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The Potentials of Pulsed Field Gradient NMR for Investigation of Porous Media

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Abstract. PFG NMR self-diffusion studies provide information on the translational mobility of fluid molecules. Since in porous media the diffusion path of fluid molecules in the pore space is affected by interaction with the pore wall, PFG NMR measurements are sensitive to structural peculiarities of the confining porous medium. The pore space properties which can be investigated depend on length scales set by the PFG NMR experiment in respect to the typical size of the structural feature studied. Based upon these length scales, an interpretation pattern for PFG NMR self-diffusion studies in porous media is given. PFG NMR self-diffusion studies in macro- and microporous systems such as sedimentary rocks and zeolite crystallites, respectively, are reviewed.

Keywords: nuclear magnetic resonance, self-diffusion, pore structure, zeolite, sedimentary rock

1. Introduction

The transport of fluids through the pore space is an essential property of porous media. It is directly influenced by the interaction between the pore fluid and the pore wall and determines effects of the porous medium on its environment and its application in technical processes, respectively. Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) represents a versatile tool to study transport phenomena of fluids in porous media (Kärger et al., 1988; Callaghan, 1991; Kimmich, 1997). The continued interest in this experimental technique which has been applied first by Stejeskal and Tanner (1965) is based on the fact that PFG NMR measurements may reveal structural properties of the porous medium through the measured molecular transport phenomena and that the technique is to a large extend independent of the porous medium, since NMR measurements of the pore fluids are performed. Furthermore, the remarkable property of PFG NMR that transport under equilibrium conditions, i.e., the self-diffusion of the molecules, can be monitored may provide unique insights into the fundamentals of interactions between the pore fluid and the porous medium.

In this article, we represent the principles of self-diffusion studies and simple interpretation pattern for investigation of structural peculiarities of porous media by PFG NMR. Investigations of restricted self-diffusion of fluids in macropores of sedimentary rocks and assemblies of zeolites are considered as examples for PFG NMR measurements, yielding structural parameters of these macropore systems. PFG NMR measurements of intracrystalline self-diffusion of sorbate molecules in microporous zeolitic adsorbents, which are used to characterise the adsorbate/adsorbent interactions, are reviewed.

2. Principle of Self-Diffusion Studies by Pulsed Field Gradient NMR

2.1. Fundamentals of the PFG NMR Method

In a fluid system under equilibrium conditions, molecular transport is controlled by the Brownian (thermal) motion. Under such conditions, no net particle flux is observed. However, in a spatially dependent concentration $c^*(\vec{r}, t)$ of labelled particles in an environment of unlabelled but otherwise identical particles, the Brownian molecular motion will cause the concentration gradient grad $c^*(\vec{r}, t)$ to vanish with time. This process is described by the diffusion equation

$$\frac{\partial c^*(\vec{r}, t)}{\partial t} = D\nabla c^*(\vec{r}, t) \qquad (1)$$

where D is the self-diffusivity (or self-diffusion coefficient). The larger the value of D, the faster is the decay of the original concentration gradient. For bulk fluids or gases, the value of D is an inherent property of the molecules. Clearly, if a fluid is contained in confined geometries, e.g., pores of porous media, the decay of an originally introduced spatially dependent concentration $c^*(\vec{r}, t = 0)$, which determines the initial condition for Eq. (1), is influenced by the walls of the porous medium. Measuring the rate of self-diffusion under such conditions does in turn provide information about the pore architecture and of the nature of the interaction between the molecules and the pore surface.

In conventional self-diffusion measurements, labelled particles, so-called tracer molecules, are introduced into the studied system from outside. The time and/or space dependence of the concentration of these tracer molecules is monitored experimentally. The self-diffusivity D is obtained by fitting these experimental data to the solution of Eq. (1) for the given initial and boundary conditions of the system.

The introduction of conventional tracer molecules in porous systems is cumbersome, if the initial concentration $c^*(\vec{r}, t = 0)$ should exhibit a significant spatial dependence on length scales comparable with or much smaller then the typical length scale of the porous medium (e.g., the pore radius). Such situation is necessary in order to study the influence of the pore wall on the self-diffusivity and the inherent self-diffusivity of the molecules within the pore system, respectively.

Nuclear magnetic resonance, in combination with an additional space- and time-dependent magnetic field, the so-called pulsed field gradients (PFG), offers a unique possibility to generate labelled molecules and to detect their mean displacements due to any transport process. The labelling is simply caused by the Larmor precession ω of nuclear spins associated with the molecules. In PFG NMR, the total magnetic field is given by the superposition of a strong, time-independent homogeneous component B_0, which is assumed to be aligned parallel to the z-coordinate of the laboratory frame of reference, and an additional space- and time-dependent magnetic field with a field gradient $\vec{g}(t)$ of this component. If—for simplicity—we assume that the field gradient is also oriented parallel to the z-direction $\vec{g}(t) = (0, 0, g(t))$, the Larmor frequency $\omega(z, t)$ can be written as

$$\omega(z, t) = -\gamma \cdot (B_0 + g(t)z), \tag{2}$$

where γ is the magnetogyric ratio of the nuclei under investigation. In such a magnetic field, the complex magnetisation density $m(\vec{r}, t)$, which represents the spatial distribution of the observed transverse nuclear magnetisation $M(t)$ as well as its evolution in time due to the Larmor precession and NMR relaxation, gets a well-defined additional z-dependence

$$m'(\vec{r}, t) = m(\vec{r}, t) \cdot \exp\left(-i\gamma z \int_0^t g(t')\, dt'\right). \tag{3}$$

The real and imaginary parts of $m'(\vec{r}, t)$ denote the x- and y-components of the magnetisation density in the PFG NMR experiment, respectively. The initial magnetisation density $m(\vec{r}, t = 0)$ is proportional to the spatial distribution of the observed nuclear spins and corresponds to the local distribution of the fluid-filled pore space of porous media.

If the magnetic field gradient $g(t)$ is turned off after a time δ, the magnetisation density is found to be embossed with a z-dependent phase factor $\exp(-i\gamma\delta gz)$

$$\begin{aligned} m'(\vec{r}, t) &= m(\vec{r}, t) \cdot \exp(-i\gamma g\delta z) \\ &= m(\vec{r}, t) \cdot [\cos(\gamma\delta gz) + i \cdot \sin(\gamma\delta gz)]. \end{aligned} \tag{4}$$

This phase factor represents the labelling of the observed molecules in PFG NMR diffusion studies. As illustrated by the second part of Eq. (4), it is a continuous twisting of the magnetisation density $m(\vec{r}, t)$ along the direction of the pulsed field gradient with a period $(\gamma\delta g)^{-1}$ in space. With the notation $k = \gamma\delta g$ one may introduce a length scale $l_{\mathrm{PFG}} = (2k)^{-1}$ over which a significant change in the phase factor and, hence, the labelling of the diffusing molecules is achieved. l_{PFG} determines an estimate for the distance over which diffusion processes of the labelled molecules will cause significant disturbance of the originally introduced spatial distribution of phases (Eq. (4)).

The self-diffusion process of the observed molecules smears out the originally present spatial distribution of phases. The measurement of this phase distribution after an observation time Δ would allow the evaluation of the self-diffusivity of the molecules. In PFG NMR, the observation of the spatial phase distribution after the time Δ is realised by a second magnetic field gradient pulse, which has the task to refocus the spatial phase distribution introduced by the first one. However, due to the displacements of the molecules caused by the self-diffusion, refocusation is not complete. Hence, the observed NMR signal $M(t)$, which follows from the integration of the magnetisation density over the sample volume, is reduced by the factor

$$\psi(k, \Delta) = \int P(z - z', \Delta) \cdot e^{ik(z-z')} d(z - z') \quad (5)$$

in comparison with a measurement without pulsed field gradients. In Eq. (5), $P(z - z', \Delta)$ denotes the probability density that a molecule within the time interval Δ was displaced by $z - z'$. It is the averaged propagator which can be calculated for the system studied by averaging the solution of the diffusion Eq. (1) over all possible starting positions. Equation (5) shows that the averaged propagator can be measured directly by PFG NMR, since it is simply given by the inverse Fourier transform of the NMR signal attenuation $\psi(k, \Delta)$ (Kärger and Heink, 1983)

$$P(z - z', \Delta) = \frac{1}{2\pi} \int \psi(k, \Delta) \cdot e^{-ik(z-z')} dk. \quad (6)$$

Equations (5) and (6) are the fundamental relations for the evaluation of PFG NMR studies with bulk fluids as well as with fluids in porous media. Due to the restriction of self-diffusion in porous media, $P(z - z', \Delta)$ contains information of the geometrical features of the pore space affecting the molecular motion of the pore fluids. Thus, the analysis of $P(z - z', \Delta)$ and $\psi(k, \Delta)$, respectively, must reveal these geometric properties. Besides the measurement of the inherent self-diffusivity of fluids in porous media, it is this investigation of pore geometries which is the key question of current PFG NMR studies (Mitra and Sen, 1992; Sen and Hürliman, 1994; Callaghan, 1995; Bär et al., 1996).

2.2. *Interpretation Pattern for PFG NMR Investigation in Porous Media*

In principle, the evaluation of fluid diffusion processes in a porous medium observed by PFG NMR using the relations (5) and (6) can only be approached by solving the diffusion equation for the considered system under consideration of the initial conditions for the magnetisation density generated by the spin distribution and pulsed field gradients (Eq. (4)). While for simple pore geometries such calculations were successful, yielding exact analytical expressions for $\psi(k, \Delta)$ (see e.g., Callaghan, 1991), in heterogeneous porous systems, consisting of irregular shaped pores an/or exhibiting a distribution of pore sizes, such calculations are not possible or at least very difficult to be carried out.

However, the feature of PFG NMR that the initial conditions for the magnetisation density and the observation time can be chosen by the NMR pulse sequence (g, δ, Δ) offers the opportunity to design experimental conditions, where the measurements are only sensitive for certain features of the pore geometry. In order to estimate possible effects of the pore geometry on the diffusion path and, thus, on the PFG NMR measurements of the diffusion process, we introduce three characteristic lengths, defined by the experimental conditions and the system studied.

The first length is l_{PFG} as introduced above. It is the length over which the phase factor of the magnetisation density changes significantly and represents an estimate for the length scale over which diffusion processes must occur in order to cause significant changes in the spin echo attenuation. The power of PFG NMR, especially for investigation of porous systems, is based on the fact that l_{PFG} and k can be easily controlled by choosing the appropriate values for the pulsed field gradient intensity g and width δ, respectively. l_{PFG} values of less then 0.1 μm (requires, e.g., for ^{1}H NMR $\delta \geq 1$ ms and $g \geq 20$ T/m) can be achieved with current state of the art of PFG NMR spectrometers (Kärger et al., 1995).

The second characteristic length is the root mean square (rms.) displacement $l_{\mathrm{Diff}} = \langle z^2(\Delta)\rangle^{0.5} = \sqrt{2D\Delta}$ of the observed molecules. It depends on the observation time Δ in the PFG NMR experiment and the diffusivity of the molecules, which in general will be influenced by the pore space. The properties of the pore structure enter into these considerations via the third characteristic length, the mean pore radius $\langle R\rangle$.

The relation between these three characteristic length scales establishes the pore space and the diffusion parameter which can be determined by PFG NMR studies. Besides the trivial case $l_{\mathrm{PFG}} \gg l_{\mathrm{Diff}}$ where no attenuation of the NMR signal due to diffusion is observed, we consider the following 4 special cases, which all require that l_{PFG} is in the same order of magnitude as l_{Diff} in order to cause significant spin echo attenuations:

2.2.1. Unrestricted, Free Diffusion Within the Pore Space, $l_{\mathrm{Diff}} \ll \langle R\rangle$. For root mean square displacements much smaller than the pore radius, most diffusing molecules do not encounter the pore wall. The self-diffusion for the vast majority of molecules is unrestricted like in the bulk fluid and the mean square displacement obeys the Einstein equation

$$\langle z^2(\Delta)\rangle = 2D\Delta \tag{7}$$

which is equivalent to the averaged propagator being a Gaussian function

$$P(z - z', \Delta) = \frac{1}{\sqrt{4\pi D\Delta}} e^{-\frac{(z-z')^2}{4D\Delta}}. \tag{8}$$

Inserting Eq. (8) into the expression (5) yields a single-exponential dependence of the spin-echo attenuation on the square of the applied PFG parameter δ and $g\,(k = \gamma\delta g)$ (see e.g., Stejeskal and Tanner, 1965; Kärger et al., 1988; Callaghan, 1991)

$$\psi(k, \Delta) = e^{-k^2 D\Delta}. \tag{9}$$

By measuring ψ as function of δg and Δ, the observation-time dependence of the self- diffusivity or the mean square displacement can be derived from the slope of the ln ψ vs. k^2 representation. The pattern for unrestricted, bulk diffusion in the pore system is a linear increase of $\langle z^2(\Delta)\rangle$ with Δ for short observation times. Short observation times mean $\Delta \ll \frac{\langle R\rangle^2}{2D}$. Only in this mode, the bulk diffusivity of a fluid in the pores may be obtained from PFG NMR measurements. Under this condition, the diffusivity does not reflect any properties of the confining pore geometry.

2.2.2. Diffusion in Well Connected Pores, $l_{\mathrm{Diff}} \gg \langle R\rangle$. The rms displacement can only exceed the typical pore size of the porous medium if the individual pores are well connected with each other. However, compared with the diffusion process in the bulk fluid, the matrix of the porous medium excludes certain diffusion path ways. Consequently, for the same observation times, the actual rms displacement in the pore space is smaller than in the bulk fluid. This reduces the diffusivity in the pore space D_{p} in comparison with the bulk diffusivity D_{o} by a tortuosity factor τ (Bear, 1972)

$$\tau = \frac{D_{\mathrm{o}}}{D_{\mathrm{p}}}. \tag{10}$$

The tortuosity factor is a pure geometric property of the porous medium. In PFG NMR, the condition $l_{\mathrm{Diff}} \gg \langle R\rangle$ can be fulfilled using long observation times $\Delta \gg \frac{\langle R\rangle^2}{2D}$. In this mode, all fluid molecules undergo interaction with the pore wall. The Einstein equation, the averaged propagator and, consequently, the spin-echo attenuation obey the same forms as Eqs. (7–9) with the reduced diffusivity D_{p} instead of D_{o}. Thus, PFG NMR diffusion measurements at long observation times reveal the tortuosity τ of the pore space via Eq. (10) if, from separate measurements, the bulk diffusivity of the pore fluid is known.

In microporous adsorbents such as zeolites, the pore radius is often in the range of a few tenths of a nanometer and by about three orders of magnitude less than the currently available minimum length scale l_{PFG} over which diffusion can be monitored by PFG NMR. Therefore, PFG NMR studies of fluid molecules adsorbed in the micropores are only able to detect diffusion processes causing rms displacements much larger than the micropore radius. Since the properties of the adsorbate are strongly influenced by the interaction of the adsorbate molecules with the internal surface of the micropores, the obtained diffusivities reflect this adsorbate/adsorbent interaction rather than the pure geometrical restrictions described by the tortuosity of the micropores (Kärger and Ruthven, 1992).

2.2.3. Restricted Diffusion in Isolated Pores, $l_{\mathrm{Diff}} \approx \langle R\rangle$, $l_{\mathrm{PFG}} > \langle R\rangle$. If the pore space consists of isolated pores, the rms displacement is limited by the pore size. At infinite observation times, it becomes independent of time and is exclusively determined by the pore size. The apparent self-diffusivity, which is also for the restricted diffusion regime defined via Eq. (7), becomes time-dependent, showing an inverse proportionality to the observation time. In the restricted diffusion mode at long observation times the end position of a molecule in a pore does not depend on the starting position in the same pore. Consequently, the spatial distribution of phases introduced by the PFG NMR experiment is averaged due to the diffusion for each pore to the averaged initial phase. The resulting spin echo attenuation is found to be independent of observation time. For small PFG intensities ($l_{\mathrm{PFG}} > \langle R\rangle$), the overall z-dependence of the spatial phase distribution (Eq. (4)) is maintained by the restricted diffusion process. Its amplitude is just slightly reduced, which results in only a slight spin-echo attenuation. Under such conditions the spin-echo attenuation is given by

$$\psi(k) = \exp\left[-k^2 \frac{\langle z^2(\Delta = \infty)\rangle}{2}\right] \tag{11}$$

which allows the direct determination of the maximum possible value of the mean square displacement in the pore space. $\langle z^2(\Delta = \infty)\rangle$ depends on pore shape and pore size. For simple geometries analytical expressions for $\langle z^2(\Delta = \infty)\rangle$ have been derived. As an example, for the restricted diffusion between parallel plates of distance a perpendicular to the field gradient, one obtains (see e.g., Kärger et al., 1988; Callaghan, 1991)

$$\langle z^2(\infty)\rangle_{\perp P} = \frac{a^2}{6} \tag{12}$$

and for diffusion within spherical pores of radius R_s

$$\langle z^2(\infty)\rangle_s = \frac{2R_s^2}{5}. \tag{13}$$

The corresponding time dependencies of the apparent diffusivities, derived from Eqs. (12) and (13) via Eq. (7) are

$$D_{\perp P}(\Delta) = \frac{a^2}{12\Delta} \tag{14}$$

for diffusion between the plates and

$$D_s(\Delta) = \frac{R_s^2}{5\Delta} \tag{15}$$

for diffusion within the sphere, respectively.

Thus, if in a PFG NMR measurement a spin echo attenuation is observed and it is found to be independent of observation time, the pore size of the porous medium can be derived from the spin echo attenuation using Eqs. (11–15) and similar equations for the corresponding pore shape, respectively.

2.2.4. Restricted Diffusion on the Pore Surface, $l_{\mathrm{Diff}} < \langle R\rangle$, $l_{\mathrm{PFG}} > l_{\mathrm{Diff}}$. For short observation times, during which the rms displacement l_{Diff} is still significantly smaller than the pore radius, the amount of molecules hindered in their diffusion path is proportional to the surface S_{P} of the pore space. If the pore surface is assumed to be non-fractal, $S_{\mathrm{P}}\sqrt{D_0\Delta}$ represents an estimate for the volume of fluid molecules which experiences the pore wall during Δ. With V_{P} denoting the total pore volume, the fraction of hindered molecules is given by $\sqrt{D_0\Delta}\frac{S_{\mathrm{P}}}{V_{\mathrm{P}}}$ (Latour et al., 1993). This quantity depends on the pore surface-to-volume ratio. If this fraction is negligible compared to the total amount of molecules, and high pulsed field gradients are applied unrestricted diffusion will be observed (as described in section 2.2.1).

In general, the restriction of a fraction of the molecules at the pore walls will cause the overall effective diffusivity to decrease with time. For not too long times Δ, the time dependence of the diffusivity $D(\Delta)$ in the pore space is given by (Latour et al., 1993; Mitra et al., 1993)

$$\frac{D(\Delta)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}} \cdot \frac{S_{\mathrm{P}}}{V_{\mathrm{P}}}\sqrt{D_0\Delta} + \Re(D_0\Delta) \tag{16}$$

were $\Re(D_0\Delta)$ are terms of higher order in $\sqrt{D_0\Delta}$ which can be neglected if one considers only the short time behaviour of $D(\Delta)$. D_{o} denotes the unrestricted diffusivity of the fluid in the pore space. The leading term in Eq. (16) contains the surface-to-volume ratio of the pore space. This means, deviations from constant diffusivities at not too long observation times are in first order proportional to the surface-to-volume ratio of the confining pores.

$D(\Delta)$ is the averaged diffusivity of all molecules. It can be measured by PFG NMR as long as l_{PFG} exceeds l_{Diff}, which corresponds to small initial spin echo attenuations observed for small values of δg. If the observed diffusivity decreases with the square root of time, the surface-to-volume ratio of the pore space and the diffusivity D_{o} can be derived from such PFG NMR measurements using Eq. (16).

3. Investigation of Diffusion in Macropores

3.1. *Examples from Petrophysics*

The translational mobility of fluids in porous rocks and sediments is an essential property determining the effects of the fluid-filled geological formation on its environment. Trapping and release of pore fluids by the rock depend on transport through the pore space. Therefore, they are macroscopic geological properties of large economical and environmental impact which, at last, have their origin in the interaction between the fluid molecules and the pore space. Being sensitive to pore space properties via the self-diffusion of the pore fluids as demonstrated above, PFG NMR represents a non-destructive method for the investigation of rock pore structures and their influence on the fluid transport. In this respect, PFG NMR must be considered as a unique petrophysical tool. After a brief introduction to NMR relaxometry which is used in petrophysics to obtain pore size distribution of a porous rock from the multiexponential relaxation behaviour of the pore fluids (Straley et al., 1991; Kenyon, 1992; Latour et al., 1995), this section reviews examples of petrophysical PFG NMR measurements.

3.1.1. NMR Relaxometry in Porous Rocks. The pores of sedimentary rocks may exhibit a wide distribution of pore sizes (from less than 10^{-6} m up to more than 10^{-3} m) and have, generally, irregular shapes. The internal pore surface is usually heterogeneous, formed by different minerals and clays during the diagenesis of the rock. From the NMR point of view, fluids occupying such pores do in fact behave fluid-like, i.e., their transverse relaxation time (T_2) is in general not much smaller than their longitudinal relaxation time (T_1) (Kleinberg et al., 1993). The NMR relaxation is governed by the interaction of the fluid molecules with the pore wall, which for not too large pores yields a proportionality between the relaxation time of the fluid in a pore and the volume-to-surface ratio $V_\mathrm{p}/S_\mathrm{p}$ and the typical size R_p of that pore, respectively (Brownstein and Tarr, 1979; Kenyon, 1992),

$$T_{1,2} = \frac{1}{\rho_{1,2}}\frac{V_\mathrm{p}}{S_\mathrm{p}} \propto \frac{1}{\rho_{1,2}}R_\mathrm{p} \quad \text{with} \quad \frac{V_\mathrm{p}}{S_\mathrm{p}} \propto R_\mathrm{p}. \tag{17}$$

$\rho_{1,2}$ denotes the surface relaxivity for longitudinal and transverse relaxation, respectively. Not too large pores are pores, where the individual fluid molecules encounter many collisions with the pore wall before they lose their contribution to the NMR signal. In this case, known as the fast-diffusion regime in NMR relaxometry of porous media (Brownstein and Tarr, 1979), the rate of molecular transport to the surface by self-diffusion is much larger than the relaxation at the surface. The opposite case is the diffusion-limited regime.

In the fast-diffusion regime, multi-exponential relaxation as usually observed for fluids in rocks, is caused by the distribution of pore sizes. Therefore, relaxation time distributions $p(T_{1,2})$ as obtained from T_1 or T_2 measurements, may be interpreted as pore size distribution $p(R_\mathrm{p})$ (Gallegos and Smith, 1988; Straley et al., 1991; Kenyon, 1992). However, the surface relaxivity which is needed to transform the relaxation times into absolute values for the pore size is usually unknown and must be determined by a separate measurement of $V_\mathrm{p}/S_\mathrm{p}$ or R_p (e.g., by nitrogen adsorption or mercury porosimtry).

3.1.2. Determination of Rock Properties from Restricted Diffusion Behaviour. It has first been recognised by Lipsicas et al. (1986) that the concept of the fast- diffusion regime used to describe the relaxation behaviour of fluids in rocks coincides with the restricted diffusion regime in PFG NMR self-diffusion studies. Therefore, the total NMR signal amplitude, measured with PFG NMR, decays by two competing mechanisms acting independently: These are (i) the dephasing of the signal due to the pulsed field gradients and (ii) the surface relaxation. The signal from the largest pores is mainly dephased by the pulsed field gradients whereas the signal from the smallest pores relaxes by surface relaxation. Thus, for a given pulsed field gradient intensity $g\delta$ pores with an intermediate pore size will dominate the NMR signal. Assuming restricted diffusion in spherical pores of radius a (Eqs. (13) and (15)), Lipsicas et al. found the dominant contribution to the signal at long observation times to be

$$-\ln\frac{M(t)}{M(t=0)} \propto \frac{1}{T_{2b}} + \left(\frac{27}{20}\rho_2^2\gamma^2\delta^2 g^2 t^2\right)^{1/3} \tag{18}$$

for the fast-diffusion regime (small pores) and

$$-\ln\frac{M(t)}{M(t=0)} \propto \frac{1}{T_{2b}} + \left(\frac{4}{5}\gamma^2\delta^2 g^2 Dt\right)^{1/2} \tag{19}$$

for the diffusion-limited regime (large pores). They proposed to use the distinct power laws to estimate the regime, and to determine the surface relaxivity, if one is in the fast-diffusion regime. Experimentally, the authors found for a dolomite rock saturated with aqueous nickel nitrate solution (1000 ppm Ni^{2+}) a scaling of the spin echo amplitude with $(g\delta)^{2/3}$ corresponding to the fast-diffusion regime (Fig. 1). The surface relaxivity was determined to be $6.7 \cdot 10^{-4}$ m/s and the sizes of the rock pores were found to be in the range of 15–27 μm, which agreed with the range of pore sizes indicated from mercury porosimetry experiments and electron micrographs of thin sections.

As the example shown in Fig. 2, most PFG NMR spin echo attenuations published for fluids in rocks exhibit a pattern deviating significantly from the single-exponential behaviour given by Eq. (9) or (11) (see e.g., Callaghan et al., 1991; Fordham et al., 1994 and Stallmach et al., 1996). Although it is commonly recognised that this behaviour is caused by the different geometrical restrictions that the fluid molecules encounter in the heterogeneous pore space, there are a number of different models for extracting relevant petrophysical parameters.

In the simplest of these models Stallmach and Thomann (1996) and Stallmach et al. (1996) assumed a two-region diffusion model, in which the spin-echo attenuation is given by the superposition of two

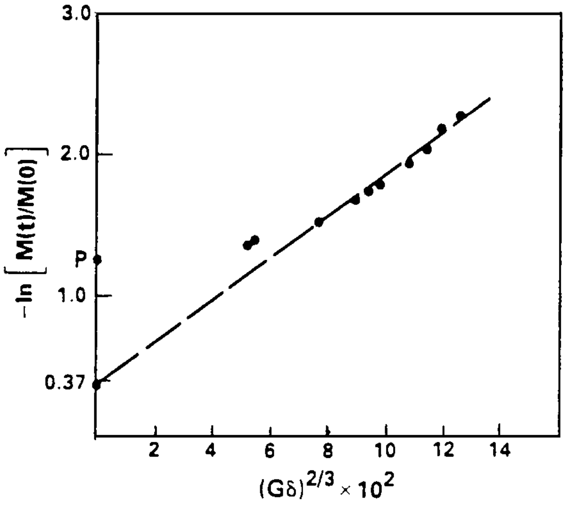

Figure 1. Plot of $-\ln[M(t)/M(0)]$ vs. $(G\delta)^{2/3}$ for PFG NMR measurements for a dolomite plug saturated with aqueous nickel nitrate solution (from Lipsicas et al., 1988). The data show the power law behaviour, predicted by Eq. (18) for the fast-diffusion regime. From the slope of the graph the surface relaxivity ρ_2 was determined to be $6.7 \cdot 10^{-4}$ m/s. The extrapolation to zero gradient yields the relaxation time of the aqueous nickel nitrate solution $T_{2b} = 76$ ms.

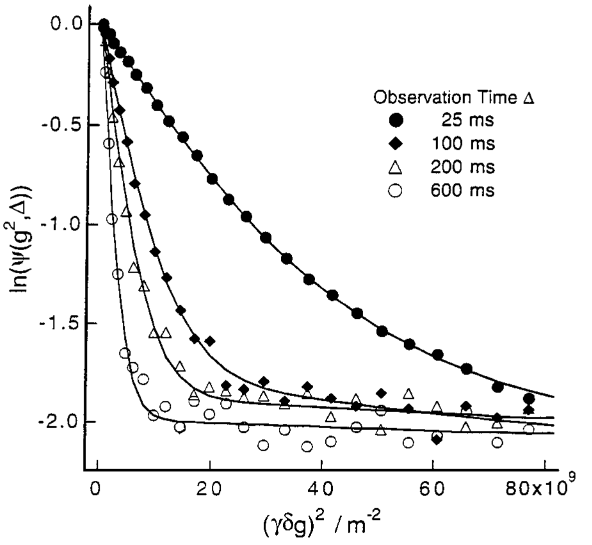

Figure 2. PFG NMR spin echo attenuations for a water-saturated Marsing sandstone in dependence on the observation time Δ (from Stallmach et al., 1996). The fit of the two-region diffusion model (Eq. (20)) to the measured data points which is given by the solid lines shows good agreement with the observed shape of the spin-echo attenuations for all observation times.

exponentials

$$\psi(k,\Delta) = p_1 e^{-k^2 D_1 \Delta} + p_2 e^{-k^2 D_2 \Delta} \quad \text{with} \quad p_1 + p_2 = 1, \qquad (20)$$

were p_i and $D_i (i = 1, 2)$ are the relative amounts of fluid molecules and their diffusivities in the individual sub-regions, respectively. This model was found to satisfactorily fit the experimental data over the whole range of pulsed field gradient intensity and observation time (Fig. 2). On the example of a Marsing sandstone, the authors demonstrate that the mean square displacement of the slow-diffusing component is constant over the whole range of observation time while it increases with time for the fast-diffusing component. Thus, the slow-diffusing component shows the pattern for restricted diffusion. Assuming spherical pore geometry a pore radius of about 8 μm was obtained. The amount of slow-diffusing molecules was found to agree for a number of different sandstones reasonably well with the amount of non-movable fluid volumes (the so-called bound volume irreducible *BVI* which is the capillary-bound fluid fraction). The authors proposed the bi-exponential fit of PFG NMR measurements as method for non-destructive determination of movable (the fast-diffusing) and non-movable (the slow-diffusing) fluid fractions in porous rocks (Stallmach and Thomann, 1996). It has the advantage of requiring no exchange or displacement of fluids as necessary for centrifugation or mercury porosimetry.

The restricted diffusion and return-to-the-origin (RTO) method of Mitra et al. (1995) is just a more general and complex approach to the same petrophysical phenomenon, that a certain fraction of the fluid molecules in a porous rock is strongly hindered in its translational mobility in small capillary-like pores. The authors show, that PFG NMR data can be used to calculate the probability that diffusing molecules will return to (or have not left) the vicinity of their initial position after a given diffusion time. In order to do this, the quantity $F(\Delta, k_{\max})$ is introduced as the fraction of molecules that after a time Δ are still within a distance of $1/k_{\max}$ of their initial location. $F(\Delta, k_{\max})$ can be directly obtained from the PFG NMR spin echo attenuation by

$$F(\Delta, k_{\max}) = \frac{3}{k_{\max}^3} \int_0^{k_{\max}} \psi(k,\Delta) k^2 \, dk. \qquad (21)$$

$k_{\max}$ is defined by the pulsed field gradient width and intensity applied. The authors present PFG NMR measurements of three different sedimentary rocks and calculated the quantity $F(\Delta, k_{\max})$ directly from the spin echo attenuations. For the largest observation time used ($\Delta = 492$ ms), the comparison of $F(\Delta, k_{\max})$ with the corresponding value of free-diffusing water illuminated the effect of the pore space on the diffusion process. In general, at large $k_{\max}$ (corresponding to small distances) the rock cores in which diffusion of water is most restricted, exhibit the largest probability to return to the origin. According to our knowledge, it has not yet been realised, that the RTO probability at long observation times should also be related to the non-movable fluid fraction as shown above.

In another approach to interpret PFG NMR data of water-saturated porous rocks, theoretical expressions for the diffusion in randomly oriented but geometrically well-defined restricting geometries as tube-like or sheet-like pores (Mitra and Sen, 1992), are fitted to the experimentally observed spin-echo attenuation (Lucas et al., 1994; Fordham et al., 1994). From the comparison between theoretical expressions and experimental data, the pore geometry which fits best the observed shape of the spin-echo attenuation is estimated and the pore size is calculated. Table 1 summarises results obtained for different rock types by this procedure.

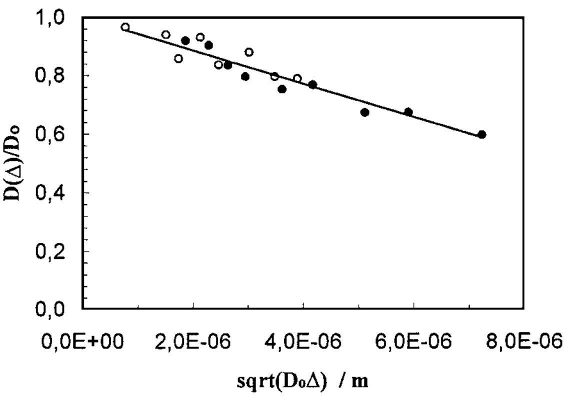

Figure 3. PFG NMR measurements of relative effective self-diffusivities $D(\Delta)/D_0$ for water (solid symbols) and hexadecane (C_{16}, open symbols) in an unconsolidated sand plotted against the diffusion distance $(D_0\Delta)^{1/2}$. The decrease of both diffusivities with increasing observation time is consistent with the short-time behaviour predicted from Eq. (16). The solid line reperesents the result of a linear regression using all plotted data points. The surface-to-volume ratio determined from the slope of the graph was found to be 0.23 μm^{-1}.

3.1.3. Measurement of the Surface-to-Volume Ratios in Rocks. First PFG NMR measurements of surface-to-volume ratios from the early time dependence of the diffusivity via Eq. (16) were reported for water and oil diffusing in packs of glass beads and for intracellular diffusion of water in onion cells (Latour et al., 1993). For water-saturated porous rocks, the method was used for a natural sandstone from Clashach quarry (Scotland) (Fordham et al., 1994) and for a Fontainebleau sandstone (Hürlimann et al., 1994). Surface-to-volume ratios of 0.05 μm^{-1} (Clashach quarry sandstone) and 0.14 μm^{-1} (Fontainebleau) were determined. The simultaneous measurement of the longitudinal relaxation time T_1 allowed the calculation of the surface relaxivities ρ_1 for both sandstones. The results are $\rho_1 = 3.1 \cdot 10^{-5}$ m/s (Clashach quarry sandstone) and $\rho_1 = 1.6 \cdot 10^{-5}$ m/s (Fontainebleau), respectively.

Figure 3 shows the time-dependence of the self-diffusivities of water and hexadecane (C_{16}) in an unconsolidated sand. Although the bulk diffusivities of both fluids differ at the measurement temperature (293 K) by almost one order of magnitude ($D_0(H_20) = 2.0 \cdot 10^{-9}$ m^2 s^{-1}, $D_0(C_{16}) = 3.1 \cdot 10^{-10}$ m^2 s^{-1}), their time-dependence in the sand follows within the scatter of the experimental points the same linear decay with the square root of time. Using Eq. (16), the surface-to-volume ratio of the sand was determined to be 0.23 μm^{-1}. With the simultaneous measurement of T_1 by the stimulated spin echo NMR sequence used for the diffusion measurements, the surface relaxivities were

Table 1. Characterization of pore spaces of water-saturated rocks by PFG NMR studies using models for the diffusion in well-defined restricting geometries like randomly oriented tubes (pore size = radius of tubes) and between randomly oriented parallel sheets (pore size = sheet separation) (Mitra and Sen, 1992).

Rock type	Pore geometry model	Pore size (μm)	Reference
Indiana limestone	Tube	10	Lucas et al. (1994)
Berea sandstone	Mixed: tube + sheet	15	Lucas et al. (1994)
Stevne Klint chalk	Tube	17	Lucas et al. (1994)
Clashach quarry sandstone	Sheet	10	Fordham et al. (1994)

found to be $\rho_1(H_20) = 1.8 \cdot 10^{-5}$ m/s and $\rho_1(C_{16}) = 9.8 \cdot 10^{-6}$ m/s for water and hexadecane in the sand, respectively.

3.2. *Macropore Diffusion in Beds of Microporous Adsorbent Particles*

Applications of microporous adsorbents such as zeolites as catalyst and adsorbents require the transport of the reactant/adsorbate molecule from outside the individual zeolite crystal into the micropores of the crystal and vice versa as well as the transport within the micropores. Since the individual zeolite crystals are usually packed together to larger assemblies, a macropore system is formed which must allow the molecules to pass from the outer surface of the individual crystals to the surface of the assembly of zeolites. Investigations of micropore diffusion in zeolites will be discussed in chapters 4 and 5. Here we demonstrate that intercrystalline diffusion can also be studied by PFG NMR. As a special case of macropore affected diffusion, we also include the restriction of the intracrystalline diffusion by the outer surface of the individual zeolite crystallites into this chapter.

3.2.1. Diffusion through the Intercrystalline Macropores of Zeolite Pellets. The best approach to investigate the intercrystalline diffusion in the macropores of zeolite pellets is to use fluid molecules which are prevented to enter into the micropores of the zeolites. This is e.g., the case for cyclo-octane in pellets of ZSM-5 type zeolites, since the cyclo-octane molecules are larger than the micropore channel diameter of the ZSM-5 zeolites. Figure 4 shows the time-dependence of the mean square displacement measured by PFG NMR for three different pellets compared with the self-diffusion of the bulk fluid. The rms displacement was found to exceed even at the shortest observation times the mean pore radius of the macropores, which was estimated to be less than 1 μm (from mercury porosimetry of similar pellet samples), significantly. Thus, the observed diffusion process corresponds to diffusion in well-connected pores (Section 2.2.2, $l_{\text{Diff}} \gg \langle R \rangle$). Furthermore, since the mean square displacements increase proportional with the observation time, the cyclo-octane diffusivities in the macropores and in the bulk could be determined. According to Eq. (10), the ratio of diffusivity in the bulk ($D_0 = 5.0 \cdot 10^{-10}$ m^2 s^{-1}) to the diffusivities in the pellets yields the tortuosity of the pore space. The examples show that the experimentally determined tortuosities may differ significantly for the pellets revealing different transport restrictions for the fluid in the macropores which must be generated during the preparation of the pellets from the zeolite material.

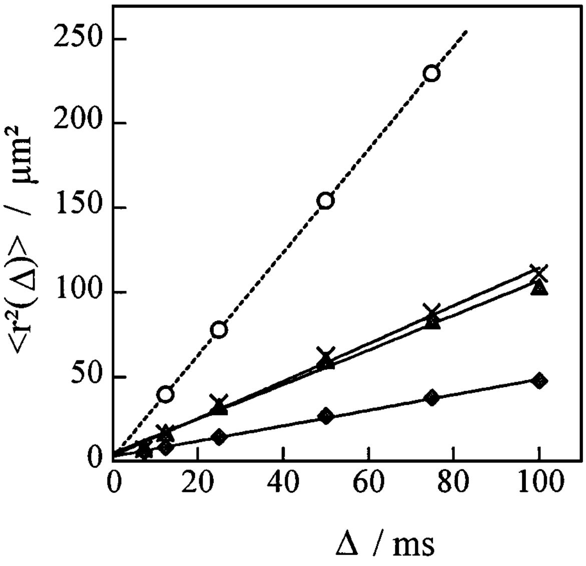

Figure 4. Observation time dependence of the mean square displacement $\langle r^2(\Delta)\rangle$ for cyclo-octane in three different pellets of ZSM-5 type zeolites (p1, ×; p2, ▲; p3, ◆) compared with the corresponding data for the bulk fluid (○). The diffusion in the pellets is reduced but the rms displacement exceeds the macropore radius (see text). The comparison of the diffusivities in the pellets with the diffusivity in the bulk ($D_0 = 5.0 \cdot 10^{-10}$ m^2 s^{-1}) reveals the tortuosities of the macropores which were found to be 2.5, 2.6 and 4.4 for the samples p1, p2 and p3, respectively.

Under the conditions of gas-phase adsorption, for sufficiently large diffusion paths (regime of “long-range” diffusion), the measured diffusivity obeys the relation

$$D \equiv D_{\text{l.r.}} = p_{\text{inter}} D_{\text{inter}} \tag{22}$$

where p_{inter} and D_{inter} denote respectively the relative number of diffusants in the macropores and their diffusivity. It has been found that values determined on the basis of Eq. (22) with a simple gas-kinetic approach for the intercrystalline diffusivity D_{inter} are in good agreement with the experimental data (Lorenz et al., 1984).

3.2.2. Restricted Intracrystalline Diffusion in Zeolite Crystallites. When during the intracrystalline diffusion the molecules encounter the crystallite surface, they may desorb or be reflected back into the micropore system of the crystallites. In both cases, the molecules

Table 2. Limiting intracrystalline mean square displacement $\langle r^2(\infty)\rangle = 3\cdot\langle z^2(\infty)\rangle$ for self-diffusion of xenon in zeolites: Comparison of data calculated from mean crystallite diameter $2\langle R\rangle$ via Eq. (13) with results determined experimentally by ^{129}Xe PFG NMR (Kärger et al., 1990) at long observation times.

Zeolite crystallite		Limiting intracrystalline mean square displacement $\langle r^2(\infty)\rangle$ (μm^2)	
Type	$2\cdot\langle R\rangle$ (μm)	By Eq. (13)	Experimental
ZSM-5	25	190	120
NaCaA	5	8	15
	13	50	75
	20	120	140

remaining in the individual zeolite crystallite will be restricted in their rms displacement by the radius of the zeolite crystallite. By measuring their mean square displacements, PFG NMR can distinguish between those molecules which were able to leave the crystallites and those which remain in the starting crystallite during the observation time (Kärger and Ruthven, 1992). For the fluid fraction which remains in an individual crystallite, the pattern of restricted diffusion (Section 2.2.3, $l_{\mathrm{Diff}} \approx \langle R\rangle$) must apply for the interpretation of the PFG NMR results.

As an example, at long observation times, the intracrystalline diffusion observed by ^{129}Xe PFG NMR (Kärger et al., 1990) for xenon adsorbed in zeolite ZSM-5 and NaCaA followed the pattern of restricted diffusion in isolated pores. Table 2 compares the measured limiting intracrystalline mean square displacements with the values calculated via Eq. (13) from the known mean diameter of the crystallites. The data show reasonable agreement.

Especially for small zeolite crystallites, the restriction of the mean square displacement at the crystallite surface may reduce the apparent self-diffusivities—as observed with PFG NMR—substantially compared with the true (unrestricted) intracrystalline self-diffusivities (Kärger and Volkmer, 1980). However, if the observed mean square displacement still depends on the observation time, the true intracrystalline self-diffusivities can be calculated from PFG NMR measurements by quantitatively taking into account the confinement exerted by the crystallite surface (Bär et al., 1996).

Recently, it has been demonstrated that also the short-time dependence of the intracrystalline diffusivity can be used to determine the surface-to-volume ratio of the outer surface of the zeolite crystallites via Eq. (16) (Sorland, 1997). He obtained for a bed of NaX zeolites with crystallite sizes from 10–20 μm loaded with n-hexane a surface-to-volume ratio of approximately 0.3 μm^{-1}. This value corresponds to a sphere diameter of about 9 μm which is in resonable agreement with the averaged size of the crystallites.

4. Diffusion in Micropores

4.1. Fields of Information

Being under the permanent influence of the internal surface, molecular diffusion in micropores reveals a number of remarkable structure-related features. Since PFG NMR is able to monitor molecular propagation without any interference with the intrinsic processes, it is a most effective method to study these properties. The present section summarizes the information provided by PFG NMR in these different fields.

4.1.1. Concentration Dependence of the Diffusivity. As a relatively stable host system, one and the same microporous material may accommodate quite different amounts of guest molecules. The concentration dependence of molecular diffusion is therefore one of the special features provided by microporous adsorbate-adsorbent systems. It turns out that corresponding to the large spectrum of different types of host-guest interactions, the concentration dependence of the diffusivities may also follow quite different patterns. In systems where the host-guest interaction energy remains essentially uniform over the internal surface, the diffusivity drops monotonically with increasing concentration. This is a simple consequence of the reduced free mean path of the diffusants. Systems following this type of concentration dependence ("type (i) pattern"—cf., e.g., Kärger and Ruthven, 1992) include n-alkanes in zeolite NaX (Kärger et al., 1980) and ZSM-5 (Caro et al., 1985). Specific interactions—as, e.g., between the cations and the π-electrons of unsaturated hydrocarbons in NaX (Germanus et al., 1985)—may effect that the diffusivities remain essentially unaffected by the concentration up to medium pore filling factors. With further increasing concentration, again a dramatic decrease in the mobility is observed (type (ii) concentration dependence). Small, polar molecules like water and ammonia in NaX exhibit a reversed concentration dependence (Förste et al.,1989); at first increasing with concentration, starting from medium pore filling factors the diffusivity remains constant (type (iii) pattern). Larger polar molecules, like methanol, combine type (ii) and (iii) behaviour by showing maximum diffusivities at medium concentrations with diffusivities decreasing monotonically for both increasing and decreasing concentration ((Brandani et al., 1995), pattern (iv)). Finally, in some cases like with alkanes in NaCaA ((Heink et al., 1994), pattern (v)) the diffusivities are found to increase with increasing loading over the total concentration range. Obviously, owing to a particularly strong host-guest interaction, in this case the guest-guest interference is completely masked.

As a consequence of the large variety of possible host-guest and guest-guest interactions, theoretical work on the *a priori* determination of zeolitic intracrystalline diffusion is only in its initial stage (Theodorou et al., 1996). This is in striking contrast to the situation with long-range diffusion (cf. Section 3.2.1) which may be treated with satisfactory accuracy by simple gas-kinetic approaches.

4.1.2. Diffusion Anisotropy. Being subjected to the adsorbent architecture, molecular diffusion has to reflect the features of the crystallographic structure. This means in particular that molecular diffusion can only be isotropic in amorphous adsorbents and in adsorbents of cubic crystallographic symmetry. In all other types of adsorbents, molecular diffusion must be described by a diffusion tensor rather than by a diffusion coefficient. Since the extensions of zeolite crystallites are typically in the range of micrometers, there are only a few attempts to trace diffusion anisotropy in this type of adsorbent by macroscopic methods (Ruthven et al., 1991; Cavalcante et al., 1997; Caro et al., 1993; Talu et al., 1998). PFG NMR has been successfully applied to determine orientation-dependent diffusivities by three different techniques. By analysing *the shape of the PFG NMR signal attenuation* (Hong et al., 1991a; Bär et al., 1988) in a powder sample one makes use of the fact that one has a superposition of exponentials of the form of Eq. (9) with orientation-dependent diffusivities $D(\varphi, \theta)$, where the contribution of the different diffusivities is determined by the probability that the corresponding orientations coincide with the direction of the external magnetic field gradient. Mathematically, the PFG NMR signal attenuation results as a monotonically decaying function with the three principal elements of the diffusion tensor as fitting parameters. There is clearly less ambiguity in the determination of the tensor elements by comparison between experiment and the theoretical expression if additional information is available. This is, e.g., the case for rotational symmetry like in trigonal, tetragonal or hexagonal structures (where two principal elements have to coincide), or if one may imply the existence of a certain correlation between the diffusivities in different direction. The conditions for the formulation of such "correlation rules" shall be discussed later in this section. The most direct way of measuring diffusion anisotropy implies the use of a *single crystal* in the mm range, where the orientation dependence of molecular mobility simply results by correspondingly changing the orientation of the crystallites with respect to the field gradient. Experiments of this type have been carried out with water in natural chabazite crystals (Bär et al., 1998). Finally, if the individual crystallites are available either as rods or plates, they may be placed within the nmr sample with a preferential orientation. In some way, one then has to do with a *quasi-single crystal* so that like with real single crystals, orientation-dependent diffusivities may be determined by varying the sample orientation. Experiments of this type have been carried out with ZSM-5 (Hong et al., 1991a and 1991b).

The existence of an interconnected network of channels and/or pores may generate a correlation between the displacements in different direction. As a most prominent example, in zeolite ZSM-5 displacements in z-direction are only possible by subsequent displacements in x- and y-directions (Kärger, 1991; Kärger and Pfeifer, 1992). Under the assumption that the individual molecules completely loose their memory on their way from channel intersection to channel intersection, the diffusivities in x-, y- and z-direction may be shown to be correlated by the expression

$$a^2/D_x + b^2/D_y = c^2/D_z, \qquad (23)$$

where a, b and c denote the unit cell extensions in x, y and z direction, respectively. Correlation rules of even simpler shape (as a consequence of the rotational symmetry of the diffusion tensor) may be derived for ZSM-11 (Kärger and Pfeifer, 1992) and chabazite (Bär et al., 1998).

4.1.3. Transport Diffusion Versus Self-Diffusion. The existence of a relatively inert pore system effects that molecular diffusion at equilibrium (i.e., under uniform concentration) and under non-equilibrium (i.e., in the presence of concentration gradients) proceed under apparently identical conditions. The relevant diffusion coefficients, the self-diffusivity D and the transport diffusivity D_{T}, must be expected, therefore, to be closely related to each other. In particular, in the limit of sufficiently small concentrations (viz., when the influence of the mutual interaction between the diffusants becomes negligibly small) both coefficients should coincide. This requirement may be easily rationalized on the basis of Fick's first law

$$\vec{j} = -D_{\mathrm{T}} grad\, c \tag{24}$$

with j and c denoting respectively the overall flux density and concentration in the case of transport diffusion, and the flux density and concentration of labelled molecules within an unlabelled surroundings of constant overall concentration in the case of self-diffusion. If molecular random walk is exclusively determined by the host-guest interaction, identical concentration gradients will give rise to identical fluxes so that the respective factors of proportionality, D and D_{T}, have to coincide. For larger concentrations, D and D_{T} are generally assumed to be related to each other by the Darken equation

$$D_{\mathrm{T}} = \frac{d \ln p(c)}{d \ln c} D, \tag{25}$$

where $p(c)$ is the pressure of the gas atmosphere necessary to keep the adsorbate at concentration c.

As an equilibrium technique, PFG NMR is able to determine the self-diffusivity. As shown in Section 2.1, the labelling is accomplished via the orientation of the nuclear spins in the plane perpendicular to the direction of the external magnetic field gradient. It should be emphasized that the energy of interaction between the nuclear spins and the magnetic field is by several orders of magnitude smaller than the thermal energy to that this way of labelling does clearly not affect the inherent dynamics of the adsorbate-adsorbent system.

It is one of the current problems of zeolite science that on comparing transport and self-diffusivities one may observe both reasonable agreement (Brandani et al., 1995; Talu et al., 1998; Nijhuis et al., 1997) and disagreement (Ruthven et al., 1991). Though there are several theoretical conceptions available (Kärger and Ruthven, 1997), a comprehensive explanation of the remaining differences does not yet exist. Presently, by novel experimental concepts being based on interference microscopy (Schemmert and Kärger, 1999) and coherent quasielastic neutron scattering (Jobic et al., 1999) for the first time the direct observation of transport diffusion inside the zeolite crystallites has become possible. It is most likely that in this way new experimental evidence shall be provided which leads to an eventual clarification of a long-standing discrepancy.

4.2. Multicomponent Diffusion

Being sensitive to a particular type of nucleus, the PFG NMR technique provides a straightforward means to record the mobility of the individual constituents in multicomponent systems. There are essentially two different routes to follow this purpose: the different compounds of the multicomponent system may contain different NMR active nuclei such as ^{1}H, ^{19}F or ^{129}Xe, or one is able to distinguish between one and the same nucleus by differences in its chemical surroundings.

While—as already noted in the case of single-component diffusion—two-component diffusion in the intercrystalline space may be well predicted by theoretical approaches (Lorenz et al., 1984), for the regime of intracrystalline diffusion there is presently no alternative for direct experimental studies.

4.2.1. Applying Different Nuclei as PFG NMR Probes. First two-component PFG NMR studies have been based on ^{1}H NMR measurements of hydrocarbons in zeolite NaX. In order to obtain the diffusivity of either component, for each adsorbate-adsorbent system a pair of samples had to be prepared, in either of which one component was used in the normal, hydrogen-containing form, while the other was applied in the deuterated form (Lorenz et al., 1984). ^{1}H PFG NMR measurement reveals the diffusivity of the hydrogen-containing component. As an inherent disadvantage of this method, the two-fold number of samples must be prepared, where, in addition, one can never be completely sure whether—exempt for isotope effects—a pair of samples is really identical.

With the more recent enhancement of the number of nuclei applied to PFG NMR studies of adsorbate-adsorbent systems, two-component PFG NMR self-diffusion measurements could be performed with one and the same sample. As an example, Fig. 5 shows the diffusivities of CH_4 and CF_4 in silicalite at 200 K as obtained by ^{1}H and ^{19}F PFG NMR at a total concentration of 12 molecules per unit cell for varying compositions. In addition, the results of multicomponent MD simulations (which are the first at all for multicomponent systems (Theodorou et al., 1996)) are presented (Snurr and Kärger, 1997). Both the general trends ($D(CH_4) > D(CF_4)$, increasing diffusivities with increasing fraction of CH_4) and the absolute values are found to be in reasonable agreement.

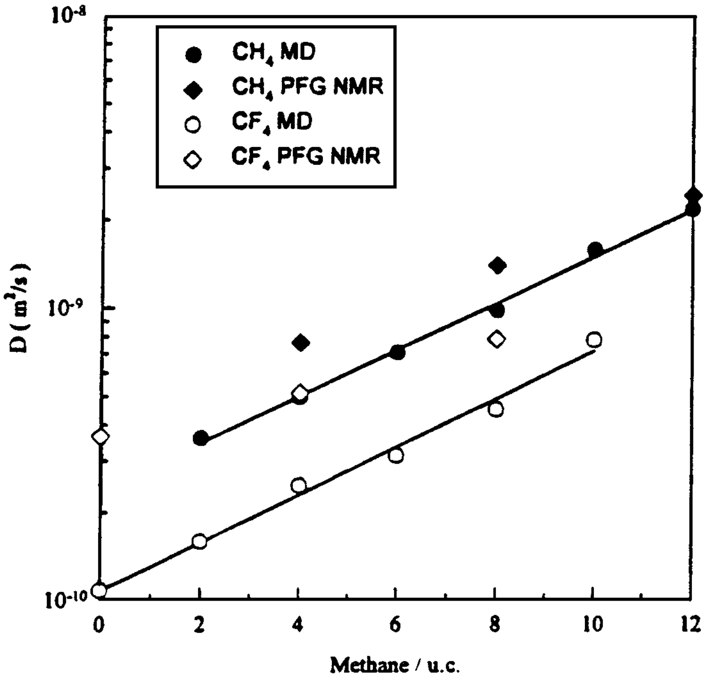

Figure 5. Self-diffusivities of methane/CF_4 mixtures in silicalite, ranging from pure CF_4 to pure methane (from Snurr and Kärger, 1997). The total loading in all cases is 12 molecules per unit cell, and the temperature is 200 K. The lines through the MD results are linear regressions, although there is no reason to expect a linear relationship. Error bars (not shown) are about ±20% for both MD simulations and PFG NMR measurements.

4.2.2. Fourier-Transform PFG NMR. The necessity to obtain the diffusivities of the different components in consecutive measurements by applying different resonance conditions (e.g., ^{1}H NMR and ^{19}F NMR, as in the example given in Fig. 5) vanishes in high-resolution PFG NMR studies, if by Fourier transforming the PFG NMR signal from time domain to frequency domain (Hong et al., 1991c; Chen et al., 1994), the individual constituents giving rise to the NMR signal may be distinguished by their different chemical shifts. Measurements of this type have been carried out with ^{1}H and ^{13}C PFG NMR. It turned out that the gain in resolution by applying ^{13}C NMR (being characterized by much larger chemical shifts) is purchased by a substantial reduction of the signal-to-noise ratio in comparison with ^{1}H NMR, resulting in much larger measuring times. In Section 5.2 this feature is discussed when considering the potentials of PFG NMR in following the transport properties during chemical reactions.

5. Measurement Under Transient Conditions

As a non-invasive technique, PFG NMR offers particularly favourable conditions for recording molecular mobilities in systems during their use under transient conditions. With microporous materials, owing to their most important technical applications, the prominent generating processes for transient conditions are the processes of molecular adsorption/desorption and internal chemical reactions. In the following, we shall report on the use of PFG NMR under either of these conditions.

5.1. PFG NMR Study During Molecular Uptake

Host-guest interaction arising during uptake of molecules may change intracrystalline transport resistances for the guest molecules during or even a long time after the adsorption process (Wernicke and Osterhuber, 1984; Tezel et al., 1984). Conventional PFG NMR studies, which are carried out under equilibrium conditions, cannot detect such effects. However, successive NMR imaging measurements combined with pulsed field gradients for self-diffusion studies enable the space- and time-dependent observation of sorbate concentration and simultaneously monitor the self-diffusion during uptake. Due to the generally short transverse nuclear magnetic relaxation times of guest molecules in zeolites and the relatively quick uptake processes in beds of zeolite samples fitting into conventional NMR spectrometer, this technique has been applied up to now only with one-dimensional spatial resolution. By aligning the direction of spatial resolution parallel to the direction of the concentration gradient, the time-dependent sorbate concentration can be monitored. With the additional pulsed field gradients for the self-diffusion measurements oriented perpendicular to this direction, effects of macroscopic concentration gradients on the measured space-dependent intracrystalline self-diffusivities can be excluded.

Using this one-dimensional PFG NMR imaging technique, space- and time-dependent self-diffusivities of *n*-hexane in NaX zeolites were in fact observed (Kärger et al., 1993). However, the time-dependence could simply be explained by the increasing intracrystalline sorbate concentration during the uptake causing the intracrystalline self-diffusivity to decrease with the *n*-hexane exposition time at a given sample position. Moreover, in experiments, where the intracrystalline sorbate concentration exhibited a step function with no *n*-hexane adsorbed in the region preceding the sorption front and maximum concentration immediately behind it, no time-dependence of the intracrystalline diffusivity was observed. Thus, at last for the system *n*-hexane/NaX, host-guest-interaction changing guest mobility during the uptake must be excluded. The PFG NMR imaging technique is expected to have large potential for studying uptake, reaction and separation processes under *in situ* conditions.

5.2. PFG NMR Study During Chemical Reaction

The effectiveness of catalysts in promoting chemical reactions is well-known to be influenced by the rate of migration of the reactant and product molecules (Kärger and Ruthven, 1992; Nivarthi and McCormick, 1995). Quantitative considerations are generally based on the Thiele modulus μ reflecting the ratio between the mean residence time of the reactant or

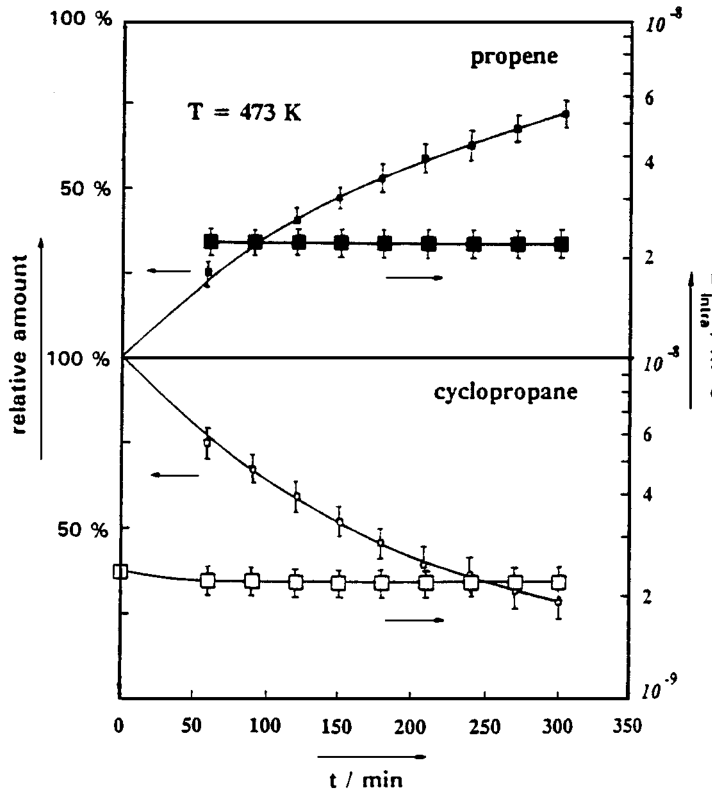

Figure 6. Time dependence of the relative amount of cyclopropane and propene during the conversion of cyclopropane to propene in NaX and their self-diffusion coefficients (□, cyclopropane; ■, propene) measuered by FT PFG NMR (from Hong et al., 1992).

product molecules in the catalyst particles and the mean reaction time. Only for $\mu \ll 1$, any essential transport inhibition of the overall catalytic reaction may be excluded. This theoretically well-established criterion suffers under the difficulty of measuring the transport properties of the individual components involved in chemical reactions. Since conventional measuring techniques like transient uptake or permeation methods fail to provide information about molecular mobilities under reaction conditions, sometimes the feasibility of defining the diffusivities relevant for estimating the Thiele modulus has been doubted. In fact, only with the advent of Fourier transform PFG NMR measurements of multicomponent diffusion in adsorbate-adsorbent systems, the determination of reaction-relevant diffusivities has become possible. As an example, Fig. 6 displays the diffusivities of cyclopropane (reactant) and propene (product) during their conversion in NaX (Hong et al., 1992). Simultaneously, the figure also shows the time dependence of the relative amount of the two components, as following from the respective intensities of the NMR signals during conversion. The numbers on the abscissa provide an idea of the typical time scale of such experiments. Processes with time constants below about 10 min will scarcely be accessible by this technique. Using ^{13}C as a probe nucleus (Schwarz et al., 1997), as a consequence of the reduced magnetogyric ratio and—as a rule—the reduced number of resonating nuclei, the signal accumulation numbers must be significantly enhanced, resulting in minimum reaction times of at least several hours.

6. Conclusion

Self-diffusion studies imply the necessity of molecular labelling. In the PFG NMR method, this may most appropriately be achieved by recording the positions of the individual molecules via the orientation of their nuclear spins. The space scale over which molecular diffusion may be followed is determined by the periodicity of this orientation. Depending on the amplitude and on the width of the field gradient pulses, this periodicity may be varied between hundreds of nanometers up to fractions of millimeters. By choosing the space scale and the diffusion length with the pulsed field gradient parameter in the NMR pulse sequence in accordance with the characteristic dimensions of porous systems, PFG NMR is able to provide information about details of both transport and structural properties of the system under study. This potential has been demonstrated by examples taken from macroporous materials like petrophysical objects as well as from zeolitic adsorbate-adsorbent systems as the most prominent class of microporous crystalline materials.

Acknowledgments

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