transport pores into the microporous bulk phase. With Equation (34) in combination with Equation (33), for cylindrical transport pores of diameter \( d \) and porosity \( e \), this reduction has been estimated to be of the order of \( eL/d \), with \( L \) denoting the particle extension. The commonly used interpretation of transport enhancement by referring it to a “reduction of the diffusion path length” is thus, under slow-exchange conditions, found to be indeed appropriate.

Under “fast-exchange” conditions, transport enhancement is correlated (see Equation (36)) with the enhancement of the
mean diffusivity due to mass transfer in the transport pores. Now it makes no sense anymore to talk about a “reduction of the diffusion path length.”

In the two limiting cases, with Equations (32), (33), and (36), the time constants of uptake and release are seen to depend on different parameters. Under slow-exchange conditions, the uptake time scales with the square of the ratio between \(R_2\) and the particle size (Equation (33)) or, respectively, the parameter \(\gamma\) (Equation (32)). Under fast-exchange conditions, the uptake time scales with the ratio between the diffusivity in the region 2 \(D_2\) and the overall diffusivity \(p_1D_1 + p_2D_2\), Equation (36). Transport enhancement by a purposeful variation of the relevant parameters should ideally be based, therefore, on the knowledge of the actual physical situation. Such information is indeed accessible via the transient concentration profiles during uptake and release, which show totally different patterns in the two limiting cases as demonstrated with Figure 1. Their potentials to record exactly such dependencies are opening up an important field for the application of microimaging via IR and interference microscopy.

Let us, in conclusion, refer to the summary of the different special cases and their quantification in Table 1. It quantifies, with the entries in bold, transport enhancement in the considered model system in the two limiting cases of slow and fast exchange between the two pore spaces. The table as well contains the limiting case of extra-slow exchange, represented by the uptake and release times in the limiting cases as demonstrated with Figure 1. Their potentials to record exactly such dependencies are opening up an important field for the application of microimaging via IR and interference microscopy.

| Table 1. Transport enhancement in a hierarchically porous particle in comparison with its purely microporous counterpart (coinciding with the limiting case of extra-slow exchange), represented by the uptake times in the limiting cases of slow and fast exchange. In addition to the actual values for two cases (written in bold, with reference to Figure 1e,h), the comparative values estimated via the relation for slow exchange under fast exchange conditions and, vice versa, the relation for fast exchange under slow exchange conditions are also given. The conditions of \(\alpha = D_1/D_2 = 10000\) and \(\beta = p_1/p_2 = 0.01/0.99\) are chosen for the present communication. |
| Uptake time constant |
|----------------------|
| \(T_{\text{extra-slow exchange}} = T_{\text{micro}}\) (Equation (27)) |
| \(T_{\text{micro}} = \frac{L^2}{2D_2}\) (Equation (27a)) |
| Slow exchange: \(\gamma = \frac{r_2}{T_{\text{micro}}} = 0.03\) |
| Fast exchange: \(\gamma = \frac{r_2}{T_{\text{micro}}} = 0.0001\) |
| \(T_{\text{slow exchange}} = \frac{p_1}{p_2}T_{\text{micro}}\) (Equation (32)) |
| \(0.03 \times T_{\text{micro}}\) (Figure 1e) |
| \(0.0001 \times T_{\text{micro}}\) (Figure 1h) |
| \(T_{\text{fast exchange}} = \frac{D_2}{p_1D_1 + p_2D_2}T_{\text{micro}}\) (Equation (36)) |
| \(0.01 \times T_{\text{micro}}\) (Figure 1e) |
| \(0.01 \times T_{\text{micro}}\) (Figure 1h) |

where the first terms on the right-hand sides have been obtained by repeated integration by parts. \(\psi_i\) denotes the contribution of the molecules in the region \(i\) to the signal attenuation. One has to be aware of the fact that, with the notation as given by Equations (39) and (40), any influence of nuclear magnetic

4.2. PFG NMR with Pore Hierarchies

We may start our considerations by use of the very same equations, Equations (5) and (6), which have already been the basis of discussing the various patterns of concentration profiles considered in the previous section. Now, however, on solving the diffusion equations, we have to consider the initial and boundary equations as required under the conditions of the PFG NMR experiment as explained and specified in Section 2.2 with, notably, Equation (1). This is, in particular, to choose the initial and boundary conditions relevant for the determination of the mean propagator \(0.03\) i.e., the probability (density) of molecular shifts over a distance \(x\), in the direction of the applied magnetic field gradient.

In order to directly transfer the concentrations as appearing in Equations (5) and (6) into probabilities, we use the normalized concentrations \(c_{i,\text{norm}} = c_i/(c_{1,eq} + c_{2,eq})\). Then, the relevant initial and boundary conditions, by which the solution of Equations (5) and (6) becomes the mean propagator, are

\[
\psi_{i,\text{norm}}(x, t = 0) = p_0\delta(x)
\]

and

\[
\psi_{i,\text{norm}}(x = \pm \infty, t) = 0
\]

\(\delta(x)\) denotes the Dirac delta function. Choosing the limits \(x = \pm \infty\) in the boundary conditions means that the extension of the particle under study is implied to significantly exceed the mean diffusion path lengths of the guest molecules within this particle.

We must have in mind that the primary information provided by PFG NMR is the attenuation \(\psi(q, t)\) of the NMR signal as a function of the pulsed field gradient intensity \(q\). This is, with Equation (1), the Fourier transform of the probability distribution of molecular displacements, i.e., of the concentration profiles of labeled molecules starting from a joint origin, rather than the concentration profiles themselves as in microimaging. Therefore, the Fourier transform of the concentrations resulting from a solution of the diffusion equation for hierarchically porous materials has to be determined. For attaining these Fourier transforms, we multiply Equations (5) and (6) (now, with normalized concentrations) with \(\cos(qx)\), resulting in

\[
\frac{\partial \psi_1}{\partial t} = -q^2D_1\psi_1 - \frac{\psi_1}{\tau_1} + \frac{\psi_2}{\tau_2}
\]

(39)

\[
\frac{\partial \psi_2}{\partial t} = -q^2D_2\psi_2 - \frac{\psi_2}{\tau_1} + \frac{\psi_1}{\tau_2}
\]

(40)
relaxation on the signal attenuation curve has been omitted. This is easily seen to be allowed if, during the timespan of the experiments, signal attenuation due to nuclear magnetic relaxation is indeed negligibly small. The influence of nuclear magnetic relaxation can as well be left out of consideration if it is identical in either pore spaces. Otherwise, Equations (39) and (40) have to be complemented by a relaxation term. Determination of the relevant diffusion parameters under such conditions becomes more complicated, but is still possible.[30]

As a solution of Equations (39) and (40), one obtains[10b,11a,12b,c]

$$\psi(t) = \psi_1(t) + \psi_2(t) = p'_1 \exp\left(-q^2 D'_1 t\right) + p'_2 \exp\left(-q^2 D'_2 t\right)$$

(41)

with

$$D'_{1(2)} = \frac{1}{2} \left( D_1 + D_2 + \frac{1}{q^2} \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \right) \pm$$

$$\left[ D_2 - D_1 + \frac{1}{q^2} \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right)^2 + \frac{4}{q^2 \tau_1 \tau_2} \right]^{1/2}$$

(42)

and

$$p'_1 = 1 - p'_2, \quad p'_2 = \frac{1}{D'_1 - D'_2} \left( p_1 D_1 + p_2 D_2 - D'_1 \right)$$

(43)

Thus, total PFG NMR signal attenuation (Equation (41)) is found to be given by the superposition of two attenuation curves as typical for normal diffusion (Equation (3)), with their diffusivities ($D'_{1(2)}$) and relative contributions ($p'_1$,$p'_2$) following (via Equations (42) and (43)) from the diffusivities in the two regions, their relative populations and the exchange rate between them. These are exactly the four parameters, which, in Section 3, have been demonstrated to be needed for the description of mass transfer in hierarchically structured pore systems.

As the limiting case of significantly large diffusion paths during observation time $t$ (i.e., $t \gg \tau_i$), Equation (41) is reduced to a single exponential

$$\psi(q,t) = \exp\left(-q^2 D_{\text{mean}} t\right)$$

(44)

with an effective diffusivity

$$D_{\text{mean}} = p_1 D_1 + p_2 D_2$$

(45)

emerging as the mean value of the diffusivities in the two regions.

One the other hand, for observation times much shorter than the mean lifetimes (i.e., $t \ll \tau_i$), signal attenuation exhibits the superposition of two exponentials, just as diffusion in the two regions was measured simultaneously, but independently from each other, in two separate samples

$$\psi(q,t) = p_1 \exp\left(-q^2 D_1 t\right) + p_2 \exp\left(-q^2 D_2 t\right)$$

(46)

The formalism based on Equations (5) and (6) has been introduced for facilitating the analysis of diffusion measurement in beds of zeolite crystals.[12c] Regions 1 and 2 were assigned to, respectively, the molecules in the space between the crystals and the interior of the individual crystals. On critically assessing the preconditions of the application of this model (as detailed in Section 3) to beds of zeolite crystals we easily come across a number of inconsistencies. They notably include that, within our model, there are no limitations in the diffusion path lengths in both regions. This, however, is not the case with the region of intracrystalline diffusion where the diffusion path lengths are clearly confined by the size of the crystals. The two-region model has nevertheless been found to serve as a useful first-order estimate for reproducing the results of PFG NMR diffusion studies with beds of zeolite crystallites[30f,h,i] as well as in many more “compartmented” systems,[11d,30e,31] notably for organic tissues, with biological cells as the compartment.[11e,30b,g,32] It is this community where the formalism has become popular under the name Kärger model with, respectively, Equations (5), (6), and (41)-(43) referred to as the Kärger equations.[10b,11a-c,f,30c-33]

We are now going to show that, with materials of hierarchical pore structure, we have a system whose transport properties are almost ideally compatible with the requirements of the two-region model of PFG NMR diffusion studies.

Diffusion in two-region systems consisting of transport pores permeating a microporous bulk phase may, generally, be assumed to proceed under the side conditions (see Equations (9) and (10)) $p_1 \ll p_2 = 1$ and $D_1 \gg D_2$. With them, Equation (41) is simplified to

$$\psi(q,t) = \exp\left[-q^2 \left( D_2 + \frac{p_1 D_1}{q^2 \tau_1 p_1 D_1 + 1} \right) t\right]$$

(47)

The conditions giving rise to this simplification are referred to as the “third limiting case,” which Zimmerman and Brittin have already mentioned in their classical paper[34] on nuclear magnetic relaxation in two-component systems. There, in place of the terms $q^2 D_i$, appeared the nuclear magnetic relaxation rates $1/T_{1i}$ (with $i = 1, 2$ and $l = 1, 2$ for the longitudinal and transverse nuclear magnetic relaxation rates, respectively).[12a,34,35] This limiting case is distinguished by the fact that, as a consequence of the extremely high values of the intrinsic diffusion (or relaxation) rate, overall diffusion (or relaxation) behavior may be found to be affected by a region whose population $p_1 \ll p_2$ is negligibly small in comparison with the total entity of molecules contributing to the NMR signal. We note that, deviating from the situation considered with the starting equations, overall mass transfer depends on only three parameters since the relative population and the diffusivity in the transport pores appear only together as the product $p_1 D_1$. Note that, in the “third limiting case” of PFG NMR diffusion measurement, the preconditions with reference to relaxation attenuation are less stringent since the mean lifetime in the region 1 is extremely short and, moreover, attenuation due to nuclear magnetic relaxation can be expected to be anyway only very faint in the range of high molecular mobility.

With Equation (47), NMR signal attenuation is, once again, seen to follow an exponential. However, deviating from the situation described in Equation (3) for normal diffusion and in Equation (44) for a two-region system under the conditions of fast exchange, a semilogarithmic plot versus the squared pulsed field gradient intensity $q^2$ does not necessarily yield, anymore, a straight line.
Straight lines would, obviously, appear if the second term in parenthesis, \( p_1D_1/(q^2\tau_1p_1D_1+1) \), is negligibly small in comparison with \( D_2 \). This may occur either in a simple case that \( p_1D_1 \ll D_2 \) so that mass transfer along the transport pores does not anyway contribute to overall mass transfer, or for sufficiently large values of \( q^2 \) so that \( q^2\tau_1p_1D_1 \gg 1 \). In the latter case, \( \ln \psi(q, \tau) \) versus \( q^2 \) would become a straight line and the vertical intercept of its extrapolated line would be \( \exp(-1/\tau_2) \).

Alternatively, \( \ln \psi(q, \tau) \) versus \( q^2 \) would as well yield a straight line if \( q^2\tau_2p_1D_1 \ll 1 \) or \( \tau_2 \ll 1/(q^2p_1D_1) \), in which one recognizes the fast-exchange condition, yielding \( p_1D_1 + p_2D_2 = p_1D_1 + D_2 \) as the mean diffusivity. This has been the situation in PFG NMR studies with mesoporous zeolites where, as a rule, the observation times had to be chosen to be significantly larger than the mean lifetime in the region 2 (micropores) \( \tau_2 \).[6i,36]

As soon as the observation time approaches the order of the mean lifetimes in the pore systems, however, \( \ln \psi(q, \tau) \) versus \( q^2 \), will exhibit curvature.

As an example of such studies, Figure 2 shows the PFG NMR attenuation curves determined with \( n \)-hexane in binderless zeolite Y-type molecular sieve.[37] Spherical granules of the zeolite Y-type molecular sieve have been chosen as a model system for simulating the properties of hierarchically structured pore spaces. In the material under study, the continuous microporous phase is formed by an assemblage of zeolite crystals, interconnected by zeolite bridges generated in a secondary stage of crystallization. The space of micropores and transport pores (here: the free space between the microporous spaces) is, therefore, by far not as homogeneous as implied in the formalism of the two-region model, even given the fact that in PFG NMR diffusion studies the “zeolite bridges” between the various crystals have been found to accelerate mass transfer in comparison with binder-pelleted zeolite molecular sieves.[38] With the included PFG NMR attenuation curves, it is demonstrated that Equation (47) indeed serves as a reasonable estimate. Given the rather complex structure of the host material, complete agreement with the predictions based on rather simplified conditions can anyway not be expected. This refers, in particular, to the fact that data analysis via Equation (47) implies uniformity of the material properties all over the sample, which is clearly not the case in reality.

By inserting the values \( p_1D_1 = 4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), \( D_2 = 1.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), and \( \tau_2 = 2 \text{ ms} \), which result in a reasonable fit between the two-region model and the experimentally determined attenuation curves, into Equation (14) one attains \( R_2 = 2 \mu \text{m} \). In comparison with the image shown in Figure 2c, such a value may indeed be accepted as a reasonable estimate of the distance covered by the guest molecules within the space of zeolite micropores in between two (short) period of transport within the transport pores.

Best fits are, obviously, attained with medium observation times of \( t = 8 \) and 11 ms. For shorter times, the calculated attenuation curves show a less pronounced decay than observed in the measurements, while the opposite is true for larger observation times. Diffusivities are thus seen to decrease with increasing observation time. Such behavior, deviating from normal diffusion, might be referred to the existence of statistically distributed transport resistances within the host material. Under their influence, the confinement “felt” by the diffusing molecules would indeed increase with increasing displacements.[6e,39]

4.3. Transient Uptake and Release with Pore Hierarchies

For elucidating the potentials of uptake and release measurement for exploring mass transfer in hierarchically porous particles we can employ the calculations performed in Section 4.1. Now we have to go one step further by considering the uptake curve, i.e., the integral of the (non-dimensionalized) concentration profiles

\[
F(T) = \int [C_1(X,T) + C_2(X,T)] \, dX
\]

(48)
In the slow-exchange region, i.e., for $0.1 \geq \gamma \geq 0.01$, on the other hand, the molecular uptake and release has been found to follow the linear driving force model, Equations (30) and (31), with the mean lifetime $\tau_1$ becoming the time constant (i.e., the uptake time).

As shown in Figure 3, uptake and release measurements are seen to be ideally suited for quantifying the enhancement of mass transfer in hierarchically structured porous materials. The theoretical expressions for uptake and release presented for the different special cases of transport enhancement, however, are seen to reveal only small differences. These differences are, moreover, most likely a consequence of the simplifying approach by Equations (5) and (6) and must be anyway expected to be masked by the variation of the material properties within a given sample, notably including the particle and pore sizes. The options of the uptake and release measurements for providing substantial insight into the origin of transport enhancement must therefore be expected to remain limited.

5. Conclusion

Hierarchically organized nanoporous materials have proved to offer most promising prospects for transport enhancement under maintenance of guest confinement within the micropores as a prerequisite for their application for matter upgrading by shape-selective catalysis or separation. Quantification of the gain in diffusivity, however, is complicated by the structural complexity of such systems.

In order to quantify mass transfer in hierarchically porous materials, we have introduced a formalism referred to as the two-region model. It has found a broad range of applications in NMR diffusion studies with compartmented systems but, to the best of our knowledge, has not yet been used for a modeling of mass transfer in hierarchically porous materials. When applied to compartmented systems, the two-region model has some distinctive shortcomings, which gave rise to a series of papers dealing with its improvement. These shortcomings do not exist for its application to hierarchically organized porous materials with mutually interpenetrating pore spaces. This is, in particular, true with any materials consisting of a microporous bulk phase penetrated by a network of transport pores. They have been in the focus of the present study. An extension of the applicability of the two-region model to systems with “extended” interfaces is the topic of ongoing work.

While the transport properties of purely microporous materials, in addition to the particle size, are mainly determined by the diffusivity, mass transfer in hierarchically porous materials depends on, at least, four independent parameters, including the diffusivities in the micro- and transport pore spaces, their relative populations and the rate of exchange between these two spaces. As a consequence of this variety of influencing parameters, transport enhancement may be achieved by various mechanisms.

In the limiting case of “fast exchange,” molecular fluxes during uptake and release occur in both pore spaces in parallel. This gives rise to an enhancement of the diffusivity in comparison with a reference material consisting of only the space of
micropores, while the extension of space to be filled or emptied remains unchanged, i.e., the whole particle.

If, alternatively, molecular uptake along the transport pores is sufficiently fast, transport pores must be expected to be, essentially, filled before a major part of the microporous space is occupied by the guest molecules. Under such conditions, molecular uptake mainly proceeds via the interface between the transport pores and the space of micropores. Overall uptake time is, hence, controlled by $D_2$ as in a purely microporous material. Now, however, the dimensions of the pore space to be filled by molecular uptake are dramatically reduced, namely, from the particle size $L$ to a quantity referred to as $R_g$, which is a measure of the range that the molecules typically have to cover on their diffusion path from the transport pores into the space of micropores for their complete filling (Equations (32) and (34)). Obviously, transport enhancement in pore hierarchies is, under such conditions, correctly referred to a dramatic reduction of the diffusion path length. Such a description, however, would not make much sense and might even be misleading in the opposite case, i.e., the case of fast exchange.

Experimental measurement of mass transfer in pore hierarchies has to meet essentially two requirements, namely, the quantitation of transport enhancement in comparison with the purely microporous counterpart and the elucidation of the mechanisms, which have given rise to the observed enhancement. The first requirement is most directly satisfied by uptake and release measurements, without an immediate access to the underlying mechanisms of mass transfer. This access is provided by the application of microimaging, which allows a clear distinction between the two limiting cases. While the limiting case of slow exchange is revealed by an essentially monotonic increase in loading, which is uniform throughout the particle (Figure 1d,e), fast exchange becomes apparent in uptake patterns (Figure 1g,h) coinciding with those for adsorption by purely microporous particles.

Preliminary studies of monitoring benzene uptake and conversion to cyclohexane in nickel- and platinum-loaded porous glass plates$^{[16]}$ by IR microimaging$^{[20]}$ have already shown the potentials for such type of measurements. They will become applicable as soon as hierarchically porous particles of suitable structure, i.e., as thin plates with the (top and bottom) surfaces sealed for the molecules under study but permeable for light of the relevant wave lengths, are available. Preparation of such particles, suitably cut out of the zeolite material shown in Figure 2b,c, is in progress.

It should be mentioned that there exists an alternative way of distinguishing between the two limiting cases. By inserting either directly measured or estimated values of the relevant quantities into Equations (32) and (36), it is possible to attain theoretical estimates of the uptake times in the two limiting cases. Following our reasoning at the conclusion of Section 4.1 with reference to the entries in Table 1, this limiting case should be the more likely one, which gives rise to the larger time constant.

Differing from uptake and release experiments in combination with either microimaging or by monitoring mass increase in gravimetric measurements, PFG NMR is operating under equilibrium conditions, with its focus on the probability distribution of molecular displacements as a function of time. Data analysis is notably facilitated if the dimensions of the particle under study are much larger than the longest diffusion pathway. It is under this precondition that the formalism of PFG NMR (Equation (1)), combined with the starting equations of the two-region model (Equations (5) and (6)), leads to a set of theoretical expressions for the PFG NMR signal attenuation as provided by Equations (41)–(43) which is, in the limiting case of sparsely populated transport pores of high diffusivity, simplified to Equation (47). This relation offers immediate access to all parameters of relevance under the given conditions, namely, the diffusivity $D_2$ in the micropores, the product $p_D D_2$ of the relative amount of molecules in the transport pores and their diffusivity and the mean lifetime $\tau_2$ in the micropores. By choosing zeolite beads (Figure 2b) as a model system for illustrating the procedure we did at least comply with the requirement that the size of the particles under study notably exceeds the mean diffusion path lengths during the PFG NMR experiments. Sample heterogeneities, as becoming visible in already the image (Figure 2c), and an associated distribution in intrinsic transport resistances are, most likely, the main reasons giving rise to obvious discrepancies between the measured curves and their theoretical predictions (Figure 2a). Ongoing experimental work scheduled to be based on the application of mesoporous giant zeolite crystals of type MFI is expected to provide notably better agreement also in this respect.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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