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Velocity autocorrelation spectra of fluid in porous media measured by the CPMG sequence and constant magnetic field gradient

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Abstract

Carr–Purcell–Meiboom–Gill (CPMG) 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 of in the time domain as with the two-pulse gradient spin echo. The frequency range of this 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 the medium.

Keywords: Magnetic resonance; Porous media; Diffusion; Modulated gradient spin echo; Velocity correlation function; CPMG sequence

1. Introduction

During recent years, understanding of confined fluid dynamics in different environments and modifications of its structure have 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.

Herein, we refer to the method of modulated gradient spin echo (MGSE) [1], where a sequence of radiofrequency (RF) pulses combined with magnetic field gradient pulses or waveforms periodically modulates the spin phase in order to obtain the spin echo attenuation proportional to the velocity autocorrelation spectrum. 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. As the velocity autocorrelation (VA) function is a fundamental quantity relating the dynamic processes on the molecular level to the thermodynamic properties of fluids, in the case of diffusion in the porous media, the VA contains information about the molecular motion as well as about the morphology of media. In this paper, we present the application of a novel MGSE technique to scan the spectrum of molecular diffusion in pores as small as a few tenth of a micrometer and demonstrate its applicability in studying complex porous media such as its partially gelatinous structure of hydrated silica powder [2].

2. Carr–Purcell–Meiboom–Gill sequence as a modulated gradient spin echo technique

As the MGSE method relies on the rate of the gradient modulation rather than on its magnitude, the spin phase grating, created by the applied gradient, can be made always larger than the size of confinement. Thus, we can analyze the spin echo with the Gaussian phase approximation [3]. By neglecting the spin attenuation, the spin echo appears as a superposition of signals induced by a large number of spins $E(\tau) = \sum_i e^{-\beta_i(\tau)}$, where the phase shift of signal induced by the ith spin is canceled by the MGSE sequence, but the attenuation contains the effect of spin motion as

$$\beta_i(\tau) = \frac{1}{\pi} \int_0^\infty \left| G_{\text{eff}}(\omega, \tau) \right|^2 \frac{D_i(\omega)}{\omega^2} d\omega.$$

Here, the sequence of RF pulses and magnetic field gradient waveforms is supposed to act as to be formed by

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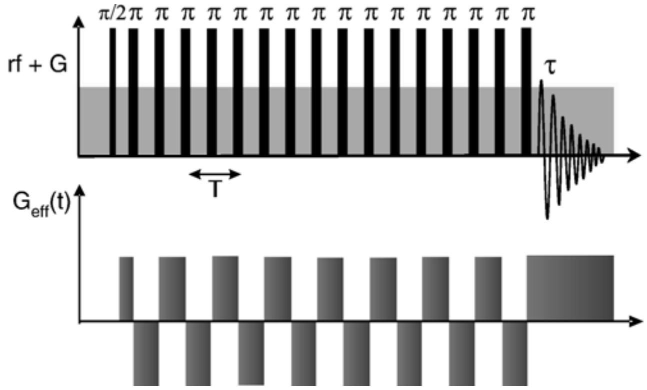

Fig. 1. CPMG sequence with the constant gradient and the time dependence of the effective magnetic field gradient.

an effective time-dependent gradient with spectrum $G_{\text{eff}}(\tau,\omega)=\int_0^\tau G_{\text{eff}}(t)e^{-i\omega t}dt$, and according to the Wiener–Khintchine theorem, the VA spectrum $D(\omega)=\frac{\omega^2}{\pi}\int_{-\infty}^{\infty}\langle\Delta z_i(t)\Delta z_i(0)\rangle e^{-i\omega t}d\omega$ is related to the time averaged autocorrelation of particle displacement $\langle\Delta z_i(t)\Delta z_i(0)\rangle$ in the direction of the applied magnetic field gradient.

In the pulsed gradient version of the MGSE method [1,4–7], the upper limit to the sampling frequency is determined by the rate at which gradient pulses can be switched. No such upper limit applies to the Carr–Purcell–Meiboom–Gill (CPMG) train of π-RF pulses applied at the constant magnetic field gradient. Such sequence was already proposed in Ref. [1], but never studied in detail. Generally, the train of RF pulses superimposed to the magnetic field gradient excites multiple spin coherence pathways that accumulate the spin dephasing in different manners [8,9]. Thus, the effective gradient of selected pathway depends on the gradient waveform and on the parameter of coherence pathway that changes stepwise between −1, 0 and +1 upon the application of RF pulses. In Fig. 1, we show the effective gradient spectra of different coherent pathways for the case of CPMG sequence with four π-RF pulses applied with the constant gradient. Only the spectrum of direct coherence pathway shows a distinctive peak at $\omega_{\text{m}}=2\pi/T$, if π-RF pulses are repeated at $T/2$ intervals. Thus, the sequence application as a MGSE technique requires the isolation of the direct coherence pathway contribution to the signal that can be done in various ways [8]. As the side peaks contribute only 1.5% to the measured value of VA spectrum, the attenuation of direct coherence pathway can be taken as determined only by the dominant peak as $\beta(NT,\omega_{\text{m}})=\frac{8\gamma^2G^2}{\pi^2\omega_{\text{m}}^2}D(\omega_{\text{m}})NT$, where N is the number of rf pulses. The measurements of the spin echo attenuation at various T give the spectrum $D(\omega)$.

3. Velocity autocorrelation of 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 the boundaries. In the structure of interconnected, permeable or partially opened pores, the general form of the VA spectrum can be written [10,11] by $D(\omega)=D\alpha+\sum_k b_k\frac{\tau_k^2\omega^2}{1+\tau_k^2\omega^2}$, where D is the diffusion constant of fluid, α is the tortuocity of media, b_k are the structure factors and τ_k are the characteristic times of restricted diffusion modes. In low-frequency approximation, $D(\omega)\xrightarrow{\omega\to0}D\left(1-b_1\tau_1^2\omega^2+\ldots\right)$, with τ_1 being about the time of particle displacement across the compartment. With the use of the Cauchy formula, the summation over diffusion modes can be substituted by integration [12] to get the high-frequency limit of the VA spectrum as

$$D(\omega)\xrightarrow{\frac{1}{\omega}\to0}D\left(1-1.11\frac{4S}{\pi V}\sqrt{\frac{D}{\omega}}+\ldots\right)$$

This limit goes in proportion to the surface-to-volume ratio of porous structure, S/V, and perfectly matches the exact calculations for the closed planar, cylindrical and spherical pores. The velocity autocorrelation spectrum contains information about time-dependent diffusion quantities. Thus, the particle mean squared displacement along the magnetic field gradient can be calculated from

$$\left\langle(z(t)-z(0))^2\right\rangle=\frac{4}{\pi}\int_0^\infty[1-\cos(\omega t)]\frac{D(\omega)}{\omega^2}d\omega.$$

4. Experimental results and discussion

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. The sample bed was a 15-mm-long cylindrical cell with a diameter (d) of 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 with a length (δ) of 2.8 μs applied to spins in the static magnetic field gradient was used to

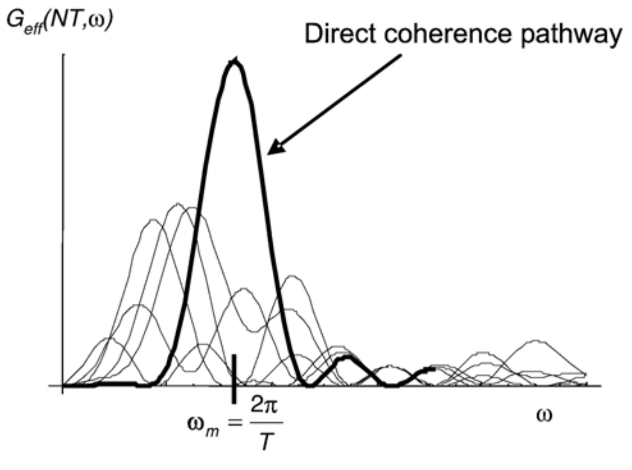

Fig. 2. The spectra of the effective magnetic field for different coherence pathways in the case of CPMG sequence with four π-RF pulses and constant gradient.

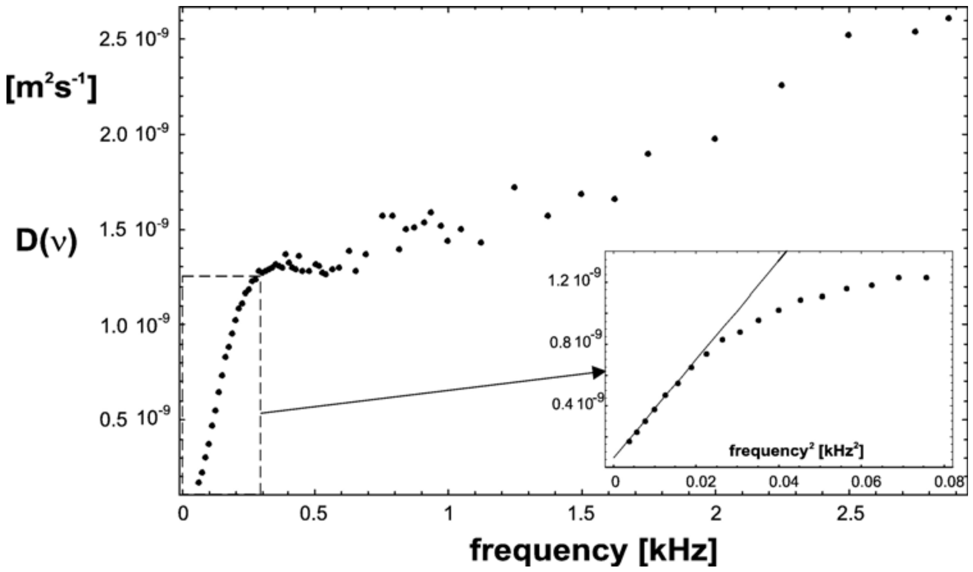

Fig. 3. Velocity auto-correlation spectra of molecular diffusion in water-saturated silica powder. Enlarged low-frequency part of the spectrum versus the squared frequency exhibits initial linear dependence with the slope proportional to the mean fourth-power of pore size.

measure the molecular velocity autocorrelation spectra in a water-saturated powder of finely ground microcrystalline silica. The sample has declared distribution of particle sizes between 0.5 and 10 μm (Sigma-Aldrich). A similar system was already studied by using the PGSE method, where bi-exponential echo decay was explained by the diffusion between and within the porous particles [2]. The parameters of measurement correspond to the range of offset frequencies $\Delta\omega/\omega_1=\pm0.14$, which is narrow enough that the observed peak of spin echo contains only the direct coherence pathway as shown in Fig. 2 [13]. In order to exclude the effect of spin relaxation, the acquisition time was kept constant at $NT=20$ ms, with N changing from 4 to 116. Fig. 3 shows the velocity autocorrelation spectrum as measured from 100 Hz to 2.9 kHz. The transition into a gentle slope occurs at frequencies about to the inverse time of spin displacement across the space of confinement, which gives the first estimation of the mean pore size of $a=4$ μm. The slope in the enlarged low-frequency part of $D(\omega)$ plot vs. ω^2 in Fig. 3 gives the mean value of $a=4.7$ μm, with an error of 4%. The line intersection with the ordinate gives the long-time diffusivity of porous media $D_\infty=6\times10^{-11}$ m^2/s,

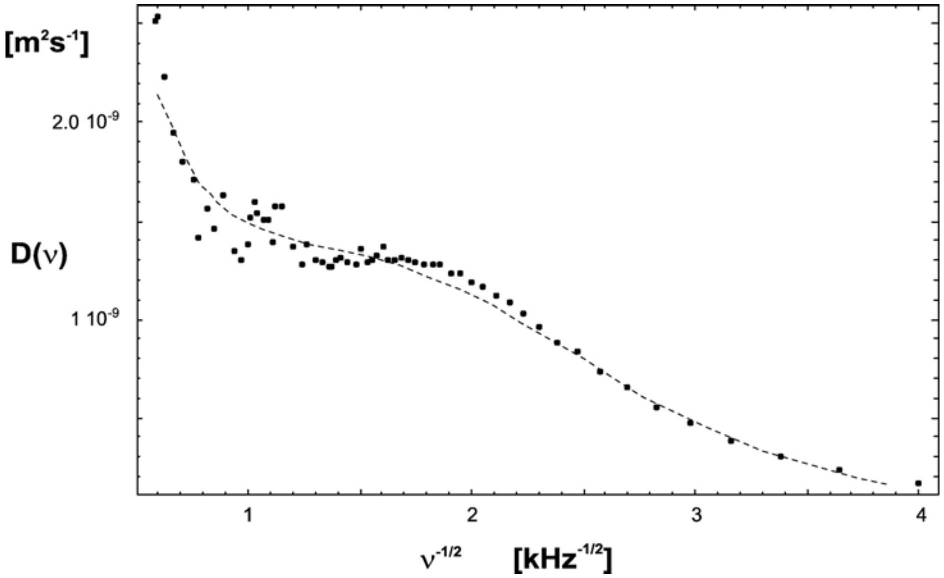

Fig. 4. VA spectum versus inverse-squared-root of frequency where the initial slope has to be proportional to the surface-to-volume ratio of the porous structure. The dotted curve is the fit by the spectrum of diffusion in the system with 90% spherical pores with the size of 3.4 μm and 10% with the size of 0.7 μm.

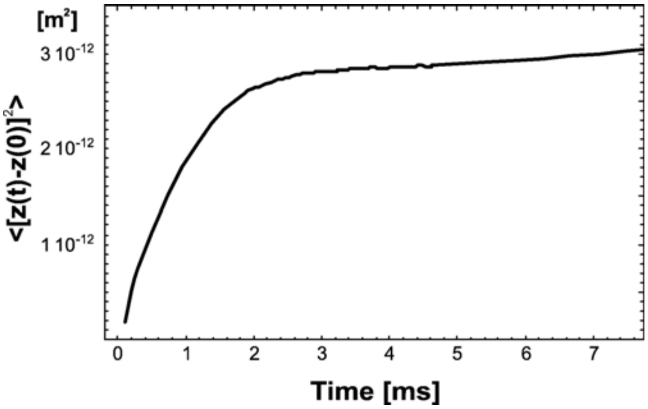

Fig. 5. Time dependence of the mean squared displacement obtained from the Fourier transform of $D(\omega)$ demonstrate the time resolution of the method.

which indicates a very slow interpore 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 intrapore diffusion rate.

The initial slope of $D(\omega)$ vs. $1/\sqrt{\omega}$ is proportional to the surface-to-volume ratio of the porous structure. Rather than a line at low $1/\sqrt{\omega}$ values, Fig. 4 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 of between 0.25×10^6 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. 4. It shows that a precise measurement of the high-frequency part of the spectrum can give good information about the pore size distribution. Fig. 5 depicts the time dependence of the spin mean squared displacement as calculated according to its relation to $D(\omega)$.

The lowest frequency of measurement determines the longest mean squared displacement (MSD) of spins in time of 8 ms, while the highest frequency gives the time resolution of MSD, which was 0.33 ms.

5. Conclusion

The results of this report show the CPMG sequence with the constant magnetic field gradient as an efficient MGSE technique. The ability of this novel technique to modulate spin-phase dephasing in the pace of applied π-RF pulses shifts up the high-frequency limit of method and enables to scan the molecular diffusion spectra in porous media with pores as small as a few tenth of a micrometer as shown with the measurement of the water diffusion in the interspaces between the packed grains of fine-grounded silica powder.

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