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Low-frequency velocity correlation spectrum of fluid in a porous media by modulated gradient spin echo

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Abstract

In addition to the fast correlation for local stochastic motion, the molecular velocity correlation function in a fluid enclosed within the pore boundaries features a slow long time-tail decay. Here we present its study by the NMR modulated gradient spin-echo method (MGSE) [1] on a system of water trapped in the space between the closely packed polystyrene beads. With MGSE pulse sequence, a repetitive train of RF pulses with interspersed gradient pulses periodically modulates the spin phase. It gives the spin echo attenuation proportional to a value of the molecular velocity correlation spectrum at the modulation frequency. Covering the frequency range between Hz and MHz, it is a complement to the quasi-elastic neutron scattering, and so a suitable technique for the investigation of low frequency molecular dynamics in fluids. In our experiment, it enables to extract the low frequency correlation spectrum of water molecules confined in porous media. The function exhibits a negative long time-tail characteristic (a low frequency decay of the spectrum), which can be interpreted as a molecular back scattering on boundaries. The results can be well fitted with the spectrum calculated from the solution of the Langevin equation for restricted diffusion (which exhibits an exponential decay) [2] as well as with the spectrum obtained when simulating the hydrodynamics of molecular motion constrained by capillary walls (which gives an algebraic decay) [3]. Despite much work on theories and simulation, which predict slow negative long time tail of molecular velocity correlation dynamics in confined fluids, the obtained velocity correlation spectrum is the first experimental evidence to confirm these effects.

The obtained dependence of spin echo attenuation on time, gradient strength and modulation frequency is also the first experimental verification of the recently developed approach to the spin echo in porous media, that uses the spin phase average with the cumulant expansion to get the attenuation as a discord of spin spatial coherence [4].

Keywords: Molecular velocity correlation; Nuclear magnetic resonance; Spin echo; Restricted; Confined self-diffusion; Spin spatial coherence; Periodic spin dephasing; Modulated magnetic field gradients; Porous system

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1. Introduction

The computer simulations of fluid hydro-dynamic by Alder reveals the existence of slow molecular motion, that appears as a long time tail of the velocity correlation function superposed on the fast exponential decay, corresponding to the average collision time of molecules. It has been well established on theoretical grounds that the long tail features a non-Markovian character of molecular dynamics. Another type of long time tail exists for fluid diffusion in porous media, where, a negative multi-exponential long-time tail results from the solution of Langevin equation [2] for systems in which pore boundaries restrict molecular motion. Moreover, the simulation of molecular motion in a system constrained by capillary walls gives also a long negative but algebraic decay explained as a diffusive decay of density perturbations [3]. Despite much work on theories which predict slow molecular dynamics in fluids, there has been little experimental evidence to confirm these effects, whether in a confined fluid or in a system experiencing free Brownian diffusion. Thus any technique, that is able to provide details in this range of molecular motion, is most welcome.

Spin echo methods, which detect molecular displacements through precession of their atomic nuclear spins in a non-uniform magnetic field, play an important role among the techniques for measurement of molecular motion in fluids. This contribution concerns the use of a new type of spin echo method in which the applied magnetic field gradient periodically modulates the spin phase, enabling direct

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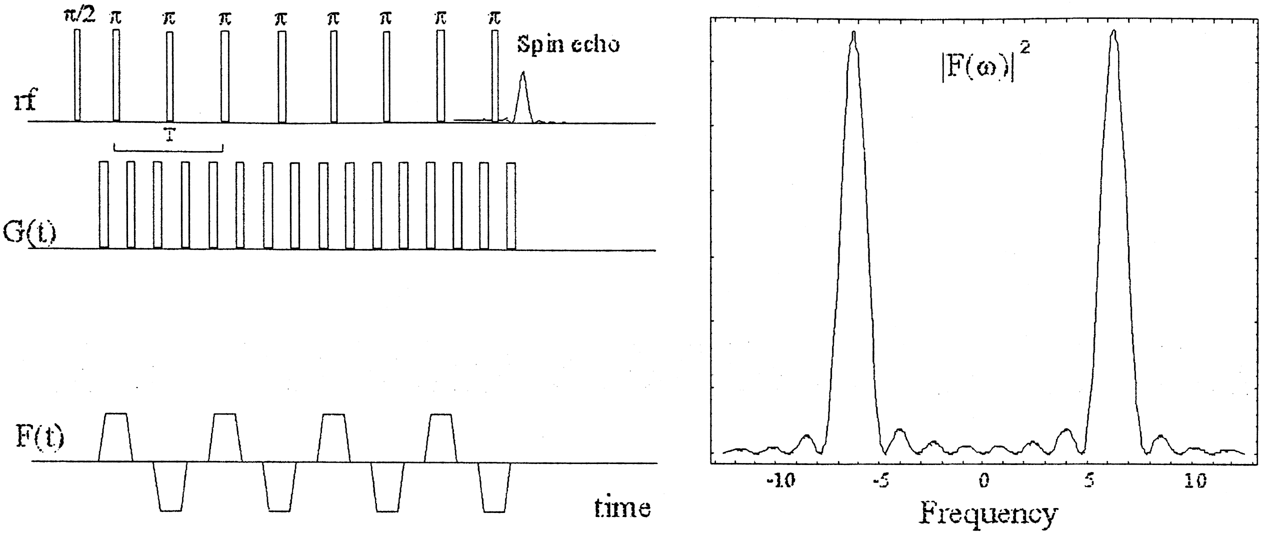

Fig. 1

insight into details of fluid dynamics on molecular level. The modulated gradient spin echo (MGSE) provides details of molecular motion by sampling the spectrum of the velocity correlation function $\langle \mathbf{v}(t)\mathbf{v}(0)\rangle$ relevant to a quantitative description of molecular dynamics. The rate of the gradient pulse application determines the temporary scale of the MGSE method being between Hz to MHz frequencies what is about a characteristic range of slow molecular dynamics in fluids. When studying molecular dynamics in fluids MGSE method can be used as a complement to the neutron measurement, which covers GHz to THz frequency range.

2. Theory

With the use of MGSE sequence we have to pays regards to the application of long lasting gradient waveform where a formation of non-uniform spin phase structure, (i.e., a spatial coherence of spin phase) is accompanied by motion of particles tending to destroy its build up. Interference of molecular motion into the creation of spin spatial phase coherence describes the factor of *mean spin dephasing* at the peak of spin echo at time τ

$$\mathbf{F}_a^2(\tau) = \frac{1}{R_g^2(\tau)} \int_0^{\tau}\int_0^{\tau} \mathbf{F}(t_1)\langle \mathbf{v}(t_1)\mathbf{v}(t_2)\rangle \mathbf{F}(t_2)\,dt_1 dt_2$$

$$= \frac{1}{\pi R_g^2(\tau)} \int_0^{\tau\infty} |\mathbf{F}(\omega)|^2 \mathbf{D}(\omega)\,d\omega,$$

where $\mathbf{F}(\omega)$ is the Fourier transform of $\mathbf{F}(t) = \gamma\int_0^t \mathbf{G}(t)dt$ with $\mathbf{G}(t)$ as effective amplitude of applied gradient sequence. $R_g^2(\tau)$ is the mean square displacement of particles along the applied gradient during the time of sequence application and the Fourier transformation of the velocity correlation function defines the diffusion spectrum $D(\omega)$. For an unbounded diffusion it gives the spin echo attenuation at time τ in the form

$$E(\tau) = E_0 \exp\left[-\frac{1}{2}\mathbf{F}_a^2(\tau)\,R_g^2(\tau)\right]$$

$$= E_0 \exp\left[\frac{1}{\pi}\int_0^{\tau\infty} |\mathbf{F}(\omega)|^2 \mathbf{D}(\omega)\,d\omega\right]$$

It contains product of two spectra: that of the velocity correlation function and the spectrum of spin phase modulation. Thus, one can probe the shape of motional correlation spectrum by an appropriate choice of gradient modulation.

The modulated gradient spin echo (MGSE) sequence such as that shown on Fig. 1 consists of a repetitive CPMG train of rf pulses with interspersed gradient pulses of period T. Its spectrum, $\mathbf{F}(\omega)$, has only one frequency peak at $\omega_m = 2\pi/\mathrm{T}$ with the width, depending on number of period repetitions N where $\tau = \mathrm{NT}$. With $\mathrm{N} > 4$ the spectrum is reasonably narrow so that the factor of mean spin dephasing can be approximated as

$$\mathbf{F}_a^2(\tau) \approx \frac{\alpha}{R_g^2} D(\omega)\tau$$

with

$$\alpha = \frac{1}{2}(\gamma\delta G)^2\left(1 - \frac{4\delta}{3T}\right),$$

a factor which includes the parameters of the gradient pulse. By changing the period T, while keeping τ constant, the frequency can be adjusted in position in order to trace out just the frequency dependence of the correlation function.

The confinement of fluid in porous structure imposes constrains to the allowed states of spin-bearing particles resulting in the spin phase spatial coherence being expressed as a composite of plane waves

$$\exp(i\mathbf{F}\mathbf{r}) = \sum_{\mathbf{k}} S_{\mathbf{k}}(\mathbf{F}) \exp(i\mathbf{k}\mathbf{r}).$$

Here, the nonzero wave vectors k denote allowable momentum states of confined particles, while the terms $S_k(F)$ are the components of spin phase structure in reciprocal space. In case of interconnected pores it provides the spin echo response in a very general form as [4]

$$E(\mathbf{F},\tau) = \int d\mathbf{r} E_0(\mathbf{r}) \sum_{\mathbf{k}} S_{\mathbf{k}}(\mathbf{F}_a) \exp\left[i(\mathbf{F}_a - \mathbf{k})\mathbf{r} - \frac{1}{2}\mathbf{k}^2 R_g^2(\tau,\mathbf{r}) \right]$$

In the short-time limit, when we can neglect the location dependence of $R_{g,}$ it gives the same form as for the spin echo of unbounded motion. Another extreme is the long time limit when the mean particle displacement within the structure of interconnected pores is larger than dimension of the single pore. It provides the spin echo signal

$$E(\mathbf{F},\tau) \approx |S_0(\mathbf{F}_a)|^2 = \left| \int d\mathbf{r} \exp(i\mathbf{F}_a(\omega)\mathbf{r}) \right|^2$$

Here only the zero-th Fourier component of spin phase structure is retained. This is in fact the integral of spin phase over the space of confinement i.e., the one-dimensional Fourier component of pore along the direction of applied gradient where the wave-vector is $k \approx F_a$.

MGSE technique requires a fast gradient modulation, so that the coil inductance will generally limit the gradient amplitude, thus allowing the approximation where the grating of phase coherence is larger than the pore size, $F_a d \ll 2\tau$. In this case the zero-th Fourier component of phase structure may be written as $|S_0(\mathbf{F}_a)|^2 \approx \exp[-\mathbf{F}_a^2(\omega) M_2]$. In the system of randomly distributed interconnected pores, M_2 represents an averaged second moment of pore volume along the direction of applied gradient. Thus the method provides information about pore morphology despite the fact that a gradient of only small amplitude is used.

3. Measurement and results

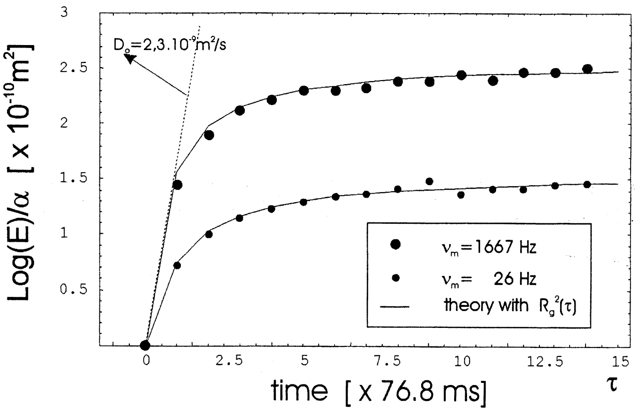

Fig. 2

By using a commercial spectrometer with a specially constructed quadrupole gradient coil, we have employed the MGSE method to measure low frequency dynamics of water molecules in a porous system. The system of interconnected pores consists of closely packed polystyrene beds of radius 15 μm. We have used the MGSE sequence of repetitive train of RF pulses with interspersed gradient pulses of width $\delta = 70$ μs. By changing the period of MGSE sequence T we varied the spin phase modulation frequency $\nu_m = 1/T$ between 210 Hz to 1.67 kHz. In addition, we changed the current through the gradient coil so as to vary the gradient field between 1 and 7 T/m. Thus we obtained the spin echo as a function of three variables: the frequency $\nu_{m,}$ the number of the sequence periods $\tau = NT$ and the gradient amplitude G. In order to allow direct comparison of the data obtained with different gradient pulse parameters, the measurements are presented on Fig. 1 in the form $-\text{Log}[E(\nu_{m,}\tau,\alpha)]/\alpha$. This type of plot should exhibit an attenuation rise in the short time limit as $D(\nu_m)\tau$, while the asymptotic value at long time limit is equal to $D(\nu_m)/D_\infty M_2$. Thus the measurement of the signal in both limits provides the motional spectrum as well as information about the system morphology, which is included in M_2 if the diffusion rate through interconnections, $D_\bullet$, is known.

The result of measurements for two different modulation frequencies is presented on Fig. 2. As a function of time, $\tau = NT$, the measured points follow the anticipated dependence with a linear increase at short times and an asymptotic levelling in the long time limit. The change of modulation frequency alters the initial slope and the height of the long time asymptote in the proportion as it was expected. It means that the frequency modification of spin echo dependence on time, in the short as well as the long time limit, is due solely to the frequency variation of the motional correlation spectrum. The series of measurements at different frequencies in the range between 26 Hz to 1.667 kHz have given the velocity correlation spectrum $D(\omega)$ in the low frequency (long-time tail). They provide the long time diffusion rate $D_{\bullet,}$ as an upward shift of correlation spectrum as presented on Fig. 3.

Using a range of theoretical results for low frequency correlation spectra of confined fluids has fit the measured spectrum. The solid line is a fit using the solution of the Langevin equation for a Brownian particle in a finite system (i.e., in the presence of walls) [2]. Similarly the low fre-

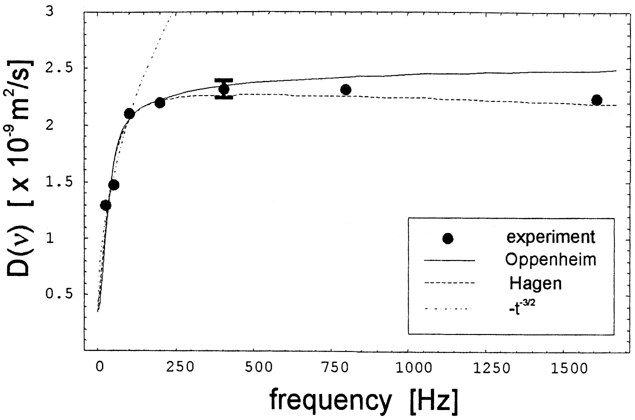

Fig. 3

quency data can be nicely fitted to the results of reference [3] where the calculation for molecular motion in a viscous fluid in the capillary has been performed on hydrodynamic grounds (hatched line). Another fit is according to long-time velocity correlation as $-t\{^{-3/2}\}$ (dotted line) that holds only at very low frequencies (long times). Evidently this last type of algebraic decay is not very convincing for the long time-tail of correlation function in the interrogating system.

A novel NMR theory [4] that can treat the effects of arbitrarily shaped gradient pulse sequence to spin echo measurement of restricted diffusion can nicely describe the obtained dependence of spin echo attenuation on time, gradient strength and modulation frequency. Thus it is also the first experimental verification of the approach that uses the average with the cumulant expansion to get the attenuation as a discord of spin spatial coherence.

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