Pulsed field gradient NMR diffusion measurement in nanoporous materials

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Abstract

Labeling in diffusion measurements by pulsed field gradient (PFG) NMR is based on the observation of the phase of nuclear spins acquired in a constant magnetic field with purposefully superimposed field gradients. This labeling does in no way affect microdynamics and provides information about the probability distribution of molecular displacements as a function of time. An introduction of the measuring principle is followed by a detailed description of the ranges of measurements and their limitation. Particular emphasis is given to an explanation of possible pitfalls in the measurements and the ways to circumvent them. Showcases presented for illustrating the wealth of information provided by PFG NMR include a survey on the various patterns of concentration dependence of intra-particle diffusion and examples of transport inhibition by additional transport resistances within the nanoporous particles and on their external surface. The latter information is attained by combination with the outcome of tracer exchange experiments, which are shown to become possible via a special formalism of PFG NMR data analysis. Further evidence provided by PFG NMR concerns diffusion enhancement in pore hierarchies, diffusion anisotropy and the impact of diffusion on chemical conversion in porous catalysts. A compilation of the specifics of PFG NMR and of the parallels with other measurement techniques concludes the paper.

Keywords NMR diffusometry · Nanoporous material · Mixtures · Catalysis · Hierarchies · Anisotropy

List of symbols

A_{12} (m ²)	Interfacial area between region 1 and 2 in a two-region system	d (m)	Diameter of a cylinder
B_0 (T)	Constant external magnetic field	D (m ² s ⁻¹)	Self-diffusivity
B_{add} (T)	Additional inhomogeneous magnetic field in the direction of B_0	D_{eff} (m ² s ⁻¹)	Effective self-diffusivity
$c_{1(2)}$ (mol m ⁻³)	Guest concentration in region 1(2) of a two-region system	$D_{\text{eff restr}}$ (m ² s ⁻¹)	Effective self-diffusivity under confinement
$c_{\text{bound.}}$ (mol m ⁻³)	Guest concentration close to the crystal boundary, just beyond the surface barrier	$D_{x'x'}, D_{y'y'}, D_{z'z'}$ (m ² s ⁻¹)	Diagonal elements of diffusion tensor
$c_{\text{Eq.}}$ (mol m ⁻³)	Guest concentration at the crystal boundary, in equilibrium with the surrounding gas phase	D_{inter} (m ² s ⁻¹)	Self-diffusivity in intercrystalline space
		D_{intra} (m ² s ⁻¹)	Self-diffusivity in intracrystalline space
		D_g (m ² s ⁻¹)	Self-diffusivity in the direction of the field gradient pulses
		D_{min} (m ² s ⁻¹)	Lower limit of self-diffusivity measurable by PFG NMR
		$D_{\text{par(perp)}}$ (m ² s ⁻¹)	Self-diffusivity parallel (perpendicular) to the symmetry axis
		g (T m ⁻¹)	Magnetic field gradient pulse
		j (mol s ⁻¹ m ⁻²)	Molar flux entering a crystal
		k_D (mass%)	Breakthrough capacity
		l (m)	Axial length of a cylinder
		$\langle l^2 \rangle$ (m ²)	Mean squared jump length
		M_1 (s)	First statistical moment

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$M_{1,\text{barr}}$ (s)	First statistical moment under limitation by surface barrier	t_{max} (s)	Maximum possible observation time
$M_{1,\text{diff}}$ (s)	First statistical moment under limitation by diffusion	T (s)	Averaging time
$M_{1,\text{fast (slow)exchange}}$ (s)	Time constant of molecular uptake and release under fast (slow) exchange conditions	$T_{1(2)i}$ (s)	Longitudinal (transverse) nuclear magnetic relaxation time in the i th region
$p(\mathbf{r})$ (m^{-1})	A priori probability density to find a molecule at position $\mathbf{r}$	T_2 (s)	Transverse nuclear magnetic relaxation time
p_i (–)	Relative number of nuclei (or molecules) in the i th region	$T_2^{\text{MAS echo}}$ (s)	Effective transverse nuclear magnetic relaxation time in magic angle spinning (MAS) PFG NMR
p_{inter} (–)	Relative amount of molecules in intercrystalline space	V_1 (m^3)	Volume of region 1 in a two-region system
$p_{\text{necks (bridges)}}$ (–)	Probability of the occurrence of channel-constricting “necks” (channel-connecting “bridges”)	V_{cryst} (m^3)	Crystal volume
$P(\mathbf{r}, z, t)$ (m^{-1})	(conditional) probability that, during time t , a molecule initially located at position $\mathbf{r}$ is shifted over a distance z	x, y, z (m)	Cartesian coordinates; position of a molecule in x, y or z direction
$P(z, t)$ (m^{-1})	Mean propagator	$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$ (m^2)	Mean square displacement in x, y or z direction
$P_0(z, t)$ (m^{-1})	Probability distribution of molecular displacements after time t	$\langle (\Delta z)^2 \rangle_{\text{min}}^{1/2}$ (m)	Minimum displacement in z direction
q (m^{-1})	“Area” or “dephasing strength” of the field gradient pulse (= $\gamma g \delta$)	Greek letters	
$\mathbf{r}$ (m)	Position vector; displacement vector of a molecule	α (m s^{-1})	Permeability (or permeance) of surface barrier
$\langle \mathbf{r}^2 \rangle$ (m^2)	Mean square displacement in three dimensions	$\alpha_{x'}, \alpha_{y'}, \alpha_{z'}$ (rad)	Angles between the field gradient direction and the principal axes of diffusion tensor
R (m)	Radius of a spherical particle (Eq. 24); mean radius of the region to which diffusion is confined (Eq. 29)	γ ($\text{rad T}^{-1} \text{s}^{-1}$)	Gyromagnetic ratio
R_2 (m)	Radius of the equivalent sphere with the same surface-to-volume ratio as region 2 of a two-region system	$\gamma(t)$ (–)	Fraction of molecules which have left the crystallites during the observation time t
s (m)	Molecular displacement in the z direction ($= \sqrt{\langle z^2 \rangle}$)	δ (s)	Duration (width) of the field gradient pulse
S (a.u.)	Intensity of the NMR signal	Δ (s)	Distance between two effective field gradient pulses
$S_{\text{f(b)}}$ (–)	PFG NMR signal attenuation for free (bound) water (Fig. 11)	θ, ϕ (rad)	Azimuthal and polar angles of crystal orientations with respect to the direction of the field gradient pulses
t (s)	Observation (= “diffusion”) time	κ (–)	Time exponent
$t_{1(2)}$ (s)	Sum of time intervals within PFG NMR pulse sequence during which the signal attenuates due to longitudinal (transverse) relaxation	τ (s)	Mean life time between subsequent jumps
		$\tau_{1(2)}$ (s)	Mean life time in region 1(2) of a two-region system
		τ_{intra} (s)	Intracrystalline mean life time
		$\tau_{\text{intra}}^{\text{Diff}}$ (s)	Intracrystalline mean life time for diffusion-limited exchange
		ψ (–)	PFG NMR signalattenuation

$\psi_{1(2)}$ (–)	PFG NMR signal attenuation associated with region 1(2) in a two-regionsystem
ω (rad s ^{–1})	Angular frequency

1 Introduction

Among the techniques of diffusion measurement, pulsed field gradient (PFG) NMR, also known in the literature as NMR diffusometry, PGSE NMR, and DOSY NMR, is distinguished by its capability of tracking molecular ensembles along their diffusion pathways. Depending on the conditions of measurement provided by the host–guest system under study, the covered distances range from hundreds of nanometers to hundreds of micrometers. PFG NMR thus has the unique ability to determine the rate of molecular transport as a function of the distance travelled. With root-mean square displacements much smaller than the diameters of the crystals, the resulting diffusivities may thus unambiguously be attributed to the intracrystalline pore space. In addition, with increasing observation times and, correspondingly, increasing displacements, information is attained about transport resistances at the external crystal surface and about “long-range diffusivities”, i.e. about the rate of transport through a bed of crystals/particles.

PFG NMR measurements are generally performed under equilibrium conditions and provide, correspondingly, the coefficient of self- or tracer diffusion. The primary information attainable is therefore different from that of classical uptake and release experiments, yielding transport (or Fickian) diffusivities [1–3]. Transport diffusivities refer to the rate of mass transfer under non-equilibrium conditions, i.e. under the influence of a concentration gradient and, thus, under conditions typical for technical application like mass separation or conversion. Though not being identical, self-diffusivities may in general be taken as a first-order approach of the transport diffusivities. They do even coincide in the limiting case of sufficiently small guest concentrations, as a simple consequence of the fact that a distinction between equilibrium and non-equilibrium phenomena becomes meaningless in systems with non-interacting elements [4].

The information provided by PFG NMR is, in general, taken from the whole of the sample under study. However, combination with magnetic resonance imaging (MRI, see, e.g. [5–7] and Price et al. this volume) also opens up the option of spatially resolved measurement.

An introduction into the fundamentals of the measuring technique in Sect. 2 is followed by a detailed discussion of the limitations of measurement, including possible pitfalls and the options to recognize and to avoid them in Sect. 3. The ample field of applications is illustrated in Sect. 4 with investigations dedicated to topics like the loading

dependence of diffusion, diffusion anisotropy, multicomponent diffusion, catalytic reactions, diffusion retardation by surface and internal barriers and diffusion enhancement by the inclusion of transport pores in hierarchically organized pore spaces. A summary of existing challenges and a view on the potentials of the use of PFG NMR as a complementary technique in combination with other methods of diffusion measurement conclude the contribution.

2 Principle of measurement

Measurement of self- or tracer diffusion requires some labeling, by which different molecules may be distinguished from each other. In “classical” measurements, this labeling is based on the application of isotopes [8–10], with the implication that their mobility remains unaffected by the labeling. Starting with purposefully chosen differences in the isotope distribution (e.g. with labeling molecules in exclusively the surrounding of the nanoporous material), one follows subsequent equilibration with direct access to the rate of tracer exchange, i.e. to self-diffusion.

Labeling in PFG NMR may easily be understood with the classical model of nuclear magnetism as shall be shown in the following. For a more general introduction we refer to the standard text books in the field [11–15], and numerous reviews including [16–20]. Within the quasi-classical perspective on nuclear magnetism, each nucleus (nuclear “spin”) combines the properties of a magnetic dipole with those of a mechanic gyroscope. Therefore, nuclear spins in a magnetic field rotate about the field direction, similarly as a gyroscope under the influence of gravity (referred to as its precessional motion). The angular frequency of this rotation (the “Larmor” frequency) is given by the relation

$$\omega = \gamma B_0. \quad (1)$$

B_0 stands for the intensity (magnetic flux density) of the external magnetic field and γ , the gyromagnetic ratio, is a characteristic quantity of the nucleus under study (e.g., 2.67×10^8 rad T^{–1} s^{–1} for ¹H; 0.67×10^8 rad T^{–1} s^{–1} for ¹³C; 0.27×10^8 rad T^{–1} s^{–1} for ¹⁵N; 2.52×10^8 rad T^{–1} s^{–1} for ¹⁹F and 0.75×10^8 rad T^{–1} s^{–1} for ¹²⁹Xe). With the individual spins, also their vector sum rotates around the direction of the magnetic field, ending up in a rotating macroscopic magnetization. Varying magnetization in a suitably positioned coil (the receiver coil in an NMR spectrometer) is known to induce a voltage, which is recorded as the NMR signal.

In PFG NMR, the constant, homogeneous magnetic field B_0 is superimposed, over short time intervals, by an additional inhomogeneous field, which is caused by the so-called field gradient pulses. For the component in the direction of the constant magnetic field we note

$$B_{add} = g\mathbf{r}. \quad (2)$$

By combining Eqs. (1) and (2), the Larmor frequency at position $\mathbf{r}$ is found to be

$$\omega(\mathbf{r}) = \gamma(B_0 + g\mathbf{r}) = \gamma(B_0 + gz) \quad (3)$$

where with the second equality, the z -coordinate is assigned to point in the direction of the magnetic field gradient. The direction of the PFGs depends on the construction of the coils by which they are generated and often (e.g. under application of opposed Helmholtz coils [21]), but not necessarily, coincides with the direction of the constant magnetic field.

With Eq. (3), the rotational frequencies ω are seen to become space-dependent under the influence of a field gradient, so that the vector sum of the magnetization over the sample will vanish. Reestablishment of macroscopic magnetization and, hence, of an NMR signal (first noted as the “Hahn echo” [22]) is brought about by a second field gradient pulse which, if incorporated in a suitable sequence of radiofrequency (RF) pulses, compensates the spreading in spin orientation caused by the first field gradient pulse. This, however, is only true if a spin has remained at the same position. Any shift over a distance z in field gradient direction will, at the end of the second field gradient pulse, lead to a remaining phase difference $\gamma gz\delta$ from the mean, where δ stands for the duration (width) of the field gradient pulses. Such spin will contribute to overall magnetization with only $\cos(\gamma gz\delta)$.

The influence of diffusion within the sample under study on the intensity $S(q, t)$ of the NMR signal in PFG NMR experiments can thus be noted as

$$S(q, t)/S(0, t) \equiv \psi(q, t) = \int_{-\infty}^{\infty} \cos(qz)P(z, t)dz, \quad (4)$$

where $q = \gamma g\delta$ has been introduced as a measure of the intensity of the field gradient pulses. It is seen that q plays the role of a scattering vector [23, 24]. $P(z, t)$ denotes the probability density that, during a time interval t , an arbitrarily selected molecule, which contributes to the NMR signal, has been shifted over a distance z in gradient direction. This time interval, which appears as the “observation time” in PFG NMR experiments, is given by the separation of the two field gradient pulses. In the PFG NMR literature, for this distance the term Δ is in common use. With the notation of Eq. (4), the observation time t is implied to be much larger than the pulse duration ($\delta \ll t$).

$P(z, t)$ is referred to as the mean propagator [25, 26]. It represents the maximum possible information on random walk within the sample as accessible by integral observation. It is directly accessible via Fourier transform of the PFG NMR signal attenuation $\psi(q, t)$:

$$P(z, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi(q, t) \cos(qz) dq. \quad (5)$$

With Eq. (5), the mean propagator is seen to be immediately accessible from the primary data of the PFG NMR experiment, i.e. the spin echo attenuation $\psi(q, t)$ as a function of the PFG intensity.

In heterogeneous systems, as typically the case with nanoporous materials, the probability of molecular propagation becomes a function of the starting point. For the mean propagator one may accordingly write [27–29]

$$P(z, t) = \int p(\mathbf{r})P(\mathbf{r}, z, t)d\mathbf{r}, \quad (6)$$

with $p(\mathbf{r})$ denoting the (a priori) probability density to find a molecule at position $\mathbf{r}$. $P(\mathbf{r}, z, t)$ stands for the (conditional) probability that, during time t , a molecule initially located at position $\mathbf{r}$ shall be shifted over a distance z in gradient direction. The conditional probability distribution $P(\mathbf{r}, z, t)$ for displacements in heterogeneous systems is, in general, quite a complicated function of the spatial coordinates. But there are special cases, including diffusion in “two-region” systems (see, e.g., Sect. 4.4 and Refs. [30, 31]), where the propagator concept may serve as a useful tool for developing the relevant analytical expressions for PFG NMR signal attenuation.

The simplest conditions for diffusion measurement by PFG NMR are given in an infinitely extended homogeneous system undergoing normal diffusion. In this case, the probability distribution $P_0(z, t)$ of molecular displacements after time t follows as a solution of Fick’s second law [1, 32–34], yielding

$$P_0(z, t) = (4\pi Dt)^{-\frac{1}{2}} \exp\left(-\frac{z^2}{4Dt}\right), \quad (7)$$

with D denoting the coefficient of self-diffusion. It is this phenomenon of self- (or tracer) diffusion, which is in the focus of the present contribution so that we are going to drop the prefix “self-”, in agreement with the general use in NMR literature.

With Eq. (7), the mean square displacement is found to be given by the relation

$$\langle z^2(t) \rangle = \int_{-\infty}^{\infty} z^2 P_0(z, t) dz = 2Dt \quad (8)$$

and, in three dimensions in isotropic space, by correspondingly

$$\langle \mathbf{r}^2(t) \rangle = \langle x^2(t) + y^2(t) + z^2(t) \rangle = 6Dt, \quad (9)$$

commonly referred to as the Einstein diffusion equation. Inserting Eqs. (7) into (4) yields for the attenuation of the NMR signal in PFG NMR diffusion experiments

$$\psi(q, t) \equiv \frac{S(q, t)}{S(0, t)} = \exp(-q^2 Dt). \quad (10)$$

With the use of Eq. (8), signal attenuation may alternatively be noted as a function of the mean square displacement:

$$\psi(q, t) = \exp\left(-q^2 \frac{\langle z^2(t) \rangle}{2}\right), \quad (11)$$

which for isotropic systems, with Eq. (9), becomes

$$\psi(q, t) = \exp\left(-q^2 \frac{\langle r^2(t) \rangle}{6}\right). \quad (12)$$

Under the conditions of normal diffusion, i.e. with the propagator given by a Gaussian (Eq. 7), the presented formalism remains even exactly applicable if the condition of negligible gradient pulse width ($\delta \ll t$) is dropped. In this case, the observation (= “diffusion”) time t appearing in the relation must be understood to be given by the relation

$$t = \Delta - \delta/3, \quad (13)$$

with Δ denoting the distance between the starting positions of two gradient pulses of a rectangular shape.

Notably crystalline nanoporous materials like zeolites and metal organic frameworks (MOFs) are often of anisotropic structure. In such cases, the place of the coefficient of intracrystalline diffusion is taken by a diffusion tensor. It is determined by its main elements $D_{x'x'}$, $D_{y'y'}$ and $D_{z'z'}$ along the principal tensor axes, forming an x' - y' - z' coordinate system. Now the time dependence of the mean square displacement becomes a function of the orientation. Along the main tensor axes, it holds

$$\langle x'^2(t) \rangle = 2D_{x'x'}t; \langle y'^2(t) \rangle = 2D_{y'y'}t; \langle z'^2(t) \rangle = 2D_{z'z'}t. \quad (14)$$

For the mean square displacement in an arbitrary direction, notably along the direction of the field gradient pulses (which we have assumed to be that of the z coordinate), one may therefore note

$$\langle z^2(t) \rangle = 2(D_{x'x'}\cos^2\alpha_{x'} + D_{y'y'}\cos^2\alpha_{y'} + D_{z'z'}\cos^2\alpha_{z'})t, \quad (15)$$

where $\alpha_{x'}$, $\alpha_{y'}$ and $\alpha_{z'}$ stand for the angles between the field gradient direction and the main tensor axes. By referring to

$$D_{x'x'}\cos^2\alpha_{x'} + D_{y'y'}\cos^2\alpha_{y'} + D_{z'z'}\cos^2\alpha_{z'} = D_g \quad (16)$$

as the “diffusivity in the direction of the field gradient pulses”, Eq. (11) is thus seen to immediately lead to the standard formula of PFG NMR signal attenuation if D_g assumes the position of the (isotropic) diffusivity D .

In PFG NMR diffusion studies with nanoporous materials one, as a rule, operates with beds of crystallites, giving rise to a random distribution of the orientation of the crystallite’s coordinate system with respect to the system of the measuring device determined by the direction of the field gradients. The signal and, hence, also the attenuation curve appears therefore as a superposition for all possible crystal orientations, ending up in the relation

$$\psi(q, t) = \frac{1}{4\pi} \int_0^{2\pi} \int_{-1}^1 \exp[-q^2(D_{x'x'}\cos^2\theta + D_{y'y'}\sin^2\theta\cos^2\varphi + D_{z'z'}\sin^2\theta\sin^2\varphi)t] d\varphi d(\cos\theta). \quad (17)$$

From this relation one easily derives

$$\psi(q, t) = \frac{1}{2} \int_0^\pi \exp[-q^2(D_{\text{par}}\cos^2\theta + D_{\text{perp}}\sin^2\theta)t] \sin\theta d\theta \quad (18)$$

for rotational symmetry with $D_{\text{par(perp)}}$ denoting the diffusivity parallel (perpendicular) to the symmetry axis, ending up in

$$\psi(q, t) = \frac{1}{2} \int_{-1}^1 \exp[-q^2 D t x^2] dx \quad (19)$$

in the extreme case of strictly one-dimensional diffusion (i. e. for $D_{\text{perp}} \ll D_{\text{par}} \equiv D$).

Equations (10) to (19), obviously, apply for PFG NMR diffusion studies with beds of nanoporous crystallites/particles (in this contribution both terms are, essentially, used synonymously), whose diameters significantly exceed the distance covered by the molecules on their diffusion pathway. Only under such a condition, the vast majority of the guest molecules do not get into contact with the crystallite surface. They behave, accordingly, as within an infinitely extended medium and the diffusivities are, correspondingly, genuine intracrystalline ones.

Equations (10) to (12) are, moreover, also exactly applicable in the limiting case of “long-range” diffusion, i.e. for mean life times of the molecules within the individual crystallites much smaller than the observation time and for diffusion path lengths notably exceeding the crystallite diameters. Then D is referred to as the long-range diffusivity and reasonably well approached by the relation [31, 35]

$$D_{\text{long-range}} = p_{\text{inter}} D_{\text{inter}}, \quad (20)$$

with p_{inter} and D_{inter} denoting, respectively, the relative amount of molecules in the intercrystalline space and their diffusivity.

In general, however, and notably with diffusion path lengths of the order of the extensions of the particles, PFG NMR signal attenuation follows more complicated dependencies. Examples may be found in the numerous reviews

and textbooks in the field [11, 13, 15, 21, 36–38]. But also under these conditions, Eq. (11) may be shown to serve as a reasonable first-order approach of the spin-echo attenuation [21]. It has thus become common use to analyze PFG NMR diffusion attenuation via Eq. (10) quite in general as a first-order approximation (notably in the initial range of sufficiently small PFG intensities) with the understanding that the diffusivity is replaced by an effective one defined by the relation

$$D_{\text{eff}}(t) = \frac{\langle z^2 \rangle}{2t} = \frac{\langle r^2 \rangle}{6t} \quad (21)$$

In general, $D_{\text{eff}}(t)$ is a time-dependent parameter. This may even enhance the versatility of PFG NMR as shall be exemplified, e.g., in Sects. 4.2 and 4.7 on demonstrating the potentials of PFG NMR for quantitating the spacing between different transport resistances and the impact of different transport resistances on the overall diffusion resistance.

Under the conditions of normal diffusion, D_{eff} is, with Eq. (9), immediately seen to coincide with the genuine diffusivity. For anisotropic diffusion in a powder sample, D_{eff} simply results as the mean (i.e. one third of the trace of the diffusion tensor)

$$D_{\text{eff}} = \frac{D_{x'x'} + D_{y'y'} + D_{z'z'}}{3} = \frac{2D_{\text{perp}} + D_{\text{par}}}{3}, \quad (22)$$

with the second equality resulting for rotational symmetry.

3 Limitations, modifications, pitfalls and checks of consistency

With the implication that for reliable diffusion measurement the PFG NMR signal attenuation should be of the order of e^{-1} , with typical values for maximum field gradient amplitudes ($g = 25 \text{ Tm}^{-1}$) and gradient pulse widths ($\delta = 2 \text{ ms}$), one obtains with Eq. (11) for hydrogen-containing molecules a minimum displacement of $\langle (\Delta z)^2 \rangle_{\text{min}}^{1/2} \approx 100 \text{ nm}$ in gradient direction. In this context it is worthwhile mentioning that quasi-elastic neutron scattering (QENS, [39, 40], see also Kruteva et al. in this issue) is able to trace, similarly like PFG NMR, the probability distribution of molecular propagation, however, with root mean square displacements that are even much smaller than this minimum distance in PFG NMR measurement. Both techniques have therefore been used truly complementary [41–43].

With Eq. (9), the lower limit of the diffusivity accessible by PFG NMR is found to be $\langle (\Delta z)^2 \rangle_{\text{min}} / (2t_{\text{max}})$, where t_{max} denotes the maximum possible observation time. We recollect that PFG NMR diffusion measurement is based on the observation of the nuclear magnetization in

the plane perpendicular to a constant magnetic field and, notably, its attenuation under the influence of field gradient pulses. The maximum observation time of a diffusion measurement is, therefore, determined by how long it takes to decay to zero for a component of magnetization in the plane perpendicular to the constant magnetic field. This time constant is the transverse relaxation time T_2 . In the simplest PFG NMR diffusion experiment, the Hahn-echo experiment, a so-called $\pi/2$ RF pulse is followed by a π pulse, with the two field gradient pulses before and after the π pulse. Larger observation times become accessible with a sequence of three $\pi/2$ pulses (stimulated echo, with the two field gradient pulses before the second and after the third $\pi/2$ pulse). They are now limited by, essentially, the longitudinal relaxation time T_1 , which in soft matter or solids notably exceeds the transverse relaxation time T_2 . With a realistic value of $T_1 = 1 \text{ s}$ one ends up with a typical value of $D_{\text{min}} \approx 10^{-14} \text{ m}^2\text{s}^{-1}$ for the lower limit of the diffusivities as accessible by PFG NMR. Nowadays, with the progress done in spin physics, a completely new option for tracing substantially longer diffusion times on the time scale of tens of seconds provided by the long-living quantum spin states has emerged [44].

Such small values for displacements and diffusivities as just estimated are, as a rule, accessible only under exceptionally favorable conditions. This is due to the fact that low diffusivities are generally accompanied by small values of T_2 . This time, however, limits the interval over which the field gradients may be applied and, thus, sets an upper limit to the duration δ of the field gradient pulses. A partial solution of this conflict is offered by the combined application of PFG NMR and MAS (magic-angle spinning, see, e.g. [45–48]). Examples illustrating the benefit of this combination, notably also including the option of high-resolution measurement, shall be presented in Sects. 4.4, 4.6 and 4.7.

With Eqs. (10) and (12), the sensitivity for the measurement of small displacements and diffusivities is seen to increase with the gradient pulse intensity $q = \gamma g \delta$. Therefore, as a consequence of the large gyromagnetic ratio, ^1H PFG NMR does indeed, in this respect, offer the best possible conditions. On the other hand, both transverse and longitudinal relaxation times are, as a rule, larger for smaller gyromagnetic ratios. This, in turn, would—as just discussed—allow the application of both larger observation times and, possibly, also broader field gradient pulses. Hence, PFG NMR diffusion measurement with, e.g., ^{13}C and ^{129}Xe , may sometimes be preferred to ^1H PFG NMR (see, e.g. [49, 50], and Baniani et al. in this issue). These nuclei offer, with the increase of their electron shell, the additional advantage of facilitating high-resolution measurement, with the option to selectively determine the diffusivity of each individual component in mixtures [38, 50–52] to which we shall refer in more detail in Sects. 4.6 and 4.7.

As a primary precondition of PFG NMR diffusion measurement, nuclear magnetism must be large enough for giving rise to an observable NMR signal. Nuclear magnetism emerges in the superposition of the magnetic fields, generated by the nuclear spins. The interaction energy between the nuclear spins and the externally applied magnetic field is, in general, extremely small in comparison with the thermal energy. As a consequence, there is only an extremely small difference in the number of spins aligned preferentially parallel and opposite to the external magnetic field. Nuclear magnetization in the ambient temperature range amounts to only about one hundred thousandth of the maximum possible value that would be realized if all spins were aligned in the same direction. Sensitivity enhancement of PFG NMR by overcoming this limitation through appropriate “hyperpolarization” procedures is a hot topic of current research [53–58].

The samples under study, in general beds of nanoporous particles/crystallites within the NMR sample tube, are by their very nature heterogeneous. Under the influence of the constant magnetic field, heterogeneities in magnetic susceptibility give rise to inhomogeneities in also the magnetic field. The constant field gradients thus generated are superimposed to the PFGs, giving rise to cross terms in the PFG NMR signal attenuation. Since the PFG intensity, as a rule, notably exceeds the intensity of these internal field gradients, their influence may, in general, be neglected. Options for a further reduction of also this influence are provided by the application of more complicated pulse sequences, including the replacement of the (unipolar) field gradient pulses in the stimulated-echo sequence by pairs of bipolar field gradient pulses, separated by a π pulse in the so-called 13-interval sequence [59]. For options of further pulse sequence refinement, see e.g. Refs. [19, 37, 60, 61].

Diffusion analysis of the PFG NMR signal attenuation is based on the implication of a perfect adjustment of the field gradient pulses involved in the employed pulse sequences since also any mismatch in gradient intensities may give rise to signal attenuation. If such a mismatch remains unrecognized, data analysis would lead to wrong conclusions about the diffusion phenomena within the sample [62]. The generation of highly stable field gradient pulses, optionally combined with an automatic mismatch compensation [63, 64], is, as a consequence, among the main tasks for the spectrometer manufacturer. The user will doubtlessly benefit from the (occasional) use of a standard sample with a known diffusivity for calibration and consistency checks.

The problem with unstable field gradient pulses does not exist anymore by operating within a strongly inhomogeneous magnetic field and by replacing, in this way, the field gradient pulses by a constant magnetic field gradient. In fact, the very first NMR diffusion studies have been performed in exactly this way [22, 65, 66]) and the initially described

measuring principle is easily understood to apply also in this case. Differing from the PFG NMR experiment, however, in constant field gradient experiments, rf pulses have to be applied and NMR signals are recorded under the presence of a strongly inhomogeneous magnetic field. It was the associated loss in sensitivity that has given rise to the development of the PFG NMR [29, 67, 68], followed by a most impressive progress in the application of NMR diffusometry, making it the possibly most versatile technique of diffusion measurement quite in general. Continuous progress in sensitivity enhancement and the options provided by novel generations of superconducting magnets have meanwhile initiated a renaissance of NMR diffusometry with also constant magnetic field gradients [69–72]. Compared to PFG NMR, however, the acquisition of a sufficiently large amount of data is still connected with a much greater expenditure of time. The benefit of this technique should therefore particularly be in the measurement of extremely small diffusion coefficients [73].

The intensity of the NMR signal, the free induction decay (FID) or the integral of their Fourier transform, is directly proportional to the concentration of nuclei contributing to this signal, if the repetition time of the signal accumulation is longer than the five-fold of the longitudinal relaxation time T_1 . After calibration, signal intensity may thus be used for an independent check of sample loading complementing, e.g., volumetric measurement of the amount adsorbed. In case of using an echo signal or a shorter repetition time, the signal attenuation due to the influence of nuclear magnetic relaxation has to be taken into account. As long as this influence is uniform over the sample for all nuclei contributing to the NMR signal, nuclear magnetic relaxation only confines the range of measurement. Any distribution of relaxation times, in combination with a distribution of the diffusivities, however, notably complicates data analysis. In such a case, the contribution of the individual regions to overall signal attenuation must additionally be weighted by the respective relaxation behavior, yielding

$$\psi(q, t) = \sum p_i \exp(-t_1/T_{1i} - t_2/T_{2i}) \exp(-q^2 D_i t), \quad (23)$$

with D_i , $T_{1(2)i}$ and p_i denoting, respectively, the effective diffusivity, the longitudinal (transverse) nuclear magnetic relaxation time and the relative number of nuclei contributing to the NMR signal in the i -th region. t_1 and t_2 denote the sum of time intervals within the PFG NMR pulse sequence during which the signal attenuates due to longitudinal and transverse relaxation, respectively. Neglecting this influence falsifies the results, in general towards too large values for the average diffusivities. This is a consequence of the fact that, as a rule, the less molecular mobility, the stronger signal attenuation by relaxation and, hence, the less contribution to the overall signal. As an extreme case it may happen,

therefore, that the contribution of the genuine intracrystalline pore space has completely disappeared as a consequence of nuclear magnetic relaxation, with the observable signal due to exclusively molecules on either the external surface or in gaps and other deviations from sample regularity [74]. Notably in such cases, it is of crucial relevance for the reliability of the PFG NMR data to dispose of reliable estimates of which fraction of molecules introduced into the sample do contribute to the PFG NMR signal observed.

Notably on considering hydrocarbons, the option to base the PFG NMR diffusion studies on either ^1H or ^{13}C , provides us with a powerful means for data confirmation. Since all the mechanisms so far discussed as a possible origin of failures in measurement depend on the nature of the nuclei under study, coincidence in the diffusivities of one and the same molecule resulting from measurements with different nuclei may be taken as a strong argument for their reliability. Recent examples of such diffusion data consistency checks using both ^1H and ^{13}C nuclei are discussed in Baniani et al. (in this issue). Examples also include measurement with ^1H and ^{19}F , e.g. on considering the diffusion of CHF_2Cl in zeolite NaX [75].

Consistency checks for demonstrating the reliability of PFG NMR diffusion data may most informatively be based on the correlation between PFG NMR signal attenuation and the time dependence of molecular propagation as provided by Eq. (12). For visualization we resort to the classical example of PFG NMR diffusion studies with water in a bed of MFI-type crystallites in different modifications [76], see also [30], as illustrated in Fig. 1.

Measurements have been performed with beds of zeolite crystals of two different sizes in closed PFG NMR sample tubes, covering a temperature range from about 0 up to 130 °C. For comparison, the same samples were also investigated with the intercrystalline space blocked by deposition of a layer of silica (from water glass) on the external surface of the crystals (filled symbols in Fig. 1).

Taking into account that differences in the loading and in zeolite structure and composition may give rise to slight differences in also the diffusivities, up to about 50 °C the PFG NMR data shown in Fig. 1 can be consistently attributed to intracrystalline diffusion, in complete agreement with our expectation for sufficiently small molecular displacements. The diffusivities in the larger crystallites are seen to continue following a linear Arrhenius dependency since, with the chosen observation time, the root mean square displacements remain small enough in comparison with the crystal sizes up to the largest temperature considered.

With the smaller crystals, the two types of samples exhibit totally different patterns. In the loose bed of crystals, temperature enhancement is found to lead to an enhancement of the diffusivity over that obtained with larger crystals. This behavior may be referred to the occurrence of long-range diffusion (Eq. 20), with the relative number p_{inter} of molecules in the intercrystalline space being large enough so that the intracrystalline diffusivity D_{intra} is significantly exceeded by the long-range diffusivity $p_{\text{inter}} D_{\text{inter}}$. In a closed NMR sample tube, like in the case considered, the activation energy of long-range diffusion is mainly given by the temperature dependence of p_{inter} , coinciding with that of the pressure within the sample, which is given by the isosteric heat of adsorption. Thus, in comparison with this latter, independently accessible quantity, also measurement of the activation energy of long-range diffusion may serve as a consistency check of PFG NMR [77].

On following, further on, the temperature dependence of the diffusivity within the “coated” small crystallites, the effective diffusivity is found to approach a constant value, as a consequence of molecular confinement to the crystal interior. For confinement to a spherical particle of radius R , e.g., it holds

Fig. 1 Temperature dependence of the effective PFG NMR diffusivity (D_{eff}) and mean square displacements for water in zeolite MFI: small (open circle, filled circle $\sim 7 \times 4 \times 3 \mu\text{m}^3$) and large (open square, filled square $\sim 16 \times 12 \times 8 \mu\text{m}^3$) crystals in a loose bed (open symbols) and with the intercrystalline space blocked (filled symbols) for an observation time $t = 1.2 \text{ ms}$. Reprinted from [76], with permission from Elsevier

$$D_{\text{eff restr}}(t) = \frac{R^2}{5t} \leftrightarrow \langle z(t)^2 \rangle_{t \rightarrow \infty} = \frac{2}{5} R^2, \quad (24)$$

with the second equation following from the first one via Eq. (8). Since particle sizes are easily accessible by experimental measurement, Eq. (24) provides us with another option for consistency checks of the validity of PFG NMR data.

Already the very fact that the signal intensity is proportional to the amount of nuclei (and, hence, of molecules) giving rise to this signal may, in principle, be used for the application of NMR in conventional tracer exchange and uptake/release experiments. This is in exactly the same way as self- and transport diffusivities have conventionally been measured. There are, correspondingly, examples where NMR spectroscopy has been applied in either way [78], e.g., by comparing the self-diffusivities of benzene in zeolite NaX as determined by PFG NMR and by tracer exchange. For

the tracer exchange experiments, zeolite crystallites initially loaded with perdeuterated benzene were brought into contact with an atmosphere of (normal, i.e., ^1H -containing) benzene, with the amount exchanged directly following from the increase of the NMR signal.

Another example of comparative PFG NMR and uptake studies is shown in Fig. 2. In the considered low-pressure region (40–45 mbar) of the host–guest system under study (cyclohexane in Vycor porous glass with a mean pore diameter of about 6 nm [79, 80]), self- and transport diffusivities are found to, essentially, coincide—as quite generally expected for sufficiently small loadings. The self-diffusivities as determined by PFG NMR (Fig. 2a) are thus, in Fig. 2c, seen to provide a perfect prediction of the uptake curve as observed in the conventional way by recording the time dependence of the amount adsorbed (in this case: from the intensity of the NMR signal). However, after a pressure step in the range of capillary condensation (from 70 to

Fig. 2 Comparison of molecular uptake with the results of PFG NMR: Adsorption isotherm of cyclohexane in Vycor porous glass as determined from the signal intensity after establishment of equilibrium after pressure variation and self-diffusivity determined via PFG NMR (a) in the same sample, with dimensions given in (b). Below shown are the uptake curves recorded via measurement of the NMR

signal intensity after pressure increase over the intervals (c) in the low-pressure range and (d) in the range of capillary condensation and adsorption hysteresis. Uptake curves, following with the PFG NMR self-diffusivities as a first-order approach of the transport diffusivities, are as well shown as the red lines. From [82], Copyright 2006, Springer Nature

75 mbar), only the very first part of the uptake curve is seen to follow an estimate based on the guest diffusivity, nicely illustrating that the slowing down of uptake in the range of capillary condensation proceeds without any reduction in molecular mobility [81, 82]. Figure 2a, simultaneously, provides an example of the strong influence of sample loading on the self-diffusivity. Further examples of such dependencies shall be provided in Sect. 4.1.

With the advent of fluorescently labeled particles, single-particle tracking (SPT) has emerged as an independent option for self-diffusion studies in nanoporous materials [83–89], (see also: Weckhuysen et al. this thematic issue). In this case, rather than by considering the “ensemble average” over all molecules during one and the same time interval via Eqs. (8) and (9) like in PFG NMR and QENS, the molecular mean square displacement is determined from the relation

$$\langle r^2(t) \rangle = \frac{1}{T-t} \int_0^{T-t} [\mathbf{r}(\tau+t) - \mathbf{r}(\tau)]^2 d\tau \quad (25)$$

as a “moving time average”, namely as the mean of the squared displacement of one and the same molecule during subsequent time intervals of duration t , during an averaging time $T \gg t$. The ergodic theorem, a cornerstone of statistical physics, predicts coincidence of the two averaging procedures. Proof of this requirement by, e.g., comparison the outcome of PFG NMR and SPT is complicated by the conflict in their measuring conditions requiring in SPT, opposite to PFG NMR, low molecular concentrations and mobilities. This is a consequence of the fact that the trajectories in SPT are constructed by “connecting the dots” [90], which emerge under flashlight observation. Such connections, however, can only give rise to genuine trajectories if any confusion in the position of a given particle in subsequent flashlight observation is excluded, requiring sufficiently low concentrations and mobilities.

With the data shown in Fig. 3, to the best of our knowledge, for the first time such a comparison has been provided. The measurements have been performed with Atto532 (ATTO532-COOH ATTO-Tec, Siegen, Germany) as a fluorescent molecule offering particularly favorable conditions for both SPT and PFG NMR. As a host-system, nanoporous glass with a mean diameter of about 3 nm has been used. It is known for its favorable properties for diffusion measurement quite in general [91], notably including SPT [85] and PFG NMR [82]. This material is, in particular, distinguished by the high homogeneity of its internal surface [92–94]. Owing to this homogeneity, in the limit of extremely low loadings as considered in the concentration range shown in Fig. 3, diffusivities may be found to become independent of concentration. With the agreement in the outcome of SPT and PFG NMR and, hence, with the coincidence of ensemble and time averages as observed with the diffusivity data

Fig. 3 Self-diffusivities of Atto532 molecules inside a nanoporous glass at room temperature recorded via single-particle tracking (SPT, red circles) and PFG NMR (black squares) as a function of loading. Reproduced from [209], with permission from John Wiley and Sons

shown in Fig. 3, the ergodic theorem of statistical physics has finally indeed found experimental confirmation for diffusion processes.

4 Examples highlighting the potentials of PFG NMR

4.1 Loading-dependent diffusivities

As a remarkable observation of the first PFG NMR diffusion studies, intracrystalline diffusion was found to vary considerably with the concentration of the guest molecules within the host pore system. Depending on the material and the molecules under study, diffusivities may follow quite different dependencies, including both their increase and decrease with increasing loading. Examples of the various types of concentration dependences experimentally observed are shown in Fig. 4.

Occurrence of both tendencies in the concentration dependence may be explained with the analog of the Einstein relation, Eq. (9), for diffusion by uncorrelated jumps

$$D = \frac{\langle l^2 \rangle}{6\tau} \quad (26)$$

with $\langle l^2 \rangle$ and τ standing for, respectively, the mean squared jump length and the mean life time between subsequent jumps. Implying a more or less homogeneous internal surface, the concentration dependence of D can be expected to be dominated by that of the mean jump length. It is not unexpected, therefore, that with n -hexane in zeolite NaX (case (i) in Fig. 4a) the diffusivity decreases over more than

Fig. 4 Concentration-dependence of guest diffusivities in zeolites. **a** Classification of the different types of concentration dependence as introduced in [96], **b** Arrhenius plots of the diffusivities of methane

two orders of magnitude with increasing loading, as a consequence of the dramatic reduction in the free volume available for molecular jumps. Under the dominating influence of adsorption sites of various intensity, as experienced e.g. by water and ammonia molecules in zeolite NaX (case (iii) in Fig. 4a), the situation is reversed since now, with increasing loading, the mean life times between succeeding jumps become increasingly shorter, leading to an enhancement in the diffusivities. Though such reasoning is an indispensable constituent of overall understanding, it can in no way replace more detailed analysis as illustrated, e.g., in Ref. [95] with reference to the various types of concentration dependence as presented in [96], see also the contribution by Coppens et al. and Baniani et al. in this issue.

Figure 4b illustrates the particular role of the cations with reference to the resulting concentration dependence. Replacement of monovalent sodium cations by bivalent calcium cations and, hence, by much stronger adsorption sites is seen to give rise to complete reversal in the loading dependence, namely (by following the nomenclature of Fig. 4a) from type (i) to (iii). At complete pore filling, the diffusivities in both host materials coincide, which may be easily understood as a consequence of the influence of the guest–guest interaction as the prevailing diffusion resistance.

The measurements shown in Fig. 4a and b have been performed with fused PFG NMR sample tubes containing

in zeolite NaX (squares) and NaCaX (circles) for different loadings. Numbers in symbols indicate concentration in molecules per supercage. Reprinted from [210], with permission from Elsevier

the host–guest system under study in equilibrium with an atmosphere of the guest molecules in the upper part of the sample tube. This arrangement allows an easy measurement of temperature dependencies as exemplified in Fig. 4b. In general, it may be implied that the amount of molecules in the gas phase remains negligibly small in comparison with the adsorbed guest molecules so that the loading remains constant. Otherwise, knowledge of the adsorption isotherm easily allows the due correction in loading [97].

Alternatively, measurement of the concentration dependence at a fixed temperature with continuously varying loading may be performed with the sample tube in contact with a gas reservoir whose pressure may be continuously varied. Diffusivity data obtained by this type of measurement have been presented in Fig. 2a.

4.2 Internal barriers

It came as a great surprise when in PFG NMR measurement of intracrystalline diffusion in various specimens of zeolite MFI, with displacements notably below the crystal diameters, the attained diffusivities were found to decrease with increasing observation time. Figure 5 shows, as an example, the diffusivity data obtained with n -butane in zeolite MFI as observed in two different samples. This dependence was, in particular, observed at low temperatures. This suggested the

Fig. 5 Intracrystalline diffusivity of *n*-butane in silicalite plotted as a function of the displacements as recorded by PFG NMR with two different samples (open and filled symbols) and results of dynamic Monte Carlo simulation (full lines), performed with the implication that the intracrystalline space is traversed by additional transport resistances with a mutual spacing of 3 μm in gradient direction. The activation energy for permeation is assumed to exceed that of genuine intracrystalline diffusion by 21.5 kJ mol^{-1} . Reprinted from [211], with permission from Elsevier

assumption that the zeolite bulk phase is permeated by transport resistances, whose influence is reducing with increasing temperature as a consequence of the increase in the thermal energy of the diffusing molecules, facilitating their passage through these resistances. Figure 5 demonstrates that the experimentally recorded trends in the diffusivities can be nicely reproduced by dynamic Monte Carlo simulations, performed with already the rather simplifying assumption that all transport resistances are identical, with an activation energy exceeding that of genuine intracrystalline diffusion by 21.5 kJ mol^{-1} and a mutual spacing of 3 μm in gradient direction. Such reasoning has meanwhile been compellingly supported by the evidence of microspectroscopy [84, 98–100]—see also the contribution of Weckhuysen et al. to this issue—and by combining PFG NMR and QENS measurements [42, 101] with transmission electron microscopy [41] and electron tomography [102].

With the effective diffusivity provided by Eq. (24) we have considered the limiting case that the diameter of the sphere to which diffusion is restricted is negligibly small in comparison with the mean diffusion path length that a molecule would cover without this restriction. An analytical expression for the time dependence of the effective diffusivity under spatial restriction may as well be derived in the opposite limiting case, for diffusion path lengths notably

below this diameter. In such cases it holds, in first-order approximation [103–107]

$$\frac{D_{\text{eff}}}{D} = 1 - \frac{4}{3\sqrt{\pi}R} \sqrt{Dt}, \quad (27)$$

where R stands for the mean radius of the region to which diffusion is confined. The structure of this relation nicely reveals, in a qualitative way, the mechanism behind this dependency: diffusion restriction is “felt” by those molecules which, during the observation time t , get into contact with the boundary of the region to which they are confined. This fraction increases with the diffusion path length (being proportional to $\sqrt{Dt}$) and the surface-to-volume ratio (being proportional to $1/R$)—just as appearing in the second term on the right hand side of Eq. (27), quantifying the drop in the effective diffusivity.

On considering the time dependence of the effective diffusivities of water (Fig. 6a) and of the lithium cations (Fig. 6b) in hydrated low-silica zeolite X (Li-LSX [108]—see the electron micrograph and scheme in Fig. 6c and d [109]), one is even able to trace two distinctly different time intervals, following the square-root-of-time dependence as predicted by Eq. (27). They are, obviously, to be attributed to diffusion within the individual crystallites and within their agglomerates, with transport resistances occurring, respectively, at the interfaces between the individual crystallites and at the external surface of the agglomerates. Crystallite and particle sizes as following with the best fit of Eq. (27) to the experimental data are of comparable order for water and the lithium cations and, moreover, close to the values which might be expected from inspecting the electron micrograph. Interestingly, the diffusivities of the lithium cations at 100 °C are of the same order as the water diffusivities at 25 °C. Diffusivities through the agglomerates are reduced in comparison with those within the crystallites, as a consequence of the transport resistance at the interfaces between the individual crystallites. Owing to the favorable properties offered by hydrated Li-LSX for the application of ^7Li PFG NMR, with these measurements for the very first time PFG NMR could successfully be applied to the diffusion measurement of exchangeable cations in zeolites quite in general—opening up a new field worth exploring.

4.3 Fast tracer exchange and surface barriers

The PFG NMR signal decay for molecular diffusion in beds of nanoporous crystallites is often found to follow the dependence as shown in Fig. 7a. The first fast decay is caused by those molecules (of fraction $\gamma(t)$) which, during the observation time t (equal to the separation Δ between the field gradient pulses), have left their crystallites. The second, slowly decaying constituent in the attenuation

Fig. 6 Effective diffusivities of water at 25 °C **(a)** and of lithium cations at 100 °C **(b)** in hydrated low-silica zeolite X (Li-LSX) as resulting via ^1H and ^7Li PFG NMR, plotted as a function of the square root of time. Diffusion occurs under confinement within both the adsorbent particles and the crystallites they consist of **(c and d)**. The diffu-

sivities and radii of confinement given in **(a)** and **(b)** result as the best fit of Eq. (27) to the experimentally determined time dependence of the signal attenuation. The Faujasite cage (bottom right of **(d)**) consists of 8 sodalite cages. Reprinted (adapted) with permission from [108]. Copyright (2013) American Chemical Society

curve is due to the molecules, which have remained. Their relative number $(1 - \gamma(t))$ is determined from the intersection of the backward extrapolation of this part (broken lines in Fig. 7a) with the ordinate. Plotting the fraction of molecules $(\gamma(t))$ that have left their crystals as a function of time represents nothing else than the tracer exchange curve as resulting in conventional tracer exchange experiments between the individual crystals and their surroundings. Differing from this conventional type of measurement, however, exchange times are now in the range of the observation times of PFG NMR, i.e. from milliseconds up to seconds. It is due to this reason that this type of measurement has been referred to as Fast Tracer Exchange PFG NMR [110].

The accuracy of determining $\gamma(t)$ increases with the difference in the slopes of $\ln \psi$ versus the squared pulse gradient intensity (here: the gradient width) and, thus, with the difference between the intracrystalline and the long-range diffusivity. Since the activation energy of long-range diffusion, as a rule, notably exceeds that of intracrystalline diffusion

(see the discussion following Fig. 1) the options for this type of measurement improve with increasing temperature.

Differing from the measurement of genuine intracrystalline diffusion, where both the crystal size and the diffusivity have to exceed a certain minimum value, there does not exist such a lower limit for the application of the technique of fast tracer exchange. In fact, the smaller the diffusivities, the smaller also the crystal sizes have to be for allowing a sufficiently large fraction of molecules to leave the intracrystalline space. Notably under such conditions, combination of PFG NMR and MAS is particularly useful since only in this way highly immobilized water molecules (like those in the sodalite cages of X-type zeolites—see Sect. 4.4 and Fig. 10) may become observable within the NMR signal.

The rate of tracer exchange may be controlled by both intracrystalline diffusion and permeation through an (additional) transport resistance on the external surface of the crystals. The time constant of tracer exchange (just like that of uptake and release), is most conveniently represented

Fig. 7 Application of PFG NMR for measurement of Fast Tracer Exchange (*n*-butane/NaX, 165 mg g⁻¹, *R* = 25 mμ, 353 K): **a** determining the relative amount $1-\gamma(t)$ of molecules, which during t ($\equiv \Delta$) have remained in their crystals, from the PFG NMR attenuation curve, **b** plotting the intercept of the broken lines with the ordinate as determined in (**a**) as a function of the observation time yields the time dependence of the relative fraction $1-\gamma(t)$ of molecules which, after time t , have not yet left their crystallites, **c** relative fraction $\gamma(t)$ of molecules which, after time t , have left their crystallites as a function of time (tracer exchange curve), with the hatched area representing the time constant of tracer exchange (first statistical moment M_1 , Eq. 28). Reproduced from [212], with permission from Wiley

by the first statistical moment [1, 111–113], defined by the relation

$$M_1 = \int_{\gamma=0}^1 t d\gamma = \int_0^\infty [1 - \gamma(t)] dt. \quad (28)$$

For diffusion-limited exchange (uptake/release), e.g., the first moment results to be

$$M_{1,\text{diff}} = \frac{R^2}{15D}, \quad (29)$$

with D denoting the self- (=tracer) diffusivity (or transport diffusivity for uptake/release). R stands for the radius of the crystal which, for simplicity, is assumed to be of spherical shape. Under limitation by surface barriers it holds

$$M_{1,\text{barr}} = \frac{R}{3\alpha}. \quad (30)$$

The parameter α is referred to as the permeability (or permance) of the surface barrier, defined by the relation

$$j = \alpha(c_{\text{Eq.}} - c_{\text{bound.}}), \quad (31)$$

where j stands for the flux entering the crystal. $c_{\text{bound.}}$ and $c_{\text{Eq.}}$ denote the guest concentrations close to the crystal surface, just beyond the surface barrier, and in equilibrium with the gas phase, respectively. The method of moments offers the advantage that the first moment under the simultaneous influence of various resistances simply results as the sum of the first moments of these resistances. For the first moment as experimentally determined via PFG NMR following Fig. 7 and Eq. (28) one may note, therefore,

$$M_1 = M_{1,\text{diff}} + M_{1,\text{barr}} = \frac{R^2}{15D} + \frac{R}{3\alpha}, \quad (32)$$

where if relevant, D has to also include the influence of internal resistances as considered in Figs. 5 and 6. Since transport resistances by surface barriers scale with only the size R of the host particle, their relevance in comparison with the diffusion resistance increases with increasing miniaturization [114–117].

Since M_1 is accessible via fast tracer desorption, R by microscopic inspection and D by “normal” PFG NMR (with a suitably chosen observation time and, hence, diffusion path length), the permeability (permance) α of the surface barrier is the only unknown quantity in Eq. (32). For its determination one has to consider the difference between M_1 and $\frac{R^2}{15D}$ which are, in general, available with only appreciable uncertainty. Estimates of surface barriers via PFG NMR are therefore, as a rule, only possible if transport resistance by surface barriers notably exceeds that by intracrystalline diffusion. It was a remarkable finding of PFG NMR that in many cases surface permeation was indeed the limiting process of molecular uptake and release with zeolites, notably under the influence of their technical application. Surface resistances were, as a consequence, often considered therefore as the origin of the sometimes dramatic differences on comparing the results of conventional uptake and release measurements with PFG NMR data on intracrystalline diffusion [118–120].

This tendency is exemplified in Fig. 8 with the parameters of molecular transport in granulated 5A zeolite as a function of time on stream in a petroleum refinery [96, 121, 213]. While the intracrystalline diffusivity D_{intra} of

Fig. 8 Intracrystalline diffusivities D_{intra} and mean life times $\tau_{\text{intra}} \equiv M_1$ of methane as a probe molecule in granulated 5A zeolite as a function of time on stream in a petroleum refinery [21, 96, 213]. The intracrystalline diffusivity D_{intra} and, hence, the intracrystalline mean life time for diffusion-controlled exchange resulting via $\tau_{\text{intra}}^{\text{Diff}} = R^2/(15D_{\text{intra}})$ remain essentially constant. The breakthrough capacity k_D , by contrast, is seen to decrease, showing that the deterioration of dynamic adsorption capacity is associated with the formation of a surface barrier. Reprinted from [96], with permission from Elsevier

the probe molecule and, hence, the intracrystalline mean life time under diffusion limitation $\tau_{\text{intra}}^{\text{Diff}}$ as following with Eq. (29) remain, essentially, unaffected, the mean life time as, actually, experimentally determined is seen to continuously increase. This has to be attributed to a continuous impediment of surface permeation with increasing time on stream. Deterioration of the molecular sieves as appearing in the decrease in the breakthrough capacity (k_D) may thus be attributed to carbonaceous (“coke”) deposits mainly close to the crystal surfaces.

It is noteworthy that in already the pristine zeolite granules as provided by the manufacturer the actual mean life time of the probe molecule ($\tau_{\text{intra}} \equiv M_1 \approx 2$ ms) notably exceeds the value ($\tau_{\text{intra}}^{\text{Diff}} = R^2/(15D_{\text{intra}}) \approx 0.2$ ms) estimated on only the basis of intracrystalline diffusion. Structural

collapse close to the surface has, obviously, led to the formation of a surface barrier already during the fabrication procedure.

4.4 Pore hierarchies and the two-region-model

The intimate contact between the guest molecules and the internal surface of the nanoporous host is among the primary prerequisites for the technical application of these materials. This notably includes the gain of value-added products by mass separation and conversion. It is, however, this intimate contact which, on the other hand, impedes the rate of molecular propagation within these systems [33, 122, 123]. This impediment in diffusivity limits the performance of their technical applications since the gain in value-added products generated within the nanoporous material can never be faster than allowed by the rate of mass transfer in their interior. A most promising route for overcoming this conflict is offered by the application of hierarchically porous materials, with the microporous bulk phase permeated by a network of (meso- or macroporous) “transport” pores [124–133].

The increasing structural complexity of such materials is, in general, accompanied by an increase in also the complexity of the mathematical formalism required for an adequate representation of internal mass transfer. While under ideal conditions, i.e. disregarding the possibility of internal and/or surface barriers, mass transfer in a purely microporous particle is completely described by the intracrystalline (= micropore) diffusivity, the number of parameters relevant for mass transfer in hierarchically porous materials enhances to four, now including the diffusivities (D_1, D_2) in the two pore systems, their relative populations ($p_1, p_2 = 1 - p_1$) and the exchange rate, i.e., the mean life times (τ_1, τ_2), where with 1 (2) we refer to the transport (micro-) pores. Life times and relative populations are correlated by the equation of detailed balance

$$\frac{p_1}{\tau_1} = \frac{p_2}{\tau_2}. \quad (33)$$

Fick’s second equation for quantitating intracrystalline mass transfer is now replaced by a set of two equations [134]

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} - \frac{1}{\tau_1} c_1 + \frac{1}{\tau_2} c_2, \quad (34)$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} - \frac{1}{\tau_2} c_2 + \frac{1}{\tau_1} c_1, \quad (35)$$

with the concentrations $c_{1(2)}$ in the transport (micro-) pores defined with reference to a unit volume, covering both micro- and transport pores and large enough so that, with

reference to this unit volume, the material may be considered to be homogeneous [135].

Equations (34) and (35) are the starting relations [21, 31] of the two-region model of diffusion yielding, for the PFG NMR signal attenuation,

$$\psi(t) = \psi_1(t) + \psi_2(t) = p'_1 \exp(-q^2 D'_1 t) + p'_2 \exp(-q^2 D'_2 t) \quad (36)$$

with

$$D'_{1(2)} = \frac{1}{2} (D_1 + D_2 + \frac{1}{q^2} (\frac{1}{\tau_1} + \frac{1}{\tau_2}) \mp \left\{ \left[D_2 - D_1 + \frac{1}{q^2} \left(\frac{1}{\tau_2} - \frac{1}{\tau_1} \right) \right]^2 + \frac{4}{q^2 \tau_1 \tau_2} \right\}^{\frac{1}{2}}) \quad (37)$$

and

$$p'_1 = 1 - p'_2; p'_2 = \frac{1}{D'_2 - D'_1} (p_1 D_1 + p_2 D_2 - D'_1). \quad (38)$$

PFG NMR signal attenuation is thus seen to result as the superposition of two attenuation curves, each of them following the relation for normal diffusion, Eq. (10). The parameters D' appearing in the exponents in place of the diffusivities and their relative contributions are, with Eqs. (37) and (38), seen to be functions of the whole parameter set describing the system, coinciding with the genuine values (p_i and D_i) in the limiting case of extremely slow exchange ($t \ll \tau_1, \tau_2$). For the systems under consideration we have, in general,

$$p_1 \ll p_2 \text{ and } D_1 \gg D_2. \quad (39)$$

Under these conditions, Eqs. (36) to (38) simplify to

$$\psi(q, t) = \exp \left[-q^2 \left(D_2 + \frac{p_1 D_1}{q^2 \tau_2 p_1 D_1 + 1} \right) t \right]. \quad (40)$$

Equations (36) to (40) have, originally, been introduced as a first-order approach of the PFG NMR signal attenuation in diffusion studies with beds of zeolite crystallites [136–138]. In this application of the formalism based on Eqs. (36) to (40), complete agreement cannot be expected since in a bed of crystallites intracrystalline diffusion is confined to the individual crystallites, in conflict with Eqs. (34) and (35), which permit unrestricted diffusion in both region 1 and 2 [139]. Equations (36) to (40), nevertheless, proved to serve as an excellent analytical tool for diffusion analysis in beds of microporous crystals [140–142] and, moreover, in compartmented systems quite in general [143–145], like, in particular, in assemblages of cells in organic tissues [146–149]. Notably in this community, the formalism has become popular under the name Kärger model [7, 13, 150–154].

The conflict of confinement to individual compartments does not exist anymore with the application of Eqs. (34)–(40) to diffusion in hierarchically porous materials. Here, in either region, propagation over unlimited distances becomes possible. As an example, Fig. 9 shows the PFG NMR signal attenuation observed with *n*-hexane in a binder-free granule of zeolite NaY [134], where the individual crystallites are mutually connected by bridges of a genuine NaY-type crystalline phase [155–158].

The experimentally determined signal attenuations are indeed found to be fairly well represented by Eq. (40). Remaining deviations of the theoretical predictions from the experimentally determined attenuation curves might be a consequence of sample heterogeneities disregarded in an approach as provided by Eqs. (34) and (35). Moreover one must have in mind that molecular exchange between the two pore spaces is only correctly represented by the terms $\frac{1}{\tau_1} c_1$ and $\frac{1}{\tau_2} c_2$ appearing in Eqs. (34) and (35) if this exchange is controlled by a transport resistance at the interface between these two pore spaces. Under diffusion limitation, Eqs. (34)

Fig. 9 PFG NMR attenuation curves for diffusion of *n*-hexane in binderless granules of zeolite NaY at room temperature (a) and microscans of a granule of the zeolite material (b) and its cross-section (c). The points in (a) are the experimental data (Exp.) and the lines are fitted curves (Fit.) of Eq. (40) to the experimental attenuation curves, with $p_1 D_1 = 4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D_2 = 1.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $\tau_2 = 2 \text{ ms}$. From [134]

and (35) can only serve as an approximation, yielding best fit to reality with the intracrystalline mean life time [134]

$$\tau_2 = \frac{(R_2)^2}{15D_2}. \quad (41)$$

The quantity R_2 stands for the “extension” of the space of micropores with reference to exchange with the network of transport pores, correlated via [134, 159]

$$R_2 = \frac{3(V_{\text{cryst}} - V_1)}{A_{12}} \quad (42)$$

with the volume of the space of micropores (resulting as the difference between the crystal volume and the volume of the transport pores) and the area A_{12} of their mutual interface.

In [142], the formalism of two-region diffusion has been extended to systems with the two regions differing, in addition to the diffusivities, in also their relaxivities and chemical shifts. Figure 10 shows, as an example of its application, the PFG NMR attenuation curves as observed with MAS PFG NMR for water in low-silicon zeolite X (LSX—see also Fig. 6) with 100% lithium exchange [109, 160]. Owing to the differences in their chemical shifts, the ^1H NMR signal of the water molecules within the sodalite units can be easily distinguished from that of the remaining water molecules. At 40 °C, PFG NMR signal attenuation for the mobile water molecules becomes clearly visible at the largest observation time, while there is not yet any indication of diffusion for the captured molecules. We observe, with increasing temperature, a significant increase in the diffusivities. They appear in a much faster decay of the signal due to the “free” water molecules outside of the sodalite cages. Simultaneously, for the largest observation time, PFG NMR signal attenuation becomes even observable with the signal stemming from the captured molecules. This is a consequence of the fact that now, during the observation time, a perceptible fraction of

the molecules within the sodalite cages have been replaced by water molecules coming from outside.

Figure 11 provides a comparison of the experimentally observed attenuation curves (Fig. 10) with the predictions of the two-region model of PFG NMR diffusion. It differs from Fig. 9 in that the water signals within the two regions (i.e. inside and outside of the sodalite cages) can be determined separately [13, 161]. Moreover, signal intensities are now considered to depend, in addition to the respective diffusivities, on also the effective transverse nuclear magnetic relaxation times $T_2^{\text{MAS echo}}$ [47, 142, 162]. They enter as a free parameter, determined in search of an optimum fit between the experimentally attenuation curves and their prediction based on Eqs. (34) and (35), complemented with a term taking account of the influence of nuclear magnetic relaxation [142].

In Fig. 11, these fits are seen to yield fair agreement between experimental measurement and theoretical prediction quite in general, but with substantial deviations for long diffusion path lengths as considered in Fig. 11c. These deviations, however, are inherent to the chosen approximation: since diffusion outside of the sodalite units, including mass transfer both within the various zeolite particles (as considered in Fig. 6a) and through the intercrystalline space, is quite a complex process, it cannot be expected to be adequately reflected by a single diffusivity, as implied with the application of Eqs. (34) and (35). By inspecting the deviations between measurement and prediction more closely one observes that for small gradient intensities—corresponding to large displacements—the experimentally determined decays are much stronger than the predicted ones, while just the opposite is true for the large gradient intensity. This, however, is exactly the expected behavior: for short displacements, the guest molecules are still mainly within the crystals undergoing intracrystalline diffusion while, on considering sufficiently large displacements, they undergo “long-range” diffusion which, under the chosen conditions,

Fig. 10 Signal attenuation of the two constituents of the ^1H MAS PFG NMR spectrum of water in 100Li-LSX at 313 K (a) and 373 K (b) for the indicated observation times. Observation of the “bound water” (captured by the sodalite units of the zeolite structure) was only possible owing to MAS (which, simultaneously, enhanced the intensity of their signal). Reprinted from [142], with permission from Elsevier

Fig. 11 PFG NMR signal attenuation plots for different observation times as a function of the squared intensity (q) of the field gradient pulses: free water (a) and bound water (b) at 40 °C; free water (c) and bound water (d) at 100 °C. Reprinted from [142], with permission from Elsevier

notably exceeds the intracrystalline diffusivity. Better agreement is therefore expected to be attained by adopting a three-region model in which the “unbound” water, presently considered as a uniform phase, is subdivided into its intra- and intercrystalline constituents.

With Eqs. (34) and (35) the pore systems 1 and 2 have been implied to be mutually penetrable and infinitely extended, with their diffusivities D_1 and D_2 independent of the observation time. The concept of effective diffusivities may be adopted quite in general to each type of material consisting of different ranges, including beds of crystals as considered, e.g., with Eq. (20) or materials with the pores separated from each other. In such cases, however, the correlation between the effective (“long-range”) diffusivity and the diffusivities in the various sub-systems is more complicated, with the latter ones becoming, as a rule, time dependent [163–166].

The description of mass transfer in a hierarchically porous system becomes straightforward under the conditions of fast exchange between the two pore systems, i.e. for exchange times τ_2 between the micro- and transport pores negligibly small in comparison between the relevant observation time. Under such conditions (which, as a matter of course, may be considered as a limiting case of Eqs. (34) and (35), mass transfer within the host particle is satisfactorily described with already a single diffusivity, resulting as the weighted sum of the diffusivities in the two regions

$$D_{\text{eff}} = p_1 D_1 + p_2 D_2. \quad (43)$$

Figure 12a illustrates the dramatic increase in intracrystalline diffusivity due to the presence of mesopores. With reference to Eq. (43), this increase is brought about by the term $p_1 D_1$, which thus is seen to exceed the term $p_2 D_2$ (being equal to the micropore diffusivity due to $p_1 \ll p_2 \approx 1$) by a factor of 100. Constancy of the diffusivities over observation times from 20 to 200 ms, corresponding with the measured diffusivities via Eq. (9) to mean molecular displacements from 200 nm up to 10 μm , demonstrate sample homogeneity.

This finding is in remarkable contrast with the message of Fig. 12b, where for ethane mesoporosity is seen to give rise to diffusivity enhancement for only the largest porosity and at the highest temperature. At lower temperatures, the existence of mesopores is even seen to reduce the diffusivity. This behavior, however, may be easily referred to the fact that, as a consequence of the similarity in the diameters of the “windows” connecting the cages in zeolite NaCaA and the molecular diameters of the n -alkanes, the smaller diameter of ethane in comparison with propane gives rise to a diffusivity enhancement [97] of more than two orders of magnitude. Thus, it turns out that for ethane the term $p_1 D_1$ in Eq. (43), in contrast with propane, remains comparable or even negligibly small in comparison with the contribution $p_2 D_2$ by micropore diffusion.

Fig. 12 Short-chain length hydrocarbons in hierarchical zeolite NaCaA of varying mesoporosity ϕ : diffusion under fast-exchange conditions. **a** Propane diffusivities at 25 °C, as a function of the observation time. Reproduced from [214], with permission from John Wiley and Sons. **b** Arrhenius plots of the ethane diffusivity (open symbols). Diffusion measurements have also been performed with the

mesopores blocked (filled symbols). Straight lines indicate the temperature dependence of micropore diffusion. The broken line (with its slope given by the heat of adsorption) indicates the temperature dependence of the relative amount p_1 of molecules in the mesopores. Reprinted from [215], with permission from Elsevier

It is, moreover, important to state that D_2 as appearing in Eq. (35) does not coincide with the diffusivity in the purely microporous material. It is rather reduced by the tortuosity resulting from the presence of the transport pores if this space is inaccessible by the guest molecules. This is, obviously, the case if the transport pores are blocked (filled symbols in Fig. 12b). The same situation is, interestingly, also approached with decreasing temperature, when—together with the guest pressure in the surrounding atmosphere—also the occupation number of the transport pores is decreasing.

With Eq. (29), the time constant of molecular uptake and release for a hierarchically porous particle under fast exchange conditions may be noted as

$$M_{1,\text{fast exchange}} = \frac{R^2}{15(p_1 D_1 + p_2 D_2)} \quad (44)$$

where the intracrystalline diffusivity in the purely microporous solid has been replaced by the effective diffusivity in the hierarchically porous solid. Adsorption and desorption proceeds with a diffusion front that propagates essentially simultaneously in both pore spaces.

In the opposite limiting case of slow exchange, the transport pores are essentially instantaneously filled during adsorption (and emptied during desorption). The time constant of this very process has already been introduced with Eqs. (41) and (42), yielding

$$M_{1,\text{slow exchange}} \equiv \tau_2 = \frac{(R_2)^2}{15D_2}, \quad (45)$$

where R_2 is a measure of the extension of the space of micropores, with reference to molecular uptake from (or release into) the transport pores, quantified by Eq. (33). Following modelling of the different limiting cases by dynamic Monte Carlo simulations [159, 167], a coherent theory of the various limiting cases based on Eqs. (34) and (35) is presented in [134].

The messages of Eqs. (44) and (45) are of fundamentally different nature. While under fast-exchange conditions transport enhancement may be achieved by both particle reduction (smaller R) and enhancement of diffusivities in the transport pores (enhancement of p_1 and D_1), exactly these quantities do not appear in Eq. (45) for uptake and release under slow-exchange conditions. Knowledge about the given conditions under which hierarchically porous solids are operating are, accordingly, of supreme practical relevance. A most direct discrimination may clearly be based on the monitoring of transient uptake profiles, which do indeed appear in quite different patterns for the various limiting cases [134]. Though the techniques of microimaging [168, 169], see also Chmelik et al. this Thematic Issue, do offer excellent preconditions for such type of measurement, practical problems with sample preparation have so far prevented such type of measurement. Much more promising, since easier to handle, appear in this context PFG NMR measurements of fast tracer exchange (see Sect. 4.3 and, notably, Fig. 7).

Figure 13 illustrates these options with the PFG NMR data for isobutane in various specimens of zeolite MFI. The figure shows the relative amount $1 - \gamma(t)$ of molecules which, after time t , have not yet left their crystallites. The intracrystalline mean life times (i.e., the first statistical

Fig. 13 PFG NMR measurement of Fast Tracer Exchange (see Fig. 7b) with isobutane in zeolite MFI at room temperature, performed with purely microporous crystals with a mean diameter of about 1 μm (filled squares) and of 0.7 μm (filled circles) and with an hierarchically mesoporous crystal with a diameter of about 1 μm (open squares). The straight lines are approaches of the decay to the function $\exp(-t/\tau)$. They have been used for a first-order estimate of the molecular exchange time (i.e. the first statistical moment M_1) of the PFG NMR trace-desorption curve as also indicated. From [30], Copyright 2020, Springer Nature

moments M_1) observed for the purely microporous zeolites are found to scale with, essentially, the square of the crystal radius as to be required, via Eq. (29), for diffusion-limited exchange. Following our expectation, molecular exchange in the mesoporous zeolite is also seen to be dramatically enhanced. The present data do not yet allow a decision about the underlying processes of mass transfer. Given the significant differences in the dependence of the time constants on the crystal size in the two limiting cases as reflected by Eqs. (44) and (45), such decision should become easily possible once mesoporous zeolite specimens of different size, but otherwise identical properties, become available.

4.5 Diffusion anisotropy

Figure 14 illustrates the potentials of PFG NMR for the measurement of anisotropic diffusion. The system under study is a water-saturated ordered mesoporous silica of type MCM-41 [170, 171]. The material contains hexagonally arranged channels with a diameter of about 3 nm. Analyzing the PFG NMR signal attenuations in powder samples following Eq. (18) yields the diffusivities (a) and, via Eq. (8), the mean square displacements (b) parallel and perpendicular to the channel direction. For comparison, Fig. 14a also shows the diffusivities in free water. Water diffusivities in channel direction are thus seen to be reduced by about one order of magnitude in comparison with the free liquid. Remarkably, though reduced by

Fig. 14 Water in MCM-41. **a** Arrhenius plots of the parallel (filled square) and perpendicular (open circle) components of the axisymmetric self-diffusion tensor as obtained via Eq. (18) from the PFG NMR signal attenuations, for an observation time of 10 ms. The full line represents the self-diffusion coefficients of super-cooled bulk liquid water. **b** Time dependence of the parallel (filled square, open square) and perpendicular (open circle, filled circle) components of the mean square displacement at 263 K in two different samples. The horizontal lines indicate the limiting values for the axial (full lines) and radial (dotted lines) components of the mean square displacements for restricted diffusion in cylindrical rods of lengths l and diameters d . The oblique lines represent the calculated time dependences of the mean square displacements for free diffusion with $D_{\text{par}} = 1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (full line) and $D_{\text{perp}} = 2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ (dotted line). Reprinted (adapted) with permission from [216]. Copyright (2000) American Chemical Society

a further order of magnitude, water is seen to diffuse in also radial direction, i.e. perpendicular to the channel axes. With diameters of about 3 nm, the channels are far too narrow to allow displacements in radial direction that are large enough for being monitored by PFG NMR in their interior. One has to conclude, therefore, that radial diffusion proceeds either through leakages in the channel walls or along the interfaces formed between individual microdomains of regular pore arrangement, which are known to form if the channels do not continuously permeate the whole particle [172–175].

With Fig. 14b we present, similarly as with Fig. 1, another example of how the PFG NMR data can be used for a self-consistency check. Since at the chosen temperature the water phase around the host particles is frozen, molecular mean square displacements within the particles approach, with increasing observation time, a well-defined value for the given geometry, as exemplified with Eq. (24) for confinement within a sphere. Similarly, for confinement within a cylinder (see top of Fig. 14), mean square displacements may be shown to approach the limiting values

$$\langle z(t) \rangle^2_{t \rightarrow \infty} = \frac{d^2}{8} \quad (46)$$

in radial and

$$\langle z(t) \rangle^2_{t \rightarrow \infty} = \frac{l^2}{6} \quad (47)$$

in axial direction. Taking account of the scattering in the particle sizes as indicated in Fig. 14b, experimental data are found to agree with the predictions. Since diffusion anisotropy is traced over the whole particle sizes, the MCM-41 particles under study do indeed appear, with reference to channel arrangement and orientation, as monocrystals. This distinguishes these specimens [173] from ordered mesoporous materials quite in general, which are commonly known to occur as polycrystals [176–178].

Electrochemical etching of (highly B-doped p-type) silicon has provided us with another, most beneficial access to ordered mesoporous materials [179–181]. The option of fabricating such materials with target-oriented pore networks has opened up a widespread field of applications, ranging from biosensing [182] to cancer therapy [183]. The possibility of a purposeful, space-dependent variation of the pore diameters, together with a variation in their connectivity, made such material also an excellent host system in fundamental research, including the investigation of freezing–melting and condensation–evaporation phase transitions under the conditions of spatial confinement [184–188].

In Fig. 15, electrochemically etched nanoporous silicon is used as a host material for illustrating the wide spectrum of diffusion-relevant phenomena that, in complex systems, might occur between the elementary steps of molecular propagation and long-range diffusion. It provides,

Fig. 15 PFG NMR measurement of diffusion anisotropy in nanoporous silicon and comparison with results of diffusion measurement by other techniques and simulation. **a** Network topology of the host material under study as attained by 3d electron tomography. **b** Schematics of a diffusion path within the pore space as provided by electron tomography, used for determination of diffusivities by dynamic Monte Carlo simulation (diamonds in (d)). **c** Simplified structure of the pore network, illustrating the occurrence of constrictions (“necks”) within and connections (“bridges”) between the channels with the respective probabilities p_{necks} and p_{bridges} . **d** Diffusivities $D = \langle z^2 \rangle / (2t)$ (normalized with the diffusivity D_0 for vanish-

ing diffusion path length and plotted as a function of displacement $s = \sqrt{\langle z^2 \rangle}$) as determined with cyclohexane as a probe molecule by QENS (squares, data coincide with the result of MD simulations), by PFG NMR with TEHOS (=tetrakis-2-ethylhexoxy-silane; triangles) and by dynamic Monte Carlo simulation, with the probabilities p_{necks} and p_{bridges} as indicated, (dotted (full) lines for diffusivities in (perpendicular to) channel direction). The broken line is the best fit of the PFG NMR data for diffusion perpendicular to the channel axes, corresponding with a time exponent $\kappa = 0.87$ in Eq. (48) for anomalous diffusion. From [102], Copyright 2007, Springer Nature

simultaneously, a survey over the potentials of PFG NMR and their limitation.

Following the evidence provided by 3d electron tomography (Fig. 15a) [189, 190] the pore network within the mesoporous silicon under study is, in first order approximation, represented by an array of parallel channels with statistically distributed constrictions (“necks”) and connections (“bridges”). Guest diffusion within this system may, correspondingly, be described by a diffusion tensor of rotational symmetry. In the schematics, shown in Fig. 15c, all constrictions and connections are assumed to be of identical geometry. Figure 15d provides a survey over the main elements of the diffusion tensor, i.e. of the diffusivities in axial and radial direction, as a function of the displacement $s = \sqrt{\langle z^2 \rangle}$ over which, depending on the applied technique, the diffusion paths have been followed.

The shortest displacements are traced by QENS (squares in Fig. 15d, [39, 191]). Here, diffusivities in axial and radial directions (full and open symbols) are seen to coincide, coinciding with also the diffusivity in the free liquid. This is the expected behavior for molecular displacements, small enough in comparison with the channel diameters. The same result is obtained in also molecular dynamics simulations. Spatial resolution of QENS is limited to a few nanometers and, hence, not sufficient for unambiguously tracing the effect of confinement.

Diamonds show the result of dynamic Monte Carlo simulation. They were performed by considering sequences of stochastic jumps between the lattice points within the free space of the host material as illustrated in Fig. 15b. The space architecture used in the simulations followed the predictions of 3d electron tomography (Fig. 15a). Now the diffusivities are observed to decrease with increasing displacements. This is, once again, in complete agreement with our understanding since the transport resistances “seen” by the molecules clearly increase with the distance covered. The effect, also expectedly, is much more pronounced for diffusion perpendicular than parallel to channel direction. Diffusion studies of this type are limited to displacements up to about 20 nm, as a consequence in the limitation in the size of the 3d replicas, which electron tomography are able fabricate.

One is no longer subject to these limitations in dynamic Monte Carlo simulations when the pore space as resulting from electron tomography so far used is replaced by the simplified pore space architecture as shown in Fig. 15c. Simulations have been performed with suitable implications on the geometry of the “constrictions” and “bridges”, which have been based on the geometries of both the pore space as available from electron tomography and the guest molecule (TEHOS). It has been selected due to its relatively low bulk-phase diffusivity ($D_0 = 7.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 20 °C), which makes it a sensitive guest molecule for probing pore spaces

over short distances. In this model, the probabilities p_{necks} and p_{bridges} for the occurrence of constrictions and bridges appear as the only free parameters.

The dotted and full lines in Fig. 15d show the best fit of these simulations to the PFG NMR data. PFG NMR measurements were performed over distances from about 80 nm to 1 μm perpendicular to and from 400 nm to 6 μm in channel direction. For normalization, the diffusivity D_0 for negligibly small displacements has been implied to coincide with that of the free liquid. With $p_{\text{necks}} = 0.35$ and with p_{bridges} equal to both 0.15 and 0.1, the simulations are seen to be in good agreement with the measurements for axial diffusion over the whole range of covered displacements. Similar coherence over the whole range of covered diffusion path lengths is not attained for diffusion in radial direction. Here, best fitting is attained with a decrease in the probability p_{bridges} for the occurrence of a bridge from 0.15 to 0.1 with increasing displacement.

We note that the initial parts of these curves (full and dotted lines in Fig. 15d) deviate from the predictions by Monte Carlo simulation in the pore replicas, notably on considering diffusion in channel direction. This, however, may be referred to the fact that the simulations have been based on the geometry as determined from a very tiny piece of the material, which may notably deviate from the average as probed in PFG NMR.

The observation that, with increasing displacements, fitting of the PFG NMR diffusivities perpendicular to the channel directions suggests a decrease in the occurrence of connecting bridges reflects a feature well known from the investigation of anomalous diffusion. It is known to occur under the influence of hierarchies of transport resistances so that confinement as “felt” by the molecules increases with increasing displacements. Under such conditions, deviating from the Einstein relation for “normal” diffusion, Eqs. (8, 9), the mean square displacement follows the relation [1, 192, 193]

$$\langle z^2(t) \rangle \propto t^\kappa, \quad (48)$$

with a time exponent $\kappa < 1$. Combining Eq. (48) with the definition of a scale-dependent diffusivity as provided by Eq. (21) yields

$$D \propto t^{\kappa-1} \propto \langle z^2(t) \rangle^{\frac{\kappa-1}{\kappa}} = s^{\frac{2(\kappa-1)}{\kappa}}. \quad (49)$$

Under the conditions of anomalous diffusion, dependence of the diffusivity on the covered diffusion path length is thus seen to also follow a power law. In Fig. 15d this scale dependence is shown with the broken straight line following the NMR diffusivities perpendicular to the channel direction. By equating the thus determined value of -0.3 with the analytical expression of the scale exponent as given with Eq. (49), the time exponent κ of the mean square

displacement is found to be 0.87 (instead of 1 as for normal diffusion).

4.6 Multicomponent diffusion

A straightforward option to selectively measure the diffusivities of the various components within a mixture is offered if the molecules under study accommodate different NMR active nuclei. As an example, [194] reports about PFG NMR measurements of the (long-range) diffusion of guest mixtures involving carbon monoxide, methane, and nitrogen within commercial 5A- and 13X-type zeolites based on the application of, respectively, ^{13}C , ^1H and ^{15}N NMR. Such measurements may be performed with one and the same sample.

If one is confined to using ^1H PFG NMR exclusively, measurements may be performed with mixtures, with only one of the components containing protons and all others in perdeuterated form. Such a procedure requires additional efforts with the preparation of more than one sample if the diffusivities of more than one component shall be studied, with the additional risk of differences between the different samples arising in the process of sample preparation.

Such complications are avoided in high-resolution PFG NMR measurement, where specific lines in the NMR spectra serve as a fingerprint of the given molecular species (just as in Fig. 10 the different lines indicate the location of the molecules). First high-resolution PFG NMR studies of two-component diffusion in zeolites were performed with ethane–ethene mixtures in zeolite NaX [195], where, at room temperature, the diffusivity of ethane was found to exceed the diffusivity of ethene by a factor of 5. This difference is a consequence of the strong interaction between ethene as the unsaturated hydrocarbon with the sodium cations, while for ethane as the saturated counterpart such a specific interaction (see also the discussion of Fig. 4b with the methane diffusivities in NaX) does not exist.

This finding is nicely corroborated in recent MAS PFG NMR measurements of single-component and mixture diffusion of a series of *n*-alkanes and *n*-alkenes in silicalite, the cation-free representative of MFI-type zeolites as shown in Fig. 16. Combination with MAS facilitated spectral resolution and allowed the unambiguous measurement of the diffusion attenuation of both components separated from each other. Given the similarity in the molecular sizes of the *n*-alkanes and *n*-alkenes, with their critical diameters notably below the pore diameters, mutual replacement of alkanes and alkenes is not expected to mean a great intervention in intrinsic dynamics. Moreover, differing from the situation in zeolite NaX, there are no specific interaction partners for the unsaturated hydrocarbons within silicalite. Correspondingly and in complete agreement with our expectation, diffusivities of *n*-alkanes and *n*-alkenes of one and

Fig. 16 Diffusivities of *n*-alkanes, *n*-alkenes and *n*-alkane/*n*-alkene mixtures in silicalite at 313 K for total loadings of and around one molecule per channel intersection (i.e., per 24 Si atoms or per ¼ unit cell). Reprinted from [217], with permission from Elsevier

Fig. 17 PFG NMR diffusivity data for *n*-octane in a fluid catalytic cracking (FCC) catalyst. Reprinted (adapted) with permission from [201] Copyright 2005 American Chemical Society

the same chain length are seen to, essentially, coincide for coinciding total loading under both single-component and mixture adsorption.

4.7 Diffusion and conversion

The gain in value-added products by chemical conversion in nanoporous catalysts can never be faster than allowed by the intrinsic rate of mass transfer. However, catalyst particles are, in general, of quite complex structure [190, 196–198]. This complicates the decision about the limiting processes of mass transfer.

For illustrating the potentials of PFG NMR in such a situation, Fig. 17 shows the results of scale-dependent PFG NMR diffusion measurements in a model catalyst as typically applied in fluid catalytic cracking FCC [199, 200]. The catalyst particles are small composite pellets of 50 to 100 μm diameter, formed from zeolite crystals (of notably zeolite Y) aggregated with a clay binder.

Figure 17 shows the results of the PFG NMR diffusion measurements with *n*-octane chosen as a probe molecule typical for the technical application of such catalysts. By an appropriate variation of both the observation time and the temperature, measurements could be performed with displacements both short enough for unambiguous measurement of intracrystalline diffusion and sufficiently long for tracing long-range (= intraparticle) diffusion [201]. Also shown is the extrapolation of the diffusivity data into the temperature range around 600 $^{\circ}\text{C}$ of their technical application.

In Fig. 17, the diffusivity within the individual crystallites, as extrapolated to the temperature of 600 $^{\circ}\text{C}$, is seen to be exceeded by about two orders of magnitude by the “long-range” diffusivity through the catalyst particle—just as also the size of the zeolite crystallites is exceeded by the size of the particles by about two orders of magnitude. Since, according to Eq. (29), the time constants of adsorption and release scale with the square of the particle sizes but linearly with the (reciprocal value of the) diffusivities, mass transfer is, hence, expected to be controlled by mainly long-range (= intraparticle) rather than by intracrystalline diffusion.

This expectation is confirmed by Fig. 18, which provides a correlation between the long-range diffusivities and the performance for four catalyst particles prepared with identical zeolite crystals but under varying conditions during

Fig. 18 Correlation between intraparticle diffusivities and catalytic performance. Measurements have been performed with catalyst particles produced under different fabrication conditions, but with identical zeolite crystallites. Reprinted from [218], with permission from Elsevier

pellet formation. Thus, the purposefully attained differences in intraparticle (= long-range) diffusivities are seen to nicely correlate with the particle performance under reaction conditions, with the highest conversion rate observed for the largest intraparticle diffusivity.

In addition to measuring the diffusivities of the various components involved in a chemical reaction, NMR spectroscopy is as well able to monitor the increase and decrease in the respective concentrations as exemplified in Fig. 2 with an uptake study. In Fig. 19, these options have been exploited for recording the conversion of isopropanol to propene in zeolite NaX, in parallel with the measurement of the diffusivities of both components [202]. Application of ^{13}C NMR allowed an easy distinction between the two components.

The formation of propene molecules and the increase in their concentration is seen to be accompanied by an increase in their diffusivity. Such a behavior is most likely to be referred to the decrease in the diffusional resistance experienced by the propene molecules by encounters with

Fig. 19 Conversion of isopropanol (bottom, full symbols) to propene (top, open symbols) in zeolite NaX at 473 K. The relative amounts (squares) and diffusivities (circles) are plotted as a function of the reaction time. Reprinted from [202], with permission from Elsevier

the bulkier isopropane molecules, whose concentration decreases in the course of the reaction.

Measurement of the diffusivities and relative concentrations of the molecular species involved requires time spans (according to Fig. 19 from minutes up to hours), which exceed the mean life time of the guest molecules within the individual zeolite crystallites as following from Eq. (29) by several orders of magnitude. For measurements as shown in Fig. 19, catalytic conversion must therefore be expected to proceed under reaction limitation, i.e. with uniform concentrations all over the sample. More detailed information, with the option of measuring the evolution of concentration profiles over the sample, is provided by the application of magnetic resonance tomography (MRT) [5, 6, 203, 204], see also (Price et al. in this issue). However, starting with already the very first attempts of such studies in uptake measurements with beds of zeolite crystallites [205], see also Sect. 12.1.5 in [1], recording of the evolution of concentration profiles within the individual crystallites has remained a challenging goal to this day. Microimaging [168, 169] with spatial–temporal resolution into the range of micrometers and seconds offers an alternative, paving the route towards even the one-shot measurement of the effectiveness factor of chemical reactions within porous catalyst particles [206–208].

5 Conclusions

PFG NMR has been shown to provide a wealth of information about the movement of the guest molecules in nanoporous host systems. This information is contained in the probability distribution of molecular displacement, which is the maximum information attainable, given the stochastic character of molecular motion quite in general. The time spans of observation are determined by the nuclear magnetic relaxation properties of the host–guest system under study and range from milliseconds to seconds. Typical distances, over which molecular pathways may be followed, are between hundreds of nanometers up to tens of micrometers. Over such dimensions, as a rule, diffusion paths must be covered for gaining unambiguous information about the rate of mass transfer in the individual crystallites, i.e., about the intracrystalline diffusivities. In composed systems, information is as well attained on possible transport-related hierarchies by a purposeful variation of the observation time and of, hence, the displacements. Such hierarchies may give rise to both diffusivity enhancement by “transport” pores and diffusivity reduction by additional transport resistances. All these measurements may be performed with the pristine material just as during its technical use, as a function of the conditions of its employment and the time on stream.

The extent of information accessible by PFG NMR depends on certain preconditions. This is, as a matter of course, the case with also any other measuring techniques. These preconditions may, as a rule, contain a number of traps giving rise to incorrect conclusions, if not properly taken into account. This concerns, among others, the influence of nuclear magnetic relaxation, which in complex systems may differently affect the signal intensity attributed to different diffusional regimes, and mismatches in the gradient pulse intensities. Fortunately, PFG NMR offers numerous options for ensuring the validity of the attained results. They include the ability of PFG NMR of recording diffusion path lengths. They may be compared with, e.g., the diameters of the individual crystallites known from microscopy as an internal standard, serving as a check of the consistency of the attained diffusion data.

PFG NMR data may, moreover, be compared with the outcome of other techniques of diffusion measurement. Many of them are truly complementary to PFG NMR. This refers, e.g., to the information by quasi-elastic neutron scattering (QENS) as another technique of diffusion measurement considering ensemble averages under equilibrium conditions. Differing from PFG NMR, however, typical time and space scales of QENS are within the range of nanometers and (hundreds of) picoseconds and, thus, by various orders of magnitude smaller than in PFG NMR. Similar space and time scales as observed in PFG NMR are in the focus of single particle tracking (SPT). However, while SPT is following the movement of single molecules, the numbers of molecules observed in PFG NMR are—with something like 10^{20} —astronomically large. The requirement of using such relatively large amounts of guest molecules may, in some applications, become a disadvantage of PFG NMR. In such cases, hyperpolarization of the guest molecules under study helps to overcome these limitations.

The message of PFG NMR on mass transfer is in the most direct way reflected by the Einstein equation of diffusion, correlating the mean square displacement of the molecules under study with the self- or tracer diffusivity. It is, however, worth emphasizing that the definition of the self- or tracer diffusivity may equivalently be based on Fick’s first and second laws, by considering the fluxes of labeled molecules within their unlabeled surroundings. From this perspective, the assessment of intrinsic mass transfer as provided by PFG NMR is seen to be of immediate relevance for material improvement aiming, as a rule, at an enhancement of molecular fluxes within the sample. In this respect, PFG NMR nicely complements the information of classical uptake and release experiments with their numerous modifications and refinements. While these techniques consider, as a rule, net effects in mass transfer as averages over the whole sample, PFG NMR may help in localizing the origin

of these effects within the sample, as a primary prerequisite for a knowledge-based improvement of their performance.

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