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Physica B 292 (2000) 296–301

PHYSICA B

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The long time tail of molecular velocity correlation in a confined fluid: observation by modulated gradient spin-echo NMR

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Received 25 November 1999

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 [1,2]. This article presents a study by the NMR modulated gradient spin-echo method (MGSE) [3] on a system of water trapped in the space between the closely packed polystyrene beads. The results prove that the obtained dependence of spin-echo attenuation on time, gradient strength and modulation frequency nicely corresponds to the recently developed NMR approach, which is able to describe the effects of arbitrarily shaped gradient pulse sequence on the spin-echo attenuation [4,5]. With an MGSE pulse sequence, a repetitive train of RF pulses with interspersed gradient pulses periodically modulates the spin-phase, giving the spin-echo attenuation proportional to a value of the velocity correlation spectrum at the modulation frequency. It enables to extract the low-frequency correlation spectrum of confined water molecules. The function exhibits a negative long time tail characteristic (a low-frequency decay of the spectrum), that can be well fitted with the spectrum calculated from the solution of the Langevin equation for restricted diffusion (which exhibits an exponential decay) as well as with the spectrum obtained when simulating the hydrodynamics of molecular motion constrained by capillary walls (which gives an algebraic decay).

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

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

1. Introduction

In his kinetic theory Boltzmann [6] introduced the assumption that the velocity correlation function decays exponentially [7] to zero over the correlation time, $\tau_c \approx 10^{-12}$–10^{-10} s, corresponding to the average collision time of molecules. However, computer simulations of fluid hydro-dynamic by Alder [8] 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 time tail exhibits a slower

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0921-4526/00/$ - see front matter
PII: S0921-4526(00)00469-5

algebraic decay as $t^{d/2}$, where d is the dimension of the system. It has been well established on theoretical grounds that the long tail features a non-Markovian character of molecular dynamics that can be ignored only in low-density gases. Another type of long time tail exists for fluid diffusion in porous media. Here, a negative multi-exponential long time tail results from the solution of Langevin equation [1] 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. This has been explained, on hydrodynamic grounds, as a diffusive decay of density perturbations [2]. 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. Such effects have been established by computer simulations but scarcely confirmed with experiments [9]. Thus, any technique, that is able to provide details in this range of molecular motion, is most welcome.

Spin echo methods [10], 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. The most frequently used technique is the spin echo with two gradient pulses separated by a well-defined time interval. While this particular method is very useful in examining molecular diffusion, it is not the ideal vehicle for the frequency domain relevant to this article. The present paper concerns the use of a new type of experiment [11,4,12] in which the applied magnetic field gradient periodically modulates the spin phase, enabling direct insight into details of fluid dynamics on a molecular level. The new method, named modulated gradient spin echo (MGSE), provides details of molecular motion by sampling the spectrum of the velocity correlation function $\langle \boldsymbol{v}(t)\boldsymbol{v}(0)\rangle$, relevant to a quantitative description of molecular dynamics. The average collision time of molecules is of course exceedingly short compared to the time regime accessible by MGSE. It can be measured by quasi-elastic neutron scattering [13,14] where the time scale of molecular measurement is determined by the instrumental energy resolution and falls in the GHz–THz frequency region. The rate of the gradient pulse application determines the temporary scale of the MGSE method being between Hz and MHz frequencies which is about a characteristic range of slow molecular dynamics in fluids. Thus, the MGSE method can be used as a complement to the neutron measurement when studying molecular dynamics in fluids.

2. Modulated gradient spin echo

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, such that the time integral of the effective gradient, $g(t)$, is zero. We can write small perturbations of spin-echo phase, due to molecular displacements in the magnetic field, as $\theta(\tau) = \gamma\int_0^\tau G(t)r(t)\,\mathrm{d}t = \int_0^\tau \boldsymbol{F}(t)v(t)\,\mathrm{d}t$, where $F(\tau) = \gamma\int_0^\tau \boldsymbol{G}(t)\,\mathrm{d}t$ and τ is the time of phase refocusing. Since the detected signal arises from the induction of an immense number of spins ($\gg 10^6$) one does not detect the frequency fluctuations of individual spins but rather a coherent superposition of signals induced by large numbers of spins. Whenever the molecular mean free path l of unimpeded molecular self-diffusion is short compared to the length of gradient spin phase grating, $Fl \ll 1$ [5] the detected fluctuations can be considered as a Gaussian process [15], even if the motion of individual spin is governed by non-Gaussian stochastic dynamics [11,4]. Using the cumulant expansion of the spin-phase average one obtains the peak of spin echo at time τ in the form

$$E(\tau) \approx E_\mathrm{o}\,\mathrm{e}^{-\frac{1}{2}F_\mathrm{a}^2(\tau)R_\mathrm{g}^2(\tau)}, \tag{1}$$

where $R_\mathrm{g}^2(\tau, \boldsymbol{r})$ is the *mean square displacement* of particles along the applied gradient during the time of sequence application. The analysis takes into account the use of long sequences of magnetic field gradients pulses or long-lasting gradient of modulated waveform by defining the factor of *mean spin dephasing* $\boldsymbol{F}_\mathrm{a}(\tau)$. This factor takes into account the property that with extended gradient application

the 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. Unlike the case of short pulses where the spin-phase structure is created in a short step, the application of long gradient pulses and the associated motion of spin-bearing particles during the extended interval of gradient application interferes with the creation of spin spatial coherence.

The Fourier transformation of the velocity correlation function [16,11] defines the diffusion spectrum

$$D(\omega) = \int_0^\infty \langle v_g(t) v_g(0) \rangle_c e^{i\omega t}\, dt, \tag{2}$$

where only the correlation between velocity components along the directions of applied gradients takes part. With the Fourier transform of spin dephasing as

$$\boldsymbol{F}(\omega,\tau) = \int_0^\tau \boldsymbol{F}(t) e^{i\omega t}\, dt \tag{3}$$

we can define the mean spin dephasing by the factor [4]

$$\boldsymbol{F}_a^2(\tau) = \frac{1}{\pi R_g^2(\tau)} \int_0^\infty D(\omega) |F(\omega,\tau)|^2\, d\omega. \tag{4}$$

Since $F_a^2(\tau)$ contains a product of two spectra: that of the velocity correlation function and the spectrum of spin phase modulation [3], one can probe the shape of motional correlation spectrum by an appropriate choice of gradient modulation as follows.

The modulated gradient spin-echo (MGSE) sequences such as that shown in Fig. 1 [3,12] consist of a repetitive CPMG train of RF pulses with interspersed gradient pulses of period T. Its spectrum $\boldsymbol{F}(\omega,\tau)$ has only one frequency peak [12] at $\omega_m = 2\pi/T$ with the width, depending on the number of period repetitions N where $\tau = NT$. With $N \geqslant 4$ the spectrum is reasonably narrow so that the factor of mean spin dephasing can be approximated as

$$|\boldsymbol{F}_a(\tau)|^2 \approx \frac{\alpha}{R_g^2} D(\omega_m)\tau \tag{5}$$

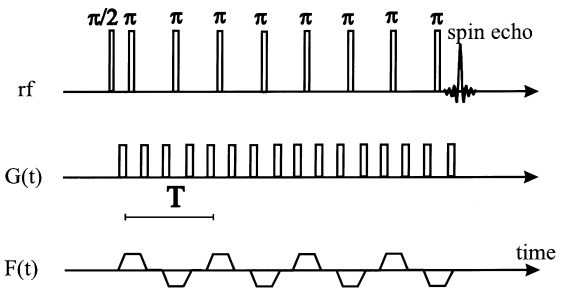

Fig. 1. MGSE pulse sequence.

with $\alpha = \frac{1}{2}(\gamma\delta|\boldsymbol{G}|)^2(1 - 4\delta/3T)$, 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. An example of the use of this method has been demonstrated for the case of disordered water flow through a column of close-packed ion-exchange beads [3]. The observed spectrum of the velocity auto-correlation exhibited characteristic features at frequencies corresponding to the angular velocity of the fluid around the beads.

This paper aims to use this method to study the molecular dynamics in a fluid confined in a porous system. Here the confinement imposes constraints on the allowed states of spin-bearing particles resulting in the spin-phase spatial coherence being expressed as a composite of plane waves

$$e^{i\boldsymbol{F}\cdot\boldsymbol{r}} = \sum_{\boldsymbol{k}} S_{\boldsymbol{k}}(\boldsymbol{F}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{6}$$

The nonzero wave vectors $\boldsymbol{k}$ denote allowable momentum states of confined particles [4] while the terms $S_{\boldsymbol{k}}(\boldsymbol{F})$ are the components of spin-phase structure in reciprocal space. A line of reasoning similar to that presented earlier can be implemented again in order to estimate the mean of spin phase in the restricted geometry, but with some limitation: Namely, the cumulant expansion can be truncated after the second order, i.e. Gaussian approximation, only for interconnected pores giving the spin-echo response as [4,5]

$$E(\boldsymbol{F}_a,\tau) = \int E(\boldsymbol{r})_0 e^{i\boldsymbol{F}_a\boldsymbol{r}} \sum_{\boldsymbol{k}} S_{\boldsymbol{k}}(\boldsymbol{F}_a) e^{-i\boldsymbol{k}\boldsymbol{r}} e^{-\frac{1}{2}\boldsymbol{k}^2 R_g^2(\tau,r)}\, d\boldsymbol{r}. \tag{7}$$

In the porous systems with completely closed pores and impermeable boundaries the use of Gaussian approximation is limited to intervals with the short particle displacement when pore size $d > R_g(\tau)$ [17]. Namely, in such systems a negative long time tail of velocity auto-correlation function may reduce convergence of cumulants series to the degree that higher-order terms of cumulant expansion cannot be omitted [5].

In the short-time limit (i.e. *the diffusion-limited region* [18]), we can neglect the location dependence of R_g and Eq. (7) gives the same form as for the spin echo of unbounded motion, Eq. (1). Another extreme is the long time limit when the mean particle displacement within the structure of interconnected pores is larger than the dimension of the single pore, $R_g > d$. Then Eq. (7) provides the spin-echo signal

$$E(\tau) \approx |S_0(\boldsymbol{F}_a)|^2 \approx \left| \int_V e^{-i\boldsymbol{F}_a(\omega)\boldsymbol{r}} d\boldsymbol{r} \right|^2. \quad (8)$$

Here only the zeroth 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 $k \approx F_a$. This formula bears a resemblance to the Fraunhofer formula of light diffraction where a similar integration is taken over the surface of aperture. Likewise, in optics where diffraction image on the screen is the Fourier spectrum of the aperture shape, the spin echo provides the diffusive diffraction patterns of the pore structure by varying the magnitude and direction of applied gradient field. In this way the method provides a direct insight into the pore geometry [19].

The 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, $F_a d \ll 2\pi$. In this case, the zeroth Fourier component of phase structure in Eq. (8) may be written as

$$|S_0(\boldsymbol{F}_a)|^2 \approx e^{-\boldsymbol{F}_a^2(\omega) M_2}. \quad (9)$$

In the system consisting of randomly distributed interconnected pores, $M_2 = 1/V_p \int_{V_p} \boldsymbol{r}_g^2 \, d\boldsymbol{r}_g$, where the integration is taken over the volume of compartment and its connections with other pores. It 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 discussion

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 beads of radius 15 μm. The MGSE pulse sequence used was a 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 and 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 $\nu_m = 1/T$, the number of the sequence periods $\tau = NT$ and the gradient amplitude G. In order to allow a direct comparison of the data obtained with different gradient pulse parameters, the measurements are presented in Fig. 2 in the form $-1/\alpha \log[E(\nu_m, \tau, \alpha)]$. This type of plot should exhibit an attenuation rise in the short-time limit as $D(\nu_m)\tau$, according to Eq. (5), while the asymptotic value at long-time limit is equal to

$$\frac{1}{\alpha} F_a^2(\nu_m) M_2 = \frac{D(\nu_m)}{D_\infty} M_2 \quad (10)$$

according to Eq. (9), where at long times we assume that $R_g^2(\tau) = 2D_\infty \tau$. 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_∞, is known.

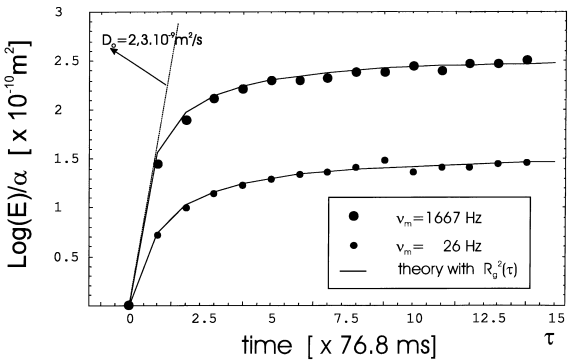

Fig. 2. Spin-echo attenuation for two different modulation frequencies fitted with the curve according to Eq. (7).

The results of measurements for two different modulation frequencies are presented in 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 leveling 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 according to Eqs. (5) and (9). 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 initial increase in attenuation starts to deflect from the linear law when the particle mean square displacement becomes comparable to the pore size, i.e. $R_g^2 = 2D_o\tau \approx l^2$ with D_o the self-diffusion rate in unbounded fluid. Thus, the point of deviation can be used to estimate an averaged pore size. The determination of the second moment of the pore volume M_2, from the asymptotic height at long times is another means of obtaining information about pore morphology.

In the case of the slow modulation frequency when the sequence period is large, there are insufficient data points in the short-time limit to allow an exact determination of the motional spectrum from the slope of curve. Therefore, we have to use the entire spin echo dependence on time calculated according to Eq. (7) to fit experimental data. Due to the fact that the gradient is projecting the pore geometry in one dimension one could approximate the confinement with a plane-parallel pore model although the actual pore geometry is different. The interconnections between pores can be regarded as a leak in planes that shifts the spectrum $D(\omega)$ upwards by a constant value equal to the diffusion rate through interconnections, D_∞. Thus, we have to consider the deviation of the time dependence of the molecular mean square displacement $R_g^2(\tau)$ from linear dependence on time [20,21]. At short times the majority of particles are not affected by walls so that the diffusion rate of unbounded molecules, D_o, can be assumed. At times $\tau_s \approx l^2/2D_o$ when the number of molecules colliding with the walls prevails over those experiencing free diffusion, the diffusion rate slows down to become D_∞ at long-time limit. Consequently, the particle mean square displacement can be approximated as $R_g^2(\tau) = 2D_\infty\tau + 2(D(\nu_m) - D_\infty)\tau_s(1 - e^{-\tau/\tau_s})$. For the parameters $D_o = 2.3\times10^{-9}$ m^2/s, $D_\infty = 0.2\times10^{-9}$ m^2/s and $\tau_s = 0.1$ s and inserting $D(\nu) = 1.4\times10^{-9}$ m^2/s for the frequency 26 Hz and $D(\nu) = 2.3\times10^{-9}$ m^2/s for 1667 kHz, we obtain a nice fit between the curves calculated according to Eq. (7) and the measurements (see Fig. 2).

The series of measurements at different frequencies in the range between 26 Hz and 1.667 kHz have given the velocity correlation spectrum D_ω in the low frequency (long time tail). They provide the long time diffusion rate D_∞ as an upward shift of correlation spectrum as presented in Fig. 3.

The measured spectrum has been fitted by using a range of theoretical results for low-frequency correlation spectra of confined fluids. 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) [1]. The original work does not take into account the pore interconnection, but we allow for this by using a constant value added to the velocity correlation spectrum. Thus, the pore leaking defines the zero-frequency value of motional spectrum. Similarly, the low-frequency data can be nicely fitted to the results of Ref. [2] 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

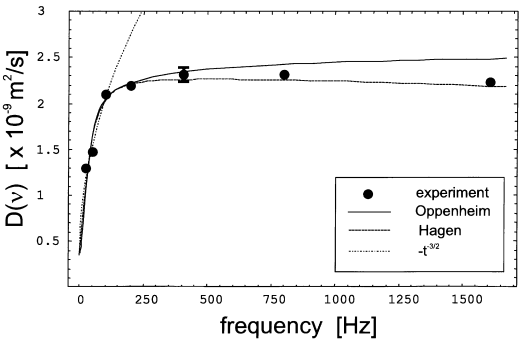

Fig. 3. The spectrum of velocity correlation function of particles confined in the porous structure of closely packed polystyrene beads of radius 15 μm as measured by modulated gradient spin echo and its fit with the theoretical results.

algebraic decay is not very convincing for the long time tail of correlation function in the interrogating system.

4. Conclusion

With the MGSE NMR method we can periodically modulate the spin phase to provide the spin-echo attenuation proportional to a value of the 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 that is in the range of GHz–THz, and so a suitable technique for the investigation of low-frequency molecular dynamics in fluids. 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 measured slow dynamics can be interpreted in terms of a cage surrounding molecules of the fluid. When molecules encounter the boundaries, back scattering occurs which results in a negative velocity correlation, which arises, theoretically, from non-Markovian character of molecular dynamics. The lowering of the diffusivity is mainly due to the geometric restriction rather than to the interaction with the surface [22].

The obtained dependence of spin-echo attenuation on time, gradient strength and modulation frequency can be nicely described by a novel NMR theory [4,5] that can treat the effects of arbitrarily shaped gradient pulse sequence to spin-echo measurement of restricted diffusion. 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.

References

[1] E. Oppenheim, P. Mazur, Physica B 30 (1964) 1833.
[2] M.H.J. Hagen, I. Pagonabarraga, C.P. Lowe, D. Frenkel, Phys. Rev. Lett. 78 (1997) 3785.
[3] P.T. Callaghan, J. Stepišnik, J. Magn. Res. A 117 (1995) 118.
[4] J. Stepišnik, J. Magn. Res. 131 (1998) 339.
[5] J. Stepišnik, Physica B 270 (1999) 110.
[6] L. Boltzmann, Wien Ber. 66 (1872) 275.
[7] G.E. Uhlenbeck, L.C. Ornstein, Phys. Rev. 36 (1930) 832.
[8] B.J. Alder, T.E. Wainwright, Phys. Rev. A 1 (1970) 18.
[9] J.P. Boon, A. Bouller, Phys. Lett. A 55 (1976) 391.
[10] E.L. Hahn, Phys. Rev. 80 (1950) 580.
[11] J. Stepišnik, Physica B 104 (1981) 350.
[12] P.T. Callaghan, J. Stepišnik, Advances in Magnetic Optical Resonance, in: Waren S. Waren (Ed.), Generalised Analysis of Motion Using Magnetic Field Gradients, Vol. 19, Academic Press, San Diego, 1996, pp. 326–389.
[13] A. Rahman, K.S. Singwi, A. Sjölander, Phys. Rev. 126 (1962) 997.
[14] G.E. Bacon, Neutron Diffraction, Oxford University Press, Oxford, 1975.
[15] N.G. van Kampen, Stochastic Processes in Physics and Chemistry, North-Holland, Amsterdam, 1981.
[16] R. Lenk, Brownian Motion and Spin Relaxation, Elsevier, Amsterdam, 1977.
[17] A. Duh, Restricted self-diffusion and edge enhancement at nmr microscopy, Thesis, 000, University of Ljubljana, 1999.
[18] L.Z. Wang, A. Caprihan, E. Fukushima, J. Magn. Res. A 117 (1995) 209.
[19] A. Coy, P.T. Callaghan, J. Chem. Phys. 101 (1994) 4599.
[20] F. Junker, W.S. Veeman, Chem. Phys. Lett. 305 (1999) 39.
[21] R.W. Mair, D.G. Cory, S. Peled, Ching Hua Tseng, S. Patz, R.L. Walsworth, J. Magn. Res. 135 (1998) 478.
[22] R. Kimmich, S. Stapf, A.I. Maklakov, V.D. Skirda, E.V. Khozina, Magn. Resonance Imaging. 14 (1996) 793.