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Spectral characterization of diffusion in porous media by the modulated gradient spin echo with CPMG sequence

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Abstract

Carr–Purcell–Meiboom–Gill train of radiofrequency pulses applied to spins in the constant magnetic field gradient is an efficient variant of the modulated magnetic field gradient spin echo method, which provides information about molecular diffusion in the frequency-domain instead in the time-domain as with the two-pulse gradient spin echo. The frequency range of novel technique is broad enough to sample the power spectrum of displacement fluctuation in water-saturated pulverized silica (SiO_2) and provides comprehensive information about the molecular restricted motion as well as about the structure of medium.

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1. Introduction

During recent years, understanding of confined fluid dynamics in different environments and modifications of its structure has often been in the focus of scientific research. The topic is of great relevance in many technological areas as well as in living systems, where essential fluid-related phenomena occur in restricted geometries of porous structures, biological cells, their membranes and surfaces, active sites of proteins, etc.

The scientific interest is centred on the development of efficient measuring methods, among which the spin echo with the non-uniform magnetic field has gained a decisive role. The signal analysis of the most commonly used two-pulse gradient spin echo (PGSE) is based on the diffusion propagator, which requires the gradient pulses much shorter than the time between the pulses. In porous media, the width of gradient pulse is limited also by the requirement that the diffusion displacement during the application of a gradient pulse has to be shorter than the size of the confinement. As a broad range of spin dephasing by applied gradient is required to sample the diffusion propagator in a small pore, it is difficult to satisfy both requirements that contradict each other. However, the PGSE method is not unique and other gradient-radiofrequency pulse sequences are possible that are able to detect the molecular motion in a different manner.

Herein, we refer to the method of modulated gradient spin echo (MGSE), where a sequence of radiofrequency (RF)-pulses combined with magnetic field gradient pulses or waveforms periodically modulates the spin phase in order to get the spin echo attenuation proportional to the power spectrum of molecular displacement (DPS) or the velocity autocorrelation spectrum, depending on the applied sequence. Instead of measuring the evolution of diffusion propagator in the time-domain, the MGSE method samples the spectrum of molecular motion in the frequency-domain by changing the period of modulation.

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The velocity autocorrelation (VA) function is a fundamental quantity relating the dynamical processes on the molecular level to the thermodynamic properties of fluids. In the case of diffusion in the porous media, the VA spectrum contains information about the evolution of molecular motion on any scale beginning from the almost free diffusion at high frequencies, to the effect of motional restriction by enclosing boundaries, and ending at low frequencies, where the permeability of media predominates. This potential of spin echo has already been exploited for the analysis of flow and diffusion in porous media and in emulsions [1–5]. The rate of spin phase modulation by the applied RF-gradient sequence determines the frequency range of the method. At the reported applications the high-frequency limit were about 1 kHz, which was not always enough to explore an entire relevant part of the diffusion spectrum.

Herein, we present the first application of a novel MGSE technique, which can scan the spectrum of molecular diffusion in pores as small as a few nano-meters, if used on an advanced NMR spectrometers. We do not test the MGSE technique on the model system, as already done by others [1,5], but demonstrate its applicability for the study of diffusion through complex porous media such as it is partially gelatinous structure of hydrated silica powder [6].

2. CPMG sequence as a modulated gradient spins echo technique

Using NMR spin echo to detect translational motion, we observe a cumulative effect of precession frequency perturbations due to the displacements of spin-bearing particles in the non-uniform magnetic field. As the MGSE method relies on the rate of the gradient modulation rather than on its magnitude, the size of confinement can be always smaller than the spin phase grating created of the applied gradient, and the signal analysis within the Gaussian phase approximation is permitted [7]. Neglecting the spin relaxation, it gives the MGSE signal as the superposition of signal induced by a large number of spins

$$E(\tau) \approx \sum_i \mathrm{e}^{-\beta_i(\tau)}, \tag{1}$$

where the motional effect is only in the attenuation of signal induced by ith spin [8] as

$$\beta_i(\tau) = \frac{\gamma^2}{2\pi} \int_{-\infty}^{\infty} G(\omega,\tau) I_{zi}(\omega) G^*(\omega,\tau) \mathrm{d}\omega. \tag{2}$$

According to the Wiener-Khintchine theorem [9], DPS is

$$I_z(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \langle \Delta z(t) \Delta z(0) \rangle \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{d}t. \tag{3}$$

Here the time average $\langle\rangle$ is taken over the autocorrelation of $\Delta z(t) = z(t) - \langle z(t) \rangle$, which is the component of particle displacement fluctuation around the mean trajectory of particle motion in the direction of the applied magnetic field gradient. DPS is related to the VA spectrum, $D_i(\omega) = I_{zi}(\omega)\omega^2$, and to the spin MSD

$$\langle [z_i(t) - z_i(0)]^2 \rangle = \frac{4}{\pi} \int_0^{\infty} I_{zi}(\omega)(1 - \cos(\omega t)) \mathrm{d}\omega, \tag{4}$$

which time-derivative yields the time-dependent diffusion constant. Evidently, DPS contains information about time-dependent diffusion quantities by definition. The spin dephasing accumulated by the sequence of RF-pulses and magnetic field gradient waveforms looks alike to be formed by an effective time-dependent gradient $\mathbf{G}_{\mathrm{eff}}(t)$, which spectrum

$$\mathbf{G}(\omega,\tau) = \int_0^{\tau} \mathbf{G}_{\mathrm{eff}}(t) \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{d}t, \tag{5}$$

defines a relation between the spin echo and the displacement fluctuations. Generally, the sequence of the magnetic field gradient waveforms superposed to the train of RF-pulses excites the multiple coherence pathways, which accumulate the spin dephasing in different manners [10]. Thus, the effective gradient of selected pathway depends on the gradient waveform $G(t)$ as well as on the parameter of coherence pathway $q(t)$ that changes stepwise between -1, 0 and $+1$ upon the application of RF-pulses. As each pathway contributes the signal with the different motional attenuation [11,12], the diffusion measurement requires an isolation of single coherence pathway. If the selected coherence pathway creates the oscillatory modulation of the spin phase, which is essential for the MGSE sequences, the corresponding spin-echo attenuation of the isotropic diffusion is

$$\beta_i(\tau,\omega_m) = 2\gamma^2\tau \sum_{n=0}^{\infty} I_{zi}(n\omega_m) |g(n\omega_m)|^2. \tag{6}$$

Here $\omega_m = 2\pi/T$ and $\tau = NT$, where N is the number of modulation periods T. $I_{zi}(n\omega_m)$ are samples of DPS at the gradient spectrum peaks, which amplitudes depend on the effective gradient waveform within a single time-period, $g(\omega) = 1/T \int_0^T G_{\mathrm{eff}}(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t$, while the peak width depends on the number of periods as ω_m/N.

The Carr–Purcell–Meiboom–Gill train of π RF-pulses (CPMG) [13] applied at the constant magnetic field gradient is an efficient MGSE sequence. Its frequency range depends only on the repetition rate of applied RF-pulses and not on the switching rate of gradient pulses limited by the coil inductance. The effective gradient spectrum of properly isolated direct coherence pathway [10] has dominant peaks at $\omega = \pm\omega_m$, if π-RF pulses are repeated at $T/2$ intervals. As side peaks at $\omega = \pm(2n+1)\omega_m$, $(n = 2,3,4,\ldots)$, contribute only 1.5% to the measured value of VA spectrum, the spin echo attenuation at $\tau = NT$ can be taken as determined just by the dominant peaks as

$$\beta_i(\tau,\omega_m) = \frac{8\gamma^2 G^2 \tau}{\pi^2} I_{zi}(\omega_m). \tag{7}$$

The measurements of the spin echo attenuation at various T enables the $I_{zi}(\omega)$ calculation.

The average over the spin ensemble converts Eq. (1) into a weighted sum of signals induced by spin subsets that are

formed of spins at various locations, but with similar motional restrictions

$$E(\tau) \approx \sum_j E_j e^{\beta_j(\tau)}. \quad (8)$$

If τ is long enough that during the application of MGSE sequence each spin-bearing particle roams over all characteristic voids of porous structure, $I_{zj}(\omega)$ describes an averaged motional spectrum identical for all spins. Otherwise, the attenuation depends on the spin location and the range of void it transverses. In this case, different spin subsets are subjected to different motional restrictions and the analysis with Eq. (8) is needed.

3. Velocity autocorrelation of molecular diffusion in porous media

The delta function is a good approximation for the VA function as long as the diffusion length is short enough that only a few molecules feel boundaries. The longer diffusion path is, the more frequent are spin encounters with the barriers leading to the VA function, which depends on the geometry of boundaries. The Langevin equation [14] or the second derivative of the mean squared displacement (MSD) derived from the diffusion equation under the boundary conditions [15] provide VA function of restricted motion. The conditional probability distribution for the restricted diffusion within the pore of an arbitrary geometry,

$$P(\mathbf{r}, t|\mathbf{r_o}) = \sum_k \psi(\mathbf{r})\psi(\mathbf{r_o})e^{-t/\tau_k}, \quad (9)$$

where τ_k is the characteristic time of the kth diffusion mode and $\psi(\mathbf{r}_o)$ is its eigenfunction [16–19], gives the MSD, which second derivative is the VA function. Its component in the direction of the applied gradient is

$$\langle v_z(t)v_z(0)\rangle = 2D\left(\delta(t) - \frac{1}{2}\sum_{k\neq 0}\frac{b_k}{\tau_k}e^{-t/\tau_k}\right), \quad (10)$$

where $b_k = \frac{1}{2D\tau_k}\frac{1}{V}\int\int d\mathbf{r}_o(z-z_o)^2\psi(\mathbf{r}\psi(\mathbf{r}_o)d\mathbf{r}_o d\mathbf{r})$ depends only on the morphology of the surrounding boundaries and D is the free diffusion constant. In short time interval, when the displacements are much shorter than the pore size, the MSD is equal to $2Dt$. It gives the condition $\sum_{k\neq 0} b_k = 1$ that furnishes the VA spectrum, which is the Fourier transform of Eq. (10), in the form

$$D(\omega) = D\sum_{k\neq 0} b_k \frac{\tau_k^2\omega^2}{1+\tau_k^2\omega^2}. \quad (11)$$

In the structure of interconnected, permeable or partially opened pores, the longest correlation time τ_1 can be much longer than the measurement time. In that case, the VA spectrum is given by

$$D(\omega) = Db_1 + D\sum_{k=2}^{\infty} b_k \frac{\tau_k^2\omega^2}{1+\tau_k^2\omega^2}, \quad (12)$$

where b_1 is the tortuosity of the porous medium. For example, a chain of N identical and identically connected pores aligned along the applied gradient has $b_1 = 1/(\zeta_p + \zeta_c)$, where ζ is the relative length $l_c/(l_c + l_p)$ of the channel (pore) divided by its relative cross-sectional area $A_c/(A_c + A_p)$.

The low-frequency approximation of Eq. (12) gives

$$\lim_{\omega\to 0} D_{rest}(\omega) = D(b_1 + b_2\tau_2^2\omega^2 + \cdots), \quad (13)$$

where for weakly connected pores $b_2\tau_2^2 = \frac{\chi^4 a^4}{D^2}$ with χ equals 0.30, 0.26 and 0.21 in the case of planar, cylindrical and spherical pores, respectively. a is the distance between planes, or the diameter of cylindrical and spherical pores. In the case of weakly permeable plan-parallel pores $\tau_2 \approx a^2/\pi^2 D$.

Using the Cauchy formula, the summation over k in Eq. (12) can be substituted by the integration [20], which gives the high-frequency limit of the VA spectrum as

$$\lim_{1/\omega\to 0} D_{rest}(\omega) = D\left(1 - \Gamma\left(\frac{3}{4}\right)\Gamma\left(\frac{5}{4}\right)\frac{4S}{\pi V}\sqrt{\frac{D}{\omega}} + \cdots\right). \quad (14)$$

The limit that goes in proportion to the surface-to-volume ratio of porous structure, $\frac{S}{V}$, perfectly matches the exact calculations for the closed planar, cylindrical and spherical pores, but differs from Eq. (6) of the reference [21] for the factor of 6. We will discuss the details of this calculation elsewhere. The dependence of VA spectrum on the surface-to-volume ratio of porous media has the correspondence in the time-domain measurement of MSD by PGSE, which exhibits a $\sqrt{t}$-early time decay in identical proportion [22].

4. Experimental procedure

Measurements were done on a TecMag NMR spectrometer with a 2.35 T horizontal bore superconductive magnet equipped with micro-imaging accessories and reversed Helmholtz gradient coils with 5.9 T/m peak magnetic field gradient. The sample bed was 15 mm long cylindrical cell with the diameter $d = 2$ mm and oriented with cylinder axis perpendicular to the static magnetic field and to the gradient direction. The CPMG pulse train of π-RF pulses, of the length $\delta = 2.8$ μs and applied to spins in the static magnetic field gradient, we used to measure the molecular DPS in a water-saturated powder of finely ground microcrystalline silica with the declared distribution of particle sizes between 0.5 and 10 μm (Sigma–Aldrich). A similar system was already studied by the PGSE method, where a bi-exponential echo decay was explained by the diffusion between and within the porous particles [6]. We optimized the first echo spacing to $T/2 - \delta/\pi$. The parameters of measurement correspond to the range of offset frequencies $\Delta\omega/\omega_1 = \gamma G d\delta/\pi = \pm 0.14$, which is narrow enough that the observe peak of spin echo contains only the direct coherence pathway. In order to exclude the effect of spin relaxation, the acquisition time was kept constant at $\tau = NT = 40$ ms.

The measurements at various modulation periods T gives DPS.

5. Results and discussion

In order to test the effect of susceptibility difference between water and silica, we applied CPMG train of π-RF pulses at a constant magnetic field gradient of 1.18 T/m and 2.36 T/m. Identical values of measured spectra approve the negligence of susceptibility effect in our measurements. The log–log plot of the measured spectrum $I_z(\omega)$ in Fig. 1 shows the frequency dependence that passes from a gentle slope at low frequencies into a straight $1/\omega^2$-dependence above 250 Hz as expected according to Eq. (12). Weak discrepancy from the straight line above 800 Hz might due to the previously mentioned signal dispersion by the induction of non-equivalent spin subsets. The transition into a straight line occurs at frequencies equal to the inverse time of spin displacement across the space of confinement, $a \approx \sqrt{2\pi D/\omega}$, which gives the first estimation of the mean pore size to be $a = 4$ μm. It shows that the diffusion displacement during 40 ms long CPMG sequence is slightly shorter compared to the length-scale of restrictive domains. Thus, the attenuation of the last echo does not give exactly an averaged DPS of molecular diffusion and a correction according to Eq. (8) is needed. The low-frequency part of the VA spectrum, $I(\omega)\omega^2 = D(\omega)$, which increases with the second power of frequency according to Eq. (13) with the factor proportional to the mean forth power of pore size, provides the another estimate of pore size. The slope in the enlarged low-frequency part of plot $D(\omega)$ versus ω^2 in Fig. 2 gives the mean value of $a = 4.7$ μm, with an error of 4%, if the geometry factor χ of 2.5 is assumed. The line intersection with the ordinate gives the long time diffusivity of porous media $D_\infty = 6 \times 10^{-11}$ m^2/s, which indicates a very slow inter-pore diffusion rate. We assumed that the gelling process on the surface of silica grains in water with pH below 7 seals the grain interspaces and impedes the intra-pore diffusion rate.

In Fig. 2, the high-frequency range of $D(\omega)$ versus ω does not show an expected leveling at the value of free water diffusion constant. An initial indication of leveling at about 200 Hz passes over in a weak rise to about 3 kHz, which is the frequency limit of our measurement. According to Eq. (14), the initial slope of $D(\omega)$ versus $1/\sqrt{\omega}$ is proportional to the surface-to-volume ratio of the porous structure. Rather than a line at low $1/\sqrt{\omega}$ values, Fig. 3 shows a curve that passes from the steep slope into a more gentle one as the frequency decreases, which may indicate a dispersed distribution of pore sizes. The slope variation gives an estimate of S/V ratio between 0.25×10^6 m^{-1} and 3×10^6 m^{-1}. The exactly calculated spectrum for the distribution of spherical pores with 90% fraction of pores with 3.4 μm radius and 10% with 0.7 μm radius gives a rough fit to the measured data shown by the dotted curve in Fig. 3. It points up that a precise measurement of spectrum in this frequency range can give good information about the pore size distribution.

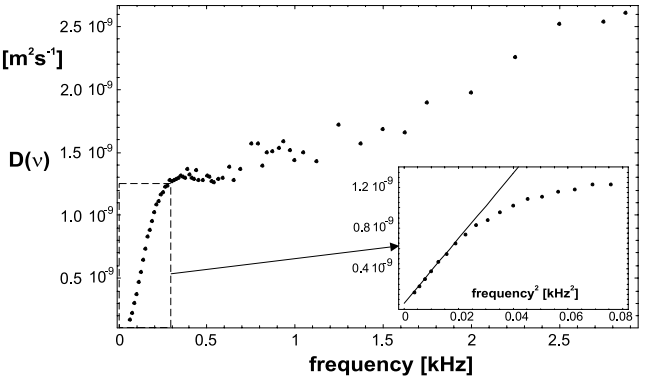

Fig. 2. Velocity auto-correlation spectra of molecular diffusion in water-saturated silica powder derived from the displacement power spectrum in Fig. 1. Enlarged low-frequency part of the spectrum versus the squared frequency exhibits a linear dependence with the slope proportional to the mean forth-power of pore size.

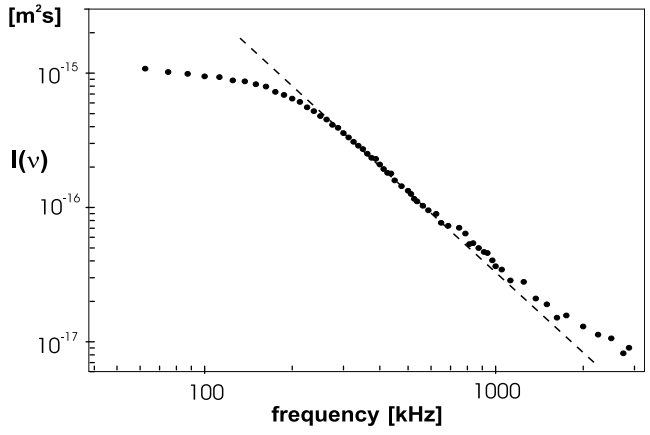

Fig. 1. The displacement power spectrum of molecular diffusion in the water-saturated silica powder with the particle size distribution between 0.5 and 10 μm.

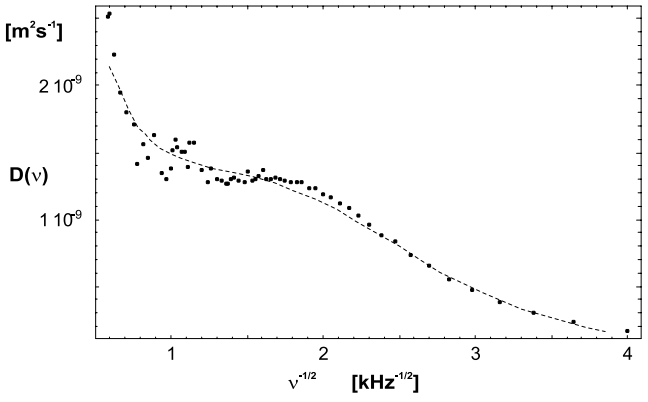

Fig. 3. Surface-to-volume of porous structure is proportional to initial slope of the VA spectrum versus inverse-squared-root of frequency plot. The dotted curve is the spectrum of diffusion in the system with the distribution of 90% spherical pores with the size of 3.4 μm and 10% with the size of 0.7 μm.

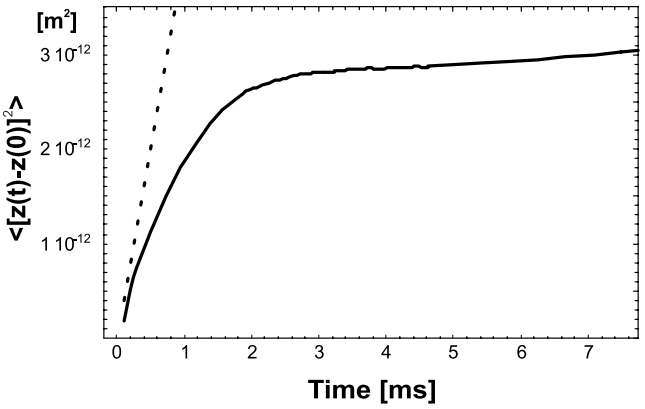

Fig. 4. Time dependence of the MSD obtained from the Fourier transform of $I_z(\omega)$ in Fig. 1 demonstrates the time resolution of the method. The dotted line is the MSD of water free at temperature of measurement (24 °C).

Fig. 4 depicts the time dependence of the spin MSD as calculated according to its relation to $I_z(\omega)$ in Eq. (4). The lowest frequency of measurement determines the longest MSD in time of 8 ms, while the highest frequency gives the time resolution of MSD, which was 0.33 ms. With the possibility to extend the frequency range of measurement to 100 kHz, the method could provide the evolution of MSD in the time intervals of 0.01 ms and provides an information about restricted diffusion in pores below 100 nm.

6. Conclusion

The results of this report disclose the CPMG sequence with the constant magnetic field gradient as an efficient MGSE technique able to scan the spectra of molecular diffusion in porous media. The ability of the novel technique to modulate the spin phase dephasing in the pace of applied π-RF pulses shifts up the high-frequency limit of method. When applied with an advanced NMR instrumentation, it could reach the frequencies about 100 kHz that permits the NMR analysis of restricted diffusion within nanopores. The MGSE measurement of the water diffusion in the interspaces between the packed grains of fine-grounded silica powder provides the information about the relation between the mass-transfer resistance and the internal architecture of the porous packing material.

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