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Probing four orders of magnitude of the diffusion time in porous silica glass with unconventional NMR techniques

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Abstract

The combined use of two unconventional NMR diffusometry techniques permits measurements of the self-diffusion coefficient of fluids confined in porous media in the time range from 100 microseconds to seconds. The fringe field stimulated echo technique (FFStE) exploits the strong steady gradient in the fringe field of a superconducting magnet. Using a standard 9.4 T (400 MHz) wide-bore magnet, for example, the gradient is 22 T/m at 375 MHz proton resonance and reaches 60 T/m at 200 MHz. Extremely short diffusion times can be probed on this basis. The magnetization grid rotating frame imaging technique (MAGROFI) is based on gradients of the radio frequency (RF) field. The RF gradients not necessarily need be constant since the data are acquired with spatial resolution along the RF gradient direction. MAGROFI is also well suited for unilateral NMR applications where all fields are intrinsically inhomogeneous. The RF gradients reached depend largely on the RF coil diameter and geometry. Using a conic shape, a value of at least 0.3 T/m can be reached which is suitable for long-time diffusion measurements. Both techniques do not require any special hardware and can be implemented on standard high RF power NMR spectrometers. As an application, the influence of the tortuosity increasing with the diffusion time is examined in a saturated porous silica glass.

Keywords: NMR; Diffusion; Porous media; Radiofrequency gradients; Fringe field gradients; Pulse field gradients

1. Introduction

The most popular principle of NMR diffusion measurements is based on the attenuation of spin echoes due to incomplete refocusing of coherences as a consequence of incoherent molecular displacements during the pulse sequence. Echo attenuation on these grounds arises in the presence of pulsed or steady gradients of the main magnetic flux density. Any sort of gradient-based echo can be used. Typical examples are the Hahn and the stimulated echo [1–3]. Here we consider the stimulated echo arising after three RF pulses in the presence of the steady fringe field gradient of a superconducting magnet. The method will be called fringe field stimulated echo (FFStE) technique.

On the other hand, there are methods employing gradients of the amplitude of the radio frequency flux density, i.e. RF field gradients [4]. Such an alternative protocol for diffusion measurements was successfully demonstrated with rotating-frame echo phenomena [3–7]. Furthermore, B_1 and B_0 gradients can be applied in mixed form. If suitably matched, such mixed combinations of gradients lead to ‘‘nutation echoes’’ [8,9] the diffusive attenuation of which can also be used for molecular displacement studies [10]. The localized character of nutation echoes [9] in principle permits remote measurements of diffusion coefficients. Moreover, it may be possible to accomplish diffusion measurements with chemical shift resolution in inhomogeneous static magnetic fields [11], provided that the directions of B_1 and B_0 gradients coincide.

With the techniques mentioned so far, a non-equilibrium magnetization distribution is first prepared in the form of a ‘‘helix’’ or—with respect to a certain component—as a

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magnetization “grid” (or “grating”). Translational diffusion then tends to level the magnetization distribution during the diffusion time. This leveling process of the magnetization grid can be monitored globally via the attenuation of spin echoes. Diffusion coefficients can then be evaluated from echo attenuation curves.

An alternative protocol is to render the magnetization profile along the gradient direction in the form of a one-dimensional image. Such a technique was proposed in Refs. [12,13] and termed magnetization grid rotating-frame imaging (MAGROFI). The appealing advantage of the MAGROFI technique in comparison with other rotating frame techniques based on rotary or nutation spin echoes is that no spatially constant gradient is required. As the magnetization grid is rendered as an image, it is only the local gradient that is relevant for the evaluation of diffusion constants. That is, the coil geometry can be optimized for strong gradients regardless of homogeneity requirements. Favorable coil geometries to be used for diffusion measurements with the MAGROFI technique turned out to be solenoids [13], conic coils [8,14] or a toroid cavity detector [15,16].

The present study focuses on the ability of the FFStE and MAGROFI techniques to probe the time dependence of the diffusion coefficient in a porous glass saturated with liquid water. The total time range to be covered with this sort of sample system is four orders of magnitude from 100 μs to 1 s. The time dependence of the self-diffusion coefficient of fluids in saturated and unsaturated porous glasses is of particular interest since it provides information on the topological constraints, the tortuosity of the pore space and the exchange dynamics between the phases.

2. Methodological background

2.1. The fringe-field stimulated echo technique

The principle of FFStE diffusometry is well-documented in the literature [1–3] and will not be discussed in detail here. We only mention that the RF pulse sequence used in the experiments reads

$$\frac{\pi}{2} - \tau_1 - \frac{\pi}{2} - \tau_2 - \frac{\pi}{2} - \tau_1 - \text{acquisition},$$

where $\tau_1 > T_2^*$ and T_2^* is the time constant of the FID attenuation in the presence of B_0 inhomogeneities. For the suppression of base-line offsets and undesired signals, the following phase cycles was used:

First RF pulse	x	x	$-x$	$-x$	x	x	$-x$	$-x$,
Second RF pulse	y	$-y$	x	$-x$	x	$-x$	y	$-y$,
Third RF pulse	y	$-y$	x	$-x$	x	$-x$	y	$-y$.

The RF pulse width was 1.8 μs so that 1 mm thick slices of the sample were excited in a fringe field gradient of 22 T/m.

For τ_2 intervals comparable with τ_1, the diffusion time is defined by $t_{\text{diff}} \equiv \frac{2}{3}\tau_1 + \tau_2 = \text{const}$ (compare Table 19.1 in Ref. [1], where the attenuation factors for diverse field gradient diffusometry techniques are given). The influence of transverse and longitudinal relaxation can be accounted for either by employing one of the diverse self-compensating pulse sequences reported in the literature [17–19] or by measuring the relaxation times separately and dividing the stimulated-echo amplitude by the corresponding factors. Since a well-defined diffusion time is of interest in the present study, we have preferred the latter measuring protocol.

2.2. The MAGROFI technique

The MAGROFI technique is based on RF field gradients [12,13]. In the following the principles of this technique will be outlined in order to clarify how the technique can be best adapted for time dependent diffusion measurements. The basic pulse sequence of a MAGROFI experiment is indicated in Fig. 1. Three intervals can be distinguished: preparation of the magnetization grid, diffusion interval and imaging of the grid. A single RF coil produces all RF pulses needed. That is, the spatial distribution of their RF fields and consequently the field gradients are identical. The RF flux density is assumed along the x' axis in the frame rotating with the resonance frequency $\omega_r = \omega_0 = \gamma B_0$. In the treatment, all interactions among the spins will be neglected. It is also assumed that gradients of the main magnetic field (B_0 gradients) of external or internal (i.e. susceptibility induced) origin neither affect the excitation of the spins nor give rise to further diffusive signal attenuation in the imaging interval. This implies that all local offsets of the main magnetic field, $\Delta B_0(\vec{r}) \equiv B(\vec{r}) - B_0$, should be negligible relative to the amplitude of the RF field, $B_1(\vec{r})$.

The shortest diffusion interval is limited by the free induction decay time T_2^*. If $\tau_2 < 5\,T_2^*$, some hard-to-control deviations from the proper coherence pathway would occur. Diffusive displacements during the preparation and imaging intervals (see Fig. 1) can be neglected if the RF pulses are much shorter than the diffusion interval. Otherwise, a formalism analogous to the well-known Stejskal/Tanner treatment for finite field gradient pulses [1–3] may be employed. In this case, the diffusion time is again defined by $t_{\text{diff}} \equiv \frac{1}{3}\tau_1 + \tau_2 = \text{const}$. In the following, we will however assume the short-pulse limit $\tau_1 \ll \tau_2$ for simplicity,

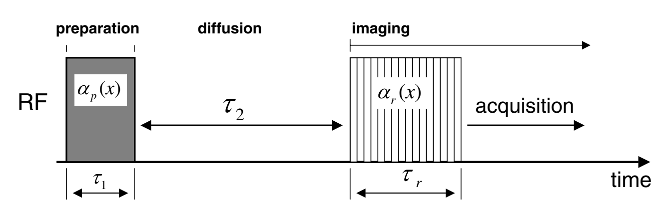

Fig. 1. The basic pulse sequence of the MAGROFI technique. The first RF gradient pulse produces a magnetization grid that will be leveled by diffusive displacements during the diffusion interval. Rotating-frame imaging of the magnetization grid permits the evaluation of self-diffusion coefficients and relaxation times.