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Physica B 307 (2001) 158–168

PHYSICA B

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Diffusion and flow in a porous structure by the gradient spin echo spectral analysis

Janez Stepišnik[a,b,*], Aleš Mohorič[a], Andrej Duh[c]

[a] *Department of Physics, FMF, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia*
[b] *J. Stefan Institute, Ljubljana, Slovenia*
[c] *Faculty of Electrical Engineering and Computer Science, Institute of Mathematics and Physics, University of Maribor, Maribor, Slovenia*

Received 3 April 2001; received in revised form 6 August 2001

Abstract

The frequency analysis of relation between the NMR gradient spin echo method and the correlation of molecular motion throws a new light upon the measurement of molecular transport in porous media by magnetic resonance. The spectral analysis provides, in some other way, a known $\sqrt{Dt}$ early time dependence of attenuation or the pulse gradient spin echo sequence, and at intermediate times, it gives a not-known $D_p t + d(1 - \exp(-t/\tau_r))$. When the displacements are getting larger than the size of compartments, the spin echo is levelling into a time-independent asymptote. In the system of packed poly-dispersed beds, the spin echo measurement of flow dispersion perpendicular to flows confirms the predicted spin echo decay. It demonstrates a clear distinction between different time regimes of signal decay, from which different properties of the porous structure can be revealed. The results gives almost identical long-time dispersion coefficient, $D' = D_p$, for different flows, but the shortening of the dispersion correlation time τ_r with the increase of interstitial velocity. In combination with the modulated gradient sequence, the method extends the measuring range of spin echo over multi-pore length scale, and opens a new way to provide information about important properties of porous media like average pore size, the interconnectivity and the tortuosity.

PACS: 33.15.V; 33.25.+f; 76.60.Lz; 61.43.G

Keywords: Nuclear magnetic resonance; Pulse gradient spin echo attenuation; Molecular velocity correlation; Restricted self-diffusion; Porous media; Flow dispersion; Modulated gradients

1. Introduction

NMR measurement, such as spin echo [1] and magnetic resonance microscopy [2] that enables the study of molecular transport, have important implication on understanding of porous media. With the modulated gradient spin echo methods (MGSE) the velocity correlation function (VCF) spectrum of self-diffusion and flow through a porous structure has been analysed [3,4], demonstrating that the method can be a powerful non-invasive probe to study molecular dynamics and structure in diverse porous media to provide new information relevant to a wide range of scientific, technological and medical inquiries such as oil

*Corresponding author. Department of Physics, FMF, University of Ljubljana, Jadranska 19, Ljubljana, Slovenia. Fax: +386-61-2517-281.

E-mail address: janez.stepisnik@fiz.uni-lj.si (J. Stepišnik).

0921-4526/01/$ - see front matter
PII: S0921-4526(01)01025-0

reservoir appraisal and management, aquifers behaviour, distillation and filtration processes, heterogeneous catalyst bed design and performance, ion channelling through membranes, cell migration in biological processes, etc.

Herein, the frequency-domain analysis is used to consider the spin echo diffusion attenuation caused by most commonly used PGSE sequence that consists of two gradient pulses of width δ and separated by a well-defined time interval Δ. The anomalous dependence of the spin echo attenuation on Δ or δ, which appears at the measurements of restricted diffusion, or at the measurements of molecular migrations in complex fluids, like polymers, liquid crystals, biological macromolecules, etc., is usually considered as the consequence of time dependent self-diffusion or mean square displacement. Here we treat it as the spin echo dependence on the spectrum of molecular motion. Such analysis provides some new relation between the spin echo attenuation and parameters of molecular motion in restricted regions and shows, among others, how the flow and appropriate gradient sequence can extend the range of the structure analysis of porous media by NMR.

2. Molecular migration and spin echo sequences

In order to trace particle migration with NMR, the magnetic field gradient, $\mathbf{G} = \nabla|\mathbf{B}|$, is used to label the position of molecule. The short gradient pulses, $\delta \ll \Delta$, creates a constant spin phase structure (or spin phase grating) in the interval between the pulses, which can be described by the spin dephasing factor, $\mathbf{F}(\tau) = \int_0^\tau \mathbf{G}(t)\,\mathrm{d}t = \gamma\mathbf{G}\delta = \mathbf{q}$. It makes the spin echo attenuation proportional to the mean squared displacement (MSD) of spins along applied gradients. Since the measurement by the PGSE sequence conveys information about the averaged motion in the interval of measurement, we can consider it as a time-domain analysis. However, the such measurement may average out certain details of motion like fast back-and-forth jumping of trapped molecules, whirling of fluid around obstacles, repetation of macromolecules etc., and to lose relevant details of translational dynamics. A thorough description of molecular dynamics is embraced in VCF, which is related to the MSD as

$$R_g^2(\tau) = \langle [r_g(\tau) - r_g(0)]^2 \rangle = \int_0^\tau \int_0^\tau \mathbf{f} \cdot \langle \mathbf{v}(t_1)\mathbf{v}(t_2) \rangle \cdot \mathbf{f}\,\mathrm{d}t_1\,\mathrm{d}t_2, \quad (1)$$

where $\mathbf{f}$ and $r_g(t)$ are the unit vector and the components of particle location along the applied gradients, respectively.

Contrary to the sequence with two short gradient pulses (narrow PGSE), the finite width gradient pulses or long gradient waveform does not create the spin phase structure in a step, but it is built up during the extended interval of gradient action. The formation of spin phase structure competes with the random molecular motion tending to destroy its build up. According to the references [5,6], the effective spatial spin dephasing (or phase grating) can be described as

$$\mathbf{F}_a = \mathbf{f}\sqrt{\frac{\beta(\tau)}{R_g^2(\tau)}}, \quad (2)$$

where $R_g^2(\tau)$ denotes the MSD along the applied gradient field and

$$\beta(\tau) = \int_0^\tau \int_0^{t_1} \mathbf{F}(t_1) \cdot \langle \mathbf{v}(t_1)\mathbf{v}(t_2) \rangle \cdot \mathbf{F}(t_2)\,\mathrm{d}t_1\,\mathrm{d}t_2. \quad (3)$$

The factor $\beta(\tau)$ includes the overlap between the gradient and the motional correlations. With the Fourier transforms of VCF tensor, $\mathscr{D}(\omega)$, and the Fourier transform of spin dephasing, $\mathbf{F}(\omega,\tau) = \int_0^\tau \mathbf{F}(t)\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t$, we can convert Eqs. (3) and (1) in more compact forms [6]

$$\beta(\tau) = \frac{1}{\pi}\int_0^\infty \mathbf{F}(\omega,\tau) \cdot \mathscr{D}(\omega) \cdot \mathbf{F}(\omega,\tau)\,\mathrm{d}\omega \quad (4)$$

and

$$R_g^2(\tau) = \frac{2}{\pi}\int_0^\infty \mathbf{f} \cdot \mathscr{D}(\omega) \cdot \mathbf{f}\; g(\omega,\tau)\,\mathrm{d}\omega, \quad (5)$$

where $g(x,y) = \sin c^2\frac{xy}{2}$.

Although Fick's diffusion equation describe molecular dynamics on a cruder level as needed for molecular motion in small compartments, the spin phase fluctuations due to molecular migration in porous structure are commonly treated by the diffusion propagator [2,7,8]. The method provides

a satisfactory explanation of the spin echo attenuation in porous media particularly when the narrow PGSE sequences are applied.

According to general theorem of probability theory, a stochastic process is fully described either by the probability distribution function, i.e. the propagator, or by the characteristic functional, which is related to the time correlations of stochastic variables [9]. In the parlance of NMR, the mean of randomly fluctuating spin phase can be treated either with the propagator method, when the distribution function is known or with the cumulant expansion method, when the moments of motional correlation (VCF) are accessible. An exact distribution function or all correlations are hardly ever available and the spin phase average can only be handled approximately. The cumulant expansion method in the Gaussian approximation, which is relevant in almost all practical application of diffusion measurement by the gradient spin method [6], neglects all cumulants higher than the second moment relating the spin echo attenuation to VCF, $\langle \mathbf{v}(t_1)\mathbf{v}(t_2)\rangle$.

As shown in the following, the VCF spectrum of the restricted diffusion exhibits the characteristic lowering in the same range of frequencies as the peak of PGSE dephasing spectrum. Thus, Torrey's formula of spin echo attenuation, which assumes a flat motional spectrum in the range of low frequencies, needs to be replaced with a more general expression of spin echo attenuation that accounts for the overlap of both spectra [10]. But in addition to it, we have to pay regards to the spatial restrictions for spin variables in the porous structure. Before averaging with the cumulant expansion method, the spatial dependence of spin phase structure created by applied gradients (phase grating) has to be expressed by the Fourier components $S_{\mathbf{k}}(\mathbf{F}_a)$, where the set of wave vectors $\mathbf{k}$ embraces spatial restriction. The final result of this approach is the gradient spin echo of restricted diffusion in the general form as mentioned in Ref. [5]

$$E(\tau) = \sum_{j,\mathbf{k}} E_{0j} S_{\mathbf{k}}(\mathbf{F}_{aj}) \mathrm{e}^{\mathrm{i}(\mathbf{F}_{aj}-\mathbf{k})\mathbf{r}_j} \mathrm{e}^{-\frac{1}{2}\mathbf{k}^2\mathbf{R}^2_{gj}(\tau)}. \tag{6}$$

Here E_{0j} is the signal of the spin sub-ensembles at the location $\mathbf{r}_j$ for which the effect of applied fields may be different. In the case of narrow PGSE sequence with $\mathbf{F}_a = \gamma \mathbf{G}\delta$, Eq. (6) acquires an identical form as that obtained by the propagator technique if assuming a flat VCF spectrum, $D(\omega) = D$. However, from the point of spectral analysis the disregard of the VCF variance is allowed only in the special cases.

In the short time limit, Eq. (6) reduces to that for the unbounded diffusion

$$E(\tau) \approx E_0 \mathrm{e}^{-\frac{1}{2}\mathbf{F}^2_a(\tau)R^2_g(\tau)} = E_0 \mathrm{e}^{-\beta(\tau)} \tag{7}$$

but with distinction that all information about the motion is hidden in the correlation function $\mathscr{D}(\omega)$ of $\beta(\tau)$. Since $\beta(\tau)$ integrates the overlap of $\mathscr{D}(\omega)$ and $\mathbf{F}^2(\omega,\tau)$, one can inspect the characteristics of restricted motion by shaping the dephasing spectrum as shown in the Refs. [3,5].

However, in the long time approximation, when the MSD is much exceeding the pore size, the spin echo develops into time-independent form depending only on the 0th Fourier component of the spin phase structure in Eq. (6) [2] giving

$$E(\tau) \approx |S_0(\mathbf{F}_a)|^2, \tag{8}$$

which is for a weak gradient, $F_a d \ll 2\pi$,

$$E(\tau) \approx \mathrm{e}^{-\mathbf{F}^2_a(\tau)M_2} = \mathrm{e}^{-(\beta(\tau)/R^2_g(\tau))M_2}. \tag{9}$$

Here $M_2 = (1/V_\mathrm{p}) \int_{V_\mathrm{p}} \mathbf{r}_g^2 \, \mathrm{d}\mathbf{r}_g$ is the second moment integrated over the volume of pore and its interconnections along the direction of applied gradient.

2.1. Spectral analysis of spin echo

The power of dephasing spectrum (DS) created by the PGSE sequence

$$|\mathbf{F}(\omega, 2\Delta)|^2 = \gamma^2 G^2 g(\omega,\delta) g(\omega,\Delta) \tag{10}$$

has a peak at the zero-frequency with width $\partial\omega = 2\pi/\Delta$ as shown in the Refs. [2,10]. Therefore, we can consider this sequence as a sampler of VCF spectrum around $\omega = 0$. In simple fluids without restriction to motion, the velocity correlation function decays exponentially to zero over the correlation time $\tau_\mathrm{c} \approx 10^{-12} - 10^{-10}$ s which corresponds to the average collision time of molecules. The resulting diffusion spectrum is relatively constant for low frequencies and is decreasing

for frequencies above $\omega \approx \tau_c^{-1}$. Since τ_c^{-1} is much greater then the highest frequency component of the DS, $\tau_c \ll \Delta$, one can write the spin echo attenuation of the isotropic diffusion as

$$\beta(\tau) = \frac{1}{\pi} D(0) \int_0^\infty |\mathbf{F}(\omega, \tau)|^2 \, \mathrm{d}\omega = D(0) \int_0^\tau |\mathbf{F}(t)|^2 \, \mathrm{d}t. \tag{11}$$

It is Torrey's formula [11], because the level of the low frequency plateau $D(0)$ is equal to the local self-diffusion coefficient D. In the case of an anisotropic diffusion, this approximation provides the Stejskal–Tanner attenuation [12], with $\mathscr{D}(0)$ being a diffusion tensor.

Theory and computer simulations of fluid hydro-dynamics reveal the existence of slow molecular motion that appears as a long time tail of the velocity correlation function superposed on the fast exponential decay. This appears with the diffusion in complex fluid systems with number of characteristic time-scales such as a characteristic negative decay in confined fluid, the tube disengagement times in entangled polymers, the complex dynamics of biological macromolecules, etc. These times are more closely related to the structure than to local motion of molecule. They usually correspond to the regime of low frequencies that can be accessed to NMR. It means that in the case of variable VCF spectrum in the range of DS, Torrey's formula needs to be replaced by more generalized form of Eq. (4). For the PGSE sequence with very narrow gradient pulses, $\delta \ll \Delta$, it gives the spin echo attenuation as

$$\beta(\tau) = \frac{(\gamma G \delta)^2}{\pi} \int_0^\infty D_{gg}(\omega) g(\omega, \Delta) \, \mathrm{d}\omega = \frac{(\gamma G \delta)^2}{2} R_g^2(\Delta). \tag{12}$$

Thus, the PGSE sequence provides information about averaged motion, i.e. the molecular displacement in the interval between gradient pulses Δ as follows from Eq. (7). However, we need to be aware that $\delta \ll \Delta$ is not the sufficient condition for the validity of Eq. (12), and an additional restriction has to be imposed in the case of restricted motion as shown in the following.

Two-pulse gradient modulation is not unique and other pulse or time-modulation sequences of magnetic field gradient are possible, in which the molecular motion can be detected in a different manner. When sufficiently fast and properly shaped sequence is applied, the gradient spin echo conveys information, not only about an average displacement, but it can reveal details of motion on a molecular level as well. It refers to a type of the spin echo experiment that probes the molecular VCF with the cyclic modulation of spin phase [3,13]. An example is a variant of the pulsed gradient multiple spin echo (PGMSE), where the combination of two PGSE is repeatedly applied $2N$ times to provide a frequency selectiveness for the motional spectrum. Generally, we consider any combination of gradient-RF pulses or gradient waveform that brings about a cyclic modulation of the spin phase as a modulated (or oscillating) gradient spin echo (MGSE). Such sequences narrows the peaks of DS with increasing number of cycles as $\partial\omega \approx 1/NT$, where T denotes the period of modulation. For $N \gg 1$, the DS can be approximated as

$$|\mathbf{F}(\omega, NT)|^2 \approx \sum_n g(\omega - n\omega_m, NT) f_n^2, \tag{13}$$

where f_n^2 are factors that includes the parameters of the gradient pulses as shown in the Ref. [4].

Some attempts have been made [14] to apply the gradient sine-wave modulation in combination with the π-RF pulses, a kind of MGSE sequence, in order to obtain an information about the restricted diffusion different from those obtained by the PGSE sequence. Unfortunately, the authors have neglected the importance of the spectral relation between the spin dephasing and the molecular motion.

A properly designed MGSE sequence that brings about the oscillation of spin phase around zero base line, has no zero-frequency peak in the SD spectrum, but the peaks at $\omega = \pm\omega_m$. The peak, which can be adjusted in position by changing the period of modulation, is a nearly ideal sampling function of VCF [3] as shown Fig. 1. By neglecting variations of $D(\omega)$ in the range of the peak width, the spin echo attenuation with this MGSE single side peak spectrum of

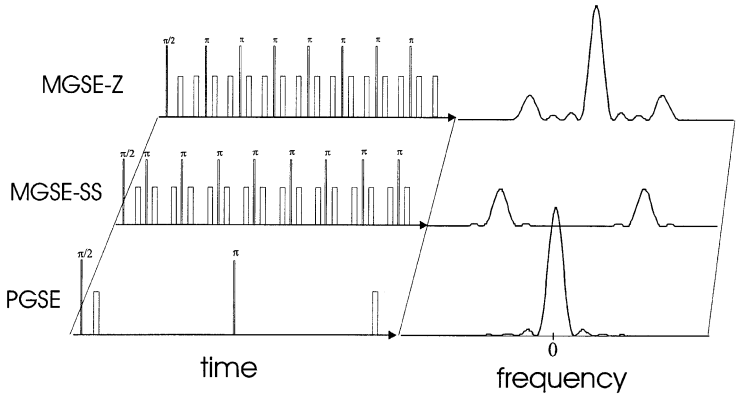

Fig. 1. MGSE-SS, PGSE and MGSE-Z sequences and their dephasing spectra.

dephasing (MGSE-SS) can be written as

$$\beta = D(\omega_m)NTf_1^2. \tag{14}$$

This sequence has been used for the spectral analysis of flow dispersion through the system of close-packed beads of 15 μm diameter [4]. It was the first experimental confirmation of Eq. (4). Another example of the MGSE-SS application was the measurement of the velocity correlation spectrum of diffusion and flow of water through the system of close-packed stack of beads with the diameters of 0.1–0.05 mm [3]. This was the first experimental verification of velocity correlation spectrum of confined molecules as obtained only by theory. The measurement also verified the approach that leads to Eq. (6) and confirms that the validity range of Eq. (7) is limited to times $\tau < M_2/D_p$, were D_p is the long range diffusivity in the porous structure.

These applications demonstrate great utility of the modulated gradient NMR technique, when the time-integral of the effective gradient waveform has the optimised spectrum, but here we are focusing to the gradient spin echo sequences like PGSE, where the overlap of the zero-frequency DS peak and the low frequency spectrum of VCF have the dominating role to the spin echo attenuation.

When the ordinary PGSE sequence is used to measure the diffusion through a porous structure by high magnetic field NMR, the susceptibility field might strongly effect the spin echo attenuation. There are different ways to avoid it. Here, we are using the method of fast spin phase cycling, which is particularly effective in the combination with the MGSE sequence as shown in the Ref. [15]. Namely, due to the difference of dephasing accumulation for the static and rapidly modulated magnetic field gradients, the fast cycling MGSE sequence removes the effect of local susceptibility gradients of heterogeneous structure from the spin echo attenuation. The combination of two gradient pulses and π-RF pulse, which is repeated $2N$-times, brings about DS spectrum as

$$|\mathbf{F}(\omega, NT)|^2 = g(\omega, NT)f_0^2 + g(\omega \pm \omega_m, NT)f_1^2, \tag{15}$$

as shown in Fig. 1. This MGSE-Z sequence brings about the lobe of DS at $\omega = 0$ and peaks at the modulation frequency $\omega = \pm\omega_m = \pm 2\pi/T$. The shape of zero-frequency peak is identical to that of the PGSE sequences, Eq. (12), considering the length of the MGSE sequence NT as the interval between two pulses, Δ. Therefore, the spin echo attenuation of the MGSE-Z sequence conveys combined information: about the MSD, as provided with the PGSE measurement, as well as about the value of VCF at modulation frequency, as obtained with the MGSE-SS sequence. With right pulse timing, the side peaks of MGSE-Z DS can be adjusted in the range with almost constant VCF spectrum, so that the MGSE-Z sequence can be a proper substitute for the PGSE sequence.

2.2. Velocity correlation function of restricted motion and spin echo

In the case of restricted diffusion, the delta function, i.e. Fick's diffusion, is a reasonable approximation for the VCF, only when the rate of intermolecular collisions is much higher than the rate of molecular impacts with walls, $\tau_c \ll t \ll \tau_w$. For longer times, the probability distribution function from Fick's diffusion equation provides a better approximation of the VCF as shown in Ref. [16]. In the case of structure of isolated pore, the average of the VCF over the pore volume can be written as

$$\overline{\langle v_g(t)v_g(0)\rangle} = 2D\left(\delta(t) - \frac{1}{2}\sum_{\mathbf{k}} B_{\mathbf{k}}\mathbf{k}^4 D\mathrm{e}^{-\mathbf{k}^2 Dt}\right). \tag{16}$$

Here D is the constant of unbounded diffusion, $B_{\mathbf{k}}$ denotes parameters of the porous structure as shown in Ref. [17], while the wave vectors $\mathbf{k}$ defines the permitted momentum states of confined particle. The identical result was obtained in Ref. [18] by solving the Langevin equation for particles enclosed between parallel planes. Its Fourier transform is the VCF spectrum as

$$D_{\mathrm{rest}}(\omega) = D\left(1 - \sum_{\mathbf{k}} B_{\mathbf{k}}\frac{\mathbf{k}^6 D^2}{\mathbf{k}^4 D^2 + \omega^2}\right) = \sum_{\mathbf{k}} B_{\mathbf{k}}\frac{\tau_{r,\mathbf{k}}\omega^2}{1+\tau_{r,\mathbf{k}}^2\omega^2}, \tag{17}$$

where $\tau_{r,\mathbf{k}} = 1/\mathbf{k}^2 D$ are the characteristic correlation times of motion between boundaries.

The negative terms of Eqs. (16) and (17), which corresponds to scattering at boundaries, can be neglected, when the diffusion displacement is much shorter then the pore size, $\sqrt{D\tau} \ll d$ or $\tau \ll \tau_{r,0}$. In the long time limit when $\tau \gg \tau_{r,k}$, the time integral of negative term cancels the positive, providing the diffusion constant $D_\infty = 0$. From the frequency point of view, the low frequency limit of the diffusion spectrum in Eq. (17) tends to zero in the case of isolated pores, $D_\infty = \lim_{\omega\to 0} D(\omega) \Rightarrow 0$. It requires that $\sum_{\mathbf{k}} B_{\mathbf{k}}\mathbf{k}^2 = 1$. In the structure of confining pores, where the interconnecting channels permit migration from pore to pore, the effective diffusion constant does not tend to zero, but to a limiting value D_p, when the interval of measurement is shorter that the longest correlation time $\tau_{r,0}$ that is about the time of diffusion across the whole sample. The tortuosity constant α is defined as the ratio between the long-range fluid diffusivity D_p and the local molecular self-diffusion coefficient D. We can use it to write $D_p/D = \alpha = B_0/\tau_{r,0}$ and the VCF spectrum of molecules in the structure of connected pores becomes

$$D_{\mathrm{rest}}(\omega) = D\alpha + \sum_{\mathbf{k}=1}^{\infty} B_{\mathbf{k}}\frac{\tau_{r,\mathbf{k}}\omega^2}{1+\tau_{r\mathbf{k}}^2\omega^2}. \tag{18}$$

Fig. 2 shows the spectrum of restricted diffusion with the characteristic lowering in the proximity of zero frequency. In the proximity $\omega = 0$, it overlaps with the lobe of the PGSE DS, which is changing, when Δ is modified. In order to get the spin echo attenuation we have to use Eq. (4) with the spectrum of motion in Eq. (18) and DS spectrum in Eq. (10) that gives

$$\beta(\Delta) = \gamma^2 G^2\left[D\alpha\delta^2\left(\Delta - \frac{\delta}{3}\right) + 2\sum_{\mathbf{k}} B_{\mathbf{k}}\tau_{r\mathbf{k}}^2 \times \left[\left(1 - \cosh\left(\frac{\delta}{\tau_{r\mathbf{k}}}\right)\right)\mathrm{e}^{-\frac{\Delta}{\tau_{r\mathbf{k}}}} + \mathrm{e}^{-\frac{\delta}{\tau_{r\mathbf{k}}}} + \frac{\delta}{\tau_{r\mathbf{k}}} - 1\right]\right]. \tag{19}$$

In the limit of narrow gradient pulses $\delta \ll \Delta$, this equation simplifies into

$$\beta(\Delta) = \gamma^2 G^2\delta^2\left[D\alpha\Delta - \frac{D\delta}{3} + \sum_{\mathbf{k}} B_{\mathbf{k}} \times \left[(1-\exp(-\Delta/\tau_{r\mathbf{k}}))\left(1+\frac{\delta^2}{12\tau_{r\mathbf{k}}^2}\right) - \frac{\delta^3}{60\tau_{r\mathbf{k}}^3}\right] + \cdots\right]. \tag{20}$$

Here, the attenuation is proportional to MSD, as assumed in Eq. (12), only for δ that is short compare to correlation times. It means that the *narrow pulse approximation* breaks down [19] for $\delta \approx \tau_{r,\mathbf{k}1} = \tau_r$.

Interestingly, this approach provides known square root dependence on the early time of PGSE attenuation restricted diffusion as has been already treated with more sophisticated theories such as the "hearing the shape of drums" [20] or the

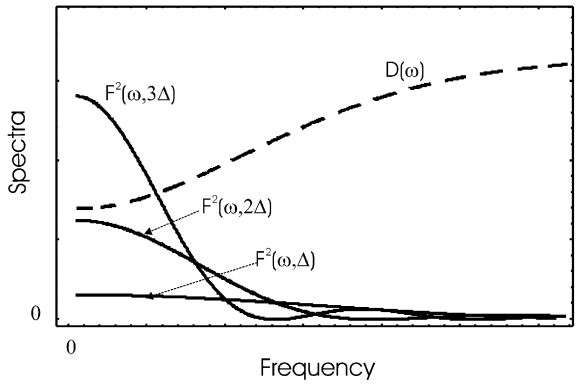

Fig. 2. The overlapping between the spectrum of restricted self-diffusion and the PGSE dephasing spectra for different Δ.

probability "returns to the origin" [21]. The spectral analysis of PGSE provides it, when the structure factor in Eq. (17) is rewritten as $C_k = B_k\mathbf{k}^4$. At least for simple geometries (planar, cylindrical and spherical) Ck exhibits a weak dependence on k so that $C_k \approx C_1$, as shown in Ref. [17]. Since the terms of a sum in Eq. (20) are monotonically decreasing function of k, the Cauchy formula can be used to substitute the summation with the integration and to write

$$\sum_{\mathbf{k}} \frac{C_1}{\mathbf{k}^4}(1-\mathrm{e}^{-\mathbf{k}^2Dt}) = \frac{b}{k_1^4}(1-\mathrm{e}^{-\mathbf{k}_1^2Dt}) + \int_{k_1}^{\infty} \frac{C}{k^4}(1-\mathrm{e}^{-\mathbf{k}^2Dt})\,\mathrm{d}k. \tag{21}$$

Here k_1 is the shortest wave vector (the longest wavelength), taken as a low limit of integration. In the short time approximation ($\Delta < \tau_{r,k}$) it gives the spin echo attenuation as

$$\beta(\Delta) = \gamma^2G^2\delta^2D\Delta\left[1-\frac{2C}{3}\sqrt{\pi D\Delta}+\cdots\right). \tag{22}$$

The result is identical to that in the Ref. [20], assuming that $C = 2S/3\pi V$, with S/V being the surface-to-volume ratio. The squared root early time dependence has been verified experimentally in liquids and gases imbibed in a variety of porous media as shown and quoted in the Ref. [22]. However, the detail of above derivation is presenting elsewhere.

For longer times, when the frequency of collision with walls increases, the attenuation is governed only by the exponential term with the longest correlation time, $\tau_r = 1/k_1^2D$. In this intermediate regime $\Delta \leqslant \tau_r$, the spin echo attenuation is approaching the linear time dependence, which has the slope proportional to inter-porous diffusion rate $D_\mathrm{p} = D\alpha$ as

$$\beta(\Delta) = \gamma^2G^2\delta^2\left[D\alpha\delta^2\left(\Delta-\frac{\delta}{3}\right) + B_{k_1}(1-\mathrm{e}^{-\Delta/\tau_r}) + \sum_{k\neq 1} B_k\right]. \tag{23}$$

At much longer times, when the number of molecules colliding with the boundaries prevails over those experiencing free diffusion, the MSD gets larger than the pore size, $R_g^2 > d^2$. In this regime, the discord of the spin phase structure takes place, developing the spin echo attenuation into the time-independent form according to Eq. (9). For the PGSE sequence with weak gradients ($\gamma G\delta d \ll 1$)

$$E(\Delta) \approx \mathrm{e}^{-\gamma^2G^2\delta^2M_2}. \tag{24}$$

3. Flow dispersion in porous media

The velocity field of a fluid flowing through a porous solid can be regarded as an array of streamlines between which the molecule moves because of the Brownian motion. Averaging over all molecules confined in the matrix leads to a statistical description of the flow pattern and to the dispersion of displacement. The dispersion of an incompressible fluid within a porous structure in the presence of flow and self-diffusion can be described by the convection–diffusion (or Focker–Planck) equation [23] by assuming that the probability profile of tracers becomes smoother in the long time limit. Depending on the magnitude of mean flow velocity $\bar{\mathbf{v}}$, it describes the dispersion of immersed particle with the coefficient D' that can be very much greater than D_0 of molecular diffusion. This Taylor hypothesis [23] is based on phenomenological argument that for high Pecklet numbers $Pe = \bar{v}d/D_0$ (d denotes the

characteristic length of porous structure), the molecular diffusion in porous media ceases to play the role and the dispersion is determined solely by spatial variation in the fluid velocity. In isotropic porous medium with the flow parallel to z-axis, the dispersion tensor can be decomposed into parallel and transverse components

$$\mathscr{D}' = \begin{bmatrix} D'_\perp & 0 & 0 \\ 0 & D'_\perp & 0 \\ 0 & 0 & D'_\parallel \end{bmatrix}, \tag{25}$$

which is related to the VCF

$$\mathscr{D}' = \int_0^\infty \langle [\bar{\mathbf{v}} - \mathbf{v}(t)][\bar{\mathbf{v}} - \mathbf{v}(0)] \rangle \, \mathrm{d}t = \mathscr{D}(0), \tag{26}$$

where $\mathscr{D}(0)$ is considered as the zero frequency tensor of VCF spectrum. The $\mathscr{D}'$ should reach constant value in the time that the particle needs to transfer over the correlation length of the porous medium. However, experimentally it was found that $\mathscr{D}'$ is changing on a much longer time scale and that the molecular diffusion actually determines the time scale on which dispersion coefficient exhibits an anomalous time dependence. Understanding these phenomena of hydrodynamic dispersion is important for modelling pollutant transport in ground water and elsewhere.

The probability density of flow dispersion particles in the porous structure obeys the convection–diffusion equation, which permits to apply the approach used for the restricted self-diffusion in previous chapter also for the analysis of flow dispersion by the gradient spin echo. Namely, the dispersion–diffusion equation provides the transverse components of the low frequency spectrum of flow VCF through porous structure in a similarly manner as that for the molecular diffusion

$$D'_\perp(\omega) = D'_\perp + \sum_{\mathbf{k}} B_{\mathbf{k}} \mathbf{k}^2 \frac{\tau_{r\mathbf{k}}^2 \omega^2}{1 + \tau_{r\mathbf{k}}^2 \omega^2}, \tag{27}$$

but with the distinction that $\tau_{r,\mathbf{k}}$ are the characteristic correlation times of flow dispersion, while $D'_\perp$ denotes the asymptotic transverse dispersion coefficient. By comparing the result of measurement, we could test the above assumptions and verify the application of spectral analysis approach to the spin echo attenuation of restricted motion, in general.

4. Measurements and discussion

The 300 MHz Bruker spectrometer and microimager was used to measure the motion of fluid through the structure of porous media by the spin echo method. The specially constructed quadrupole gradient coils were used to apply the magnetic field gradient of 4.5 T/m perpendicular to the capillary axis. With the gradient spin echo we measured the diffusion and the flow dispersion transverse to the main direction of flow velocity in the ion-exchange resin with poly-dispersed beads (100–30 μ) packed in a capillary of 2.0 mm inner diameter. A reciprocating piston pump controlled the average flow velocities. Instead of ordinary PGSE, we employed the MGSE-Z sequence that provides an identical lobe of dephasing spectrum in the proximity of zero-frequency, as that of the PGSE sequence as shown in Fig. 1, but due to fast spin phase cycling, it removes the effect of the susceptibility difference of the porous structure that appears in the high magnetic field. As shown in Ref. [15] the MGSE-Z sequence accomplishes it more effectively than just ordinary application of a Carr–Purcell train of π pulses between the first and second gradient pulse of two pulse gradient experiment. However, the modulation frequency has to be high enough to shift side peaks of MGSE-Z spectrum outside the characteristic spectrum of the flow motion. According to previous measurement on the same porous media [3], the modulation frequencies above 600 Hz is high enough to put side bands into the frequency range with the plateau that is equal to the local diffusion constant D. The experiment confirms that the side peaks are not affected by flow motion at these frequencies as long as the velocity is below 3 mm/s. In the intermediate regime with the validity of Eq. (4), MGSE-Z brings about the spin echo attenuation identical to that of PGSE sequence, but with the addition of constant $\frac{1}{2}\gamma^2 G^2 \delta^2 D \Delta$, where the length of the MGSE-Z sequence NT is considered as the interval between two pulses Δ. It adds one half to the tutousity

factor as

$$D_{\mathrm{eff}} = D\left(\alpha + \frac{1}{2}\right) + \frac{B_{k_1}}{\tau_r} e^{-\Delta/\tau_r}. \quad (28)$$

The MGSE-Z sequence with the gradient pulses of width $\delta = 70$ μs was used to measure the spin echo decay as a function of the modulation frequency and the sequence duration Δ for the stationary water and water trickling through porous structure with the average velocities 1.1 and 2.2 mm/s. The time dependence of spin echo attenuation for the flow rate of 1.1 mm/s and the modulation frequency 833 Hz displays a clear transition from the non-linear increase with the decreasing slope into the linear time dependence, as shown in the Fig. 3. At still longer times, the attenuation exhibits a tendency to level into the time-independent asymptote, which agrees with Eq. (8), but the signal in this range was just above the detection limit of spectrometer. Therefore, this part of decay is not taken into consideration.

Detailed consideration confirms that the course of the measured spin echo decay is according to Eq. (23), where the attenuation is exponentially approaching toward the linear dependence with the correlation time τ_r, and where the slope of linear part is in the proportion to the long time dispersion coefficient $D'_\perp$. The slope of linear part intersects the coordinate abscise at the point determined by structure coefficient B_1 i.e. the size

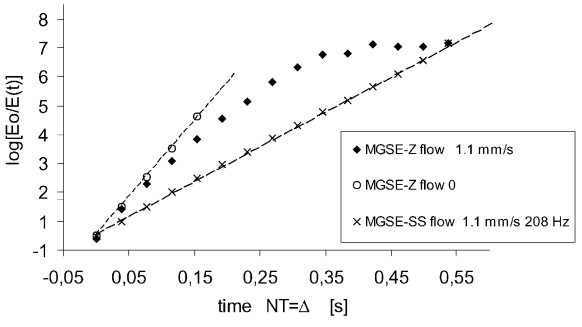

Fig. 3. The MGSE-Z attenuation with $\delta = 70$ μs, $G = 4.52$ T/m and the modulation frequency above 600 Hz of stationary water and water trickling through porous structure with the average velocity 1.1 mm/s. MGSE-SS attenuation is given for comparison to demonstrate a clear linear rise of attenuation.

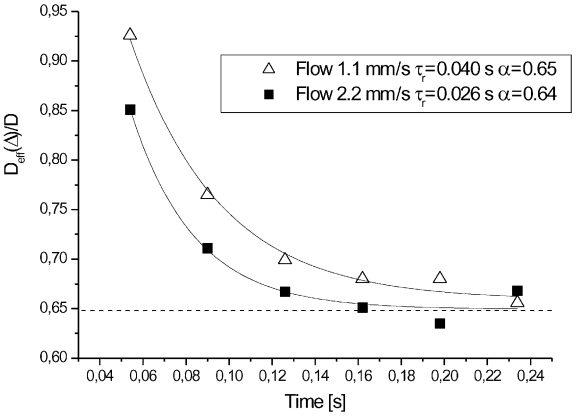

Fig. 4. Time-dependent self-diffusion as derived from the attenuation of MGSE-Z sequence applied perpendicular to the flow of water through porous structure with velocities 1.1 and 2.2 mm/s.

of structure that restricts motion. As shown in Fig. 4, the effective dispersion really decays exponentially for both flows, but with the shorter τ_r for faster flow. It also levels into a time-independent long-time asymptote but with almost identical values for both flows. This levelling provides, in case of diffusion according to Eq. (4), long-time diffusivity that is related to tortuosity of the porous structure. These experiments shows that the long-time dispersion measured perpendicular to flow seems to be unaffected by the flow rate at least for weak flows. Still more unexpected is the fact that the obtained ratio between the long-time dispersion coefficient and the molecular diffusion $D'_\perp/D$ is the same as the ratio of long- and short-time diffusion, D_{p}/D for the diffusion in gases as obtained in Ref. [24]. It could be explained with a kind of vortex motion of fluid in the pore that increases the frequency of particle coalitions at walls, but leaves the inter-pore motion perpendicular to the flow almost unaffected, at least at weak flows. Thus the flow shorten τ_r and speeds up the transition into the hydrodynamic regime determined by the inter-pore motion. From the frequency point of view, the shortening of τ_r means a broader dip of motional spectrum that decreases the spin echo attenuation as shown in Fig. 2.

As the PGSE measurement of fluid in the porous structure is poor at determining microstructural details over multi-pore length due to slow diffusion rate, Mair and co-workers used the noble gas [24], with the diffusion rate thousand times faster than that of ordinary liquid. In this way, they obtained the tortuosity of the structure of packed beads. However, the results of our experiment show that the flow through porous media amplifies the motion through porous structure with a similar effect to the spin echo attenuation as the increase of diffusion rate. However, manipulation of flow velocities allows adjusting the rate of motion properly to the dimensions of porous structure instead of looking for the fluid with the proper diffusion rate. It makes the gradient spin echo measurement perpendicular to the flow a useful tool to analyse the porous structure.

The dispersion of tracer in porous structure concerns the time, which the dispersion coefficient needs to reach an effectively constant value $D'_{\perp}$. Seymour and Callaghan have shown [25] on the system of packed spheres of about 30 μm that the dispersion coefficient reaches the asymptotic regime for times greater than 10 ms. From Taylor's view the tracer needs to convect at least over a correlation length of porous medium to be permitted the application of the dispersion–diffusion equation. Since the flow increases the convection displacement of particle, the rate of decay toward stationary D' is in proportion to the interstitial velocity. This is according to our experimental result, where the flow velocity shorten the correlation time as shown in Fig. 4 and speed up transition into stationary regime.

In our derivation, we use the convection–diffusion (or Focker–Planck) equation to calculate VCF in intervals shorter than it is permitted according to theory. Agreement between so predicted and the experimentally observed decay of the effective dispersion seems to show than Taylor's theory is valid even for shorter time intervals than the time that the particle needs to transfer over the correlation length of porous structure.

In Fig. 3 the measured spin echo decay indicates the levelling into time-independent regime at long times according to Eq. (24), but its consideration is not the subject of this paper.

5. Conclusion

The spectral analysis of the gradient spin echo measurement is a new way to understand the anomalous dependence of spin echo on the molecular self-diffusion and flow dispersion in porous media. It provides a known square root early time dependence of spin echo attenuation as well as unfamiliar time dependence at intermediate time when the coefficient of self-diffusion or flow dispersion is developing toward an effectively constant value. The measurement on the system of trickling water through a porous structure demonstrates agreement with this theory and confirms shortening of the dispersion correlation times with increased interstitial velocity, which speed up the transition into regime described by the convection–diffusion equation.

The spin echo decay displays three well-resolved time regimes from which different properties of the porous structure can be revealed. In this way, the flow assisted pulsed gradient spin echo, extends the range of NMR measurements into multi-pore length scale and makes possible to disclose the parameters of the molecular dynamics as well as of the porous structure at once. In combination with the modulated gradient sequence, it can be a powerful non-invasive probe for studying diverse porous structures, which appear in nature. The new method may be useful to a wide range of scientific, technological and medical inquiries such as oil reservoir appraisal and management, aquifers behaviour, distillation and filtration processes, heterogeneous catalyst bed design and performance, ion channelling through membranes, cell migration in biological processes, etc.

Acknowledgements

For the financial support, we are grateful to the Slovenian Ministry of Science. One of the authors has to acknowledge that the measurement with the modulated gradient spin echo method together

with first notion about the presented interpretation of restricted diffusion have started during his sabbatical year with P.T. Callaghan at the Massey University, New Zealand.

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