

# Determination of Genuine Diffusivities in Heterogeneous Media Using Stimulated Echo Pulsed Field Gradient NMR

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**Pulsed field gradient (PFG) NMR diffusion measurements in heterogeneous media may lead to erroneous results due to the disturbing influence of internal magnetic field gradients. Here, we present a simple theoretical model which allows one to interpret data obtained by stimulated spin echo PFG NMR in the presence of spatially varying internal field gradients. Using the results of this theory, the genuine self-diffusion coefficients in heterogeneous media may be extrapolated from the dependence of the apparent diffusivities on the dephasing time of the simulated echo PFG NMR sequence. Experimental evidence that such extrapolation yields satisfactory results for self-diffusion of hexadecane in natural sediments (sand) and of *n*-octanol in doped MgO pastes is provided.** © 2001 Academic Press

**Key Words:** PFG NMR; stimulated spin echo; diffusion; internal magnetic field gradients; heterogeneous media.

## INTRODUCTION

Pulsed field gradient (PFG) NMR has proven to be a powerful technique for diffusion measurements in porous media (1–3). One of the main restrictions of this method is related to the fact that the internal magnetic field in porous materials is already inhomogeneous without any externally applied field gradients. These inhomogeneities are caused by the variations between magnetic susceptibilities of the different components of heterogeneous media. The magnitude of the susceptibility-induced internal field inhomogeneities depends on the size and on the geometry of these components as well as on the strength of the polarizing magnetic field. Especially in high-field PFG NMR studies, these field inhomogeneities, which we refer to as internal magnetic field gradients, may be comparable with those produced by the externally applied pulsed field gradients. This situation is known to complicate the interpretation of the spin echo attenuation observed with PFG NMR. To suppress the influence of the internal field inhomogeneities, PFG NMR sequences with alternating polarity of the pulsed field gradients were developed (4, 5). It was shown theoretically as well as experimentally that these sequences remove susceptibility-induced artifacts in PFG NMR diffusion studies if each spin experiences a constant internal field gradient over the duration of the NMR sequence. This assumption is generally valid when the molecular displacements during the NMR sequence are much

smaller than the characteristic length scale of constant susceptibility in a heterogeneous medium. However, calculations of local magnetic fields in heterogeneous media consisting of two types of areas with different susceptibilities have shown that the field inhomogeneities due to susceptibility variations cannot be described by constant field gradients on a length scale comparable with the characteristic length of constant susceptibility (6). For molecular displacements on this length scale, the application of PFG NMR (even with alternating pulsed field gradients) cannot be assumed to be completely free from the disturbing influence of internal field gradients (7). In general, one must expect that the spin echo attenuation depends not only on the applied pulsed field gradient but, in a complicated way, also on the internal field gradients. Only in two cases, namely in the above-discussed case of displacements which are small in comparison with the characteristic length scale of constant susceptibility and in the other limiting case of much larger displacements than the characteristic length of constant susceptibility (which means that the majority of spins experience spatially rapidly varying internal gradients (8)), is the determination of the true self-diffusion coefficients by PFG NMR straightforward.

Until now an exact and complete theory of spin echo attenuation by externally applied pulsed field gradients in the intermediate case, i.e., in the presence of internal field gradients slowly varying on the displacement length scale, has not been developed. In Ref. (9), the case of spin echo attenuation due to diffusion in a parabolic magnetic field is solved exactly. It is pointed out in Ref. (9), as well as subsequently in Refs. (10, 11), that the PFG NMR spin echo attenuation in an inhomogeneous field is governed by a combination of certain intrinsic lengths.

The purpose of the present article is to report a simple experimental procedure allowing one to estimate the disturbing influence of internal field gradients on the measurement of self-diffusion coefficients by the simple PFG NMR stimulated spin echo sequence. We will consider a general case, where the internal field gradients may vary on the length scale of molecular displacements. It is frequently observed that even in such a case the logarithm of the measured spin echo attenuation  $\Psi$  is still proportional to the square of the amplitude of the magnetic field

gradient pulses ( $g^2$ ),

$$\ln(\Psi(g, \Delta)) \equiv \ln\left(\frac{M(g, \Delta)}{M(0, \Delta)}\right) = -(\gamma\delta g)^2 D_{\text{app}}\Delta, \quad [1]$$

where  $\delta$  is the duration of the gradient pulses,  $\Delta$  is the time interval between the two gradient pulses of the sequence, and  $D_{\text{app}}$  denotes the apparent diffusivity. Assuming such a proportionality, we will derive a functional relation between the apparent self-diffusivity  $D_{\text{app}}$  and the true self-diffusion coefficient  $D$ . We will show in a very general approach that in this case  $D_{\text{app}}$  is expected to depend on the dephasing delay ( $\tau_1$ ) in the stimulated spin echo sequence. Moreover, we demonstrate that the predicted  $\tau_1$ -dependence of  $D_{\text{app}}$  is in fact observed experimentally and may be used to calculate the true self-diffusivity by extrapolating to  $\tau_1 = 0$ .

### THEORETICAL MODEL

Under the conditions of internal field gradients varying over the displacement length, the results of the diffusion measurements using bipolar forms of the pulsed field gradient sequences cannot always be assumed to be free from the artifacts produced by internal field gradients (7). In this case, one way to carry out diffusion measurements using PFG NMR is to minimize the dephasing of the magnetization by internal field gradients by using a small constant magnetic field and thus reducing susceptibility-induced internal field gradients, as well as by minimizing the time interval of the magnetization dephasing by the internal field gradients. Let us consider the PFG NMR stimulated spin echo sequence [ $\pi/2-\tau_1-\pi/2-\tau_2-\pi/2-\tau_3-$ ] ( $I-3$ ). The sequence consists of three intervals, the dephasing ( $\tau_1$ ), the store ( $\tau_2$ ), and the refocusing ( $\tau_3$ ) intervals. In the dephasing time interval each spin is labeled by a phase accumulated in the local field,

$$\varphi = \gamma \int_0^{\tau_1} (\mathbf{g}(t)\mathbf{r} + B_z(\mathbf{r})) dt, \quad [2]$$

where  $\mathbf{g}(t)$  is the externally applied pulsed field gradient and  $B_z(\mathbf{r})$  is the component of the local inhomogeneous magnetic field which is parallel to the homogeneous polarizing magnetic field.  $B_z(\mathbf{r})$  is caused by susceptibility variations in the sample. We will consider a sufficiently short dephasing time interval  $\tau_1$ , so that the displacements over  $\tau_1$  can be assumed to be negligibly small. In the store time interval  $\tau_2 \gg \tau_1$  the phase information is unaffected by the field gradients. The spins are unlabeled in the refocusing interval  $\tau_3$ . The phase of the spins will not be completely restored in the refocusing interval if they moved in the direction of the field gradients. For each spin, the phase

difference can be written as

$$\varphi_{r_1} = \gamma \left( \int_0^{\tau_1} (\mathbf{g}(t)\mathbf{r}_1 + B_z(\mathbf{r}_1)) dt - \int_{\tau_1+\tau_2}^{\tau_1+\tau_2+\tau_3} (\mathbf{g}(t)\mathbf{r}_2 + B_z(\mathbf{r}_2)) dt \right) \quad [3]$$

or, using  $\tau_1 = \tau_3$ ,

$$\varphi_{r_1} = \gamma\delta\mathbf{g}(t)\Delta\mathbf{r} + \gamma\tau_1(B_z(\mathbf{r}_1) - B_z(\mathbf{r}_2)), \quad [4]$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  describe the positions of the spin in the time intervals  $\tau_1$  and  $\tau_3$ , respectively, and  $\Delta\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ . Due to the displacement of the molecules, the local magnetic fields, experienced by a spin in the defocusing and refocusing periods, are different. Hence, we can introduce an effective internal gradient  $\mathbf{g}_0(\Delta\mathbf{r}, \mathbf{r}_1)$  by

$$\mathbf{g}_0(\Delta\mathbf{r}, \mathbf{r}_1)\Delta\mathbf{r} = B_z(\mathbf{r}_1) - B_z(\mathbf{r}_2). \quad [5]$$

Now, Eq. [4] can be rewritten as

$$\varphi_{r_1} = \gamma\delta\mathbf{g}(t)\Delta\mathbf{r} + \gamma\tau_1\mathbf{g}_0(\Delta\mathbf{r}, \mathbf{r}_1)\Delta\mathbf{r}. \quad [6]$$

The spin echo attenuation for all spins with the starting point  $\mathbf{r}_1$  can be written as (3)

$$\Psi_{r_1}(g) = \int \cos(\varphi_{r_1})P(\varphi_{r_1})d\varphi_{r_1}, \quad [7]$$

where  $\Psi_{r_1}(g)$  is the attenuation of the stimulated spin echo by the field gradients for the spins with the initial position  $\mathbf{r}_1$  and  $P(\varphi_{r_1})$  denotes their phase distribution. For unrestricted diffusion, the distribution of the first term in Eq. [6], which is determined by the distribution of  $\Delta\mathbf{r}$ , is described by a Gaussian function. The phase distribution due to diffusion in the presence of non-constant, randomly distributed field gradients (the second term in Eq. [6]), in general, cannot be approximated by a Gaussian distribution (9, 12). However, when the dephasing of magnetization due to the internal field gradients is weak in comparison with that produced by the externally applied pulsed field gradients, the distribution of  $\varphi_{r_1}$  is still approximately Gaussian. For Gaussian  $P(\varphi_{r_1})$ , Eq. [7] can be written as (3)

$$\Psi_{r_1}(g) = \exp(-\langle\varphi_{r_1}^2\rangle/2), \quad [8]$$

where the brackets  $\langle \dots \rangle$  mean the averaging over the displacements  $\Delta\mathbf{r}$ . Again using the assumption that the internal gradients are weak, we will neglect the term proportional to  $\mathbf{g}_0^2$  in the

expression for  $\langle \varphi_{r_1}^2 \rangle$ . Hence, using Eq. [6], we can write  $\langle \varphi_{r_1}^2 \rangle$  as

$$\langle \varphi_{r_1}^2 \rangle = (\gamma \delta g)^2 \langle \Delta z^2 \rangle + 2\gamma^2 \delta g \tau_1 \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle, \quad [9]$$

where it was assumed that the direction of the externally applied pulsed field gradients coincides with that of  $B_0$ . For unrestricted diffusion holds

$$\langle \Delta z^2 \rangle = 1/3 \langle \Delta r^2 \rangle, \quad [10]$$

which finally yields

$$\langle \varphi_{r_1}^2 \rangle = (\gamma \delta g)^2 \langle \Delta r^2 \rangle / 3 + 2\gamma^2 \delta g \tau_1 \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle. \quad [11]$$

To calculate the spin echo attenuation of all spins  $\Psi(g)$ , we must average  $\Psi_{r_1}(g)$  in Eq. [8] over all initial positions  $\mathbf{r}_1$ ,

$$\begin{aligned} \Psi(g) &= \exp(-(\gamma \delta g)^2 \langle \Delta r^2 \rangle / 6) \langle \exp(-\gamma^2 \delta g \tau_1 \\ &\quad \times \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle) \rangle_{r_1}, \end{aligned} \quad [12]$$

where  $\langle \dots \rangle_{r_1}$  means averaging over  $\mathbf{r}_1$  and  $\langle \Delta r^2 \rangle$  was assumed to be independent of  $\mathbf{r}_1$ . The second exponent in Eq. [12] can be written as a cumulant expansion,

$$\begin{aligned} &\langle \exp(-\gamma^2 \delta g \tau_1 \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle) \rangle_{r_1} \\ &= \exp \sum_{n=1}^{\infty} ((-\gamma^2 \delta g \tau_1)^n \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^n \rangle_C / n!), \end{aligned} \quad [13]$$

where the cumulant averages can be represented as the normal averages over  $\mathbf{r}_1$ ,

$$\begin{aligned} \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^1 \rangle_C &= \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^1 \rangle_{r_1}, \\ \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^2 \rangle_C &= \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^2 \rangle_{r_1} \\ &\quad - \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle \rangle_{r_1}^2, \end{aligned} \quad [14]$$

etc.

In general, the logarithm of the PFG NMR spin echo attenuation in the presence of internal field gradients does not have to exhibit single-exponential behavior when plotted as function of  $g^2$ . However, we will now consider the case when  $\ln(\Psi(g, \Delta))$  is proportional to  $g^2$ , as given in Eq. [1], since it is often observed experimentally. In order to satisfy this condition, all terms in the cumulant expansion Eq. [13] except for the second one should be equal to zero. It is interesting to note that this corresponds to the case of the Gaussian distribution of  $\langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle$  over  $\mathbf{r}_1$ . Now, we can rewrite Eq. [12] as

$$\begin{aligned} \ln(\Psi(g)) &= -\frac{1}{6} (\gamma \delta g)^2 \langle \Delta r^2 \rangle \\ &\quad \times [1 - 6\gamma^2 \tau_1^2 \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^2 \rangle_{r_1} / \langle \Delta r^2 \rangle]. \end{aligned} \quad [15]$$

By comparison of Eq. [15] with Eq. [1], it follows that the apparent self-diffusion coefficients are given by

$$D_{\text{app}} = D [1 - 6\gamma^2 \tau_1^2 \langle \langle \mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) \Delta \mathbf{r} \Delta z \rangle^2 \rangle_{r_1} / \langle \Delta r^2 \rangle], \quad [16]$$

where we made use of the well-known Einstein relation, which defines the true self-diffusion coefficient via the mean square displacement:

$$\langle r^2(\Delta) \rangle = 6D\Delta. \quad [17]$$

Obviously, the apparent self-diffusion coefficient is smaller than the true self-diffusion coefficient. The same conclusion was attained in (13) and subsequently in (14) by considering internal field gradients, which are symmetrically distributed about  $g_0 = 0$ , but which remain constant for each individual spin over its displacement length. Equation [16] represents an extension of the theory of the stimulated echo PFG NMR in the presence of a distribution of internal field gradients (13) to the case where the internal field gradients may vary on the length scale of molecular displacements. It is important to note that Eq. [16] is only valid if the second term in the square brackets is small in comparison with the unit, i.e., for small deviations of  $D_{\text{app}}$  from  $D$ . In this case,  $D$  could be estimated from the dependence of  $D_{\text{app}}$  on  $\tau_1^2$ .

If the changes of  $\mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1)$  are small over the length scale of molecular displacements it can be expanded to first order as

$$\mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1) = \mathbf{g}_0^0(\mathbf{r}_1) + \hat{g}_0^1(\mathbf{r}_1) \Delta \mathbf{r}, \quad [18]$$

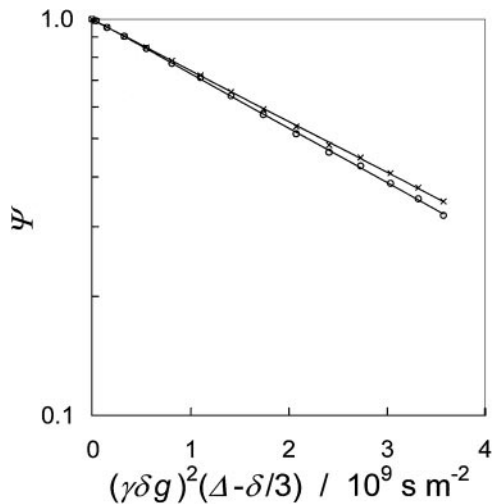
where  $\mathbf{g}_0^0(\mathbf{r}_1)$  and  $\hat{g}_0^1(\mathbf{r}_1)$  do not depend on  $\Delta \mathbf{r}$ . Substituting  $\mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1)$  in Eq. [16] by the expansion to first order (Eq. [18]) and again using Eq. [10], we obtain

$$D_{\text{app}} = D \left[ 1 - \frac{2}{3} \gamma^2 \tau_1^2 \langle \langle g_{0z}^0(\mathbf{r}_1) \rangle^2 \rangle_{r_1} \langle \Delta r^2 \rangle \right], \quad [19]$$

where  $g_{0z}^0(\mathbf{r}_1)$  is the component of the internal gradient parallel to the external one. The present paper focuses on the diffusion measurements under conditions when the changes of  $\mathbf{g}_0(\Delta \mathbf{r}, \mathbf{r}_1)$  are large on the length scale of molecular displacements. Under these conditions, Eqs. [18] and [19] are, clearly, invalid. Instead, Eq. [16] can be used to estimate the genuine diffusivities.

## RESULTS AND DISCUSSION

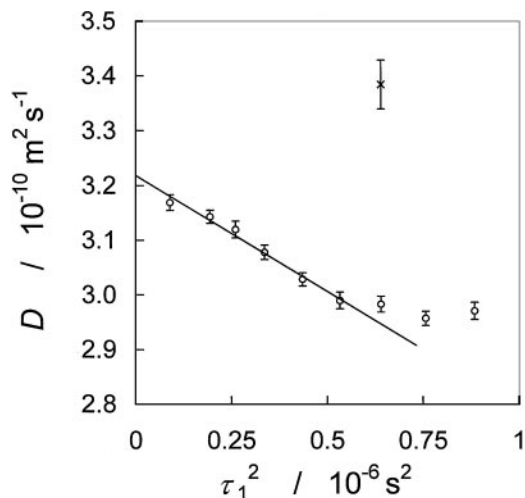
Within the experimental error, which is determined by the signal-to-noise ratios of the NMR signal, the PFG NMR spin echo attenuation curves exhibit single-exponential behavior. Figure 1 shows the attenuation curves recorded with the sand sample for two  $\tau_1$ -delays. Clearly, with increasing  $\tau_1$  the slope of the spin echo attenuations decreases, which corresponds to a decreasing apparent self-diffusivity. Note that the observation time



**FIG. 1.**  $^1\text{H}$  PFG NMR spin echo attenuations observed for hexadecane in sand at 295 K by use of the stimulated spin echo sequence with  $\tau_1$ -delays of 870 ( $\times$ ) and 300  $\mu\text{s}$  ( $\circ$ ).

and the length of the gradient pulses were kept constant. Thus, the observed  $\tau_1$ -dependence of the apparent self-diffusivity cannot be caused by restricted diffusion effects.

Figure 2 shows the dependence of the apparent diffusion coefficients measured in the sand sample on  $\tau_1^2$ . It is seen that for small  $\tau_1$  values, a linear dependence of  $D_{\text{app}}$  on  $\tau_1^2$  satisfactorily describes the experimental data. This is in agreement with Eq. [16]. For larger  $\tau_1$  values, there is a deviation from linear behavior, i.e.,  $D_{\text{app}}$  decreases less strongly with increasing  $\tau_1$  than required by a linear dependence of  $D_{\text{app}}$  on  $\tau_1^2$  observed for smaller  $\tau_1$  values. It is interesting to note that

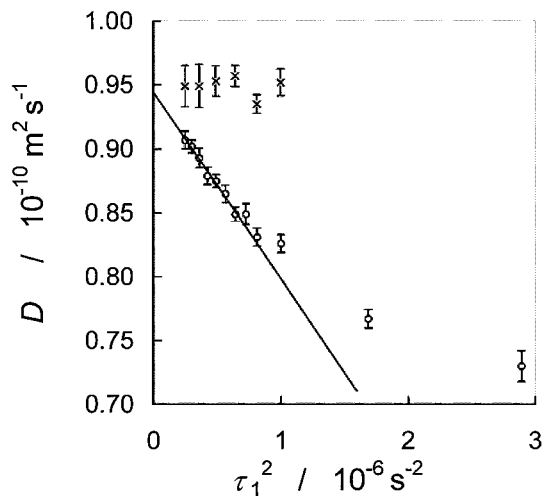


**FIG. 2.** The apparent self-diffusion coefficients obtained for hexadecane in sand at 295 K for different  $\tau_1$  values by using the stimulated spin echo sequence ( $\circ$ ) and the 13-interval sequence ( $\times$ ). The solid line is a linear fit of the dependence of the apparent diffusivities on  $\tau_1^2$  for small  $\tau_1$  values.

the linear extrapolation of the  $\tau_1^2$ -dependence of the apparent self-diffusivities to  $\tau_1^2 = 0$  yields a self-diffusion coefficient, which is in reasonable agreement with the self-diffusion coefficient measured using the 13-interval sequence. A comparison of the latter diffusivity ( $3.38 \times 10^{-10} \text{ m}^2/\text{s}$ ) with the bulk diffusion coefficient of hexadecane at 295 K ( $3.61 \times 10^{-10} \text{ m}^2/\text{s}$ ) shows a small difference between these values. This difference is attributed to a restriction of hexadecane diffusion in the sand sample (15, 16).

Also, for the doped and undoped pastes of MgO with *n*-octanol, the echo attenuation was found to decay monoexponentially within the experimental accuracy. In Fig. 3, the apparent diffusion coefficients obtained for both the undoped and the doped samples are plotted as a function of  $\tau_1^2$ . While there is no noteworthy  $\tau_1$ -dependence in the case of the undoped sample, the apparent diffusivities observed for the doped sample are found to decrease linearly with  $\tau_1^2$  for small  $\tau_1$  values, as predicted by Eq. [16]. Like in the case of the sand sample, a deviation from the linear behavior is observed for large  $\tau_1$  values (Fig. 3). Considering only the data obtained for small  $\tau_1$  values, we have found that there is a good correspondence of the extrapolation to  $\tau_1 = 0$  diffusivity in the doped sample with the diffusivities observed in the undoped reference sample: The extrapolation to  $\tau_1 = 0$  according to Eq. [16] yields  $D = (9.45 \pm 0.3) \times 10^{-11} \text{ m}^2/\text{s}$  for the doped sample and for the undoped sample we obtain a value of  $(9.49 \pm 1.6) \times 10^{-12} \text{ m}^2/\text{s}$  for all observation times (see also Fig. 3).

As we know the characteristic correlation length of the internal gradient in the doped MgO paste, we can also compare it with the root mean square displacement over an observation time of 100 ms. This displacement is about 4  $\mu\text{m}$  for the diffusion coefficient of *n*-octanol in the undoped MgO paste. Thus,



**FIG. 3.** The apparent self-diffusion coefficients of *n*-octanol measured by stimulated echo PFG NMR at 295 K in a 1%  $\text{Fe}_2\text{O}_3$ -doped MgO paste ( $\circ$ ) and in undoped MgO paste ( $\times$ ) for different  $\tau_1$  values. The solid line is a linear fit of the dependence of the apparent diffusivities in the doped sample on  $\tau_1^2$  for small  $\tau_1$  values.

the root mean square displacement corresponds to about half of the above estimated correlation length of the gradient.

The main assumption made in the presented theory is that the molecular displacements over dephasing time  $\tau_1$  are negligibly small. This also requires that the  $\tau_1$  values remain small. Hence, the experimental observation made for large values of  $\tau_1$  (Figs. 2 and 3), i.e., the deviation of the dependence of  $D_{\text{app}}$  on  $\tau_1^2$  from the predicted linear dependence (Eq. [16]), does not contradict our model.

As the experimental examples clearly demonstrate, the theory of stimulated echo PFG NMR in the presence of internal magnetic field gradients presented in this paper shows a good agreement with the experimental data. In addition to quantitatively describing the dependence of the apparent self-diffusion coefficient on the dephasing delays, Eq. [16] also offers an experimental possibility for measuring genuine self-diffusion coefficients for samples with internal magnetic field gradients without needing to use a bipolar magnetic field gradient sequence. The latter technique needs more sophisticated gradient control equipment than what is necessary for a simple stimulated echo PFG NMR experiment. Moreover, as was shown in (7), the application of bipolar PFG NMR pulse sequences does not always remove all of the distorting effects of internal field gradients on measured diffusivities when diffusing molecules experience spatially varying field gradients. Even if the internal field gradient remains constant for each molecule over the dephasing and refocusing time intervals of the bipolar 13-interval pulse sequence considered in (7), variation of the gradient over the store interval of the sequence may already be sufficient to induce errors in measured diffusivities. In the latter case, the measured diffusivities were observed to depend on the duration of dephasing time ( $\tau^*$ ) (7). Assuming a linear dependence of measured diffusivities on  $\tau^*$ , the “true” diffusivities were extrapolated to  $\tau^* = 0$  in (7). The extrapolated diffusivities were found to be close to the expected self-diffusion coefficient.

In the present work we have adopted a similar approach using the simple stimulated spin echo sequence. An impressive agreement between the diffusion coefficient measured in a reference MgO sample without internal magnetic field gradient and that extrapolated using Eq. [16] for the MgO sample with internal field gradients is a good illustration of the potentials of the proposed method of diffusion measurements in heterogeneous media.

## CONCLUSION

In this work we present a simple method which allows one to obtain true self-diffusion coefficients in heterogeneous media using the simple stimulated echo PFG NMR sequence. The method is based on Eq. [16], which is the main result of our theoretical model of PFG NMR stimulated spin echo in the presence of spatially varying internal magnetic field gradients. Using Eq. [16], genuine diffusivities in heterogeneous media can be extrapolated from the dependence of the apparent diffusivities

on the dephasing time interval of the stimulated spin echo sequence. The applicability of the presented model and Eq. [16] is restricted to small dephasing time intervals and to systems where the normal, i.e., single-exponential, attenuation curves are observed. For two heterogeneous porous systems, where the conditions of the applicability of Eq. [16] are fulfilled, the extrapolated diffusivities were found to be in agreement with the expected self-diffusion coefficients.

## EXPERIMENTAL

*Description of the NMR samples.* PFG NMR measurements with two types of heterogeneous samples were performed. The first sample is a well-sorted quartz sand saturated with hexadecane. The grains of this sand exhibit a narrow grain size distribution with an average grain radius of about 200  $\mu\text{m}$ . For sample preparation, 0.78 g of the dried sand was filled into an NMR sample tube of 7.5 mm outer diameter. This amount filled the tube up to a height of about 1.5 cm. Subsequently, a volume of 0.15 ml of hexadecane was added to the sand. This amounts only to 90% fluid saturation of the total available pore space between the grains, which prevents excess fluid in the sand. To exclude fluid loss by evaporation, the sample was sealed tightly. Prior to any NMR measurement, the sample was centrifuged, which ensured a high and repeatable packing density of the grains. Moreover, in the lower part of the sample tube, which is placed in the sensitive region of the RF and gradient coil of the NMR spectrometer, a 100% fluid saturation of the sand is achieved by centrifuging.

In the sand sample, the magnetic susceptibility distribution is given by the nature of the sand and there is no reference system without the action of an internal gradient available. As a situation with such a reference system would be highly desirable, a sample with a purposefully introduced internal gradient (and the corresponding reference sample without this gradient), namely a  $\text{Fe}_2\text{O}_3$  doped paste of MgO with octanol, along with a corresponding reference paste without the iron oxide doping was studied as well. The reference sample consists of a paste prepared with 5 g of MgO (food grade “light” magnesia, obtained from Merck, Darmstadt) and 10 ml of *n*-octanol (analytical grade, also from Merck). Potentially present internal magnetic field gradients in this paste due to different magnetic susceptibilities of MgO and *n*-octanol can be neglected, since the susceptibility difference between MgO and octanol is relatively small.

The sample with an internal gradient was produced by doping the MgO powder with 1% in weight of a  $\text{Fe}_2\text{O}_3$  powder (obtained from Reanal, Budapest) with a grain size between 2 and 5  $\mu\text{m}$ . The grain size was estimated from electron microscopy images of the dry powder. From the size of the grains and the dopant concentration, we can estimate a mean distance of 16  $\mu\text{m}$  between the  $\text{Fe}_2\text{O}_3$  grains in our sample. Hence, a characteristic correlation length of the internal field gradient is about 8  $\mu\text{m}$ . Sufficiently good mixing of the two oxides was ensured

by vigorous stirring of the powders in the dry state and again by stirring of the paste after the addition of octanol.

*Details of the PFG NMR measurements.* PFG NMR self-diffusion measurements were carried out with the homebuilt NMR spectrometer FEGRIS 400 NT operating at 400 MHz  $^1\text{H}$  resonance frequency. According to Eq. [16], the presence of internal field gradients should lead to a  $\tau_1^2$ -dependence of the apparent diffusivity measured with the stimulated spin echo sequence. In order to observe such influences, the  $\tau_1$ -delay in this sequence was varied. For the measurements with different  $\tau_1$ -delays the duration of the magnetic field gradient pulses  $\delta$  was kept constant. It was chosen to be smaller than the smallest  $\tau_1$ -delay used in the measurements. The strength of magnetic field gradients was calibrated by performing a set of PFG NMR diffusion measurements of water samples with the known diffusion coefficients. In heterogeneous samples, restriction of the self-diffusion of the observed molecules by the geometrical boundaries between the different regions of the sample also leads to an observation of time dependence of the apparent diffusivity (15, 16). To avoid such effects, the observation time  $\Delta$  and the length of the gradient pulses in PFG NMR were kept constant. For PFG NMR stimulated spin echo measurements with rectangular pulsed field gradients and a fixed delay between the RF pulses and the field gradient pulses, the observation time  $\Delta$  is given by the sum of  $\tau_1$  and  $\tau_2$ .

Thus, a constant observation time for each set of  $\tau_1$  delay variations is achieved by a corresponding compensation in the  $\tau_2$  delay. Note that in all cases  $\tau_1$  was much smaller than  $\tau_2$ . Systematic errors in the PFG NMR stimulated echo measurements may also appear due to eddy current field (17). These errors are caused by a distortion of the stimulated echo signal. Under our measurement conditions such distortion was not observed. This rules out the influence of eddy current field on our PFG NMR stimulated echo measurements. For the measurements with the hexadecane-saturated sand, the  $\tau_1$ -delay was varied between 0.3 and 0.94 ms. Measurements at an observation time  $\Delta$  of 20 ms were performed. The width of the field gradient pulses  $\delta$  was set to 0.15 ms. The spin echo attenuation was monitored for each  $\tau_1$  by increasing the intensity  $g$  of the pulsed field gradients in 15 steps from zero up to 16 T/m.

In order to evaluate the effects of the internal field gradients on the spin echo attenuation recorded by the stimulated spin echo sequence, diffusion measurements with the sand sample were also performed using the 13-interval sequence (5) with equal bipolar pulsed field gradients. The time intervals of the

13-interval sequence were chosen to correspond to those of the stimulated echo sequence. Thus, the observation time  $\Delta$  was equal to 20 ms. The width of each of the bipolar gradients was set to 0.15 ms. For diffusion measurements the intensity of the gradients varied from 0.5 to 9 T/m.

Due to the higher purity of the materials used for the MgO samples and subsequently longer NMR relaxation times, the experiments with the pastes could be performed with a longer observation time  $\Delta$  of 100 ms. The  $\tau_1$ -delays varied from 0.5 to 0.9 ms. The width of the field gradient pulses  $\delta$  was set to 0.35 ms. The spin echo attenuation was monitored for each  $\tau_1$  by increasing the intensity  $g$  of the pulsed field gradients in 15 steps from zero up to 4 T/m.

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