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Application of the short diffusion time model to diffusion measurements by NMR in microporous crystallites

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Abstract

It is evident that the study of diffusion of molecules confined in microporous material, such as zeolites, gives valuable information about the chemical and geometrical properties of the pores. However, due to the limited size of the microporous crystallites or grains, and a non-zero observation time, it is difficult to measure true intra-crystalline diffusivity directly. The measured value of the intra-crystalline diffusivity as derived from PFG-NMR measurements turns out to be dependent on the observation time even if this is very short. This difficulty is inherent to the PFG-NMR technique and due to the limited size of microporous crystallites. Here we present NMR diffusion measurements of ethane confined in H-ZSM-5 crystallites where the mean crystallite diameter was of the order of 20 μm prior to the sample preparation. We apply the short diffusion time model and extrapolate to zero observation time to obtain the unrestricted intra-crystalline diffusivity. The root-mean-square displacement in the diffusion measurements is then only a small fraction of the mean crystallite diameter. We will also describe pitfalls which are present when analysing the experimental data sets.

Keywords: Ethane; H-ZSM-5; Intra-crystalline diffusion; PFG-NMR; Short diffusion time model

1. Introduction

The short diffusion time model proposed by Mitra et al. [1] was originally used to extract information on the surface-to-volume ratio in porous rocks. At short observation times only a small fraction of the molecules within the crystallites senses the crystallite borders. Then Mitra et al. have shown that a perturbation expansion of the measured diffusivity will deviate from the unrestricted intra-crystalline diffusion coefficient, D_0, given by the following equation [1]:

$$D(t) = D_0 - \frac{4D_0^{3/2}S}{9\pi^{1/2}V}\,t^{1/2}, \tag{1}$$

where D_0 is the bulk diffusivity, S is crystallite surface area, and V is the crystallite volume. For heterogeneous systems where the bulk diffusivity D_0 is an unknown parameter, a square root of time fit of the diffusivity $D(t)$ will, in addition to the surface-to-volume ratio, yield a fitted value for D_0.

When measuring the restricted intra-crystalline diffusivity where the restriction is the size of the

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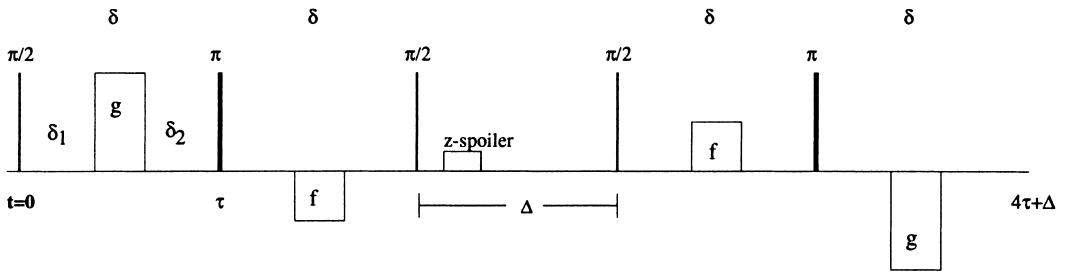

Fig. 1. The 13-interval PFGSTE sequence for unequal bipolar gradients. Δ denotes the standard observation time interval while the part prior to and after this interval represents the motional encoding and decoding intervals.

crystallite, one may use the short diffusion time model to find the unrestricted intra-crystalline diffusivity. The porous medium constitutes an ensemble of crystallites in which the diffusing particles are allowed to move. The diffusivity is orders of magnitude larger [2] for particles outside the microporous crystallites, thus entailing that the NMR signal from this small fraction is sufficiently suppressed when one is aiming at measuring the restricted intra-crystalline diffusivity using the pulsed field gradient stimulated echo (PFGSTE) experiment shown in Fig. 1 [3].

The fraction of particles being exchanged between the two regions, the inter- and intra-crystalline space, is small or negligible at short observation times. Thus, for short observation times, the root-mean-square displacement is much less than the mean diameter of the crystallites. The proposed method for measuring unrestricted intra-crystalline diffusion has been applied by Sørland [4] and Hansen et al. [5]. However, the reported values of the $D(t)/D_0$ ratio at the shortest observation times are in our opinion too small to justify the application of the short diffusion time model of Mitra et al. When the $D(t)/D_0$ ratio for the shorter observation time is down to approximately 0.7, Mitra et al. [1] demonstrated that higher order correction terms will affect the measured diffusivity. Then, as the observation time increases, the short observation time model proposed by Mitra et al. [1] is no longer valid. It was also shown experimentally [6] when measuring the restricted intra-crystalline diffusivity of ethane confined in H-ZSM-5 at room temperature that the derivative of $D(t)$ with respect to $\sqrt{t}$ changed significantly when the observation time of the experiment was reduced. The extrapolated values for D_0 then changed from 5.67×10^{-6} cm^2/s to approximately 1.0×10^{-5} cm^2/s.

In order to achieve values of the $D(t)/D_0$ ratio close to 0.9, we investigated the same system as that presented in Refs. [4,6], but reduced the temperature at which the diffusion measurements were performed. When this ratio is close to 0.9, the experimental data points are within the same domain as the data presented by Latour et al. [7] for an equivalent system, restricted diffusion of intracellular fluid in onion. Those measurements were the first ones to experimentally verify the square root of time behaviour of the diffusivity at short observation times.

2. Experimental

The experiments were performed with a Bruker Avance DMX400 spectrometer, and magnetic field gradient strengths up to 700 Gauss/cm were applied. The sample of the saturated ethane confined in H-ZSM-5 crystallites, where the mean crystallite diameter was of the order of 20 μm, was cooled to three temperatures: 213 K, 223 K and 233 K. For each temperature a set of diffusion measurements was performed as a function of observation time. The 13-interval PFGSTE pulse sequence [3] shown in Fig. 1 was applied. In contrast to other well-established modes of PFG-NMR experiments for diffusion measurements in zeolites [2], this experiment suppresses the coupling between a constant internal magnetic field

gradient and the applied magnetic field gradient by introducing 180° RF pulses into the PFGSTE sequence [8,9]. To suppress the coupling completely, we put $\delta 1 = \delta 2$ (=0.45 ms). Denoting $g = g_{cal} i$ and $f = g_{cal}(i - x)$, the echo attenuation for the given PFGSTE experiment can be written [3]:

$$\ln\frac{I}{I_0} = -\gamma^2(2\delta)^2 g_{cal}^2 D\left[\Delta + \frac{3}{2}\tau - \delta/6\right] \times \left[i - \frac{1}{2}\left(\frac{\Delta + \tau - \delta/6}{\Delta + \frac{3}{2}\tau - \delta/6}\right)x\right]^2. \quad (2)$$

Here i is the current (A), x is the difference in current amplitude between f and g, and g_{cal} is the calibrated gradient strength (Gauss/cm A). The gradient pulse length was set to 0.5 ms, and the difference in gradient strength between f and g was 2.5 Gauss/cm. The τ value then equals 1.4 ms. The observation time Δ ranged from 1 ms to 9 ms. In the fitting procedure of the experimental data sets we used the effective diffusion time which corrects for restricted diffusion during the motional encoding/decoding in the PFGSTE experiment [10]. When analysing the results from the PFGSTE experiment we also made use of the second cumulant approximation stating that the initial decay of the magnetisation as a function of g is most dependent on the lowest order of g. Since the contributions from higher orders of g are much smaller than the contribution from the second order moment at short times, the initial decay should reflect a Gaussian distribution which takes into account the non-linear attenuation in the PFGSTE experiment [11,12] (see Figs. 2 and 3).

Fig. 2 shows a typical attenuation obtained from the 13-interval PFGSTE experiment. Two fractions are clearly resolvable, for which the difference in mobility is approximately two orders of magnitude. However, to analyse the fraction arising from the intra-crystalline ethane, we had to neglect the early stages of the data set in which there is a possible contribution from rapidly diffusing inter-crystalline ethane. Due to a distribution of inter-crystalline diffusivities, it is not possible to perform a one-component fit of the fast diffusing fraction, subtract it from the echo attenuation, and analyse the remaining fraction as being solely the signal from the intra-crystalline ethane. Thus, the first point used from the echo attenuation was at the position where the NMR signal from the fast diffusing inter-crystalline ethane was suppressed by a factor of approximately $e^{-5} = 0.0067$. This is the same criterion as the one used to determine the recycle delay due to the longitudinal relaxation time constant in multi-scan experiments [13].

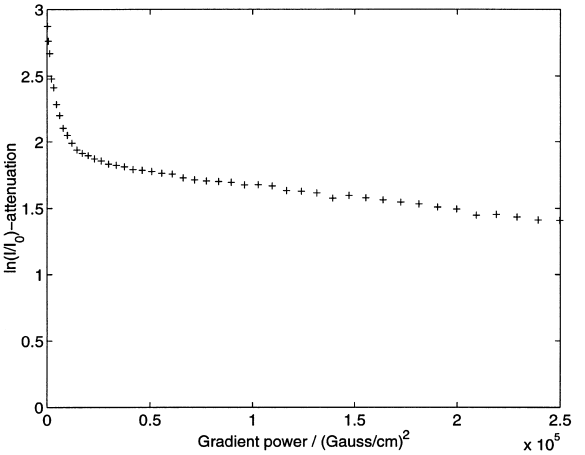

Fig. 2. Natural logarithm of the echo attenuation obtained from a 13-interval PFGSTE experiment of ethane in a saturated H-ZSM-5 sample at 213 K.

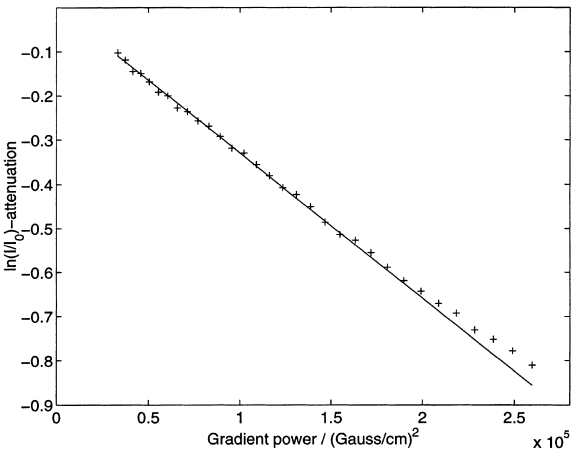

Fig. 3. Natural logarithm of the echo attenuation when the signal contribution from inter- and intra-crystalline ethane simultaneously present has been neglected. The $\ln(I/I_0)$ attenuation was linear down to approximately -0.4 for all data sets.

The intra-crystalline diffusivity was found by a weighted least-squares fit to the initial slope of the remaining points in the echo attenuation. This is in accordance with the second cumulant approximation [11]. Fig. 3 shows such a fit after removing the initial points which might contain a contribution from the inter-crystalline ethane. The $\ln(I/I_0)$ attenuation is linear down to approximately -0.5 where it starts to deviate from a straight line. This is expected, since we observed the same behaviour when studying an ideal system, i.e restricted diffusion of water among compact mono-sized spheres at short observation times [12]. Since restricted diffusion during the motional encoding in the PFGSTE experiment was taken into account when analysing the experimental data, our approach is significantly different from the one used by Hansen et al. [5].

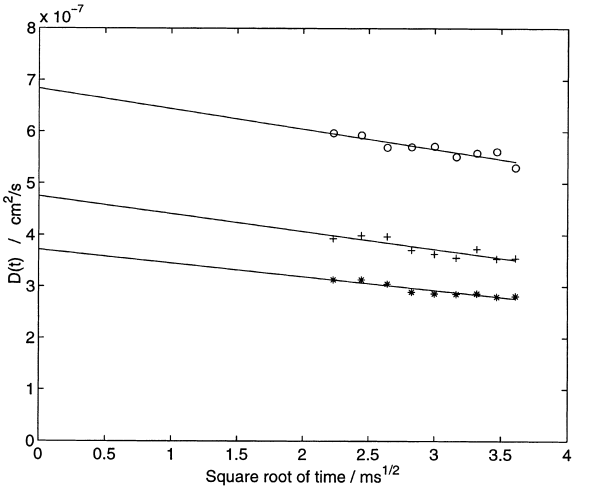

Fig. 5. Short observation time diffusion measurements at different temperatures (* = 213 K, + = 223 K, ○ = 233 K). The solid line indicates the fit to the unrestricted intra-crystallite diffusivity.

3. Results and discussion

To illustrate the benefit from using the 13-interval PFGSTE sequence, we have compared a 13-interval PFGSTE experiment with a standard PFGSTE experiment using the same effective observation time (see Fig. 4). As expected, using the ordinary PFGSTE sequence, the fitted value of the restricted intra-crystalline diffusivity is significantly smaller than the value found when using the 13-interval PFGSTE sequence [9]. The diffusivity obtained from the 13-PFGSTE experiment is more than 40% larger than the diffusivity extracted from the ordinary PFGSTE experiment. The number of scans in the experiments is the same, and one clearly sees that the signal-to-noise ratio obtained when using the ordinary PFGSTE sequence is poor compared to that from the 13-interval PFGSTE sequence. This effect is caused by the 180° RF pulses, which refocus the NMR signal due to diffusion in an inhomogeneous magnetic field. The effective transverse relaxation time, T_2^*, is then significantly increased for the 13-interval PFGSTE sequence.

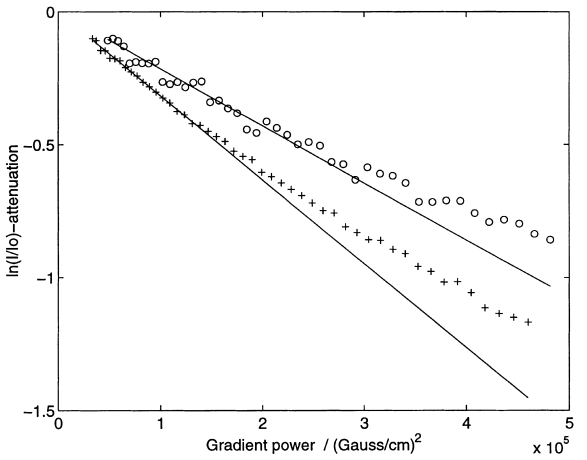

Fig. 4. Comparison of data from the 13-PFGSTE experiment (+) to the ordinary PFGSTE experiment (○) for a sample of ethane confined in H-ZSM-5. The observation time is the same for the two experiments; $D^{+} = 5.51 \times 10^{-7}$ while $D^{\circ} = 3.85 \times 10^{-7}$.

Fig. 5 shows the result for $D(t)$ at three different temperatures: 213 K, 223 K, and 233 K. The first fitted measuring point for the three data sets yields a value of $D(t)/D_0$ which varies from 0.84 to 0.87 (see Table 1). Being this close to the fitted D_0, we believe that the experiments show that it is possible to extract the value for the unrestricted intra-crystalline diffusivity using the short observation time model proposed by Mitra et al. [1]. Without

Table 1
Unrestricted intra-crystalline diffusivities for ethane confined in H-ZSM-5 at different temperatures

Temperature (K)	D_0 (10^{-7} cm^2/s)	$D(t_{min})/D_0$	$D(t_{max})/D_0$
213	3.71	0.84	0.74
223	4.75	0.84	0.74
233	6.83	0.87	0.79

this short diffusion time fit, the measured intra-crystalline diffusivity would have been underestimated by at least 10% depending on the setting of the observation time.

The fitted surface-to-volume ratio for the experiments yielded a mean crystallite diameter of 5 μm which is significant smaller than the actual mean value. The discrepancy can be explained in the following way: there is a distribution of crystallite diameters, and the restricted geometry is first sensed by the molecules confined in the crystallites with smaller diameters. Thus, the values for the surface-to-volume ratio obtained from the diffusion experiments will be more affected by the smaller than the larger crystallites. This will result in an observed crystallite diameter which is smaller than the actual mean crystallite diameter.

Using the fitted unrestricted diffusivity, the root-mean-square displacement during the observation time is found to be approximately 1 μm or less. The values at the shortest observation time, 2.5 ms, approach 0.5 μm. This indicates that the first measured points are within the region where the square root of time fit is valid. At longer observation times, the fraction of molecules experiencing the crystallite surfaces increases. The model proposed by Mitra et al. [1], which assumes that only a small fraction of the molecules are experiencing the crystallite surfaces, will then be violated. However, due to the variance in our measured restricted diffusivities at the longer observation times, up to 10.5 ms, it is not possible to reveal a deviation from the square root of time fit (Fig. 5).

At even longer observation times the picture of isolated crystallites is not valid, as exchange between the inter- and intra-crystalline space takes place. Therefore, the measured restricted intra-crystalline diffusivities at longer observation times do not fit into the short diffusion time model. Furthermore, any deviation from linearity at longer observation times cannot be used to obtain reliable information on the surface relaxivity or curvature of the crystallites by adding higher order terms to Eq. (1) [1]. Another point is that, to cancel the cross-terms between the applied and internal magnetic field gradients using the 13-interval PFGSTE sequence, one must assume that each molecule is experiencing a constant value of the internal magnetic field gradient during the observation time [14]. As the observation time increases it becomes more likely that the molecules by the end of the observation time will have moved so far away from the starting point that neither the value nor the polarity of the internal magnetic field gradient will be the same at the end of the motional decoding as at the beginning of the motional encoding. The result is then a 13-interval PFGSTE sequence which is not as efficient in cancelling the cross-terms at longer compared to shorter observation times. This results in an erroneous value of the measured diffusivity at longer observation times, which is affected by the coupling term between the applied and internal magnetic field gradients.

4. Conclusions

We have shown that it is possible to use the short time diffusion model proposed by Mitra et al. [1] to indirectly measure unrestricted intra-crystalline diffusion. However, it is important to be aware of the several pitfalls which follow this procedure.

The first measuring point of the $D(t)/D_0$ ratio should be larger than 0.80 in order to have only a small fraction of intra-crystalline molecules sensing the crystallite surfaces.

Due to the expected large distribution of inter-crystalline cavity sizes, the measured averaged inter-crystalline diffusivity will reflect a distribution of diffusivities. When measuring the intra-crystalline diffusivity from the echo attenuation, one should therefore exclude the early stages of the PFGSTE attenuation which may contain a possible contribution from inter-crystalline molecules.

The initial slope of the PFGSTE attenuation should be used to obtain the true intra-crystalline diffusivity in order to correct for the non-linear attenuation in the PFGSTE experiment. Corrected effective diffusion times should also be used when analysing the measured restricted intra-crystalline diffusivities to take into account the restricted diffusion during motional encoding.

At longer observation times effects from higher order correction terms of the observation time, exchange between inter- and intra-crystalline molecules, and a failure to suppress the coupling between applied and internal magnetic field gradients will affect the measured diffusivity.

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References

[1] P.P. Mitra, P.N. Sen, L.M. Schwartz, Phys. Rev. B 47 (1993) 8565.
[2] J. Kärger, D.M. Ruthven, Diffusion in Zeolites and other Microporous Solids, Wiley, New York, 1992.
[3] G.H. Sørland, B. Hafskjold, O. Herstad, J. Magn. Reson. 124 (1997) 172.
[4] G.H. Sørland, Ph.D. Thesis, NTNU; IFK report 51, 1997.
[5] E.W. Hansen, F. Courivaud, A. Karlsson, S. Kolboe, M. Stöcker, Micropor. Mesopor. Mater. 22 (1998) 309.
[6] G.H. Sørland, D.W. Aksnes, L. Gjerdåker, J. Magn. Reson. 137 (1999) 397.
[7] L.L. Latour, P.P. Mitra, R.L. Kleinberg, C.H. Sotak, J. Magn. Reson. A 101 (1993) 342.
[8] L.E. Drain, Proc. Phys. Soc. 80 (1965).
[9] J. Zhong, R.P. Kennan, J.C. Gore, J. Magn. Reson. 95 (1991) 267.
[10] E.J. Fordham, P.P. Mitra, L.L. Latour, J. Magn. Reson. 121 (1996) 187.
[11] P.P. Mitra, B.I. Halperin, J. Magn. Reson. 113 (1995) 94.
[12] G.H. Sørland, J. Magn. Reson. 126 (1997) 146.
[13] J.K.M. Sanders, B.K. Hunter, Modern NMR Spectroscopy. A Guide for Chemists, Oxford University Press, Oxford, 1993.
[14] R.M. Cotts, M.J.R. Hoch, T. Sun, J.T. Markert, J. Magn. Reson. 83 (1989) 252.