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A new view of the spin echo diffusive diffraction in porous structures

J. Stepišnik(*)

Physics Department, FMF, University of Ljubljana
Jadranska 19, 1000 Ljubljana, Slovenia
and J. Stefan Institute - Jamova 39, 1000 Ljubljana, Slovenia

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Abstract. – Analysis with the characteristic functional of stochastic motion is used to clarify details of the diffraction-like effect at the gradient spin echo measurement of self-diffusion in porous structures. This approach shows that the phase interference of spins rebounding at boundaries brings about the diffraction, when the mean displacement of scattered spins is equal to the phase grating caused by the applied magnetic field gradient. The diffraction patterns convey information about morphology of the surrounding media only at times long enough that boundaries restrict further spin displacements. The method explains the dependence of diffraction on the time and width of gradient pulses, as observed at the experiments and the simulations.

Introduction. – Measurements of the molecular displacements through the precession of their atomic nuclear spins in non-uniform magnetic field by the magnetic resonance spin echo [1] has gained a most decisive role in the studies of molecular transport within porous structures. These comprise diverse system as sandstone rocks, catalysts, colloids, or biological tissue. The field has an extensive literature and a wide range of experiments has been performed. The methodology of the Pulsed Gradient Spin Echo (PGSE) [2] have been successfully implemented to measure diffusion in systems for which the constrained molecular motion causes a deviation from Fickian behavior. Based on the diffusion propagator formalism [3], the spin echo can be considered as a Fourier transform of the probability distribution [4], from which the concept of diffusive diffraction of spin echo in a porous media has been developed [5]. This effect makes it possible to extract information not only about the motion but also about the morphology of the surrounding medium [6–9]. Unlike NMR Imaging where molecular positions are recorded to a resolution on the order of $10\,\mu$m, the method is able to achieve the resolution of displacement measurement some two to three orders of magnitude better, and pushes the lower limit of NMR resolution into a nanometer range.

However, the probability distribution function is just a way to consider the transport properties of spins in terms of the mean characteristics of the elementary events. The method of characteristic functional, *i.e.* the Fourier transform of the probability distribution [10], is an

(*) E-mail: Janez.Stepisnik@fiz.uni-lj.si alternative way to get the average of the spin phase fluctuation. With the cumulant expansion in the Gaussian approximation, a simple derivation of spin echo attenuation for any gradient pulse sequence is provided and the relation between the spin echo and the spectrum of the single-particle velocity correlation function (VCF) is obtained [11–13]. The method shows that a sufficiently fast and a properly shaped gradient sequence [14, 15], conveys information about macroscopic flow and diffusion, but also about the details of motion on the molecular level. The method has been successfully implemented to measure the diffusion spectrum and the flow dispersion in porous media [16, 17].

This study is an attempt to apply the method for the analysis of the spin echo diffusive diffraction. Our aim is to clarify details of diffraction dependences on the time, the width of gradient pulse and the type of applied gradient sequences. It may explain the results of experiments and computer simulations [18–20], which remain unanswered in the frame of propagator theory. The new approach could elucidate the dependence of diffraction on the mechanism of spin scattering at walls as well.

Spin echo and average of spin phase fluctuation. – Whenever in NMR a non-uniform magnetic field is used to encode the spin magnetization for motion rather than position, the spin echo is used to refocus any spin phase shift, due to absolute spin position. Thus, the perturbations of spin phase, due to displacements $\boldsymbol{r}(t)$ of spins in the non-uniform magnetic field gradient $\boldsymbol{G}(t)$, can be written as $\theta(\tau) = \gamma \int_0^\tau \boldsymbol{G}(t)\cdot\boldsymbol{r}(t)\,\mathrm{d}t = -\int_0^\tau \boldsymbol{F}(t)\cdot\boldsymbol{v}(t)\,\mathrm{d}t$, where $\boldsymbol{F}(t) = \gamma\int_0^t \boldsymbol{G}(t')\,\mathrm{d}t'$ is a factor of spin dephasing, τ is the time of refocusing, and $\boldsymbol{v}(t)$ is spin velocity. Regarding their location in a non-uniform magnetic field and rf excitation, one can distinguish subgroups of spins according to their precession frequency to obtain the spin echo as [21]

$$E(\tau) = \sum_j E_{j0}\langle e^{-i\int_0^\tau \boldsymbol{F}_j(t)\cdot\boldsymbol{v}_j(t)\,\mathrm{d}t}\rangle, \tag{1}$$

where E_{j0} is the normalized amplitude and $\langle\cdots\rangle$ is the motion average of particles in the j-th sub-ensemble. In the case of a sequence with two sharp gradient pulses of widths δ and interspaced for Δ, *i.e.* a sharp PGSE sequence where $\boldsymbol{F} = \boldsymbol{q} = \gamma\delta\boldsymbol{G}$, the mean of the spin phase fluctuation can be worked out with the conditional probability distribution (the diffusion propagator) $P(\boldsymbol{r}', t'|\boldsymbol{r}, t)$ [3–5]. It gives the spin echo as

$$E(\tau, \boldsymbol{q}) = \sum_j E_{j0}\langle e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_j(\tau)-\boldsymbol{r}_j(0))}\rangle \longrightarrow \int E(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}' \int \mathrm{d}\boldsymbol{r} P(\boldsymbol{r}, \tau|\boldsymbol{r}', \Delta) e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}. \tag{2}$$

Here, the spin echo is a Fourier transform of the probability distribution with respect to parameter $\boldsymbol{q}$ [4]. Thus, the measured $E(\tau, \boldsymbol{q})$ may provides the diffusion propagator. When properly strong gradients are applied, it gives the diffusive diffractions at long diffusion times [5].

According to statistical physics, the stochastic process is determined knowing either the probability distribution or the characteristic function, which is defined as the Fourier transform of probability distribution [22],

$$\langle e^{ifr}\rangle = \int e^{ifr} P(r)\,\mathrm{d}r. \tag{3}$$

The characteristic function exists even when the probability does not. By passing the stochastic properties from the variable r to v, where $r = \int_0^t v(t')\,\mathrm{d}t'$, the characteristic function is transformed into the characteristic functional. It can be worked out with the cumulant expansion method as

$$\langle e^{i\int_0^t f(t')v(t')\,\mathrm{d}t'}\rangle = e^{i\int_0^t f(t')\langle v(t')\rangle\,\mathrm{d}t' - \frac{1}{2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 f(t_1)\cdot\langle v(t_1)v(t_2)\rangle_c f(t_2) + \cdots}. \tag{4}$$

with $f(t)$ being an arbitrary function. The cumulant expansion relates the characteristic functional to the expectation $\langle v(t)\rangle$, and to the set of correlation functions, of which the second order is $\langle v(t_1)v(t_2)\rangle_c = \langle v(t)v(0)\rangle - \langle v(t)\rangle^2$. The expansion to the second term, the Gaussian approximation, is often used to describe physical processes and can be justified in many processes in the magnetic resonance as well.

These basic facts from the theory of stochastic processes lead to understanding that the average of the spin phase fluctuation can be resolved in different manners depending on the applied gradient sequence. With the sharp PGSE sequence, the position of spin-bearing particle $\boldsymbol{r}(t)$ is considered as a stochastic variable that permits to treat the spin phase fluctuation by using a probability distribution as shown in eq. (2). When the short gradient pulse approximation fails, as in the cases of finite gradient pulses, multi-pulse gradient sequences or gradients of general waveform, the stochastic properties can be passed to the velocity of spin, $\boldsymbol{v}$. Since the mean of spin echo has a form of characteristic functional, it can be treated by the well-developed methods of statistical physics. Its cumulant expansion in the Gaussian approximation gives the spin echo as

$$E(\tau) = \sum_j E_{j0} e^{i\phi_j(\tau)-\beta_j(\tau)}. \tag{5}$$

where the phase shift depends on the local mean spin velocity

$$\phi_j(\tau) = -\int_0^\tau \boldsymbol{F}(t)\langle \boldsymbol{v}_j(t)\rangle \, \mathrm{d}t, \tag{6}$$

and the spin echo attenuation is related to the local velocity correlation function

$$\beta_j(\tau) = \frac{1}{2}\int_0^\tau \int_0^\tau \boldsymbol{F}_j(t_1)\cdot\langle \boldsymbol{v}_j(t_1)\ \boldsymbol{v}_j(t_2)\rangle_c \cdot \boldsymbol{F}_j(t_2)\,\mathrm{d}t_1\,\mathrm{d}t_2. \tag{7}$$

For a free motion in a simple fluid, the mean velocity is assumed to be zero $\langle v_{gj}(t)\rangle = 0$, while VCF is commonly approximated with $\langle v_{gj}(t)\ v_{gj}(0)\rangle = 2D\delta(t)$, due to a short memory of molecular collisions. Substitutions into eq. (5) gives the exponential decay of spin echo that is proportional to the spin mean-squared displacement.

For the motion in complex systems, there are a number of characteristic time scales, which correspond to frequency regime of spin echo. These include a long-tail decay of VCF in liquids [23,24], tube disengagement times in entangled polymers [25], a characteristic negative decay of VCF in confined fluids [26,27]. Such times are more closely related to the structural dynamics of a liquid than to local particle motion, and usually results in an anomalous time-dependent spin echo attenuation.

In the previous use of this method for the spin echo measurement of restricted motions [13, 28], the terms of cumulant expansion were averaged over the volume of confinement. It averaged out the phase shift $\overline{\langle \boldsymbol{v}\rangle} = 0$, and the attention had been focused to the second term of expansion. Such approximation provides a known relation between the spin echo attenuation and VCF [17], but is permitted as long as the gradient sequence is short enough or when the gradients are weak enough. In general analysis, the role of local distributions of the spin phases and spin echo attenuation must be carefully considered.

Distribution of velocity correlation function and mean velocity of confined motion. – For the diffusion in restricted geometries, the approximations, with $\langle v_g(t)\rangle = 0$ and with the VCF as a delta-function, are reasonable as long as the number of molecular impacts at walls is small compared to the number of intermolecular collisions, $\tau_\mathrm{c} \ll t \ll \tau_\mathrm{w}$. At longer times,

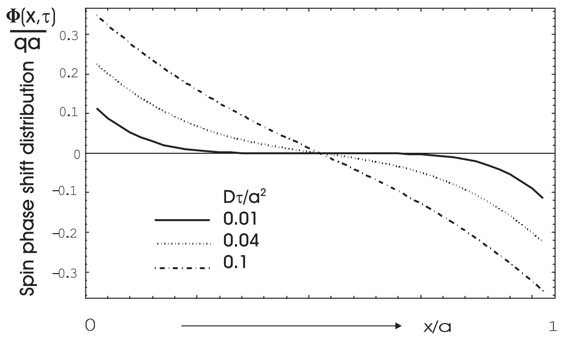

Fig. 1 – Distribution of the spin phases for the diffusion between plan-parallel planes with the sharp PGSE.

we need better approximations. The solution of the Langevin equation for diffusion between parallel planes provides such VCF [27], which is identical to that obtained with the use of the probability distribution of Fick's diffusion equation [29]. Using the last method, the conditional probability function of the restricted diffusion can be written in general as

$$P(\boldsymbol{r}, t \mid \boldsymbol{r}_o, t_o) = \sum_k \psi_k(\boldsymbol{r})\psi_k(\boldsymbol{r}_o)e^{-k^2 D|t-t_o|},$$

where k and eigenfunctions $\psi_k(\boldsymbol{r})$ characterize the compartment geometry. The mean spin velocity follows from the first derivative of the mean spin displacement as

$$\langle \boldsymbol{g} \cdot \boldsymbol{v}(\boldsymbol{r}, t)\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\int_V \boldsymbol{g} \cdot (\boldsymbol{r} - \boldsymbol{r}')P(\boldsymbol{r}, t \mid \boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}', \tag{8}$$

where the unit vector $\boldsymbol{g}$ is aligned along the magnetic field gradient. The second derivative of the mean-squared displacement is the VCF as

$$\langle \boldsymbol{g} \cdot \boldsymbol{v}(\boldsymbol{r}, t)\boldsymbol{v}(\boldsymbol{r}, t) \cdot \boldsymbol{g}\rangle = \frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\int_V (\boldsymbol{g} \cdot (\boldsymbol{r} - \boldsymbol{r}'))^2 P(\boldsymbol{r}, t \mid \boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'. \tag{9}$$

In order to enlighten this point of view to the diffusive diffractions, we considered the simplest case, *i.e.* the use of the sharp PGSE sequence for the self-diffusion measurement

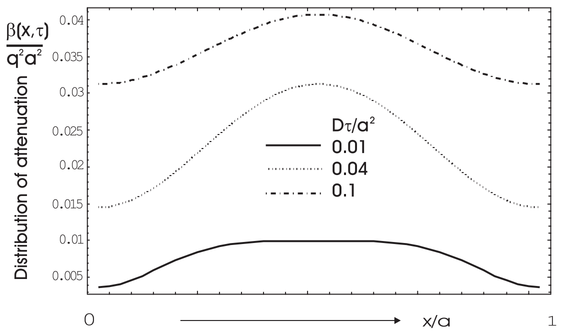

Fig. 2 – Distribution of the spin echo attenuation for the diffusion between plan-parallel planes with the sharp PGSE.

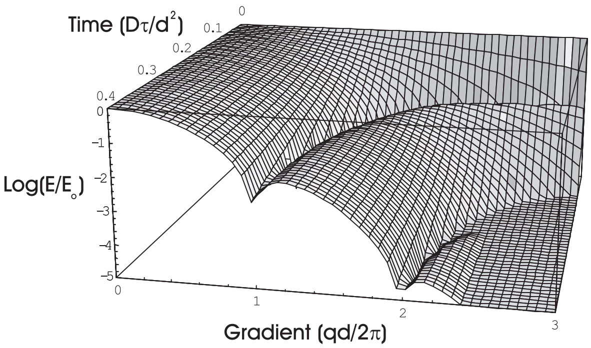

Fig. 3 – Time and gradient dependence of the diffraction patterns for diffusion between plan-parallel planes as observed with the sharp PGSE.

between parallel planes. With the use of eqs. (6), (7), (8) and (9), the distributions for the phase shifts and the spin echo attenuation at different times are provided, as shown in fig. 1 and 2. At early times after the first gradient pulse, only spins in the proximity of the wall are involved in the scattering. The component of mean velocity, aligned outward of boundaries, gives the resulting phase shift proportional to spin displacement, $\phi(\tau, \boldsymbol{r}) \approx q\sqrt{Dt}$, but with the opposite sign at the facing planes. At longer times, when the number of scattered spins increases, the phase shift develops into almost linear dependence on position in the pore, $\phi(\tau, \boldsymbol{r}) \approx \boldsymbol{q}(\boldsymbol{r} - \langle \boldsymbol{r} \rangle)$. As displayed in fig. 2, at early times, the distribution of the spin echo attenuation is almost uniform but with small dales in the proximities of the walls, but develops into a well-defined distribution with a maximum in the center of compartment with long diffusion displacements.

Such strong dependences of spin phases and attenuation on the location in the pore requires the analysis that includes the local details of motion. It does not permit an averaging over the space of compartment. Thus, in the continuum limit, the spin echo has to be written

$$E(\tau) = \int_V E(\boldsymbol{r})\, e^{i\,\phi(\tau,\boldsymbol{r}) - \beta(\tau,\boldsymbol{r})}\, \mathrm{d}\boldsymbol{r}^3, \tag{10}$$

where $\phi(\tau, \boldsymbol{r})$ and $\beta(\tau, \boldsymbol{r})$ describe the distribution of the spin phase and of the spin echo attenuation, respectively.

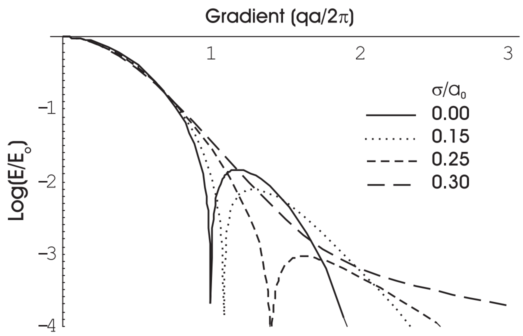

Fig. 4 – Long-time diffraction patterns for the irregularly displaced plan-parallel planes.

In the case of diffusion between parallel planes and when a sharp PGSE sequence is applied, the integration of eq. (10) gives diffraction-like patterns as shown in fig. 3. Diffusive diffractions exhibit the dependence on gradient magnitude q as well as on time τ. At short times, the diffraction minima are shifted toward larger q, and depend on the spin displacement as $2\sqrt{D\tau}q \approx n2\pi$. At large displacements, when each spin is starting to experience scattering at the opposite boundaries, the minima appear at value of $qa \approx n2\pi$, where a is the size of the pore. According to fig. 3, it occurs at the displacements above $2D\tau > 0.3a^2$. At these times, the spin echo with the sharp gradient pulses gets the form

$$E(\tau) \approx e^{-\frac{1}{2}\boldsymbol{q}^2(M_2-\boldsymbol{M}_1^2)}\left|\int_V e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{M}_1)}\,\mathrm{d}\boldsymbol{r}\right|, \tag{11}$$

where $\boldsymbol{M}_1 = \int_V \boldsymbol{r}\,\mathrm{d}\boldsymbol{r}$ and $M_2 = \int_V \boldsymbol{r}^2\,\mathrm{d}\boldsymbol{r}$.

When the planes are interspaced for a, it gives

$$E(\tau) \approx e^{-\frac{1}{24}(qa)^2}\left|\frac{2\sin(qa/2)}{q}\right|, \tag{12}$$

what is in the limit of small q

$$E(\tau) \approx e^{-\frac{1}{12}(qa)^2}. \tag{13}$$

Although the last result is the same as that obtained with the propagator approach [5], the dependence of the spin echo diffraction patterns on q and on the interval of measurement are very different, as shown in fig. 3.

Real porous media have a complex void associated with a distribution of pore size. In order to demonstrate the effect of diffraction in polydispersed porous media, the average over the pore size distribution is needed. Assuming the normal pore size distribution with the mean pore size a_0 and its variance as σ^2, the long-time approximation for diffusion between irregularly interspaced plan-parallel planes provides the diffraction patterns as shown in fig. 4. The broader the distribution, the larger the shift of the first minimum toward higher qa, until, for $\sigma/a_0 > 0.3$, the shape of diffraction patterns is getting less and less pronounced.

Conclusion. – The analysis with the cumulant expansion of the characteristic functional provides some new details of diffraction-like features that occur at the gradient spin echo measurement of diffusion and flow in porous media. It shows that the diffraction appears as the interference of phase shifts due to the back-flow of spins rebounding at walls. It conveys information about morphology of the surrounding media only at long times, when the boundaries restrict spin motion. The approach explains the diffraction dependence on the time and the duration of gradient pulses, as observed at the experiments and the simulations and shows the effect of the pore size distribution.

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