

A Pulsed Field Gradient Spin-Echo Method for Diffusion Measurements in the Presence of Internal Gradients

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Over the past decade several pulsed field gradient stimulated-echo methods have been presented for diffusion measurements in heterogeneous media. These methods have reduced or eliminated the coupling between the applied magnetic field gradient and a constant internal magnetic field gradient caused by susceptibility changes throughout the sample. For many research purposes the *z*-storage delay between the second and third $\pi/2$ RF pulse has been included in order to increase the decay of the echo attenuation to an appropriate level and to increase the signal-to-noise ratio by avoiding T_2 relaxation of the magnetization in parts of the pulse sequence. For these reasons a stimulated-echo method has been applied instead of a spin-echo method. When studying systems where it is necessary to keep the duration of the pulse sequence at a minimum, and one is not dependent on using *z*-storage time to increase the echo attenuation or to study diffusion as a function of observation time, a spin-echo method should be chosen. Here we propose a bipolar pulsed field gradient spin-echo method which is well suited to this purpose, and preliminary diffusion measurements are presented as illustration.

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Key Words: pulsed field gradient spin-echo method; bipolar magnetic field gradients; short observation time; restricted intracrystallite diffusion; zeolites.

INTRODUCTION

In work with diffusion measurements in heterogeneous media it has become evident that a bipolar form of the pulsed field gradient sequence is a powerful method for reducing the cross term between the applied and internal magnetic field gradient (1) and in reducing the eddy current dead time (2). Without a bipolar version of the gradient pulse sequences, the measured diffusivities might be underestimated (3, 4), and errors due to eddy current field are likely to occur when analyzing a Fourier transformation of the FID of the echo signal (2). The basic assumption for elimination of the effect caused by the cross term when deriving the echo attenuation is that all molecules are experiencing a constant internal magnetic field gradient during the pulse sequence. This assumption is at its highest validity when having the shortest duration on the pulse sequence applied.

For porous systems where porous grains or crystallites are of the same order of magnitude as the distance traveled by the

molecules during the pulse sequence, it is important to keep the diffusion time short. With shorter diffusion times the distance traveled by the molecules during the pulse sequence is reduced. Depending on the crystallite sizes it will then be possible to extract true intracrystallite diffusion coefficients instead of a diffusion coefficient which is significantly affected by restrictions at the crystallite surfaces.

The application of bipolar magnetic field gradients in the preparation and read intervals introduces two or more π RF pulses in the pulse sequence. Depending on the RF-field homogeneity this may result in a significant signal contribution from unwanted coherence transfer pathways (5) to the echo attenuation, which again will lead to an erroneous interpretation of the analysis of the echo attenuation (6, 7). This unwanted echo signal can be greatly reduced or removed by applying sophisticated phase cycling schemes (2), orthogonal spoiler gradients (6), or unequal bipolar gradients (7).

As the present NMR diffusion probes and gradient power supply may generate magnetic field gradient strengths that make the *z*-storage period unnecessary, a bipolar version of the pulsed field gradient spin echo (PFGSE) can be employed instead of a stimulated-echo sequence. Karlicek *et al.* (8) presented a set of PFGSE sequences which are spin echo analogues to the stimulated echo sequences presented by Cotts *et al.* (1), starting from the 17-interval sequence and upward. Here we present the spin-echo analogue to the 13-interval stimulated-echo sequence given by Cotts *et al.*, the so-called 11-interval bipolar PFGSE sequence.

The benefit from using the proposed sequences is that the constant background gradient assumption is at its highest validity, the diffusion time is reduced to a minimum, and less unwanted echo signal is generated compared to the 13-interval (pulsed field gradient stimulated-echo (PFGSTE) sequence and to the PFGSE sequences presented by Karlicek *et al.* (8).

THEORY

The general PFGSE method for measuring diffusion consists of two intervals, the preparation and the read interval (Fig. 1).



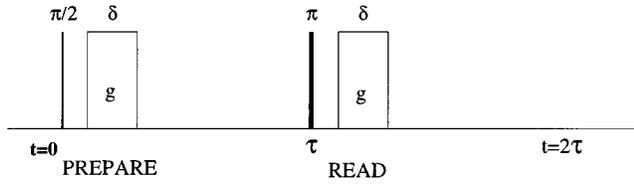


FIG. 1. The PFGSE sequence where the prepare interval labels the phases of the spins, and the read interval unlabels the spins.

In the preparation interval the molecules are labeled with a phase proportional to the integral of the effective gradient $g(t)$ in the longitudinal direction,

$$\phi = \gamma \int g(t) z(t) dt, \quad [1]$$

where γ is the gyromagnetic ratio and $z(t)$ the longitudinal position of the molecules. In the read interval, the spins are unlabeled, and if molecules have moved in the direction of the applied magnetic field gradient during the sequence, this will result in a dephasing of the magnetization given by

$$\Delta\phi = \gamma g \delta (Z_{\text{com}}^{\text{read}} - Z_{\text{com}}^{\text{prepare}}), \quad [2]$$

where g is the amplitude of the pulsed magnetic field gradient, δ is the duration of the gradient pulse, and $(Z_{\text{com}}^{\text{read}} - Z_{\text{com}}^{\text{prepare}})$ is the center of mass distance traveled by the molecules during the pulse sequence (9). When dephasing due to diffusion is taken into account, the logarithm of the normalized echo attenuation of a homogeneous system is generally written (8)

$$\ln \frac{I}{I_0} = -\gamma^2 D \int_0^t \left(\int_0^{t'} g(t'') dt'' \right)^2 dt', \quad [3]$$

where D is the diffusion coefficient.

The proposed 11-interval PFGSE sequence is shown in Fig. 2. When splitting the sequence into its separate RF and gradient parts, one observes that the RF-pulse sequence is a double spin echo while the gradient sequence is identical to the bipolar

version presented by Sørland *et al.* (7). The part of the 13-interval PFGSTE sequence which stores the magnetization in the longitudinal direction is simply omitted. This is the shortest bipolar PFGSE sequence which is possible to construct when one is aiming at reducing or eliminating the effect of diffusion in the presence of strong internal magnetic field gradients. In contrast to the ordinary PFGSTE sequence there is no store period in which the spins are allowed to diffuse between labeling and unlabeled, and a significant echo attenuation will thus be more dependent on the features of the diffusion probe and gradient power supply.

Following the procedure of Cotts *et al.* (1) we divide the sequences into 11 parts where the effective $g(t)$ is not changed by the RF pulses or onset/offset of applied magnetic field gradient pulses. Then we may perform the evaluation of Eq. [3] sequentially. Denoting $g = g_{\text{cal}} \cdot i$ and $f = g_{\text{cal}} \cdot (i - x)$ where g_{cal} is the gradient strength per ampere, and i and $(i - x)$ are current amplitudes, the result for the 11-interval sequence is given by

$$\ln \frac{I}{I_0} = -\gamma^2 D g_{\text{cal}}^2 (2\delta)^2 \left[\frac{3}{2} \tau - \frac{\delta}{6} \right] \left[i - \frac{x}{2} \left(\frac{\tau - \delta/6}{\frac{3}{2}\tau - \delta/6} \right) \right]^2 - \gamma^2 D g_{\text{cal}} \delta (\delta_1 - \delta_2) \tau (2i - x) G_0 + \text{offset}, \quad [4]$$

where x is the difference in gradient strength between f and g . The offset is a small constant term due to this difference in amplitude of f and g , and is given by

$$\text{offset} = -\gamma^2 D \delta^2 \left(\frac{(\tau - \delta/6)^2}{\frac{3}{2}\tau - \delta/6} - (\tau - \delta/3) \right) x^2. \quad [5]$$

The time constants are defined according to Fig. 2. When $x = 0$ there is no difference in amplitudes of f and g , and the offset term equals 0. Equations [4] and [5] are thus valid for both equal and unequal bipolar gradients. A small cross term is left between the applied and the internal magnetic field gradient as for the 13-interval PFGSTE sequence. This term is canceled provided $\delta_1 = \delta_2$.

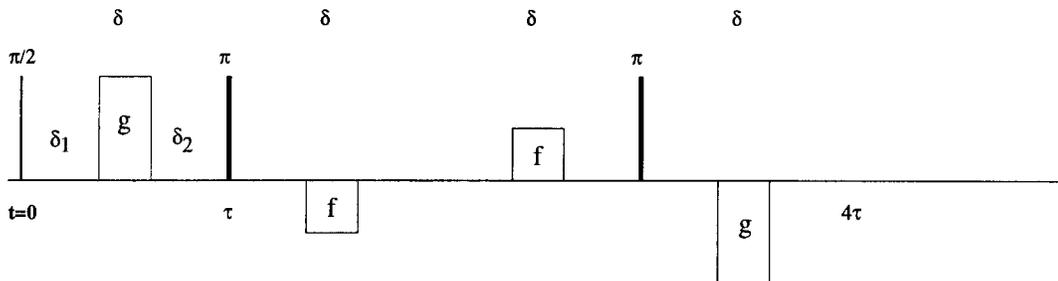


FIG. 2. The 11-interval PFGSE sequence with bipolar gradients.

TABLE 1
A Phase Sequence Which Removes Unwanted Coherence Transfer Pathways in the 11-Interval Spin-Echo Sequence

Number	$\pi/2$	First π	Second π	Receiver
1	+x	+y	-y	+x
2	+x	+y	+y	+x
3	+x	+y	-x	-x
4	+x	-x	+y	-x

EXPERIMENTAL

The experiments were performed with a Bruker Avance DMX200 spectrometer using a homebuilt diffusion probe and a DMX400 spectrometer using a commercially available Bruker diffusion probe. For the homebuilt diffusion probe the maximum gradient strength applied was approximately 1 T/m while one had access to 9 T/m using the Bruker diffusion probe.

The echo attenuations resulting from the diffusion experiments were recorded in real time domain at the time of the echo; $t = 4\tau$. Thereby any impact from magnetic field transients on the experimental datasets was minimized. No shift in the appearance of the echo peak was observed, and any significant mismatch between the time integral of the applied effective gradient in the preparation and read interval is for this reason not present. Applying gradient preemphasis with three exponential correction terms, the eddy current dead time was less than 350 μs for both diffusion probes. Without preemphasis adjustment the dead times were approximately 1–2 ms, depending on pulse sequence and gradient pulse lengths employed.

For the calibration measurements we made use of distilled water, while the diffusion measurements for illustration of the proposed sequence were performed on ethane confined in H-ZSM5 zeolites.

The H-ZSM5 diffusion measurements at the longest observation times were done with the homebuilt diffusion probe applying gradient pulse lengths of 1 ms with amplitudes up to 1 T/m. The 13-interval stimulated-echo sequence (7) had to be used as proper signal-to-noise required a storage of the NMR signal in the longitudinal direction when studying the apparent intracrystallite diffusion at relatively long observation times. Since the longitudinal relaxation time for ethane in H-ZSM5 is of the order of 100 ms while the transverse relaxation time is of the order of 1 ms, the observation time was varied by changing the duration of the store period (7). For the shortest observation times we used the proposed 11-interval spin-echo sequence and a maximum gradient strength of 4.5 T/m for the 0.5-ms-long gradient pulses. The observation time was then changed by increasing δ_2 from 850 μs and upward. δ_1 was set to 50 μs for all experiments.

The phase sequence employed for the 11-interval spin-echo sequence is given in Table 1, and it is constructed for removing

unwanted coherence transfer pathways as $p = 0 \rightarrow -1 \rightarrow -1 \rightarrow -1$ and $p = 0 \rightarrow -1 \rightarrow 0 \rightarrow -1$. Unwanted coherence transfer pathways as $p = 0 \rightarrow 1 \rightarrow -1 \rightarrow -1$ will not contribute to the NMR echo signal as the sequence of effective gradient pulses does not result in a gradient echo with this coherence transfer pathway.

RESULTS AND DISCUSSION

As in Sørland *et al.* (7), we performed a set of magnetic field gradient calibration experiments in order to check the degree of removal of signal arising from possible unwanted coherence transfer pathways. The duration of the $\pi/2$ and π RF pulses was deliberately set to values different from the correct ones, and for each experiment a gradient strength was fitted to the monoexponential echo attenuation (Fig. 3). As can be seen in Fig. 3 there is no significant RF-pulse dependence for the two curves using equal and unequal bipolar magnetic field gradients. All values are within 0.218 ± 0.002 T/m A, but there seems to be a small systematic difference in calibrated gradient strength when comparing the gradient strength values from the equal bipolar gradient experiments with the values from the unequal bipolar gradient experiments. If this difference were due to a failure in removing the unwanted NMR signal when using equal bipolar gradients, this should result in a nonlinear behavior in the logarithm of the spin-echo attenuation. Figure 4 shows a recording of the echo attenuation using equal bipolar gradient, and one may see that there indeed is a linear behavior down to at least -8 . The small systematic difference may be explained in the following way. There is a difference in magnetic field transients induced by a pair of equal bipolar gradients compared to a pair of unequal bipolar gradients. The larger

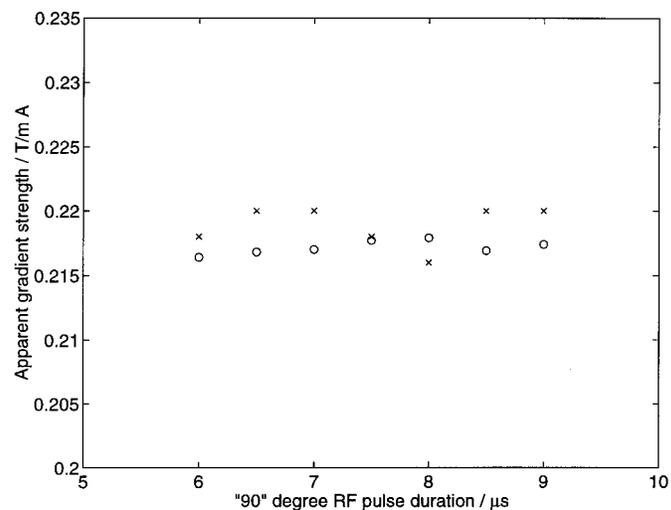


FIG. 3. Apparent gradient strength as a function of the length of the “90°” RF pulse. (○) Apparent gradient strength values for the sequence with equal bipolar gradients; (×) Values for the sequence with unequal bipolar gradients. The real 90° pulse was found to be 7.5 μs .

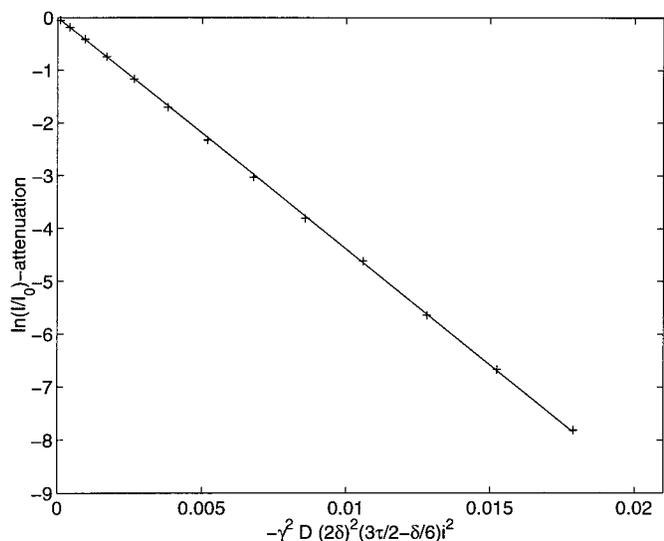


FIG. 4. The $\ln(I/I_0)$ attenuation for the 11-interval PFGSE sequence using equal bipolar gradients ($x = 0$). The solid line represents the linear calibration with gradient strength 0.209 T/m A.

the difference is in absolute magnitude between the gradient pulses in a bipolar pair, the less efficient is the cancellation of the magnetic field transients following the pair. As the calibrated gradient strength is dependent on the time integral of the magnetic field gradient over the test sample, one should therefore expect higher calibration values when using unequal bipolar gradients.

The 11-interval spin-echo analogue to the 13-interval stimulated-echo sequence is not as sensitive to whether one is using equal or unequal bipolar gradients, and for the illustrative diffusion experiments on ethane in H-ZSM5 we have made use of equal bipolar gradients. In Fig. 5 we have displayed the two sets of diffusion measurements as described under Experimental. Due to the shorter duration of the gradient pulses and no store period applied when using the 11-interval spin-echo sequence, we were able to reduce the minimum effective diffusion time from 3.8 ms using the 13-interval PFGSTE sequence to 2.1 ms. The achieved reduction in observation time revealed useful information on the measured intracrystallite diffusion, as we observe that by decreasing the observation time, the measured diffusivity increased. This can be explained by the fact that as observation time decreases, fewer intracrystallite ethane molecules are experiencing the restrictions at the surface barriers, and fewer restrictions are imposed on them. Those molecules leaving the crystallites during the diffusion experiment are not contributing to the spin-echo attenuation as the echo signal from the fast-diffusing intercrystallite ethane is suppressed by the applied magnetic field gradient pulses. The increase in the measured diffusivity is not an eddy current effect because the gradient strength used in the 11-interval spin-echo sequence was calibrated for each value of δ_2 , and the error in the calibrated gradient strength was within $\pm 2.5\%$.

This error varied randomly when decreasing δ_2 down to 350 μs . For our preliminary measurements, the shortest δ_2 applied was 850 μs .

The shorter the observation time the closer we are to measuring the true intracrystallite diffusion. When the observation time is sufficiently short, one should be able to fit the experimental dataset into the short diffusion time model proposed by Mitra *et al.* (10). Then, the fitted value at zero observation time should give the true intracrystallite diffusivity. Our preliminary diffusion measurements are not close enough to perform such a fit with proper accuracy since the course of the curve in Fig. 5 is not determined for shorter observation times. However, the slope indicates that the true intracrystallite diffusivity is approaching $1.0 \cdot 10^{-9} \text{ m}^2/\text{s}$. The measurements do, however, demonstrate the need for measuring diffusion at as short observation times as possible, and it is for this purpose we have designed the 11-interval PFGSE sequence for diffusion measurements in the presence of internal magnetic field gradients.

CONCLUSION

We have introduced the 11-interval spin-echo analogue to the 13-interval stimulated-echo sequence for accurate diffusion measurements in the presence of significant internal magnetic field gradients. The 11 intervals yield the shortest sequence which is possible to construct when one is aiming at canceling the cross terms between the applied and internal magnetic field gradients by using bipolar gradient pulse pairs. The proposed sequence is less sensitive to unwanted coherence transfer pathways when using the proposed phase cycle, leading to a linearity of the logarithm of the echo attenuation down to at least -8 . The measurements of the apparent intracrystallite diffu-

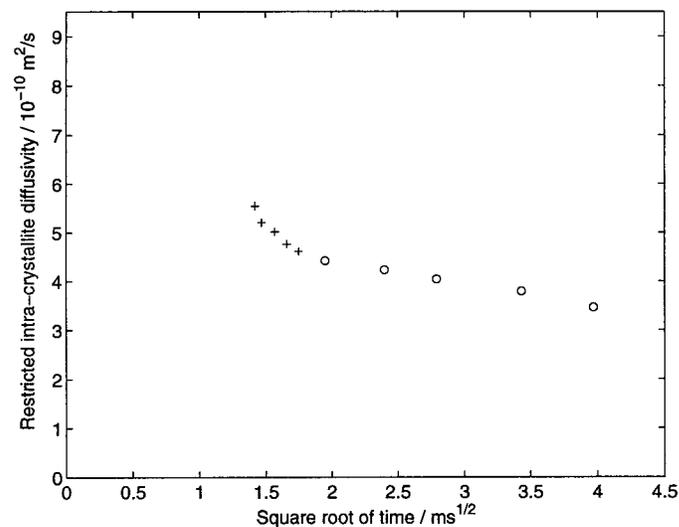


FIG. 5. Measured restricted intracrystallite diffusivity of ethane in H-ZSM5 at different diffusion times. +, data acquired with the 11-interval PFGSE sequence; and O, data acquired with the 13-interval PFGSTE sequence.

sion of ethane in H-ZSM5 illustrate that important information on the behavior of the measured diffusivity is revealed when decreasing the observation time by using the shortest pulse sequence possible.

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REFERENCES

1. R. M. Cotts, M. J. R. Hoch, T. Sun, and J. T. Markert, *J. Magn. Reson.* **83**, 252 (1989).
2. D. Wu, A. Chen, and C. S. Johnson, Jr., *J. Magn. Reson. A* **115**, 260 (1995).
3. J. Zhong, R. P. Kennan, and J. C. Gore, *J. Magn. Reson.* **95**, 267 (1991).
4. J. M. Dereppe, C. Moreaux, and F. Humbert, *Microporous Mesoporous Mater.* **21**, 645 (1998).
5. A. D. Bain, *J. Magn. Reson.* **56**, 418 (1984).
6. L. L. Latour, L. Li, and C. H. Sotak, *J. Magn. Reson. B* **101**, 72 (1993).
7. G. H. Sørland, B. Hafskjold, and O. Herstad, *J. Magn. Reson.* **124**, 172 (1997).
8. R. F. Karlicek and I. J. Lowe, *J. Magn. Reson.* **37**, 75 (1980).
9. P. P. Mitra and B. I. Halperin, *J. Magn. Reson. A* **113**, 94 (1995).
10. P. P. Mitra, P. N. Sen, and L. M. Schwartz, *Phys. Rev. B* **47**, 8565 (1993).