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Displacement power spectrum measurement by CPMG in constant gradient

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Abstract

The modulation of spin phase produced by Carr–Purcell–Meiboom–Gill (CPMG) sequence in combination with constant magnetic field gradient is appropriate to probe the displacement power spectrum (DPS). The spin-echo attenuation is directly proportional to the DPS value at the applied modulation frequency. Relaxation and selective excitation effects can be factored out while probing the DPS. The modulation frequency is adjusted by varying the pulse separation time while the gradient strength and the time of acquisition are kept constant. In designing the experiment gradient strength limitations, imposed by off-resonance effects, as well as limitations arising from using Gaussian phase approximation must be considered. An effective experimental strategy is presented, supported by experimental results for free and restricted diffusion.

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1. Introduction

Porous materials have been successfully studied by means of NMR diffusion measurements. For this purpose mainly pulsed field gradients (PFG) are used. In confined geometry such as porous materials the diffusion process is described by time-dependent diffusion coefficient [1]. This quantity can be used for determination of porous material properties such as permeability or tortuosity of pore walls and surface-to-volume ratio [2,3]. A common approach which uses PFG to study morphology is based on the average displacement propagator measurements and is known as q-space microscopy [4,5]. It measures the time evolution of spin displacements distribution.

Signal analysis based on the averaged propagator to probe the time-dependent diffusion coefficient is possible only in the case of short gradient pulses. As the propagator sampling requires a broad range of dephasing wavelengths, the application of this method for studying diffusion in porous media is limited also by the condition that the diffusion displacement during application of a gradient pulse is shorter than the extent of the confinement. In small pores the propagator has to be sampled at a short time scale, thus large gradients have to be used in order to achieve adequate signal attenuation. A different perspective on spin-echo attenuation due to spin motion is offered by frequency-domain analysis proposed by Stepišnik and Callaghan, known as the modulated gradient spin-echo method (MGSE) [6–8]. In this case, the RF pulse sequence periodically modulates the spin phase and thus provides adequate signal attenuation at a shorter time scale than can be achieved by the PFG method.

The fundamental assumption in the MGSE approach is that the spin-echo signal has a form of the characteristic functional of stochastic motion. In this case the spin position is considered to be a stochastic variable and the gradient modulation waveform is used as an argument of the

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stochastic functional [9]. The spectrum of the gradient modulation waveform acts as a frequency window for probing stochastic motion. Under the condition of Gaussian phase approximation, this approach enables the application of experiments that do not necessarily use short gradient pulses like in the case of averaged propagator approach. Instead of describing motion in terms of time-dependent diffusion coefficient, the concepts of the displacement power spectrum (DPS) or the diffusion spectrum are used. Interpretation of some restricted diffusion measurements has been refined from this perspective [10,11]. The DPS incorporates information about stochastic motion, such as the velocity autocorrelation function and the mean square displacement. More details are given in the next section.

In order to probe the DPS, the spectrum of gradient modulation waveform has to be narrowly centered around a chosen modulation frequency. A pulse sequence has to allow the experimenter to systematically adjust the modulation frequency. Many gradient modulation forms meet these requirements [7,8], but they mainly utilize pulsed gradients or harmonically shaped gradients. Due to technical limitations in fast gradient switching and other side effects a constant gradient is a better choice for achieving higher modulation frequencies. It has been noted that the spectrum of gradient modulation produced by CPMG sequence in combination with constant gradient has promising qualities for probing the DPS [7]. The sequence is known for its capability of measuring the relaxation as well as diffusion properties of a sample while achieving optimized signal-to-noise ratio by cycling the phase of radio-frequency (RF) pulses. However, so far it has not been yet exploited for frequency-domain diffusion measurements.

The CPMG sequence has been studied extensively in order to understand diffusion and relaxation effects in stray-field experiments. If RF pulses are applied in a strong inhomogeneous field, the ''on-resonance'' condition is meet only in a limited portion of the sample. Hürlimann has developed a formalism for analyzing spin-echo amplitudes and shapes in the presence of off-resonance effects [12]. Song has categorized coherence pathways in order to efficiently analyze diffusion effects for larger numbers of refocusing pulses [13]. Based on this approach different relaxation and time-dependent diffusion measurement techniques have been developed [14–16].

The objective of this article was to present an experimental strategy for using CPMG in frequency-domain measurements. We demonstrate the feasibility of using CPMG for DPS measurement and discuss the advantages and limitations of this approach.

2. Echo attenuation by spin motion

The spectral analysis of spin-echo attenuation due to spin motion in the case of CPMG sequence shows that the attenuation is proportional to the selected frequency component of the DPS, which is related to the diffusion spectrum, i.e., the spectrum of velocity autocorrelation function.

The spin-echo attenuation is determined by the effective gradient waveform that can be written as $G_{ef}(t) = G_0 p(t)$, where the parameter $p(t)$ denotes the selected coherence pathway. The phase factor is defined as $q(t) = \gamma \int_0^t G_{ef}(t')\,dt'$. If a direct echo pathway is selected in the case of CPMG sequence, the effective gradient waveform $G_{ef}(t)$ changes sign upon each successive π pulse in time intervals T_π and the phase factor oscillates periodically around zero with the modulation period $T_m = 2T_\pi$. The pulse sequence with corresponding effective gradient and phase factor form is presented in Fig. 1. The echo condition is fulfilled each time the phase factor accumulates to zero.

Temporal and subsequent ensemble average over all equivalent spins gives the echo signal as $S = S_0\langle \exp(i\gamma \int_0^{t_e} G_{ef}(t)x(t)\,dt)\rangle$ [11], where S_0 denotes the signal in the absence of motion. The ensemble average can be expressed by cumulant expansion [9]. In Gaussian approximation the signal is written in terms of signal phase ϕ and attenuation factor β as $S = S_0 e^{i\phi} e^{-\beta}$ [7]. It has been shown that such an approximation is justified whenever the phase grating wavelength $1/q_0$ induced by gradient modulation is greater than the mean free path of moving particles [17]. In the case of CPMG sequence the factor q_0, the gradient strength G_0 and the modulation period are related as $q_0 = \gamma G_0 T_m/4$. This imposes the upper limit to the gradient strength, which is in the case of liquids above the practical attainability by the conventional coil.

While the MGSE sequence cancels the signal phase ϕ, which depends on the net particle drift velocity, only the attenuation β is sensitive to stochastic fluctuations of spin position [6]. Thus, from signal attenuation measurements the information about random fluctuation superposed on the mean flow can be extracted. The attenuation factor at the time of echo acquisition t_e equals

$$\beta = \frac{\gamma^2}{2}\int_0^{t_e}\int_0^{t_e} G_{ef}(t_1)G_{ef}(t_2)\chi(t_1 - t_2)\,dt_1\,dt_2, \quad (1)$$

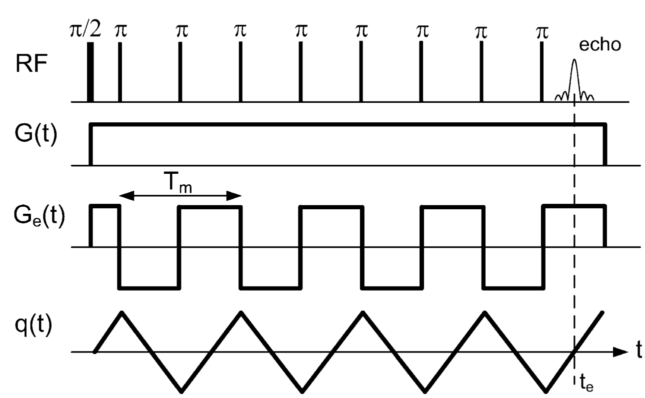

Fig. 1. The MGSE sequence: On the top is the CPMG RF sequence; the echo signal is measured at the constant echo time t_e. Below are following: the constant gradient, the effective gradient $G_{ef}(t)$ and the phase factor $q(t)$. The last two oscillate around zero with the modulation period T_m.

where $\chi(t) = \langle \delta x(t)\delta x(0)\rangle$ is the autocorrelation function of position fluctuations $\delta x = x - \langle x\rangle$. In a porous medium the spins from various locations may experience different restrictions to motion on a short time scale. With t_e long enough that spins can roam the entire range of motion, the spin-echo attenuation contains information about an average autocorrelation function $\chi(t)$ of all the detected spins. In frequency domain the attenuation (1) is expressed by the integral of two overlapping spectra, namely the square of absolute gradient spectrum $|G(\omega)|^2$ and the DPS. The gradient modulation spectrum $G(\omega)$ is defined as Fourier transform of the effective gradient form $G_{ef}(t)$, while the DPS is given by Wiener–Khintchine theorem [9] as the spectrum of $\chi(t)$ that we will denote by $I(\omega)$.

In the case of CPMG sequence $|G(\omega)|^2$ has distinctive peaks at odd multiples of the modulation frequency $\omega_m = 2\pi/T_m$ (see Fig. 2). The width of the peaks is inversely proportional to the number of modulation periods N. Note that for N modulation periods $2N$ refocusing pulses are required.

For more than about 10 modulation cycles, the attenuation factor for CPMG can be expanded in terms of DPS values at odd multiples of modulation frequency [18]. It can be written as

$$\beta(\omega_m) = K\left(I(\omega_m) + \frac{I(3\omega_m)}{81} + \frac{I(5\omega_m)}{625} + \frac{I(7\omega_m)}{2401} + \cdots\right) \approx KI(\omega_m), \quad (2)$$

where $K = \frac{8}{\pi^2}\gamma^2 G_0^2 t_e$. With accuracy to within a few percents the attenuation is directly proportional to the DPS component $I(\omega_m)$.

The modulation frequency ω_m is adjusted by varying the pulse separation time T_π. To factor out the relaxation effects the echo time has to be kept constant, implying that the separation time T_π and the number of π pulses have to be adjusted appropriately to give $t_e = 2NT_\pi$. In order to operate with large number of pulses $2N$ the echo time should be set as long as possible.

The DPS and $\chi(t)$ are related to the other quantities, which are used to describe stochastic motion [9]. The velocity autocorrelation function $\chi_v(t)$ is obtained by the second derivative of $\chi(t)$. Thus, in frequency domain the DPS and the spectrum of $\chi_v(t)$, i.e., the diffusion spectrum $D(\omega)$, are related by

$$D(\omega) = I(\omega)\omega^2. \quad (3)$$

By using the relation (3) in Eq. (2) one can see that in case of the CPMG sequence in constant gradient the attenuation is proportional to the selected component of the diffusion spectrum. The diffusion spectrum contains information about properties of porous materials [10,18]. From the low-frequency part of the restricted diffusion spectrum the average pore size and the tortuosity constant can be extracted, while the high-frequency part, where the spectrum approaches the free diffusion regime, gives the information about the pore's surface-to-volume ratio.

The usual time-dependent diffusion coefficient, defined as $D(t) = \langle \Delta x(t)^2\rangle/2t$, is related to the diffusion spectrum via the mean square displacement, which can be expressed by the displacement autocorrelation function as $\langle \Delta x(t)^2\rangle = 2\chi(0) - 2\chi(t)$ or equivalently by the Fourier transform of $I(\omega)$

$$\langle \Delta x(t)^2\rangle = \frac{4}{\pi}\int_0^\infty I(\omega)(1 - \cos\omega t)\,d\omega. \quad (4)$$

3. Signal dependence on sequence parameters

To determine the attenuation $\beta(\omega_m)$ one has to know the signal amplitude S_0. Important question in applying the method is how the sequence parameters G_0, T_π, and N affect S_0. As the gradient field is applied in combination with RF pulses, two effects arise. First, the selective excitation significantly influences S_0, what is shown in Fig. 3. Second, in a strong gradient field the assumption of direct echo pathway is no longer valid [13]. We will discuss how

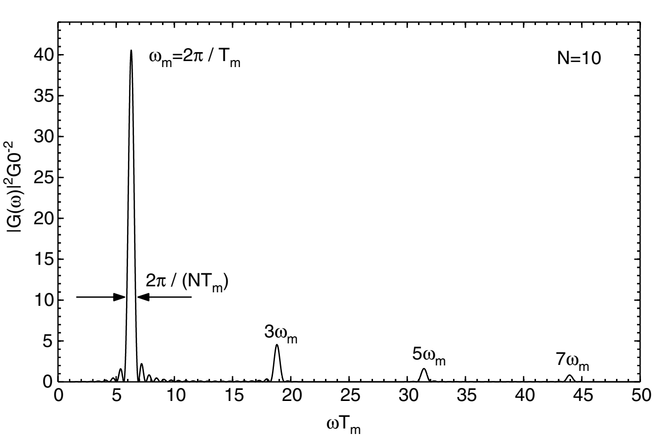

Fig. 2. The effective gradient spectrum $|G(\omega)|^2$ for 10 modulation periods.

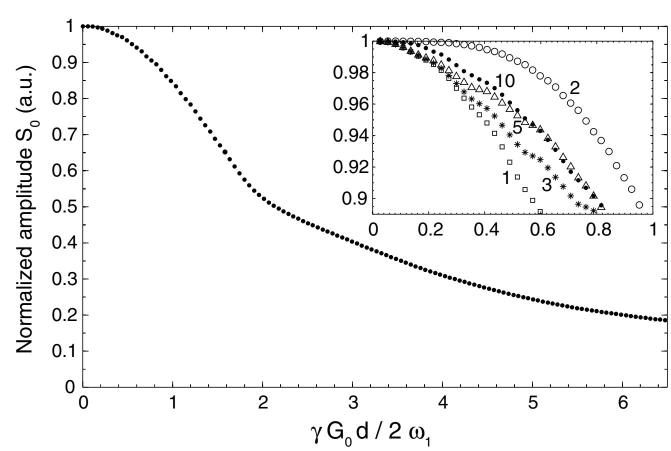

Fig. 3. Calculation of normalized amplitude S_0 versus $\gamma G_0 d/2\omega_1$ for a homogeneous sample of a regular shape ($2N = 10$ and $T_\pi = 1$ ms). The inset shows a transient behavior for numbers of pulses smaller than 10 in the range $\gamma G_0 d/2\ \omega_1 < 1$. The labels next to curves correspond to the numbers of pulses.

S_0 can be determined first, and then consider the gradient strength limitations.

3.1. Determining the amplitude S_0

The volume of the sample within which the on-resonance condition can be assumed decreases with increasing the gradient strength. This results in a strong echo amplitude dependence on gradient strength $S_0(G_0)$ (Fig. 3). The abscise in Fig. 3 is given in units of $\gamma G_0 d/2\omega_1$, where d is the length of a homogeneous sample and ω_1 is the RF field strength. As the offset of local Larmor frequency at position x is given by $\Delta\omega = \gamma G_0 x$, the value of $\gamma G_0 d/2\ \omega_1 = 1$ corresponds to the maximum frequency offset $|\Delta\omega_{\max}| = \omega_1$. By increasing the number of π pulses $S_0(G_0)$ quickly approaches an asymptotic form. The result presented in Fig. 3 has been obtained by solving the Bloch equations numerically for 10 refocusing pulses, which suffices to obtain the asymptotic dependence. The transient behavior of $S_0(G_0)$ at small number of pulses, presented in the inset of Fig. 3, is related to the transient behavior of $S_0(N)$ that will be discussed latter. Because there is no exact analytical solution for $S_0(G_0)$ dependence it is very difficult to take this into account. For this reason it is more convenient to factor out this effect by keeping the gradient strength constant while probing the spectrum $I(\omega)$. The choice of keeping gradient strength constant is further justified because unknown internal gradients can be induced in a porous sample, by susceptibility differences between the solid and the pore filling fluid. These gradients can be neglected if a much stronger external gradient is applied. The only variable parameters that remain are thus N and T_π.

The echo amplitude is given by the integral over the entire signal spectrum. It is not easily seen from the shape of the spectrum, how parameters N and T_π influence the signal amplitude S_0. For this reason we have numerically solved Bloch equations in order to obtain $S_0(N,T_\pi)$. In Fig. 4A the echo amplitude is plotted versus the number of refocusing pulses for different separation times T_π. It can be seen that the amplitude approaches an asymptotic value after the initial transient behavior. Similar results are presented also in Ref. [12] obtained by summation over different coherence pathways. Based on analytical theory of composite pulses [19] it has been shown that the shape of the effective magnetization profile approaches an asymptotic form very quickly by increasing the number of refocusing pulses [20]. The asymptotic profile results in an asymptotic amplitude S_0.

In addition to the pulse number dependence we have also analyzed the dependence on the pulse separation time (Fig. 4B). A transient behavior is observed for very short separation times. This can be interpreted as a non-efficient averaging of the oscillatory contributions shown in [20]. As for short T_π the oscillation period is large, the oscillatory contributions do not completely average out due to finite spectral width. The amplitude S_0 can be considered constant at least within 1% of accuracy for pulse numbers larger than about 10 and for pulse separation time longer than about twice the π pulse length, which is near the limit of most RF amplifiers. For pulse numbers fewer than 10 and very short pulse separation time the signal S_0 departs from the asymptotic value by less then 10%. Due to inaccurate RF pulses the transversal magnetization component is slightly reduced, but the asymptotic behavior is retained, so that the S_0 can be considered constant. The effects of inaccurate RF pulses are similar to the off-resonance effects [13,21].

If large enough modulation frequencies are reached, S_0 can be determined directly from the DPS measurement. The natural logarithm of the signal is proportional to the DPS as $\ln S(\omega_m) = \ln S_0 - KI(\omega_m)$. At large modulation frequencies the free-diffusion regime is eventually reached and the DPS decreases as ω^{-2}. Note that for smaller pores higher frequencies are required to enter the free-diffusion regime [10]. The offset $\ln S_0$ can be determined by probing

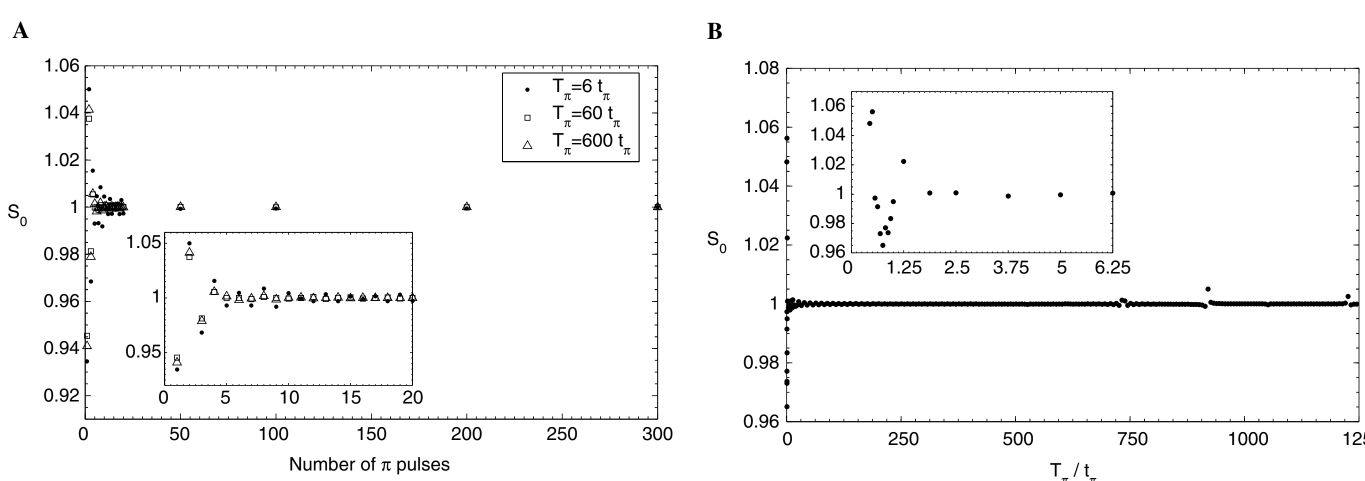

Fig. 4. (A) Calculated echo amplitudes S_0 versus number of π pulses for pulse spacings $T_\pi = 6t_\pi$, $60t_\pi$, and $600t_\pi$, where t_π is the π pulse duration. (B) Spin echo amplitudes S_0 versus the ratio T_π/t_π for $2N = 10$. The calculation was performed at $\gamma G_0 d/2\ \omega_1 = 0.54$.

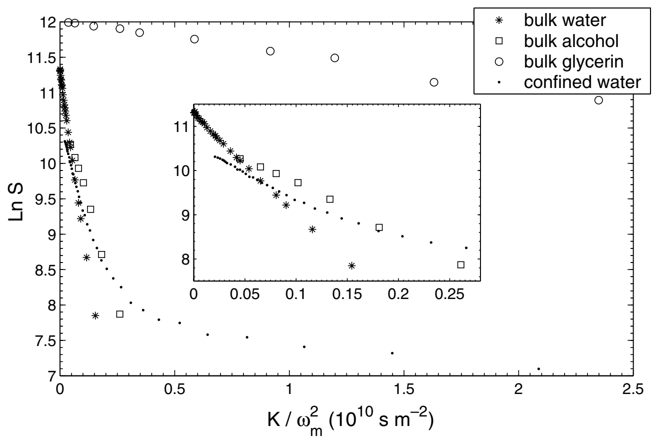

Fig. 5. Spin echo signal of unrestricted diffusion (∗, water; □, alcohol; ○, glycerin) and restricted diffusion (·) in a porous sample (silica Sol–Gel) with pore sizes between 0.5 and 10 μm.

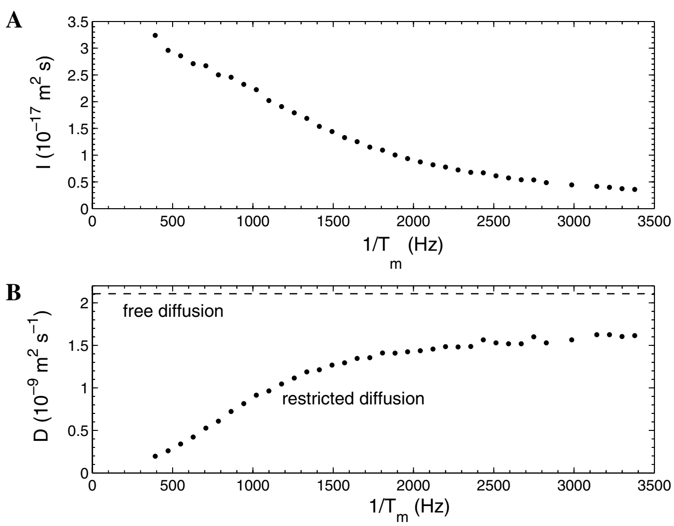

Fig. 6. Restricted diffusion case: (A) DPS and (B) diffusion spectrum corresponding to the data presented in Fig. 5.

the ω^{-2} dependence and extrapolate it to $\omega^{-2} = 0$. Such determination of the offset $\ln S_0$ can be pictured from the inset of Fig. 5. If the free-diffusion regime cannot be reached the amplitude S_0 has to be determined by measuring the signal attenuation for variable number of pulses at constant pulse separation time. In this case a separate relaxation measurement at $G = 0$ is required. Once S_0 is known, the DPS spectrum can be determined using Eq. (2) and the diffusion spectrum is calculated from Eq. (3). The two spectra are presented in Fig. 6.

3.2. Gradient strength limitations

In a strong field gradient multiple coherence pathways are excited. Different coherence pathways exhibit diffusion sensitivity on different time scales. By classification of coherence pathways [13] it has been found that there are mainly two kinds of coherence pathways that contribute

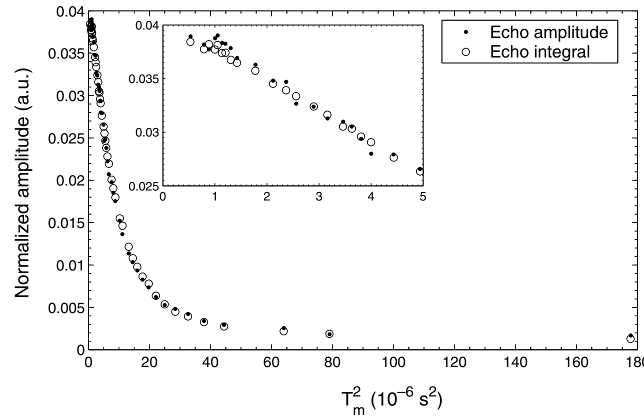

Fig. 7. Restricted diffusion data: comparison of normalized echo amplitudes (dots) and echo integrals (circles) taken over the time interval of about $11t_\pi$. The differences are within the experimental error confirming that the off-resonance effects can be neglected.

to the echo amplitude. The contributions that are composed of direct echo segments and singly stimulated segments sum up to about 95% of the signal. The inclusion of additional coherence pathways in the off-resonance contributions does not extend significantly the diffusion time scale compared to that of the direct echo. The stimulated segments increase the average signal attenuation by 32%. However, it is demonstrated in Ref. [13] that for detection bandwidth limited to $|\Delta\omega| < \omega_1$ the signal is mainly composed of the direct echo pathway. The attenuation factor rapidly increases beyond ω_1 interval. This suggests that as the signal bandwidth is limited to the range $\pm\omega_1$ the direct echo pathway contribution is a good approximation and the frequency-domain analysis based on the direct echo pathway can be considered.

In order to select the direct echo pathway, a narrow signal bandwidth has to be used. This can be achieved either by digital filtering, as shown by Hürlimann [12], or by using samples with limited length in the field gradient direction. The result presented in Fig. 7 demonstrates that by using a short sample only the direct echo pathway is successfully selected in our experiment.

4. Experimental results

Measurements where performed by using the 100 MHz superconducting horizontal bore Oxford magnet with Tec-Mag Apollo MRI spectrometer equipped with micro-imaging accessories and reversed Helmholtz gradient coils with 5.9 T/m peak magnetic field gradient. The gradient strength used was 1 T/m and the excitation pulse was $t_{\pi/2} = 1.4$ μs ($\omega_1 = 1.12 \times 10^6$ s^{-1}). The DPS was acquired by measuring the echo signal at $T_{\pi/2}$ after the last π pulse in the CPMG sequence. Different frequency components were determined by varying the modulation period T_m in the range between 0.1 and 8 ms, while keeping the acquisition time constant at $t_e = 40$ ms. In order to optimize the signal-to-noise ratio, the time interval between the excitation pulse and the first π pulse was adjusted to $T_{\pi/2} - 2t_{\pi/2}/\pi$ [22].

Experimental results show an evident distinction between bulk and restricted diffusion. The slope of data presented in Fig. 5 is proportional to the diffusion spectrum. To test the method three known free diffusion spectra at 22 °C were measured. The data for free diffusion exhibit an expected linear slope in Fig. 5 as the diffusion spectrum is constant $D(\omega) = D_0$. For glycerin we obtained $D_0 = 6.1 \times 10^{-11}\ \mathrm{m^2/s}$, for ethyl alcohol $1.1 \times 10^{-9}\ \mathrm{m^2/s}$ and for tap water $2.1 \times 10^{-9}\ \mathrm{m^2/s}$. These results confirm that the signal amplitude S_0 can be regarded as independent of sequence parameters. For comparison restricted diffusion has been probed in a water-saturated powder of microcrystalline silica(Sol–Gel) with the declared distribution of particle sizes between 0.5 and 10 μm (Sigma–Aldrich). The results of Sol–Gel porous sample show that the diffusion spectrum increases with modulation frequency (Fig. 6B).

Although our detection bandwidth was about 3 MHz the spectral width was limited by the length of the sample $d \approx 1.5$ mm, determining $|\Delta\omega_{\mathrm{max}}| \approx 2 \times 10^5\ \mathrm{s^{-1}}$. The ratio $|\Delta\omega_{\mathrm{max}}/\omega_1| < 0.18$ ensures that contributions from stimulated pathways can be neglected. This is confirmed by experimental data if a narrow bandwidth filter is applied by means of integrating each echo over a long time interval. In Fig. 7 the normalized echo amplitudes are compared to the normalized echo integrals taken over a time interval of about $11t_\pi$. The differences are seen to be within the limits of experimental error, confirming that the echo amplitudes are not influenced by off-resonance effects.

5. Conclusion

We have presented the experimental strategy for using CPMG sequence in frequency-domain diffusion measurement. Different DPS components can be measured by systematically adjusting the pulse separation time while keeping the echo time constant. Due to the S_0 dependence on gradient strength, that is caused by selective excitation, also the gradient strength has to be kept constant in probing the DPS at different modulation frequencies. The gradient strength can be adjusted in order to achieve the desired sensitivity. For probing the DPS at higher modulation frequencies a larger gradient strength is needed (see Eq. (2)). The transient behavior of the echo amplitude shows that the shortest pulse separation time T_π should be at least twice as long as the π pulse length, which is near the capability limits of most RF amplifiers. Thus, the highest achievable frequency is determined by the duty cycle of the RF amplifier. The lowest frequencies are limited by the relaxation time T_2 and the minimal number of π pulses required to avoid the transient behavior of the echo amplitude. A sufficiently narrow spectral lobe of the gradient waveform is achieved with 10 modulation periods (20 π pulses), which suffices to avoid the transient behavior. If the echo time is set to the relaxation limit, the lowest achievable frequency can be estimated by $10/T_2$. The gradient strength restrictions are imposed by Gaussian approximation of the cumulant expansion (1) and by off-resonance effects. The first restriction gives the upper limit on the order of 100 T/m for liquids and 40 T/m for gasses in case of $T_{\mathrm{m}} = 4$ ms. The second restriction is conditioned by the strength of RF pulses. It implies that the signal bandwidth should be smaller than the RF field strength $|\Delta\omega/\omega_1| < 1$. This can be achieved either by data filtering or by using an appropriately short sample.

Our experimental results confirm that the presented strategy is efficient in probing the DPS, which is in close relation to the diffusion spectrum. Thus, the presented technique can be used for characterization of porous materials via frequency-domain analysis of restricted molecular dynamics.

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