PHYSICAL REVIEW E VOLUME 57, NUMBER 6 JUNE 1998

Fringe field NMR diffusometry of anomalous self-diffusion in molecular sieves

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(Received 18 December 1997)

Superconducting magnet fringe field NMR diffusometry is applied to an adsorbate–molecular sieve system in order to obtain intracrystalline self-diffusion of adsorbed molecules. Effects of self-diffusion, exchange, relaxation, and dipolar correlation are discussed. The proper equations for one- and two-dimensional anomalous self-diffusion with and without macroscopic order are derived. The method is applied to investigate methane self-diffusion in the molecular sieve silicoaluminophosphate, type 11 (SAPO-11). It is concluded that the nature of the methane displacements in the sieve channels is single-file self-diffusion. [S1063-651X(98)03906-3]

PACS number(s): 47.55.Mh, 66.30.−h, 76.60.−k, 81.05.Rm

I. INTRODUCTION

Molecular sieves are microporous materials, which possess a huge internal volume capable of adsorbing molecules of proper size. There is a large variety of intracrystalline structures restricting adsorbate displacements so that anomalous self-diffusion processes can be expected. Usually one investigates adsorbate diffusion in thermal equilibrium. In terms of a model with two states, ‘‘adsorbed’’ and ‘‘free,’’ that is, desorption and adsorption of molecules are balanced.

In such systems at least three different time scales can be distinguished for the self-diffusion properties of the adsorbates [1]. In the short-time limit relative to the exchange rates, all molecules retain their initial state, i.e., exchange is not yet effective. In that case adsorbate displacements can be classified either as intra- or intercrystalline diffusion. On the other extreme, the long-time limit, all adsorbate molecules have been subject to many exchange processes and self-diffusion must be considered as a weighted average of the two states. Between these two extremes an intermediate time scale is found, where self-diffusion is directly affected by the exchange rate.

Pulsed field gradient (PFG) NMR diffusometry was successfully applied to the study of adsorbate diffusion [1]. However, this method has its limitations when the intracrystalline part of self-diffusion is to be examined. Molecular sieve samples are usually powdery and consist of small crystalline particles with diameters on the order of micrometers. The observation of purely intracrystalline self-diffusion therefore is only possible if the adsorbate displacements do not exceed the intracrystalline length scale. That is, the diffusion time to be probed is severely restricted. The consequence is that very strong field gradients must be employed in order to achieve perceptible echo attenuations by intracrystalline displacements.

Strong gradient pulses, however, are unavoidably accompanied by pulses of magnetic forces on the samples and the probe head. These forces can be of an inductive nature with respect to the conducting parts of the probe head or they are induced by the varying magnetic susceptibilities of the sample and all other materials surrounding the sample in the gradient coils. Such forces can be a source of artifacts, limiting the applicability of PFG experiment for intracrystalline self-diffusion measurements [2].

In the present study we have therefore employed the superconducting magnet fringe field (SFF) NMR diffusometry technique as an alternative method for monitoring intracrystalline self-diffusion. Instead of using pulsed field gradients, the experiments were carried out in the fringe field of a superconducting magnet. The corresponding field gradient is stationary and is very strong (60 T/m in our case). The radio-frequency (rf) pulse sequence consists of three 90° pulses. The echoes of interest are the primary echo (PE) and the stimulated echo (STE). The experimental protocol implies the evaluation of the quotient of the amplitudes of these echoes so that the influence of relaxation on the attenuation curves compensates itself under suitable circumstances [3].

In the following a corresponding formalism for molecular sieve–adsorbate systems will be derived taking into account the factors influencing the STE and PE amplitudes, i.e., self-diffusion, exchange, dipolar correlation, spin-spin, and spin-lattice relaxation. The results for isotropic anomalous self-diffusion obtained in previous studies for the case of steady gradients are extended to one- and two-dimensional anomalous self-diffusion without macroscopic order. This formalism will then be applied to methane adsorbed in a molecular sieve of the silicoaluminophosphate of type 11 (SAPO-11, strucutre code AEL).

SAPO-11 has straight channels of elliptical cross section and no interconnections. In such a system one-dimensional self-diffusion without macroscopic order is expected. Moreover, the similar diameters of methane and the cross section of the SAPO-11 channels suggest that the diffusing molecules cannot pass each other. The consequence is that the displacement of a molecule in one direction stipulates return steps in the reverse direction with a higher probability than

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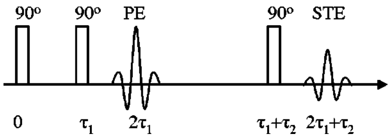

FIG. 1. Three-pulse method with stationary gradients for self-diffusion measurements in the fringe field of superconducting magnets. The amplitudes of the primary (PE) and the stimulated echo (STE) are evaluated and divided by each other.

for the continuation along the original displacement direction. That is, the mean square displacement (MSD) of molecules is proportional to the square root of time in contrast to the ordinary linear Einstein relationship [4]. This phenomenon is termed single-file self-diffusion. It has been the subject of several theoretical [4] and simulation investigations [5–8], whereas experimental evidence of single-file self-diffusion has been found only recently with PFG NMR diffusometry [9–11].

II. THEORY

A. Response of a two-phase system to a three-rf-pulse–steady field gradient sequence

NMR self-diffusion studies are based on the measurement of spin echo amplitudes under the effect of main- or rf-field gradients. In the presence of a stationary main-field gradient, the echo formation times are varied in contrast to the more familiar PFG diffusometry schemes, in which the gradient pulses are incremented instead. This introduces the problem to separate relaxation and self-diffusion effects in the evaluation procedure. A solution is to measure the STE and PE amplitudes as a function of τ_1 while τ_2 is kept constant (see Fig. 1). The echo amplitudes depend on several factors [3,12]

$$A_{STE}(2\tau_1+\tau_2)=A(0)A_{r1}(\tau_2)A_{r2}(2\tau_1)\times A_{dc}(2\tau_1+\tau_2)A_{diff}(2\tau_1+\tau_2), \tag{1}$$

$$A_{PE}(2\tau_1)=A(0)A_{r2}(2\tau_1)A_{dc}(2\tau_1)A_{diff}(2\tau_1), \tag{2}$$

where $A(0)$ is proportional to the equilibrium magnetization. The attenuation factors are due to the effect of dipolar correlation A_{dc} [13], self-diffusion A_{diff}, and longitudinal A_{r1} and transverse relaxations A_{r2}. In the quotient of STE and PE the transverse-relaxation factors cancel, while $A_{r1}(\tau_2)$ is constant for constant τ_2. Hence, in the absence of the dipolar correlation effect, the only variables in the quotient are the attenuations due to self-diffusion.

In the molecular sieve–adsorbate system under consideration here, the situation is more complex due to the different environments existing. We distinguish two phases of the adsorbate molecules: adsorbed a and free f. The PE and STE amplitudes evolve differently for these phases and are further modified for the fraction of adsorbate molecules that is subject to exchange in the course of the pulse sequence. Consequently, the PE and STE amplitudes are composed of three terms each:

$$\begin{aligned}A_{STE}(2\tau_1+\tau_2)=&\,p_a(2\tau_1+\tau_2)A^a_{STE}(2\tau_1+\tau_2)\\&+p_f(2\tau_1+\tau_2)A^f_{STE}(2\tau_1+\tau_2)\\&+p_{ex}(2\tau_1+\tau_2)A^{ex}_{STE}(2\tau_1+\tau_2),\end{aligned} \tag{3}$$

$$\begin{aligned}A_{PE}(2\tau_1)=&\,p_a(2\tau_1)A^a_{PE}(2\tau_1)+p_f(2\tau_1)A^f_{PE}(\tau_1)\\&+p_{ex}(2\tau_1)A^{ex}_{PE}(2\tau_1).\end{aligned} \tag{4}$$

The functions $p_a(t)$ and $p_f(t)$ are the proportions of molecules adsorbed and free during the whole period t, respectively, and $p_{ex}(t)$ is the fraction exchanged in that period. In this case none of the factors cancels in the quotient of the STE and PE amplitudes and a complex function of relaxation, self-diffusion, and dipolar correlation parameters for the different environments results.

For adsorbed and free molecules the self-diffusion coefficients usually differ by several orders of magnitude due to the restrictions imposed by the intracrystalline constraints and the mutual interactions of molecules. Therefore, the displacements of particles that have changed their environment during the time scale of the experiment t are dominated by the displacements achieved while intermittently residing in the free phase [1]. Consequently, the MSD of molecules having been subject to exchange is

$$\langle r^2_{ex}(t)\rangle=\langle r^2_a(t_a)\rangle+\langle r^2_f(t_f)\rangle\approx\langle r^2_f(t_f)\rangle, \tag{5}$$

where r_a and r_f are the displacements in the adsorbed and free states, respectively, and t_a and t_f are the times spent in the corresponding environments.

The echo attenuations due to self-diffusion reflect the MSD of the molecules during the experiment (see below Sec. II B). Because of the large differences in the MSD values, it is possible to find such a value for the stationary gradient, that $A^f_{diff}(t),A^{ex}_{diff}(t)\approx 0$, while $A^a_{diff}(t)$ is still finite. In that case the amplitude quotient of STE and PE simplifies to

$$\begin{aligned}Q(\tau_1,\tau_2)&=\frac{A_{STE}(2\tau_1+\tau_2)}{A_{PE}(2\tau_1)}\\&\approx A^a_{r1}(\tau_2)\underbrace{\frac{p_a(2\tau_1+\tau_2)}{p_a(2\tau_1)}}_{Q_{ads}(\tau_1,\tau_2)}\underbrace{\frac{A^a_{dc}(2\tau_1+\tau_2)}{A^a_{dc}(2\tau_1)}}_{Q_{dc}(\tau_1,\tau_2)}\\&\quad\times\underbrace{\frac{A^a_{diff}(2\tau_1+\tau_2)}{A^a_{diff}(2\tau_1)}}_{Q_{diff}(\tau_1,\tau_2)},\end{aligned} \tag{6}$$

depending only on the properties of the adsorbed molecules. The quotient then in principle consists of four factors representing the influences of longitudinal relaxation $A^a_{r1}(\tau_2)$, the fractions of adsorbed molecules $Q_{ads}(\tau_1,\tau_2)$, the dipolar correlation $Q_{dc}(\tau_1,\tau_2)$, and the self-diffusion $Q_{diff}(\tau_1,\tau_2)$.

In order to extract the information on intracrystalline self-diffusion, the effects of dipolar correlation and changes in the fractions of adsorbed molecules must be separated. In the most simple case the quotients $Q_{dc}(\tau_1,\tau_2)$ and $Q_{ads}(\tau_1,\tau_2)$ are constant for varying τ_1, so these factors are compensated for in the normalization procedure anyway required in order to take into account spin-lattice relaxation.

A constant quotient $Q_{ads}(\tau_1,\tau_2)$ means that the relative change of $p_a(t)$ during the time intervals $[2\tau_1, 2\tau_1+\tau_2]$ does not depend on τ_1 (τ_2 is kept constant in the course of each experiment anyway). Clearly this is a matter of the exchange process and must be discussed correspondingly (see below). The case that $Q_{ads}(\tau_1,\tau_2)\approx 1$ stipulates that the exchange is slow relative to the first pulse interval.

The dipolar correlation effect can only be observed if a residual dipolar coupling exists on the time scale of motional averaging. This residual coupling may then fluctuate on the much longer time scale of the stimulated-echo experiment [13]. In molecular sieves, adsorbate motions are restricted due to narrow cavities. Residual couplings therefore must be considered. If the restrictions vary with the position in the cavities, fluctuations of the residual dipole-dipole interaction may arise.

The potential relevance of the factors $Q_{ads}(\tau_1,\tau_2)$ and $Q_{dc}(\tau_1,\tau_2)$ in the evaluation procedure of the diffusion attenuation term $Q_{diff}(\tau_1,\tau_2)$ can be checked experimentally by simply repeating the experiment with different field gradient strengths. This affects the gradient dependent quotient $Q_{diff}(\tau_1,\tau_2)$, whereas the other terms remain constant. However, with such gradient variation experiments it must be made sure that all previous assumptions $[A^{f}_{diff}(t), A^{ex}_{diff}(t)\approx 0]$ are still valid.

If both $Q_{dc}(\tau_1,\tau_2)$ and $Q_{ads}(\tau_1,\tau_2)$ can be approximated by 1, Eq. (6) simplifies to

$$Q(\tau_1,\tau_2)\approx A^{a}_{r1}(\tau_2)Q_{diff}(\tau_1,\tau_2). \tag{7}$$

The τ_1 dependence of this function is solely due to the intracrystalline self-diffusion properties of the adsorbate.

B. Self-diffusion quotient

The mutual translational impedance and the confinement of adsorbate molecules in the pore space of molecular sieves causes deviations from the ordinary self-diffusion behavior given by the linear Einstein relation for the time dependence of the mean square displacement. Instead one may assume a power law of the form

$$\langle r^2(t)\rangle = 2\zeta\alpha t^{\kappa}. \tag{8}$$

If $\kappa=1$, diffusion is ordinary. Otherwise one speaks of ''anomalous'' diffusion. The case $\kappa<1$ is of particular interest in this context. $\zeta=1,2,3$ is the dimensionality of the *isotropic* environment, that is, the diffusion of adsorbate is confined in one, two, or three dimensions.

Kärger *et al.* [14] have shown that anomalous three-dimensional isotropic self-diffusion leads to an attenuation factor

$$A_{diff}(\tau_1,\Delta)=\exp[-2\alpha\ a(\tau_1,\Delta)], \tag{9}$$

where

$$a(\tau_1,\Delta)=\frac{\gamma^2G^2}{(\kappa+1)(\kappa+2)}\left[\frac{1}{2}(\Delta+\tau_1)^{\kappa+2}+\frac{1}{2}(\Delta-\tau_1)^{\kappa+2}-\Delta^{\kappa+2}-\tau_1^{\kappa+2}\right]. \tag{10}$$

The diffusion time Δ is equal to τ_1 for the PE and is given by $\tau_1+\tau_2$ in the case of the STE [12,14]. The quantities γ and G are the gyromagnetic ratio and the field gradient strength, respectively.

In the case of one- or two-dimensional anomalous diffusion one must take into account that the self-diffusion attenuation factor depends on the displacements along the field gradient direction (i.e., along z axis), which is

$$\langle z^2(t)\rangle = 2\alpha\ (\cos^2\ \theta)t^{\kappa} \tag{11a}$$

in the one-dimensional case and

$$\langle z^2(t)\rangle = 2\alpha\ (\sin^2\ \theta)t^{\kappa} \tag{11b}$$

in the two-dimensional case. θ defines the angle between the gradient and diffusion direction in the former, and between the gradient and plane normal in the latter case. The above results for $\kappa=1$ are similar to those for the MSDs for cylindrically symmetric *anisotropic* ordinary diffusion in the limit of vanishing diffusion in one or two directions, respectively [15]. The corresponding diffusive attenuation factors become

$$A_{diff}(\tau_1,\Delta)=\exp[-2\alpha\ (\cos^2\ \theta)a(\tau_1,\Delta)], \tag{12a}$$

$$A_{diff}(\tau_1,\Delta)=\exp[-2\alpha\ (\sin^2\ \theta)a(\tau_1,\Delta)], \tag{12b}$$

respectively.

In a molecular sieve–adsorbate system the possible one- or two-dimensional diffusion arises from the restrictions in the cavities of crystallites. The individual crystallites can be oriented in any direction relative to the gradient direction with equal probability. Consequently, the attenuation varies in each crystallite and the total attenuations are the weighted averages of Eqs. (12a) and (12b) over the angle θ [16]. Then the total attenuation factors are

$$A_{diff}(\tau_1,\Delta)=\frac{\int_0^{\pi}\exp[-2\alpha(\cos^2\ \theta)a(\tau_1,\Delta)]\sin\ \theta\ d\theta}{\int_0^{\pi}\sin\ \theta\ d\theta}=\sqrt{\frac{\pi}{8\alpha a(\tau_1,\Delta)}}\ \mathrm{erf}[\sqrt{2\alpha a(\tau_1,\Delta)}], \tag{13a}$$

$$A_{diff}(\tau_1,\Delta)=\frac{\int_0^{\pi}\exp[-2\alpha(\sin^2\ \theta)a(\tau_1,\Delta)]\sin\ \theta\ d\theta}{\int_0^{\pi}\sin\ \theta\ d\theta}=\sqrt{\frac{\pi}{8\alpha\ a(\tau_1,\Delta)}}\ \exp[-2\alpha\ a(\tau_1,\Delta)]\times(-i)\mathrm{erf}[i\sqrt{2\alpha\ a(\tau_1,\Delta)}] \tag{13b}$$

in the one- and two-dimensional cases, respectively.

III. EXPERIMENT

In this study the diffusion properties of ^{13}C enriched methane gas loaded into the molecular sieve material SAPO-11 was investigated. The diffusometry experiments were carried out using proton NMR. The purpose of the ^{13}C enrichment was to permit ^{13}C spectroscopy of the adsorbate at low densities.

The sample preparation can be found elsewhere (the ''static'' sample in Ref. [17]). The channels in SAPO-11 are straight without interconnections and possess an elliptical cross section of 3.9×6.3 Å [18]. The loading with methane was approximately 0.7 molecules/unit cell at room temperature. The proportion of methane in the adsorbed state was about 60% as determined using ^{13}C-{^{1}H} NMR spectroscopy [17]. The unit cell has an $AlPO_4$-11 type structure and implies four possible adsorption sites [19,20], so that 17.5% of the sites are occupied.

The amplitudes of proton STE and PE were recorded in the fringe field of a 9.7-T superconducting magnet. The magnet and the probe were screened from floor vibrations using air-inflated damping units. The resonance frequency of protons was 201.5 MHz and the gradient strength 60 T/m. The 90° pulse width was 1.7 μs. Up to 64 k-point transients were accumulated for each value of τ_1 and τ_2 allowing for a relaxation delay of 150 ms. In all experiments τ_1 was varied while keeping τ_2 constant.

Single-pulse and two-dimensional (2D) exchange ^{13}C-{^{1}H} spectra were recorded on a Bruker DPX400 spectrometer at a frequency of 100.5 MHz. The 2D exchange spectra were acquired in the phase-sensitive mode sampling 64×256 data points with a mixing time of 10 ms and a recycling delay of 100 ms. For each t_1 value, 256 transients were accumulated. Prior to Fourier transformation, the matrix of the t_1 dimension data was zero filled to 256 points. A 50-Hz exponential line-broadening function was applied in both dimensions.

IV. RESULTS AND DISCUSSION

For the optimization of the superconducting magnet fringe field diffusometry experiments, a first test of the efficiency of echo attenuation by self-diffusion in the free phase was carried out with the aid of the conventional PFG technique. The minimum diffusivity in the free methane phase D_f was estimated as 1.2×10^{-6} m^2/s. The self-diffusion coefficient of the molecules subject to exchange D_{ex} can be estimated using Eqs. (5) and (8) ($\alpha=D$, $\zeta=3$, and $\kappa=1$),

$$D_{ex}\approx p_f(0)D_f, \tag{14}$$

where $p_f(0)=t_f/t$ [1]. The proportion of free methane is about 0.4 as determined from ^{13}C-{^{1}H} spectroscopy data [17]. The self-diffusion coefficient for exchanging molecules therefore is 5×10^{-7} m^2/s.

According to this estimation, the magnetizations of the free and the exchanged adsorbate molecules decay in the SFF gradient (60 T/m) to less than 5% in 35 μs. This value was calculated assuming isotropic ordinary self-diffusion [Eq. (9), $\alpha=D$, $\zeta=3$, $\kappa=1$, and $\Delta=\tau_1$]. The fast attenuation of the free-methane magnetization is observed indeed as the initial drop of the PE curve (Fig. 2) between the first ($\tau_1=10$ μs) and the second data point ($\tau_1=110$ μs). For comparison, in the corresponding STE curve recorded with $\tau_2=3$ ms no such drop is visible because the magnetizations of the free methane phase were completely defocused after the much longer diffusion time in the STE experiment. That is, the echo signals acquired in the SFF experiments should solely be due to the adsorbed molecules.

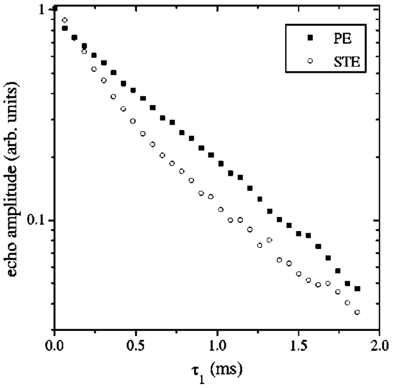

FIG. 2. Decays of the STE amplitude (○) for $\tau_2=3$ ms and the PE amplitude (■) as a function of τ_1.

Figure 3 shows a semilogarithmic plot of the quotient of STE and PE amplitudes as a function of $\tau_1^2\tau_2$. There is clear deviation from a linear decay, which would be expected for ordinary self-diffusion [see Eqs. (7) and (9)] in the absence of dipolar-correlation and exchange effects.

Likely the dipolar-correlation effect is not the source of the anomalous behavior. Apart from the interactions between adjacent molecules, the channel walls can lead to some anisotropy of the methane rotational diffusion. All these interactions fluctuate on relatively short time scales so that only averages matter. That is, a preferential orientation of the methane molecule relative to the channel walls is expected. As the channels are known to be straight, this orientation should be stationary as long as the molecule is inside its initial channel. Consequently, no dipolar-correlation effect should occur.

On the other hand, previous ^{13}C investigations showed that there is no residual dipolar coupling between ^{13}C and ^{1}H [17]. However, another anisotropic interaction was

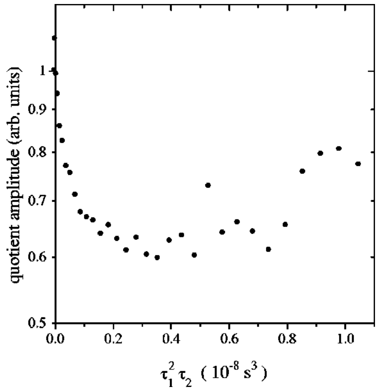

FIG. 3. Quotient of the STE and PE amplitudes as a function of $\tau_1^2\tau_2$.

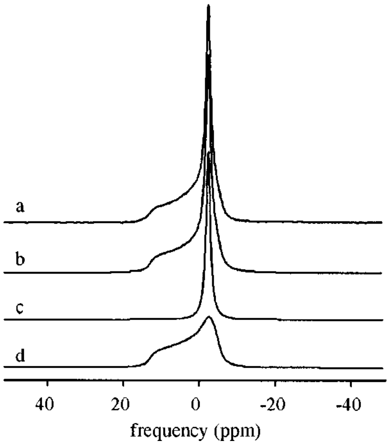

FIG. 4. (a) Experimental and (b) simulated ^{13}C-$\{^1H\}$ spectrum of methane in SAPO-11. The simulated spectrum consists of (c) a singlet and (d) a chemical-shift powder pattern arising from free and adsorbed methane, respectively.

found, namely, the shielding anisotropy of ^{13}C in methane. This somewhat surprising result indicates that the channel walls induce an average deformation of the originally symmetric shielding tensor, whereas they cannot prevent methane from rotating nearly isotropically.

Methane exchange between the adsorbed and free states was investigated by 2D exchange ^{13}C spectroscopy [21]. In Ref. [17] it was shown that free and adsorbed methane can be identified from the ^1H decoupled ^{13}C spectrum as a singlet and a chemical shift powder pattern, respectively (see Fig. 4). A corresponding 2D exchange spectrum is shown in Fig. 5. Cross correlations are obvious, indicating that a significant exchange occurs in an exchange time of 10 ms. Because of the unknown relaxation times and the short exchange time compared to the preparation and the observation intervals, no quantitative analysis has been tried so far.

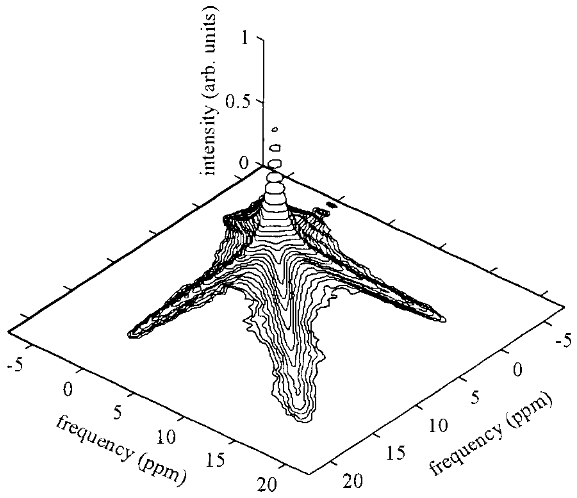

FIG. 5. ^{13}C-$\{^1H\}$ 2D exchange spectrum of methane in SAPO-11 recorded with a mixing time of 10 ms.

The echo amplitude quotient (see Fig. 3) is a decreasing function of τ_1, whereas $Q_{ads}(\tau_1,\tau_2)$ should increase with τ_1. The exchange of molecules from the intracrystalline channels takes place through the channel openings to the intercrystalline space. The molecules situated next to the openings therefore more likely exchange their environment than those in the middle of the channels. That is, the fraction of molecules staying in the adsorbed state during the whole pulse sequence decreases faster near the openings than in the middle of the channels.

A priori information suggests that for methane in SAPO-11 self-diffusion should be one dimensional without macroscopic order. From Eqs. (7) and (13a) the amplitude quotient of the STE and PE can be derived as

$$Q(\tau_1,\tau_2)=A^a_{r1}(\tau_2)\sqrt{\frac{2(2^\kappa-1)\tau_1^{\kappa+2}}{\frac{1}{2}(2\tau_1+\tau_2)^{\kappa+2}+\frac{1}{2}(\tau_2)^{\kappa+2}-(\tau_1+\tau_2)^{\kappa+2}-\tau_1^{\kappa+2}}}$$

$$\times\frac{\operatorname{erf}\left\{\sqrt{\frac{2\alpha\gamma^2G^2}{(\kappa+1)(\kappa+2)}\left[\frac{1}{2}(2\tau_1+\tau_2)^{\kappa+2}+\frac{1}{2}(\tau_2)^{\kappa+2}-(\tau_1+\tau_2)^{\kappa+2}-\tau_1^{\kappa+2}\right]}\right\}}{\operatorname{erf}\left\{\sqrt{\frac{2\alpha\gamma^2G^2}{(\kappa+1)(\kappa+2)}2(2^\kappa-1)\tau_1^{\kappa+2}}\right\}}. \tag{15}$$

Futhermore, the diameters of the SAPO-11 channel cross section (3.9×6.3 Å) and of the methane molecule (3.8 Å [22]) suggest that the adsorbed molecules cannot pass each other. Consequently, the nature of self-diffusion should be of the single-file type and the MSD of methane is proportional to the square root of time ($\kappa=1/2$) [4]. This is to be contrasted with the ordinary-diffusion case where the MSD depends linearly on time ($\kappa=1$).

The least-squares-fits to the experimental amplitude quotients are shown in Fig. 6 for both cases. The data points refer to the adsorbed phase of the adsorbate and were recorded with the SFF NMR diffusometry as described above. The two fitting parameters were a constant scaling factor and the one-dimensional diffusivity α. The first data point in the plot of Fig. 6 recorded for the shortest τ_1 value is obviously affected by the fast initial decay of the quotient function, that

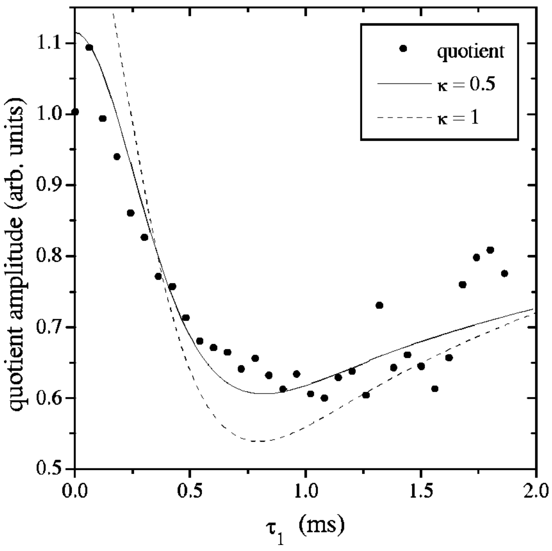

FIG. 6. Amplitude quotient of STE and PE for a τ_2 value of 3 ms as a function of τ_1. The lines represent fits of the one-dimensional self-diffusion model [see Eq. (15)] for ordinary (- - -) and single-file (—) self-diffusion. Note that the first point has been excluded from fits.

is, by those molecules that are close to the channel openings and consequently subject to fast exchange. This data point was therefore excluded from the fitting procedure. The constant scaling factor is proportional to the spin-lattice relaxation attenuation factor. The single-file self-diffusion formalism evidently fits better to our data. The resulting single-file diffusivity turned out to be $(9.6\pm 1.2)\times 10^{-13}$ m$^2/\sqrt{\mathrm{s}}$.

The above single-file diffusivity value is reasonable as can be estimated considering the mean absolute displacement $(\langle|z|\rangle=\sqrt{2\langle z^2\rangle/\pi})$ during the pulse sequence. For the longest pulse interval in the experiments (7 ms), it is about 0.32 μm. Field emission scanning electron micrograph of SAPO-11 shows that the crystal sizes are in the micrometer range (see Fig. 7). That is, adsorbate molecules in the middle of the channels have a good chance to remain in the adsorbed state during the whole pulse sequence. The corresponding fraction of molecules dominates the SFF diffusometry decays shown in Fig. 6.

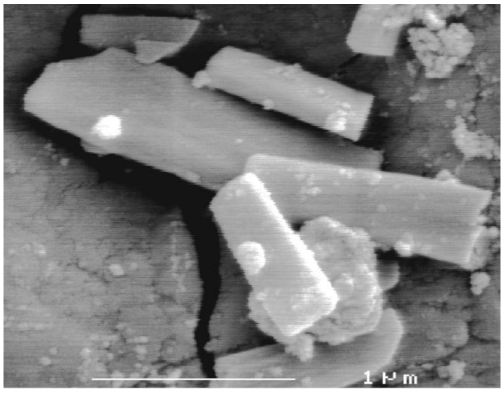

FIG. 7. Field emission scanning electron micrograph of SAPO-11.

This finding can be rationalized by formally factorizing the fraction of molecules adsorbed during the whole pulse sequence:

$$p_a(2\tau_1+\tau_2)=p_a(2\tau_1)\ p_a(2\tau_1,\tau_2), \tag{16}$$

where $p_a(2\tau_1,\tau_2)$ is the fraction still in the channels after the interval τ_2 of those molecules that were still in the channels after the initial interval $2\tau_1$. That is, $p_a(2\tau_1,\tau_2)$ must be considered as a fraction of a fraction (note the comma instead of the plus sign in the argument). The first factor on the right-hand side strongly depends on τ_1, but cancels in the quotient

$$Q_{ads}(\tau_1,\tau_2)=p_a(2\tau_1,\tau_2). \tag{17}$$

On the other hand, the second factor that determines the quotient Q_{ads} according to Eq. (17) is a very weak function of the pulse intervals. The pulse interval τ_2 is kept constant in the experiments so that no time dependence enters this way. The only time dependence that might be relevant here may arise from the spatial distribution of molecules still being adsorbed at the beginning of the subsequent τ_2 interval. This distribution may slightly vary with different τ_1 values. Beacuse τ_1 is usually adjusted to be shorter than τ_2 interval, any time dependence of this sort must be minor and $Q_{ads}(\tau_1,\tau_2)$ can be considered to be virtually constant. The quality of the fitted curves corroborates this conclusion. It is further supported by a Monte Carlo simulation suggesting that the exchange of adsorbed particles in finite single-file systems predominantly occurs during the first short interval at the beginning (see Fig. 7 in Ref. [5]), the fractions p_a of which cancel in the quotient Q_{ads}.

The single-file diffusivity is proportional to the clearance between the adjacent molecules and to the self-diffusion properties of single molecule alone in the channel [4]

$$\alpha=\underbrace{l\frac{1-f}{f}}_{\text{clearance}}\sqrt{\frac{D}{\pi}}, \tag{18}$$

where l is the elementary jump length of a molecule, f is the relative occupancy of the channel, and D is the self-diffusion coefficient of a single molecule in a channel. A molecular-dynamics simulation of xenon in AlPO$_4$-11 shows that xenon moves by jumping from adsorption cell to another [20]. As the diameters of xenon and methane molecules on the one hand and AlPO$_4$-11 and SAPO-11 channels on the other are similar, we conclude that methane should perform the same kind of jumps in SAPO-11. Under these circumstances the clearance can be estimated to be ~20 Å ($l=4.2$ Å and $f=0.175$), so that $D=0.7\times 10^{-6}$ m^2/s. This value is two orders of magnitude higher than the molecular-dynamics simulation result for xenon in AlPO$_4$-11 (6.5×10^{-9} m^2/s).

Previous PFG NMR diffusometry investigations [9–11] of single-file diffusion of various adsorbates in AlPO$_4$-5 and theta-1 molecular sieves referred to higher crystallite lengths (above 25 μm). The single-file diffusivities obtained under these circumstances varied from 7×10^{-13} m$^2/\sqrt{\mathrm{s}}$ to 1×10^{-10} m$^2/\sqrt{\mathrm{s}}$ at different temperatures. In order to compare the results, the effect of loading, i.e., the clearance between the molecules, must be taken into account. For the estimation of the clearance in AlPO$_4$-5, we have assumed two adsorption sites per unit cell with a distance of half of the unit cell length. This assumption is supported by molecular-dynamics simulations [6]. Our result for the single-molecule self-diffusion coefficient D is close to the values calculated for tetrafluoromethane ($\sim 1\times 10^{-6}$ m^2/s), whereas methane and ethane have considerably higher values, 8×10^{-4} m^2/s and 1.1×10^{-4} m^2/s, respectively, in AlPO$_4$-5 at room temperature. The lower D values are explained by the smaller channel diameter of SAPO-11 (7.3 $\times$7.3 Å for AlPO$_4$-5) and the larger adsorbate diameter of tetrafluoromethane (4.7 Å) as compared to methane or ethane in AlPO$_4$-5.

V. CONCLUSION

We have shown that the steady gradient (SFF) NMR diffusometry method permits the selective investigation of self-diffusion in microheterogeneous systems, where the differences in self-diffusion between the different environments are large. The effects of relaxation, exchange, and dipolar correlation have been considered. In particular, the factors affecting the adsorbate–molecular sieve systems are discussed. The amplitude attenuation factors for the PE and STE in the presence of a stationary gradient are derived for anomalous one- and two-dimensional self-diffusion with and without macroscopic order. Then the results are applied to investigate the intracrystalline self-diffusion of methane in SAPO-11. The conclusion is that methane undergoes single-file self-diffusion with an anomalous diffusivity of 9.6×10^{-13} m$^2/\sqrt{\mathrm{s}}$. This value compares favorably with values in significantly larger crystals of molecular sieves that can be studied with the ordinary PFG NMR diffusometry.

ACKNOWLEDGMENTS

J.J. and M.Y. thank the Academy of Finland for financial support. Moreover, M.Y. is grateful to the Tauno Tönning foundation and the University of Oulu for grants. UOP is thanked for providing us with SAPO-11.

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