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PULSE GRADIENT SPIN ECHO MEASUREMENT OF FLOW DYNAMICS IN A POROUS STRUCTURE: NMR SPECTRAL ANALYSIS OF MOTIONAL CORRELATIONS

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1. Introduction

NMR measurement of spin migrations by the spin-echo [1] and magnetic resonance microscopy [2] have important implication on understanding of the molecular transport in porous media. Among various approaches, the analysis of self-diffusion and flow through a porous structure by Modulated Gradient Spin Echo method (MGSE) demonstrated that a properly shaped gradient sequence can be is a powerful non-invasive probe for study of molecular dynamics by measuring the low frequency features of the velocity self-correlation function (VCF) [3, 4]. The method provides new information that might be relevant 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.

Although the experiments have confirmed a great potential of spectral analysis in revealing details of translation motion through a porous structure, it also opened a puzzling problem, when treating results of flow measurement through the porous structure by the two Pulse Gradient Spin Echo (PGSE) sequence in a traditional way. Namely, in contrast to the MGSE measurement, which shows an increase of the effective diffusion constant with the flow, it decreases when measure by the PGSE sequence as shown in the figure 1. This phenomena can be explained by the analysis of the spectral relation between the gradient spin echo NMR and the molecular motion in porous media as follows.

2. Spin echo and restricted self-diffusion

Whenever in NMR a non-uniform magnetic field is used to encode the spin magnetization for motion rather than position, it is appropriate to refocus any spin phase shift due to absolute spin position by means of a spin echo, so that the time integral of the effective gradient $G(t)$ is zero. Therefore we can write small perturbations of spin-echo phase, due to molecular displacements in the non-uniform magnetic field, as $\theta(\tau) = \int_0^\tau \mathbf{F}(t)\, v(t)\, dt$, where $F(\tau) = \gamma \int_0^\tau \mathbf{G}(t) dt$ and τ is the time of phase refocusing. The propagators of Fick's diffusion equation are commonly used to average the $\theta(\tau)$ fluctuation [5, 6, 2]. Although the Fick's diffusion equation may describe a process on a cruder level as needed for molecular motion in small compartments, this method provides quite satisfactory explanation of the spin echo attenuation in porous media when PGSE sequence with a sharp gradient pulses is applied, $\delta \ll \Delta$. However, the spin phase average with diffusion propagator is not unique and other ways are possible, in which the molecular motion can be described in a different manner. Namely, according to theorems of probability theory, a stochastic process is fully described either by the probability distribution function, i.e. the propagator, or by the correlation functions [7]. An exact distribution function or all correlations of spin phase fluctuation are hardly ever available and one has to use approximations. Since NMR does not detect the individual spin, but rather a coherent superposition of small signals that arise from the induction of immense number of spins ($\gg 10^6$), the spin phase fluctuations can be considered as a Gaussian process [7], if certain conditions are fulfilled. In the case of the gradient spin echo, the molecular mean free path l must be short compare to the length of gradient spin phase-grating, $F.l \ll 1$ [8]. This condition is met at the most practical applications of the gradient spin echo for the diffusion measurement. The average of spin phase fluctuations by the cumulant expansion method in the Gaussian approximation, permits to neglect all cumulants higher than the second moment. Thus, the spin echo attenuation is related to the VCF $\langle \mathbf{v}(t_1)\mathbf{v}(t_2)\rangle$ [9, 10]. With the Fourier transforms of the VCF tensor $\mathcal{D}(\omega)$, and the Fourier transform of spin dephasing $\mathbf{F}(\omega,\tau) = \int_0^\tau \mathbf{F}(t) e^{i\omega t}\, dt$ the spin attenuation is written as

$$\beta_j(\tau) \;=\; \frac{1}{\pi} \int_0^\infty \mathbf{F}(\omega,\tau) \cdot \mathcal{D}(\omega) \cdot \mathbf{F}(\omega,\tau)\, d\omega \qquad (1)$$

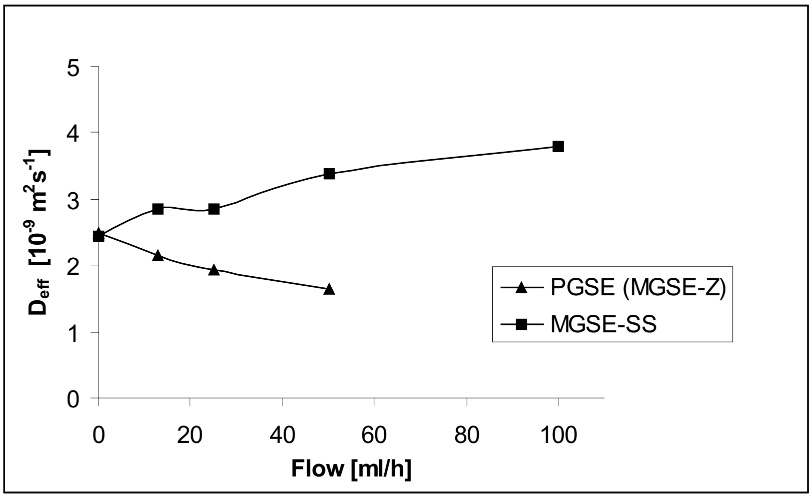

Figure 1. The effective self-diffusion coefficient of flow through porous media as measured by MGSE sequence at the frequency 400 Hz and PGSE (MGSE-Z) sequences with the gradient perpendicular to the flow.

Here the overlap of the gradient spectrum $\mathbf{F}(\omega, \tau)$ and the motional spectrum $\mathcal{D}(\omega)$ can be used to probe the molecular dynamics as shown in the references [3, 4].

2.1. VELOCITY CORRELATION FUNCTION

In simple fluids without restriction to motion, the velocity correlation function decays exponentially to zero over the correlation time $\tau_c \approx 10^{-12} - 10^{-10}s$, 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 gradient modulation, $\tau_c \ll \Delta$, the Torrey's formula [11] can be used to describes the spin echo attenuation. However, the theory and the 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 occurs with the molecular motion in the complex fluids, in confined fluids as the characteristic negative decay, in entangled polymers as the tube disengagement times etc. These times are more closely related to the structure than to local motion of molecule, and may correspond to the low frequencies regime accessible by NMR.

The delta function is a reasonable approximation for the VCF of restricted diffusion 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 calculation of VCF with the probability distribution function from Fick's diffusion equation provides a better approximation [12]. With a full set of characteristic eigen functions $\psi_k(\mathbf{r})$, which characterizes the motional restriction, the generalized form of probability distribution function can be written as $P(\mathbf{r}, t|\mathbf{r_o}, t_o) = \sum_k \psi_k(\mathbf{r})\psi_k(\mathbf{r}_o)e^{-k^2 D|t-t_o|}$. In the case of isolated pore, it provides the average of VCF spectrum over the pore volume as

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

Here D is the constant of unbounded diffusion, $\tau_{r,\mathbf{k}} = \frac{1}{\mathbf{k}^2 D}$ are the characteristic correlation times for the restricted motion and B_k are the parameters of porous structure

$$B_k \;=\; \frac{1}{2}\int_V \int_{V_o} [\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_o)]^2 \psi_k(\mathbf{r})\psi_k(\mathbf{r}_o))\; d^3\mathbf{r}\; d^3\mathbf{r}_o, \tag{3}$$

where $\mathbf{f}$ is the unit vector along the applid gradient. An identical result is obtained by solving the Langevin equation for diffusion between parallel planes [13]. The low frequency limit of VCF is the long time diffusion constant, D_∞, which tends to zero in the case of isolated pores, $\lim_{\omega\to 0} D(\omega) \Rightarrow 0$. It imposes the following condition: $\sum_{\mathbf{k}} B_{\mathbf{k}}\mathbf{k}^2 = 1$.

In the case of diffusion in structures of interconnected pores, with the tortuosity constant α defined by the ratio between the long range fluid diffusivity $D_\infty = D_p$, and the local molecular self-diffusion coefficient D, the low frequency limit of the diffusion spectrum has to be $\lim_{\omega\to 0} D(\omega) \Rightarrow D.\alpha$. It changes the structure terms in a way that $\sum_{\mathbf{k}} B_{\mathbf{k}}\mathbf{k}^2 = 1-\alpha$.Thus, the characteristic VCF spectrum of motion in the structure of interconnected pores is

$$D_{rest}(\omega) = D\left(\alpha + \sum_{\mathbf{k}} B_{\mathbf{k}}\mathbf{k}^2 \frac{\tau_{r\mathbf{k}}^2\omega^2}{1+\tau_{r\mathbf{k}}^2\omega^2}\right). \tag{4}$$

The spectrum at the zero frequency is shifted upward for $D_p = D.\alpha$, but retains the characteristic lowering in the proximity of zero frequency. Since the spectrum of spin dephasing, created by the PGSE sequence, exhibits a peak around zero frequency as well, Torrey's formula needs to be replaced with the more generalized expression, where the effect of VCF on the spin echo time dependence is taken into account.

However, Eq.1 can be used to describe the spin-echo of restricted diffusion in the system of interconnected pores as long as the diffusion displacement is short or comparable to the inter-pore distance. When the displacement is much larger that spin jumps between pores, in addition to the effect of motional correlation, the pore structure imposes a restriction to the spatial definition range of spin variables. It means that prior performing the average of spin phase, one has to incorporate the spatial limit of spin phase structure created by applied gradients (i.e. the phase grating). It can be described by the discrete Fourier components $S_{\mathbf{k}}(\mathbf{F}_a)$ in the inverse space, where the wave vectors $\mathbf{k}$ defines the volume occupied by spins and $\mathbf{F_a}$ is an effective spin dephasing created by applied gradients. As shown in reference [14], it gives the spin echo in a very general form as

$$E(\tau) = \sum_{j,\mathbf{k}} E_{0j} S_{\mathbf{k}}(\mathbf{F}_{aj}) e^{i(\mathbf{F}_{aj} - \mathbf{k})\mathbf{r}_j(0)} e^{-\frac{1}{2}\mathbf{k}^2 \mathbf{R}^2_{gj}(\tau)}, \tag{5}$$

where j denotes the summation over the sub-ensembles of spins for which the effect of applied fields may be different. In the case of PGSE with narrow gradient pulses $\mathbf{F}_a = \gamma \mathbf{G} \delta$, but for the sequences with finite pulses or long gradient waveform, the general form of effective spatial spin dephasing (or phase grating) is

$$\mathbf{F}_a = \mathbf{f} \sqrt{\frac{2\beta(\tau)}{R^2_g(\tau)}}. \tag{6}$$

Here $R^2_g(\tau)$ is the mean squared displacement along the gradient [14, 8].

In the short time limit, Eq. 5 reduces to that for the unbounded diffusion

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

where information about a restricted molecular motion is hidden in $\beta(\tau)$.

At long displacements, when $R^2_g(\tau)$ becomes much larger than the pore size, only the zero-th Fourier component of the spin phase structure is retained in Eq. 5, giving the spin echo attenuation independent of time

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

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

$$E(\tau) \;\approx\; e^{-\frac{\beta(\tau)}{R^2_g(\tau)} B_o}, \tag{9}$$

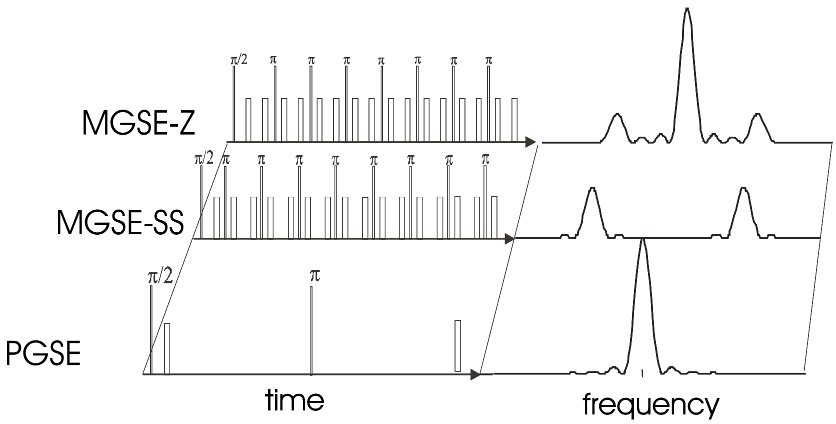

Figure 2. MGSE-SS, PGSE and MGSE-Z sequences and their dephasing spectra.

where B_o is defined by Eq.3. It can be considered as an averaged second moment of the pore volume and its interconnections along the direction of applied gradient.

The spectrum of two-pulse PGSE gradient sequence

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

is dominated by the zero-frequency lobe with the width $1/\Delta$. Therefore, it is unsuitable to extract high-frequency information about $D(\omega)$. In the case of restricted diffusion, it covers the range of the VCF spectrum that has a dip in the proximity of $\omega = 0$. It means that Torrey's formula has to replaced by the expression for $\beta(\Delta)$ in Eq.1, in which the spectral overlap is taken into account. For the PGSE sequence with the finite pulse widths, the calculation gives the spin echo attenuation in the form

$$\begin{aligned} \beta(\Delta) \;=\; & \gamma^2 G^2 \Big[D\alpha\delta^2(\Delta - \frac{\delta}{3}) + 2\sum_{\mathbf{k}} B_{\mathbf{k}} \tau_{r\mathbf{k}}^2 \Big[\Big(1 - cosh(\frac{\delta}{\tau_{r\mathbf{k}}})\Big) e^{-\frac{\Delta}{\tau_{r\mathbf{k}}}} + \\ & + e^{-\frac{\delta}{\tau_{r\mathbf{k}}}} + (1 - \frac{\delta}{\tau_{r\mathbf{k}}}) \Big] \Big]. \end{aligned} \tag{11}$$

It simplifies in the limit of narrow gradient pulses as

$$\begin{aligned} \beta(\Delta) \;=\; & \gamma^2 G^2 \delta^2 \Big[D\alpha(\tau - \frac{\delta}{3}) + \sum_{\mathbf{k}} B_{\mathbf{k}} \Big[\Big(1 - e^{-\frac{\Delta}{\tau_{r\mathbf{k}}}}\Big)(1 + \frac{\delta^2}{12\tau_{r\mathbf{k}}^2}) - \\ & - \frac{\delta}{3\tau_{r\mathbf{k}}} \Big] + ... \Big]. \end{aligned} \tag{12}$$

We need to emphasize that these result differs from the known relations with respect to the term with $D\alpha$. It also confirms a breakdown of the *narrow pulse approximation* [15] for $\delta \approx \tau_{r\mathbf{1}} = \tau_r$, which imposes the upper limit to the gradient pulse width $\delta \ll \tau_r$, to where the spin echo attenuation is in proportion to the mean squared displacement of particles.

If the structure factor in Eq.3 is written as $B_k = C_k^2/k^4$, because the constants C_k exhibit a weak dependence on wave vector at least for simple geometries (planar, cylindrical and spherical) [18], we can obtain the early-time dependence of the spin-eco. Since the terms in the sum of Eq.12 monotonically decrease with the increasing k, the Cauchy formula permits to substitute the summation with the integration. In the short time approximation ($\Delta < \tau_r$), it gives

$$\beta(\Delta) \;=\; \gamma^2 G^2 \delta^2 D\Delta[1 - \frac{2\,C}{3}\sqrt{\pi D\Delta} + ...) \tag{13}$$

This result is the same as that already obtained with a more sophisticated theories such as the "hearing the shape of drums" [16] or the probability "returns to the origin" [17], if assuming $C = \frac{2S}{3\pi V}$. Here $\frac{S}{V}$ is the surface-to-volume ratio of porous media. 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 references [19].

In the intermediate regime $2D\Delta \approx d^2$, when the collision frequency with walls increases, all correlation times but the longest one τ_r, can be neglected. It transforms Eq.12 into

$$\beta(\Delta) \;=\; \gamma^2 G^2 \delta^2 [D\alpha\Delta + B_{k_1}(1 - e^{-\frac{\Delta}{\tau_r}}) + \sum_{k\neq 1} B_k], \tag{14}$$

where the spin echo attenuation exponentially approaches the linear time dependence that has the slope proportional to inter-porous diffusion rate $D_p = D\alpha$.

At still longer times, when $R_g^2 > d^2$ is getting much larger than the pore size, the number of molecules colliding with the boundaries prevails over those experiencing free diffusion, the discord of the spin phase structure must be taken into account Eq. 9.

2.3. FLOW DISPERSION IN A POROUS MEDIA

In the case of the flow, the velocity field in the porous structure 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 [20] by assuming that the probability profile of tagging molecule becomes smoother in the long time limit. Depending on the magnitude of mean flow velocity $\bar{\mathbf{v}}$, it describes the flow dispersion with the effective coefficient D' that can be very much greater than D of molecular diffusion. With the flow along z-axis in a porous media, the parallel and transverse components of dispersion tensor

$$\mathcal{D}' = \begin{bmatrix} D'_\perp & 0 & 0 \\ 0 & D'_\perp & 0 \\ 0 & 0 & D'_\| \end{bmatrix}, \tag{15}$$

are related to the zero frequency tensor of VCF spectrum as

$$\mathcal{D}' = \int_0^\infty \langle [\bar{\mathbf{v}} - \mathbf{v}(t)][\bar{\mathbf{v}} - \mathbf{v}(0)] \rangle \, dt = \mathcal{D}(0). \tag{16}$$

The flow dispersion obeys the convection-diffusion equation that allows us to apply the same approach as used for the restricted self-diffusion when analysing the spin echo experiment on the porous media. The probability density of flow dispersion gives the transverse frequency spectrum of VCF as before

$$D'_\perp(\omega) = D'_\perp + \sum_{\mathbf{k}} B_{\mathbf{k}} \mathbf{k}^2 \frac{\tau^2_{r\mathbf{k}} \omega^2}{1 + \tau^2_{r\mathbf{k}} \omega^2}, \tag{17}$$

but with the distinction that $\tau_{r,\mathbf{k}}$ are the characteristic correlation times of flow dispersion, and $D'_\perp$ denotes the asymptotic transverse dispersion coefficient. The measurement of the that dispersion coefficient needs to reach a constant value might clarify the understanding of the flow dispersion phenomena, which is important in different field of science and technology; for example to model the pollutant transport in the ground water.

3. Measurement and discussion

The spin echo decay caused by the flow motion through the porous structure was measured on the 300 MHz Bruker spectrometer/micro-imager, which has a specially constructed quadrupole gradient coil. Porous media was a column of ion-exchange resin with poly-dispersed beads ($100 - 30\ \mu$) packed in a capillary of 2.0 mm inner diameter. With the magnetic field gradient of 4.5 T/m applied perpendicular to the capillary axis, the spin echo of

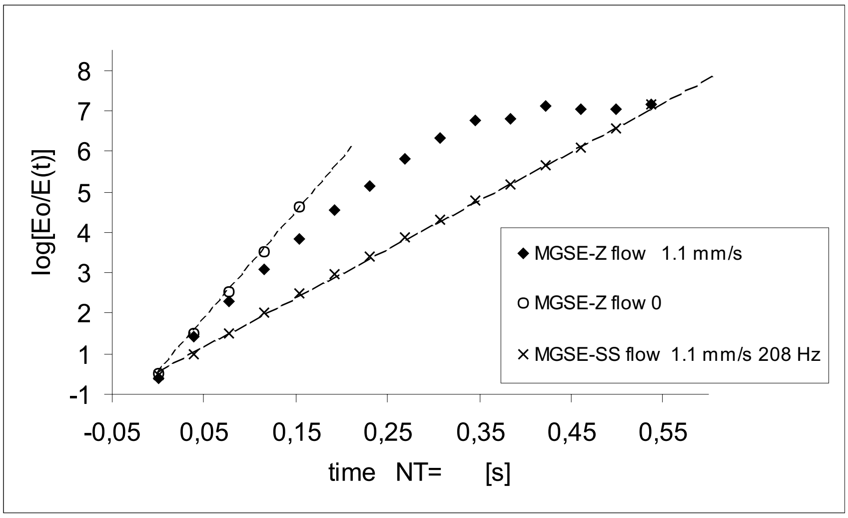

Figure 3. The MGSE-Z attenuation with $\delta = 70\ \mu s$, $G = 4.52\ T/m$ and the modulation frequency above 600 Hz of stationary water and water trickling through porous structure with the average velocity 1.1 mm/s. MGSE-SS attenuation is given for comparison to demonstrate a clear linear rise of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

stationary water, and water trickling though the media was measured. The reciprocating piston pump is used to control the flow velocities. In the high magnetic field, the susceptibility difference of the heterogeneous porous structure can spoil the anticipated time dependence of the spin echo. Commonly, these effects are drowned by the use of large external gradients, but it also shortens spin echo decay and makes impossible to trace a long-time inter-pore diffusion. In order to eliminate the susceptibility attenuation, we used another method: the fast spin phase cycling with the modulated gradient spin echo sequence [21]. For this purpose, we employed the MGSE-Z sequence instead of PGSE. MGSE-Z sequence brings about the identical lobe of diffusion spectrum in the proximity of zero-frequency, as the PGSE sequence (Fig.2), but the modulation frequency has to be high enough to remove susceptibility attenuation and simultaneously shifts the side peaks of MGSE-Z spectrum outside characteristic frequencies of motion. It brings about a spin echo attenuation almost identical to that of PGSE sequence. According to previous measurement [3], the modulation frequencies of 600 Hz is high enough to shift the side peaks in the range that is not affected by flows as long as velocity is below 3 mm/s. Above this range the motional spectrum levels into a plateau equal to the local diffusion constant D. Considering the length of the MGSE-Z sequence NT as the interval between two pulses,Δ, the expression for the spin echo attenuation is the same as that of PGSE sequence, but with the addition of the linear

TABLE I. The parameters of the fit by Eq.18, error 5%.

parameters	1.1 mm/s	2.2 mm/s
α	0.59	0.62
τ_k	88 ms	46 ms
B_1	$1.5 \cdot 10^{-10} m^2$	$1.25 \cdot 10^{-10} m^2$
B_o	$7.1 \cdot 10^{-10} m^2$	$7.7 \cdot 10^{-10} m^2$

term equal to $\frac{1}{2}\gamma^2 G^2 \delta^2 D\Delta$. At intermediate times, the only distinction with respect to the PGSE attenuation is in the addition of one half to the tutousity factor as

$$\beta(\Delta) \; = \; \gamma^2 G^2 \delta^2 [D(\alpha + \frac{1}{2})\Delta + B_{k_1}(1 - e^{-\dfrac{\Delta}{\tau_r}}) + \sum_{k \neq 1} B_k]. \qquad (18)$$

The MGSE-Z sequence with the gradient pulse width $\delta = 70\mu s$ was used to measure the spin echo attenuation as a function of the sequence duration NT for the stationary water and water trickling with the velocity 1.1 mm/s and 2.2 mm/s through porous structure.

The result for the flow rate of 1.1 mm/s is shown in the figures 3. The spin echo attenuation displays a clear transition from the exponential increase into the linear time dependence, which levels into almost time independent asymptote at long times. This time evolution agrees with the theoretical predictions according to Eq.14 and Eq.9. The fit to Eq. 18 provides almost identical slopes of the linear part for both flows but with a shorter τ_r for faster flow as shown in Tab.I. It reads that the flow motion enlarges the bouncing rate with the walls, while leaving the inter-pore motion perpendicular to the flow less affected, at least for weak flow rates. It demonstrates that the flow dispersion is more effective within a pore than between pores. The quantitative analysis with the fit of Eq.18 to the experimental results provides the parameters as shown in TableI In figure 3 the spin echo attenuation obtained by the MGSE-SS sequence is added to show the distinct contrast between its linear time dependence and the non-linear dependence of the MGSE-Z (or PGSE) attenuation in different time regimes.

Conclusion

The approach with the spectral analysis of spin and molecular motion confirms the non-linear time dependence of the PGSE attenuation in the fluid trickling through a porous structure. Apparently, the flow motion shorten the time-of-flight between boundaries, so that the spin echo decay displays three distinct time regimes from which different properties of the porous structure can be revealed. The experiments demonstrate that the flow assisted pulsed gradient spin echo, extends the range of NMR measurements into multi-pore length scale, and is able to disclose the parameters of the molecular dynamics and 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.

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