Molecular exchange of \textit{n}-hexane in zeolite sieves studied by diffusion–diffusion and $T_1$-diffusion nuclear magnetic resonance exchange spectroscopy

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Abstract. Molecular exchange properties and diffusion of \textit{n}-hexane embedded in a bimodal pore structure with characteristic length scales in the order of nano and micrometres, respectively, formed by packing of zeolite particles, are studied. Two-dimensional (2D) nuclear magnetic resonance (NMR) diffusion correlation experiments together with relaxation–diffusion correlation experiments are performed at low magnetic field using a single-sided NMR scanner. The exchange time covers a range from $10^{-3}$ to $10^{-1}$ s. The molecular exchange properties are modulated by transport inside the zeolite particles. Different exchange regimes are observed for molecules starting from different positions inside the porous sample. The influence of the spin–lattice relaxation properties of the fluid molecules inside the zeolite particles on the signal intensity is also studied. A Monte Carlo simulation of the exchange process is performed and is used to support the analysis of the experimental data.
1. Introduction

Transport in porous media is an important part of many engineering processes, such as chromatography, petroleum recovery, reactor design, environmental remediation, catalysis, ion exchange, etc. The diffusive displacement of molecules in confinement is mostly determined by the pore geometry and the interactions with the pore walls [1]. Nuclear magnetic resonance (NMR) spin–lattice relaxation and molecular self-diffusion measurements [2] provide important insights into the molecular organization and dynamics of solvents in porous media. The transport properties of fluids in these kinds of systems differ dramatically from bulk. NMR diffusometry and relaxometry are ubiquitous techniques to probe this last statement [3].

In recent years, two-dimensional (2D) NMR spectroscopy in the time domain has emerged as a powerful new tool for probing the macroscopic dynamics of fluids confined in porous media [4]–[7]. In particular, the development of correlation spectroscopy in the time domain [4] has extended the possibilities of describing dynamical processes such as diffusion and exchange in more detail. The introduction of a reliable algorithm for the inversion of the Laplace transform (ILT) in two dimensions [8] facilitated the analysis and interpretation of these kinds of experiments.

The possibility of measuring diffusion in the stray field of mobile NMR devices in a short time and in a reliable way was demonstrated recently [9]. The use of the conventional stimulated-echo (STE) sequence in such devices requires a minimum number of scans in order to suppress unwanted effects generated by the radiofrequency (RF) pulses in the presence of strong magnetic field inhomogeneities [10, 11].

In previous work, the dynamics of n-hexane inside a zeolite-based porous sample were investigated using the NMR diffusion–diffusion (D–D) correlation technique [12] at low magnetic fields in the presence of a strong, constant field magnetic gradient. In this paper, a more detailed study of the molecular dynamics of the solvent inside zeolite 13X porous media, taking numerical simulations of molecular motion into account, is presented. A detailed interpretation of the experimental data by means of Monte Carlo simulations is attempted. In addition, a supplemental relaxation–diffusion correlation study is reported.

2. Experimental methods

The sample is based on a zeolite 13X porous sieve purchased from Sigma Aldrich Chemie GmbH, Germany (catalog number 283592). This consists of grains with a mean-particle
Table 1. NMR relaxation times and diffusion coefficient of bulk and confined in zeolite $n$-hexane at room temperature. $T_1$ is measured with the saturation-recovery pulse sequence. $T_{2,\text{eff}}$ is measured with a CPMG pulse sequence with an echo time of 53.5 $\mu$s. (†) Measured with 1D STE pulse sequence. (††) See [12].

|             | n-hexane |               | n-hexane |
|-------------|----------|---------------|----------|
|             | bulk     | inter-particles | intra-particles |
| $T_1$ (ms)  | 2160 ± 10| 18.8 ± 0.6    |          |
| $T_{2,\text{eff}}$ (ms) | 67 ± 3    | 48 ± 3        | 9 ± 1    |
| $D$ ($\times 10^9$ m$^2$ s$^{-1}$) | 4.56 ± 0.01(†) | 3.55 ± 0.05(††) | 0.04 ± 0.01(††) |

Diameter of the order of 2 $\mu$m and an inner pore size of 0.8 nm [13]. In order to eliminate residual water content, the zeolite was kept at 150 $^\circ$C for 70 h. The porous sieve of zeolites was put into a glass vial filled with liquid $n$-hexane, shaken for several minutes and subsequently centrifuged to ensure a high packing density of the grains. As a result, a bimodal pore structure was created, with two kinds of interconnected porous spaces, the mesoporous phase composed of particles of zeolites, and the inter-particle space with a characteristic pore space of the order of one micrometre. The NMR relaxation times and diffusion coefficient of $n$-hexane confined inside the zeolite sieves are shown in table 1.

The NMR $T_1$-diffusion correlation pulse sequence is based on the combination of a saturation-recovery pulse sequence, which encodes the recovery times for determination of the spin–lattice relaxation time $T_1$, followed by a STE module, used for measuring diffusion. The pulse sequence is shown in figure 1(a). Note that no exchange time is defined. The recovery time $\tau_{\text{rec}}$, however, is the most relevant period of time regarding exchange during this experiment.

The $D$–$D$ correlation pulse sequence is based on two successive STE pulse sequences separated by the interval $t_{\text{exch}}$, defining the timescale for exchange (see figure 1(b)). The STE modules are characterized by the two independently varied encoding times $\tau_1$ and $\tau_2$, and the constant time $\Delta$, which defines the timescale of the diffusion measurements. The last part of both sequences is the Carr–Purcell–Meiboom–Gill (CPMG) pulse train with an echo time of $\tau_{\text{echo}}$, where the train of echoes is acquired and added up in order to increase sensitivity. As can be seen in figure 1(b), this pulse sequence scheme includes, before the CPMG-part, seven 90°-pulses, requiring the design of an adequate cycling scheme for the phases of each RF-pulse. A phase cycle of 128 steps was introduced in order to select the desired coherence pathways [10]–[12]. The encoding times $\tau_1$ and $\tau_2$ were varied from 5.5 $\mu$s to 0.75 ms. The diffusion time $\Delta$ was fixed at 1.6 ms. The minimum and maximum experimental exchange times, $t_{\text{exch}}$, were 1 and 80 ms, respectively, covering two orders of magnitude in time scale. This scale is enlarged in the simulations until 500 ms.

The echo time in the CPMG-part of the pulse sequences is 53.5 $\mu$s and the number of echoes is 256, giving a total acquisition time of the order of 14 ms. The different transversal relaxation times of molecules in the inter-grain space on the one hand and in the inner part of the zeolite particles on the other lead to a modulation in the decay of the echo amplitudes that is independent of the exchange time $t_{\text{exch}}$, possibly leading to an apparent asymmetry in the exchange coefficients as explained later.
Figure 1. (a) NMR $T_1-D$ correlation pulse sequence. (b) NMR $D-D$ correlation pulse sequence. The time intervals are explained in the text. Each RF-pulse (r.f.) is denoted by the flipping angle. The constant gradient is denoted as $g$.

The experiments were performed using the stray field of a single-sided NMR sensor (profile NMR-MOUSE, ACT GmbH, Germany) with a $^1$H resonance frequency of 11.7 MHz, providing a time-constant magnetic field gradient of 11.5 T m$^{-1}$ in the sensitive volume. The magnet and sample are kept at room temperature within 0.5 °C. The temperature of the magnet was monitored during the whole process, possessing a variation of ±0.5 °C. At the position of the sample, a minor increase in the temperature was detected due to the heating of the RF coil. This heating was well below 0.5 °C and did not significantly affect the diffusion process.

3. Theory and simulation

Although $D-D$ exchange data inherently contain information about the transport inside the sample, Monte Carlo simulation and $T_1-D$ experiments provide more insight into residence and exchange times of molecules in the different phases of the sample.

A phenomenological model for the molecular transport of $n$-hexane inside the sample (packing of zeolites) is considered on the basis of excluded volume, diffusion and relaxation. Simulations based on this model describe very well the experimental facts observed in the exchange coefficients. As will be described below, the adjustment of simulation parameters permits the correlation between experiment and simulation.

In the following, the model of transport inside the porous sample is introduced, which, despite its simplicity, is adequate for interpretation of the experimental results. This describes
Figure 2. (a) Sphere packing used in the simulations. (b) Schematic cross-section of figure 2(a) and scheme of exchange. The time constants $\tau$ are described in the text.

the mechanism of molecular exchange in the sample via a radial layers-exchange mechanism.
The model distinguishes between molecules that are found in $N$ imaginary layers or compartments within the zeolite particle. Each of the layers has a volume $V_i$, which is the same for all $i = 1 \ldots N$ and contains an equal number of molecules $n_i$ in order to maintain a constant total density inside the particle. The dynamic equilibrium condition is satisfied between layers. For illustration, see figure 2.

The exchange time between different layers is denoted as $\tau_{ij}$. The mean time necessary for a molecule to move out of the particles, starting from layer $i$, is the exchange time $\tau_{i0}$, where 0 indicates the outside (inter-particle) region. A mean-exchange time can be defined as $\langle \tau \rangle = \sum_i V_i \frac{1}{V_T} \tau_{i0} = \frac{1}{N} \sum_i^n V_i$, where $V_T = \sum_i V_i$ is the total particle volume and $\tau_{10}$ is the shortest exchange time (below 1 ms) corresponding to exchange from the outermost layer of the particle. It can be estimated from the fastest decay in the curve of the $a_{ij}$ coefficients obtained from the simulations (see below).

The timescales of the exchange process are:

(i) the slow-exchange limit
$$t_{\text{exch}} \ll \tau_{10};$$

(ii) the intermediate-exchange limit
$$\tau_{10} \ll t_{\text{exch}} \leq \langle \tau \rangle$$

(iii) the fast-exchange limit
$$\langle \tau \rangle \ll t_{\text{exch}}.$$

The mean-exchange time $\langle \tau \rangle$ has to account for the exchange time of molecules in the different regions of the zeolite particle. A rough approximation for the largest exchange times can be found by assuming $\langle \xi^2 \rangle = (2 \mu m)^2$, where $\langle \xi^2 \rangle$ is the mean-squared displacement of the molecules inside the zeolite particles. Considering the characteristic diffusion constant of $n$-hexane confined in the zeolites as $D_{in} = (2 \mu m)^2/(2D_{in})$ leads to 50 ms, which is, as it will
be found below, a lower-limit approximation, compared with the residence times found in the simulation. For the timescale of the experiments, each of the three limits defined in the conditions (i)–(iii) can be found, depending on which layer is considered. Therefore, it is expected that the experimental data can only be described successfully by a distribution of exchange times.

4. Description of the simulation

Two models were used to simulate the exchange coefficients $a_{ij}$. Both use a random packing of 30 non-overlapping spherical particles with a narrow lognormal distribution of radii with a mean radius $\langle r \rangle$ and packing density $(1 - \phi_{\text{out}})$. A 3D lattice was generated from this ensemble by discretizing into $300^3$ cubic elements and a label was assigned to each point of the lattice. For the first model, these labels were used to distinguish between inter- and intra-particle positions, defining the regions A and B, respectively. The more complex radial layers-exchange model described above, in addition, distinguishes between different radial distances from the centre of the particles by defining $N = 10$ concentric spherical shells of equal volume corresponding to the regions 1–10, where 1 denotes the outermost shell that is nearest to the inter-particle region (see figure 2), labelled ‘0’. This corresponds to the region A in the simple model described before.

For the layer model the condition of constant density arising from volume exclusion effects was introduced for the distribution of molecules in the intra-particle region. This model does not include more adjustable parameters than the simple one. The layer model keeps the number of molecules in each of the shells constant and discarding simulation steps that violated this condition. In the first model, on the other hand, only the number of molecules inside the particles was kept constant, with no restrictions on the distribution of molecules inside this region.

In both models, no restriction was applied to the distribution of molecules in the inter-particle region. Molecules starting from different positions within this region are not expected to show different exchange dynamics because these molecules are, on the timescales of the exchange process, able to cover all distances to the neighbouring particles due to the much higher diffusion coefficient compared with the intra-particle layer.

The inner porosity $\phi_{\text{in}}$ of the particles was considered by controlling the number of molecules in the intra- and inter-particle regions, which were randomly placed at the beginning of the simulation, according to this relation,

$$\frac{N_{\text{in}}}{N_{\text{out}}} = \frac{\phi_{\text{in}} (1 - \phi_{\text{out}})}{\phi_{\text{out}}},$$

where $N_{\text{in}}$ and $N_{\text{out}}$ are the number of molecules in the intra- and inter-particle regions, respectively.

A random walk on the above-mentioned labelled lattice was simulated by performing isotropic discrete steps of length $1/300$ (in normalized units) independently in each dimension with a probability $P_i$,

$$P_i(\Delta x) = \frac{a_i}{2} \delta \left( \Delta x - \frac{1}{300} \right) + \frac{a_i}{2} \delta \left( \Delta x + \frac{1}{300} \right) + (1 - a_i) \delta(\Delta x),$$

where

$$a_i = \frac{2D_i \Delta t 300}{s^2},$$

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Figure 3. $D-D$ diffusion spectrum of the sample obtained from Laplace inversion of the echo decays, for three different exchange times. The factors $a_{i,j}$ correspond to the intensity of the peaks, as explained in the text. The presence of the off-diagonal peaks is the signature of the exchange process present in the sample.

and $\Delta t$ is the length of a simulation time-step, $D_j$ is the self-diffusion constant in regions $i$ and $s$ is a scaling factor that is defined by comparing the mean-particle size $\langle r \rangle$ in real units with the size of the packed particles in the units of the simulation where the simulation space is defined within a box of size 1: $s = \langle r \rangle_{\text{real}} / \langle r \rangle_{\text{sim}}$.

All molecules were labelled and for each simulation step their assignment to one of the regions and layers was recorded. Spin-lattice relaxation was considered by assigning a factor to each molecule resembling the magnitude of magnetization. These factors were multiplied by $\exp(-\Delta t/T_{1,i})$ at each simulation step, where $T_{1,i}$ depends on the region that the molecule was assigned to during the step. Depending on the model, different coefficients $a_{i,j}$ can be computed by calculating the sum of the relaxation factors of the corresponding molecules. For example, $a_{1,0}(t_{\text{exch}})$ can be obtained by finding the molecules that start in region 1 and end in region 0 after a time $t_{\text{exch}}$, and subsequently calculating the sum of their relaxation factors. These coefficients, along with the distributions of residence times, defined by the total time that a molecule spends inside a particle, were calculated for the radial layers model.

5. Results and discussions

For the $D-D$ experiment, the data were analysed using two approaches. The first was an Inverse Laplace inversion algorithm developed by Venkataramanan et al [8] that is applied on the 2D experimental echo decays $S(\tau_1, \tau_2)$ in order to obtain a 2D $D-D$ spectrum. As it was explained in previous work [12], the attenuation factor due to the relaxation time $T_2$ in the echo decays is $\exp(-\xi \tau_1 / T_2)$ where the coefficient $\xi$ is 2 or 4 depending on whether the experiment is 1D STE or 2D $D-D$, respectively. The influence of $T_2$ on the measured diffusion coefficients is when the echo decay factor for all encoding times is small compared with the diffusion decay factors in equation (1).

Figure 3 shows the result of the $D-D$ correlation experiment of $n$-hexane confined in the bimodal porous sample. It presents three ILT maps at different evolution times $t_{\text{exch}}$. The two diagonal peaks show a distribution of diffusion constants corresponding to the diffusion
of the solvent molecules in the intra- and inter-particle regions. The respective areas of these
diagonal peaks are proportional to the population of molecules that either did not exchange,
or have returned to their initial region, during the corresponding $t_{\text{exch}}$ period. The diffusion
coefficients at the centre of each peak correspond to those values obtained when the single STE
experiment is used and there is good agreement with literature values for this solvent using
PFG diffusometry [15]. The off-diagonal peaks reveal the presence of exchange of the solvent
molecules between the different regions of the porous sample. The peak $a_{AB}$, for instance,
corresponds to the molecules that, during $t_{\text{exch}}$, started in the inter-particle space and ended
inside the zeolite particles. It can be seen in these figures that at longer waiting times, the
relative intensities of the diagonal peaks decrease, while the intensities of the off-diagonal
peaks increase. The apparent imbalance of the intensities of the $a_{i\neq j}$ coefficients observed
for $t_{\text{exch}} = 25$ ms can be explained by the transversal relaxation during the CPMG acquisition
segment, which is faster in the intra-particle phase than in the inter-particle phase. Since the
sum of the integrated echoes, which is giving the signal intensity for the $D-D$ exchange
experiment, is weighted by transversal relaxation, less signal intensity is observed for molecules
that are residing in the intra-particle phase during the CPMG segment. Therefore, the apparent
imbalance in amplitude coefficients is an indication that transversal relaxation is faster for
molecules inside the zeolite grains.

The second step for data analysis is the time-domain fitting using the function
\[
S_{\text{fit}}(\tau_1, \tau_2) = \sum_{i,j=A}^{B} a_{ij} \exp(-q_1 D_{1,i}) \exp(-q_2 D_{2,j}),
\]  
where $D_{1,2}$ are the diffusion constants for the inter- and intra-particle regions, respectively. The
coefficients $a_{AB}$ are proportional to the peak integral in the 2D ILT-maps and reveal both the
exchange dynamics as well as the $T_1$ NMR relaxation process present in the sample. The results
of both analytical procedures are in agreement with each other. The advantage of the time-
domain fitting procedure is a better fidelity of the results, knowing that the ILT algorithm is
quite likely to produce artefacts.

Figure 4 shows the coefficients $a_{ij}$ obtained from the time-domain fitting of the exchange
experiments as a function of the exchange time. Note the good matching with the simulated
coefficients, which are plotted as lines.

Besides the exchange process, which leads to a decay of the coefficients $a_{AA}$ and $a_{BB}$ but
to an increase in $a_{AB} + a_{BA}$, spin–lattice relaxation processes have to be regarded. They mainly
take place during $2\Delta$ and $t_{\text{exch}}$, and lead to an attenuation that depends on the exchange time and
consequently produce an extra decay of all coefficients.

The influence of spin–spin relaxation is of a different kind: due to the short maximum
encoding times of $\tau_{1,2}^{\text{max}} = 0.85$ ms during which the spins are affected by spin–spin relaxation,
this relaxation process has only a minor influence on the STEs. During the CPMG-part of the
experiment, on the other hand, a weighting factor arises from spin–spin relaxation, which is
independent of $t_{\text{exch}}$: molecules that are in the inter-particle region during the CPMG-part and
will exhibit relaxation with a time constant $T_{2,\text{inter-particle}}$, whereas those inside the particles
will relax with a time constant $T_{2,\text{inside}} < T_{2,\text{inter-particle}}$. As a result, the relative intensities of the
coefficients $a_{AA}$ and $a_{BB}$ will be modulated by this weighting and an apparent difference
in the intensity of the $a_{i\neq j}$ coefficients may be produced. For comparison of simulated and
experimental data, this effect has been considered by scaling the simulated coefficients $a_{ij}$
individually to fit the experimental ones.
Figure 4. Coefficients $a_{ij}$ obtained from the time-domain fitting of the exchange experiments together with the corresponding relaxation-weighted coefficients obtained from the simulation. Index A corresponds to region 0 in the simulation ($a_{A,A} = a_{0,0}$). Index B corresponds to region 1 in the simple model and to a sum over the regions 1 to 10 ($a_{B,A} = \sum_{i=1}^{N} a_{i,0}$ and $a_{B,B} = \sum_{i=1}^{N} \sum_{j=1}^{N} a_{i,j}$) in the layer model. For the individual $a_{i,0}$, see figure 5(a). The results obtained from the first model, where different layers of the inner region are not considered, is compared with results obtained from the layer model, where the number of molecules is kept constant in each of the layers. The inset shows the results of the simulated coefficients for longer $t_{exch}$ times. Note that above 200 ms, all of the coefficients decay with the same rate due to the effective $T_1$ in the fast exchange regime. Note that in the case that is not visible, the error bars are smaller than the symbol size.

The mean-particle radius and porosity are determined from the experimental data by adjusting these two parameters in the simulation in order to obtain good agreement with the experimental results, as shown in figure 4. The parameter corresponding to the porosity was set to $\phi_{in} = 30\%$, in agreement with the value reported in [14], and the mean particle radius $\langle r \rangle = 2 \mu$m. For spin–lattice relaxation, only the relaxation time of the inner region $T_{1, in}$ was adjusted, keeping $T_{1, out} = 2.2$ s (according to the value for n-hexane in bulk from table 1). This is because the decay of the coefficients $a_{i,j}$ is predominantly affected by the much shorter spin–lattice relaxation time of the inner region. The settings that provided the best fit were $T_{1, simple} = 45$ ms for the first model and $T_{1, layer} = 20$ ms for the layer model. Note that the second value is in good agreement with the relaxation time obtained from the $T_1$-diffusion experiment, which is a further supporting argument for the necessity to consider the distribution of the exchange times within the particles into account. The diffusion constants
$D_{1,2}$ were set according to table 1 and a set of randomly packed particles with a packing density of $(1 - \phi_{out}) = 56.3\%$ was chosen.

The root-mean-squared displacement $\sqrt{2D_{\text{bulk}} \Delta} = 3.8 \mu m$ during the diffusion times $\Delta$ of the STE segments in the sequence (where $D_{\text{bulk}}$ is the diffusion coefficient measured for the bulk sample of $n$-hexane), and the fact that $D_{\text{inter}} \ll D_{\text{bulk}}$ (where $D_{\text{inter}}$ is the higher one of the diffusion coefficients obtained from time-domain fitting of the $D - D$ exchange experiments) show that the inter-particle pore size has to be smaller than $3.8 \mu m$, which can also be expected considering the given size of the zeolite grains (suggesting inter-particle pore sizes of about $1 \mu m$). However, $D_{\text{inter}}$ is also affected by exchange during the time $\Delta$.

From $D_{\text{intra}} \ll D_{\text{bulk}}$, it can be concluded that the intra-particle pores have to be much smaller than the above-mentioned root-mean-squared displacement. For liquids in pores of nm-dimensions, fast-exchange conditions are generally fulfilled so that a time dependence of $D$ itself cannot be detected, and the actual value of $D_{\text{intra}}$ is an indication of the intra-particle tortuosity for the given molecule.

In the following section, the details of the observed exchange process will be investigated based on the results obtained from the Monte Carlo simulation.

The exchange process of molecules starting in one of the intra-particle layers and ending in the inter-particle region, that is described by the coefficients $a_{i,0}$, depends on the initial position, i.e. the initial region. Molecules starting near to the centre of a particle exhibit a slower exchange process compared to those starting near to the surface. Figure 5(a) shows these coefficients versus exchange time, illustrating the different timescales for this process. The fastest exchange process is of the order of $100 \mu s$ (for the outermost region) and cannot be monitored by the time sampling in this graph. Due to the much faster spin–lattice relaxation inside the particles, molecules from the inner layers, which spend a longer time inside before exchanging, contribute less to the experimentally observed exchange coefficient $a_{BA} = \sum_{i=1}^{N} a_{i,0}$. Therefore, only molecules from within the outermost $40\%$ of the particle volume contribute to the exchange process that can be observed in the experiment. In analogy to this argument, the coefficient $a_{AB}$ comprises only those molecules that end in the outer $40\%$ of the particle volume. This is in accordance with experimental data where a maximum for $a_{AB} + a_{BA}$ is observed for $t_{\text{exch}} \approx 26 \text{ ms}$ (compare $a_{3,0}$ and $a_{4,0}$ in figures 4 and 5(a)).

Also note that all of the coefficients $a_{i,0}(t_{\text{exch}})$ decay with the same rate for higher exchange times. This decay arises from the motionally averaged spin–lattice relaxation, indicating that the exchange process has reached the equilibrium.

In figure 5(b), the coefficients $a_{i,1...10}$, which correspond to molecules starting in layer $i$ ending in any of the intra-particle layers, are plotted against exchange time. Two processes affect the decay of these coefficients with different impact depending on the initial layer of the molecules. One decay process arises from the exchange of molecules to the inter-particle region, which is most significant for small $i$ corresponding to initial layers near to the surface of the particles and, on the timescale of this graph, cannot be observed for high $i$ corresponding to molecules starting near to the centre. The other decay process is determined by spin–lattice relaxation, which provides additional insight into the exchange dynamics. Different limits for the motional averaging of the effective spin–lattice relaxation time $T_{1,\text{eff}}$ due to the exchange process are observed. For the outermost layer, the fast-exchange limit applies for practically all observable exchange times, leading to a constant averaged relaxation decay. The regions 2–5 exhibit intermediate exchange for a range of exchange times and show fast exchange at higher $t_{\text{exch}}$. For regions 6 and above, the slow-exchange limit applies, leading to a fast and constant...
Figure 5. (a) Spin–lattice relaxation weighted coefficients $a_{i,0}$ corresponding to the molecules starting from one of the intra-particle layers and ending in the inter-particle region after $t_{\text{exch}}$. Note the slower exchange process and higher relaxation attenuation for molecules that started nearer to the centre of the particles compared with those that started near to the surface. (b) Spin–lattice relaxation weighted coefficients $a_{i,B}$ corresponding to molecules that started from an intra-particle layer $i$ and end in any of the inner layers again after $t_{\text{exch}}$. Two processes, the exchange of molecules and spin–lattice relaxation, affect the decay of these coefficients with a different impact depending on $i$.

decay of the corresponding coefficients, which arises solely due to spin–lattice relaxation inside the particles.

Figure 6 shows the distributions of residence times for molecules starting from different inner layers. A lognormal distribution was fitted in order to obtain the mean-residence times.

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Distribution of residence times for molecules starting from different inner layers. The mean values are given in the figure.

⟨τ_{resid}⟩ of molecules starting from the regions 1–5. The mean-residence time of the layers 6–10 could not be obtained due to the restricted timescale of the simulation.

In the T_1−D measurements, two components can be distinguished, which are in agreement with the relaxation times and diffusion constants given in table 1. Figure 7 shows two diagonal peaks. Their relaxation times are attributed to T_1 of the n-hexane molecules inside the zeolite particles and the motional averaged T_{1,eff}. T_1 in the inter-particle region cannot be measured because this relaxation takes much longer than the exchange process. This relaxation time is assumed to be close to the bulk value of around 2.2 s. On the other hand, the timescale of the STE-part of the sequence is below the characteristic exchange times of most of the molecules inside. Therefore, the observed diffusion constants are expected to resemble the ‘true’ values corresponding to diffusion inside and outside of the zeolite particles, respectively.

The single non-diagonal peak arises from molecules that exhibit spin–lattice relaxation in the fast-exchange limit but end within a particle for the STE-part of the sequence. The other diagonal peak is not observed. The reason is that most of the molecules that start inside and exhibit fast spin–lattice relaxation do not exchange on the timescale of the corresponding recovery times.

6. Conclusions

Two different 2D NMR exchange experiments have been designed for investigations in low magnetic field strengths in the presence of a strong magnetic field gradient. The possibility of using strong gradients expands the applicability of the technique to small self-diffusion coefficients and/or shorter exchange times.

Even for a simple system with well-defined geometries and two strongly different fluid environments, characterized by two sets of relaxation times and diffusion coefficients for
intra- and inter-particle voids, the simple two-site exchange model did not lead to values of the geometric parameters that fitted the actual circumstances. The improved two-site exchange model proposed here, allowing for a coarse spatial assignment of molecules within the porous material, resulted in a much improved fitting compared to individually measured $T_1$ and $D$ values, and demonstrated the presence of a wide range of exchange times between the two environments. This approach becomes necessary whenever slow or intermediate exchange prevails in a sample, and will therefore be of interest for applications in a range of porous media with micrometre-sized domains, or with smaller confinements but highly viscous fluids. For many materials, the strong static magnetic field gradient used in these experiments will dominate over internal gradients so that the latter may be neglected in the analysis of the data. A quantitative consideration of short $T_1$ and $T_2$ relaxation times is the topic of ongoing research.

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