

A Stimulated-Echo Method for Diffusion Measurements in Heterogeneous Media Using Pulsed Field Gradients

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The pulsed-field-gradient stimulated-echo method is a well-established technique for studying molecular motion without disturbing the system under investigation. In porous media, the effects from internal magnetic field gradients make it necessary to perform compensatory sequences. Short relaxation times make it necessary to use as short pulse a sequence as possible. Here a pulse sequence which gives reliable diffusion measurements without the need for orthogonal spoiler gradients is presented, and the number of $\pi/2$ and π pulses is kept at a minimum. Experimental verification for the removal of unwanted echoes using the proposed PFGSTE sequence is provided, and preliminary diffusion measurements for ethane in a saturated H-ZSM5 zeolite are presented. © 1997 Academic Press

INTRODUCTION

In work with diffusion measurements in porous media using low magnetic field gradients, there is a need for pulse sequences which cancel or reduce the effect from the cross term between the applied and internal magnetic field gradient. Due to differences in magnetic susceptibilities in heterogeneous media, internal gradients will be induced, and the measured diffusivity in the presence of internal gradients of the same order of magnitude as the applied magnetic field gradients will be lower than the actual diffusivity. This can be explained as follows: Assuming that there is a diffusion distribution function for the spins, the internal magnetic field gradients will weigh this distribution function at the time of the echo. This is because the degree of unwanted dephasing caused by the internal gradients is a function of the diffusivity. At the time of the echo, a fraction of fast diffusing spins from the distribution function will be more attenuated due to internal gradients than a fraction of slow diffusing spins. This results in a measured mean diffusivity that is biased toward the slow diffusing spins, and not the mean diffusivity given by the correct distribution function.

There are in principle two approaches to circumvent or reduce the effect from the internal magnetic field gradients: One can use a considerably larger applied gradient so that the cross term between the applied and internal gradient

becomes small compared to the square of the applied gradient (I). The other approach is to use bipolar gradients together with RF pulses in such a manner that the cross terms are canceled or reduced (2).

Introducing several RF pulses into the sequence induces unwanted echoes which interfere with the uptake of the stimulated echo of interest. There exist numerous inventive sequences to suppress the unwanted echoes by using phase cycles according to the correct coherence-transfer pathway (3, 4) and/or orthogonal spoiler gradients (5, 6).

For diffusion probes without the facility of orthogonal spoiler gradients, we have found, as did Latour *et al.* (5), that a four-step phase cycle as proposed by Fauth *et al.* (3) does not suppress the unwanted echoes to a desired degree. Instead of imposing orthogonal gradients, we make use of the four-step phase cycle together with bipolar gradients of different strength. The so-called CPMG echo, which arises from the $\pi/2-\tau-\pi-\tau$ -echo sequence, will then not refocus, provided that the difference between the bipolar gradients is large enough.

THEORY

The PFGSTE sequence for measuring diffusion consists of three intervals, the prepare, the store, and the read intervals (Fig. 1). In the prepare interval the molecules are labeled with a phase proportional to the integral of the effective gradient $g(t)$

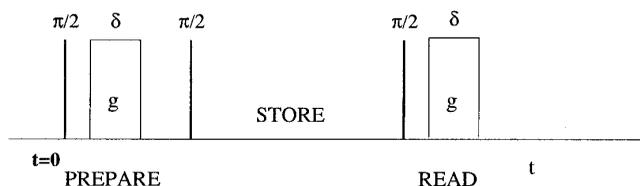


FIG. 1. The PFGSTE sequence where the prepare interval labels the phases of the spins, the store interval allows the spins to diffuse, and the read interval unlabels the spins.

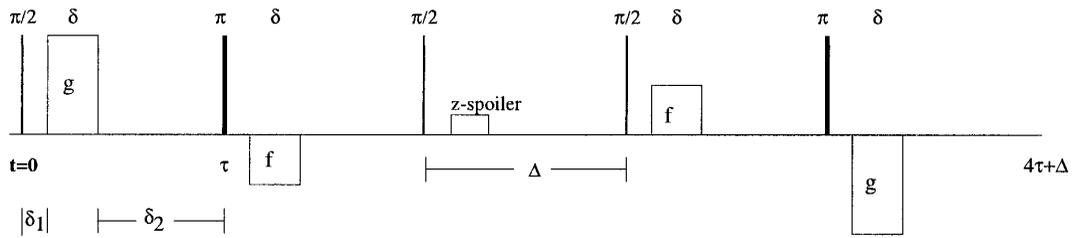


FIG. 2. The PFGSTE sequence with bipolar gradients. The gradient labels given in the text refer to the gradients in chronological order (the z spoiler is disregarded).

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

where γ is the gyromagnetic ratio. After the application of the second $\pi/2$ pulse, the net spin is stored in the longitudinal direction, and is thus unaffected by the presence of any longitudinal gradients. In the read interval, the spins are unlabeled, and if the molecules have moved in the longitudinal direction during the sequence, this will be apparent in the logarithm of the pulsed-field-gradient stimulated-echo attenuation $[\ln(I/I_0)]$ as a function the diffusion time and the gradient strength (2). In heterogeneous media, the usual way of performing this kind of experiment is to fix the experimental or diffusion time and vary the applied magnetic field gradients. In that manner the number of surviving molecules with respect to relaxation effects will be constant,

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

where D is the diffusion coefficient. Equation [2] is the solution of the equation of motion of the spins assuming a fixed diffusion time (2). As the signal strength of the stimulated echo is limited by the relaxation processes, we have chosen to use a PFGSTE with a minimum number of RF pulses, the 13-interval sequence (2).

The idea behind choosing the two pairs of bipolar gradi-

ents of different strength comes about when considering which pairs are coupled to effective internal gradients of opposite signs. By pairs, we mean one gradient pulse from the prepare interval and one from the read interval. Figure 3 shows the effective gradients and one can see that the bipolar pairs with opposite internal gradients are gradient numbers 1 and 4 and gradient numbers 2 and 3.

Following the procedure of Cotts *et al.* condition I (2), we divide the time intervals into 13 parts and perform the evaluation of Eq. [2] sequentially. Condition I means that the polarities of the gradients are the same in the prepare as in the read interval. In Fig. 3 we have omitted the π pulses and shown the effective gradients according to the desired coherence-transfer pathway: $p = 0 \rightarrow +1 \rightarrow -1 \rightarrow 0 \rightarrow -1 \rightarrow +1$. The appropriate 13 integrals arising from $\int_0^t g(t'') dt''$ are given in Table 1.

The result for the given sequence is presented in the following equation, where we have relabeled the times according to Fig. 2:

$$\ln \frac{I}{I_0} = -\gamma^2 \delta^2 D \left[\left(\Delta + 3\tau - \frac{\delta}{3} \right) g^2 + \left(\Delta + \tau - \frac{\delta}{3} \right) f^2 + 2(\Delta + \tau)gf + \delta(\delta_1 - \delta_2)\tau(f + g)G_0 + \frac{4}{3}\tau^3 G_0^2 \right]. \quad [3]$$

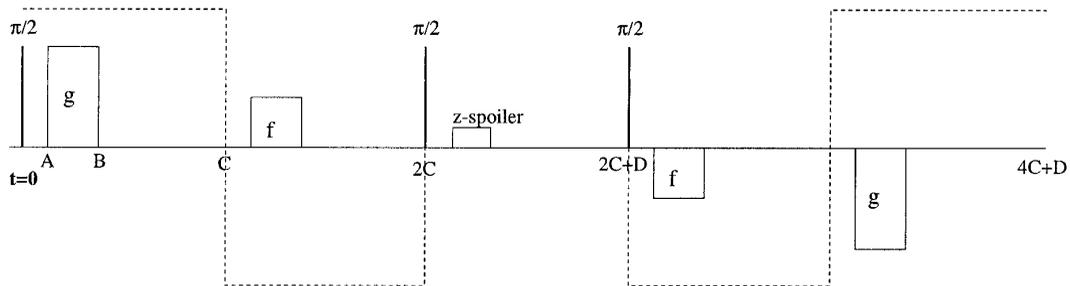


FIG. 3. The PFGSTE sequence with effective internal (dotted lines) and applied gradients according to the desired coherence-transfer pathway. The times for switching on/off the applied gradients are the same in the prepare and read intervals.

TABLE 1
Effective Gradients and Integrals

Time	Gradient	$\int_0^{t'} g(t'') dt''$
(0, A)	$-G_0$	$-G_0 t'$
(A, B)	$-G_0 + g$	$-G_0 t' + g(t' - A)$
(B, C)	$-G_0$	$-G_0 t' + g(B - A)$
(C, C + A)	$+G_0$	$G_0(t' - 2C) + g(B - A)$
(C + A, C + B)	$+G_0 + f$	$G_0(t' - 2C) + g(B - A) + f[t' - (C + A)]$
(C + B, 2C)	$+G_0$	$G_0(t' - 2C) + g(B - A) + f(B - A)$
(2C, 2C + D)	0	$g(B - A) + f(B - A)$
(2C + D, 2C + D + A)	$+G_0$	$+G_0 [t' - (2C + D)] + g(B - A) + f(B - A)$
(2C + D + A, 2C + D + B)	$+G_0 - f$	$+G_0 [t' - (2C + D)] + g(B - A) + f(B - A) - f[t' - (2C + D + A)]$
(2C + D + B, 3C + D)	$+G_0$	$+G_0 [t' - (2C + D)] + g(B - A)$
(3C + D, 3C + D + A)	$-G_0$	$-G_0 [t' - (4C + D)] + g(B - A)$
(3C + D + A, 3C + D + B)	$-G_0 - g$	$-G_0 [t' - (4C + D)] + g(B - A) - g [t' - (3C + D + A)]$
(3C + D + B, 4C + D)	$-G_0$	$-G_0 (t' - 4C + D)$

G_0 is the internal magnetic field gradient. In the derivation of the $\ln(I/I_0)$ attenuation, a constant G_0 is assumed.

EXPERIMENTAL

The experiments were performed with a Bruker DMX200 spectrometer using a homebuilt diffusion probe featuring actively shielded gradient coils constructed after the target field approach (7). The gradient coils were supplied by Dr. Paul Callaghan and Dr. Phillip Back, Massey University (New Zealand). The eddy-current time after a gradient pulse was found to be around 1 ms. When applying gradient pre-emphasis with the possibility of a three-exponential correction term we achieved stable free-induction decays from 200 μ s and upward. That is, there were no signs of eddy-current transients in a free-induction decay from a RF pulse applied 200 μ s after a single gradient, regardless of available gradi-

ent strength (0–100 G/cm). For all the experiments performed we applied a gradient dead time (δ_2) of 300 μ s.

The uptake of the attenuation was done by sampling the echo signal in real time. This was done to ensure that any field transients introduced by bipolar gradients of different strength should not affect the uptake. The calibration experiments were performed using water slightly doped with Cu_2SO_4 .

The size of H-ZSM5 crystallites (20–50 μ m) made it possible to perform intercrystalline diffusion measurements of ethane. Figure 4 shows two SEM pictures of the H-ZSM5, and, as can be seen, the majority of the crystallites are larger than 20 μ m. Before the H-ZSM5 was activated the sample was evacuated to a pressure of 1×10^{-7} Bar and a final temperature of 650 K for more than 12 hours. After evacuation, the H-ZSM5 was saturated with ethane at a pressure of 1.2 Bar at room temperature, and then sealed off.

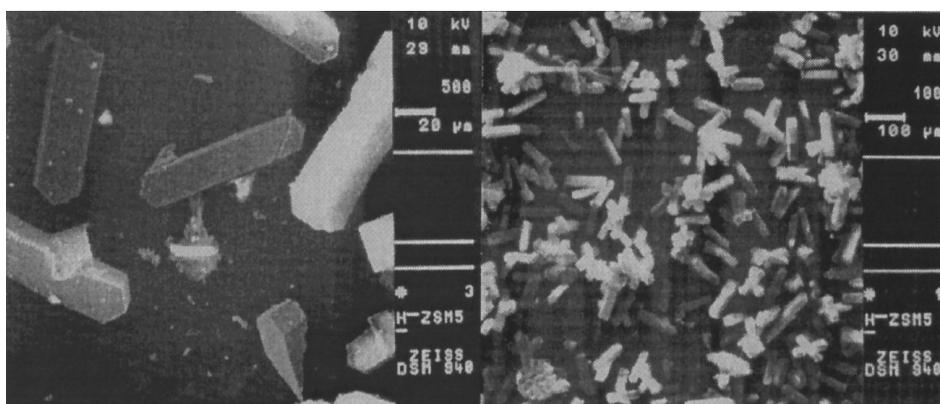


FIG. 4. H-ZSM5 crystallites. The large diameter of the crystallites (20–50 μ m) indicates that it should be possible to perform intracrystalline diffusion measurements if the diffusivity is of the order 10^{-10} m^2/s and the diffusion time is a few milliseconds. The mean squared displacement is then of the order of a few micrometers.

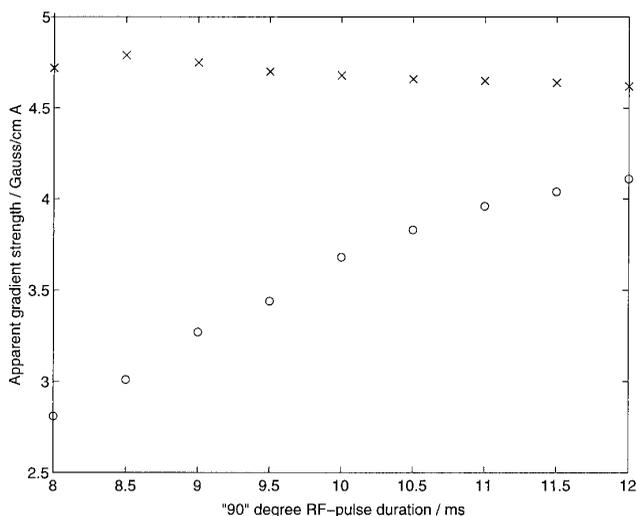


FIG. 5. Apparent gradient strength as a function of the length of the “ $\pi/2$ ” RF pulse. The symbols \circ show the apparent gradient strength values for the sequence with equal bipolar gradients and the symbols \times show the values for the sequence with unequal bipolar gradients. The real $\pi/2$ pulse was found to be $10.5 \mu\text{s}$.

RESULTS AND DISCUSSION

To verify the removal of the CPMG echoes, we performed a set of experiments with and without equal bipolar gradients and deliberately set the values for the $\pi/2$ and π pulses different from the real values. By doing this one should expect that if there were a considerable amount of signal from unwanted echoes, the apparent gradient strength would

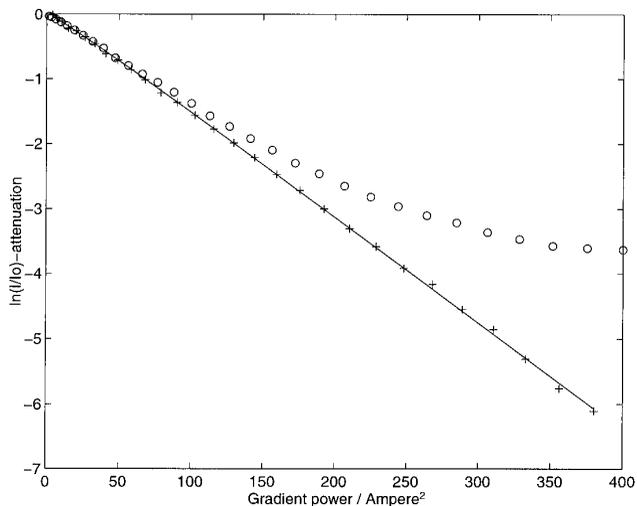


FIG. 6. The $\ln(I/I_0)$ attenuation for the 13-interval PFGSTE sequence using equal bipolar gradients (\circ) and unequal bipolar gradients ($+$). The solid line represents the linear calibration with gradient strength 4.45 G/cm A using the experiment with unequal bipolar gradients.

change. Thus the apparent diffusivity would change and indeed be a function of the duration of the RF pulses. Figure 5 shows the calibrated gradient strength using a sample of known diffusivity as a function of the duration of RF pulses.

As can be seen in Fig. 5, there is a large difference in the response to the offset of the $\pi/2$ pulse for the two sequences. While the apparent gradient strength changes from 2.8 to 4.1 G/cm A for equal bipolar gradients, it is within $4.7 \pm 0.1 \text{ G/cm A}$ for the unequal bipolar gradients.

Figure 6 shows two sets of experiments using bipolar gradients of equal and unequal strength. While the $\ln(I/I_0)$ attenuation is linear only down to -1 for equal bipolar gradients, it is linear down to -6 for unequal bipolar gradients. As the diffusion time and the applied gradient power are the same for both experiments, one should expect an overlap of the two $\ln(I/I_0)$ attenuations. This is clearly not the case for $\ln(I/I_0)$ attenuation larger than -1 , and we believe it can be explained using the experimental result in Fig. 5. As the unequal bipolar gradient experiment shows no significant dependency on the offset of the RF pulses from the true $\pi/2$ and π pulses, we observe a considerable dependency when using equal bipolar gradients. As no other parameters have been changed, the effect must be caused by the change from unequal to equal bipolar gradients. Considering the read interval, one sees that the unwanted coherence-transfer pathway as $p = 0 \rightarrow +1 \rightarrow +1$ causes an unwanted echo at the same time as the wanted PFGSTE echo. This is the most likely error, which results in the nonlinear behavior for the $\ln(I/I_0)$ attenuation using equal bipolar gradients. Due to the experimental results, our conclusion is that the amount of unwanted echoes is removed or greatly reduced by the use of unequal bipolar gradients. Taking into account the uncer-

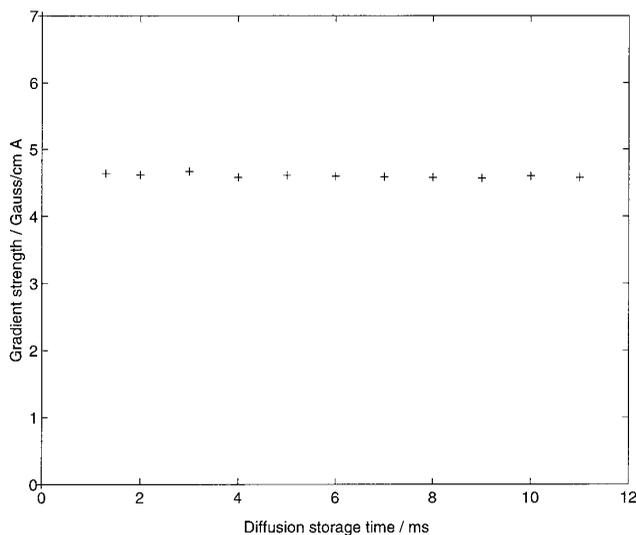


FIG. 7. Gradient strength as function of the diffusion storage time.

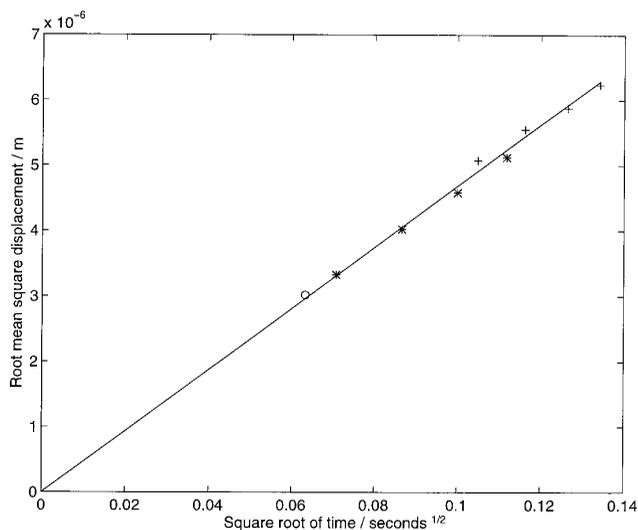


FIG. 8. Measured diffusivities at different diffusion times and gradient delta times. *, 1.5 ms gradient pulses; +, 1.0 ms gradient pulses; and O, 2.0 ms gradient pulses. The linear fit gives a mean diffusivity of $3.66 \times 10^{-10} \text{ m}^2/\text{s}$.

tainty from the RF dependence, we have found the total error for the gradient strength to be within $\pm 2.5\%$.

To test the correctness of the derived expression for the $\ln(I/I_0)$ attenuation (Eq. [3]), we performed a set of experiments where the diffusion time Δ was changed from 11 ms down to 1.3 ms. As can be seen in Fig. 7, the deviation from the calibrated gradient strength is not significant, and it is within the experimental error of the measurements (2.5%). There is no sign of systematic deviations due to errors in the derivation of the attenuation for bipolar gradients of different strengths.

Figure 8 shows a preliminary result using the proposed sequence, a diffusion measurement of ethane in a saturated H-ZSM5 zeolite. The $\ln(I/I_0)$ attenuations were linear down to at least -1 and the diffusion coefficient is found to be $3.8 \pm 0.3 \cdot 10^{-10} \text{ m}^2/\text{s}$. Using a standard PFGSTE experiment without bipolar gradients, we found the diffusion coefficient to be $1.5 \pm 0.2 \cdot 10^{-10} \text{ m}^2/\text{s}$. This is consistent with the picture we have of a measured mean diffusivity that is biased toward the slower diffusing molecules. The difference between inter- and intracrystalline diffusion was so large that we observed monoexponential decay with the gradient strengths applied. That is, the signal from the ethane outside the crys-

tallites had decayed substantially already at the smallest applied gradient strength. Even if the first data points showed no significant deviation from the linear behavior, we decided to rule out the first three data points due to the possible signal contribution from intercrystalline ethane.

Measurements have been performed with different duration of the gradient pulses. If the assumption of a constant internal gradient was not valid for the diffusion times and gradient pulse times applied, one should expect that changing the length of the gradient pulses would change the measured apparent diffusion coefficient. We have found that with different gradient pulse lengths up to 2.0 ms there was no significant change in the measured diffusivities.

CONCLUSION

We have derived the $\ln(I/I_0)$ attenuation for the 13-interval PFGSTE using bipolar gradients of different strength. Experiments have demonstrated a considerable improvement using this sequence as compared to the 13-interval PFGSTE sequence using equal bipolar gradients. By using the proposed sequence, we have eliminated the need for orthogonal spoiler gradients. Preliminary diffusion measurements of ethane in a H-ZSM5 zeolite were also presented.

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