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Averaged propagator of restricted motion from the Gaussian approximation of spin echo

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Abstract

Apart from the propagator theory of spin-echo diffusion measurement, the average of spin phase fluctuation by the cumulant expansion is developed. The expansion to the second order, the Gaussian phase approximation (GPA), is able to explain the diffusion and flow measurement by the spin echo with the generalized magnetic field gradient sequence, which can be designed in a way to extract information not only about the macroscopic self-diffusion coefficient, but also about the details of the molecular velocity correlation spectrum. By taking into account the distribution of local spin properties resulting from restriction to motional by boundaries, the GPA method covers a broad range of spin echo decay, which throws a new light upon the diffraction-like phenomena, different from that, obtained by the averaged propagator method. The corrections of GPA by the higher order terms of cumulant expansion introduce only small changes to the tail of spin echo decay. The paper demonstrates the advantage of the GPA in this generalized form to deal with the space–time correlations of diffusion and flow in porous medium, closing a fictive gap between NMR diffusometry and *q*-space NMR.

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Keywords: Gradient spin echo; Nuclear magnetic resonance; Restricted self-diffusion; Porous media; Cumulant expansion; Diffusive diffraction

1. Introduction

The magnetic field gradient spin echo [1] provides a means to encode motions in the spin phase distribution in a manner, that enables to elucidate the macroscopic parameters of molecular translation dynamics. The methodology of the pulsed gradient spin echo (PGSE) [2] has been implemented to measure diffusion in systems for which the constrained molecular motion causes a deviation from simple Brownian motion. In heterogeneous systems, where boundaries restrict spin motion, the short pulse gradient spin echo (SPGSE) appears as the most efficient

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approach to probe molecular diffusion in small confining geometries, such as biologic tissues, chromatographic sieves, heterogeneous catalysts, concrete, rocks or clays, etc. The propagator method of spin echo explains the diffraction-like phenomena of spin echo [3], which can extract information not only about the motion but also about the morphology of the surrounding medium [4–7]. Unlike NMR imaging where molecular positions are recorded to a resolution on the order of 10 μm, the so-called spin echo diffusive diffraction is a promising tool to achieve the resolution of displacement measurement for two to three orders of magnitude better.

The first theoretical approach to the effect of molecular motion on the spin echo proposed by Hahn [1] and refined by Carr and Purcell [8] follows the translation motion of the individual spin-bearing molecules in the inhomogeneous magnetic field by evaluating the observable total magnetic moment of spins at the end. This approach proved extremely difficult to extend beyond the simplest spin echo sequence [9]. By introducing a diffusion term in the Bloch equation, Torrey [10] has proposed the hydrodynamic approach, where the spatial inhomogeneities of spin properties has to be small over the mean free path of molecular Brownian motion. This commonly used approach results in the diffusion propagator method (APM) [11], in which the spin echo appears as a Fourier transform of the probability distribution, which provides a clear visual perception of the tracer spreading in a medium [12].

In the theory of Brownian motion, the very fundamental method is grasping the thermal molecular motion as a stochastic process, which can be treated by the method of statistical physics. The spin echo averaging by the cumulant expansion method [13] is an alternative to the propagator method, but also an approach that paves the way for the revival of Hahn–Carr–Purcell method, which follows the detailed evolution of individual spin before the observable signal is evaluated. The cumulant expansion to the second order is sufficient for a kind of stochastic processes, named the Gaussian processes, where fluctuations are small in comparison to the averaged value. In the case of the gradient spin echo, the application of the Gaussian phase approximation (GPA) requires a weak the spin echo phase fluctuations due to spin motion in the non-uniform magnetic field. This method provides a link between spin echo signal and the properties of single spin i.e. the mean spin velocity and the mean velocity auto-correlation function [14,15]. Properly designed gradient-RF sequence is able to extract information not only about the macroscopic self-diffusion coefficient, but also about the details of the molecular velocity correlation spectrum of diffusion and flow dispersion [16–18]. Although, the velocity auto-correlation spectrum of unrestricted diffusion is flat, the molecular collisions with the barriers give rise to additional features, which might be in the frequency range accessible by the gradient spin echo sequences. As demonstrated by experiments on a water-saturated packed bed of 15 μm radius polystyrene spheres [19] and on emulsion droplets below 1 μm radius [20], this method has an access to a shorter time scales of diffusion measurement than the traditional two-pulse PGSE experiment.

Although, the GPA method provides an additional physical insight into spin echo relation to the microscopic details of diffusion and flow, it is commonly considered as an unsatisfactory condition in the case of restricted diffusion [3]. This allegation is a consequence of improper applications of the GPA method with the cumulant terms averaged over the space of motion. The GPA with ensemble-averaged cumulants (GPA-EA) cancels the first cumulant, which is particularly important, when the gradient phase grating is comparable to the characteristic length of heterogeneity in the porous medium. Consequently, the method fails to describe the effect of the diffusive diffraction [21,22], but provides correct results at a weak spin dephasing as shown in the appendix. Namely, the GPA-EA method reveals the spin echo decay in the intermediate range between the early square-root time dependence and its asymptotic transition into tortuocity regime not known before [23].

However, the analysis of MRI diffusive edge enhancement by the GPA-EA and the APM [24] came up with the fact that none of them is able to fit the result of simulation at long diffusion times. Both methods give correct edge-enhancement distribution at small displacements, but disagree with simulated image at long displacements and strong gradients. Corrections to the GPA-EA spin echo by higher order cumulants [25] brings attenuation distribution closer to the APM results, which demonstrates that the cumulant expansion series with the ensemble-averaged terms converges into the results of the APM. Therefore, we consider the GPA-EA method as an approximation to the APM in the case of restricted diffusion, which is sufficient condition only at weak gradients as shown in the appendix. However, the disagreement between the results of simulation and the theories points out a deficiency of present approaches to analyze the phenomena, where local spin properties may play significant role. Namely, the classic propagator method starts with the probability, which is averaged over all spins in the confinement, while the GPA-EA method uses the averaged velocity and the averaged velocity correlation.

We need an alternative approach, which takes into account local properties of moving spins. The analysis with the GPA method in a generalized form [22], which includes the local distribution of spin phase and attenuation, is able to describe a broader range of spin echo decay, including the phenomena of diffusive diffraction. However, the diffraction dependence on time and magnitude of applied gradient obtained by the generalized GPA method is quite different, when compared to the results of APM. It either indicates a conceptual problem with the GPA treatment or demonstrates the limits of the propagator formalism, because it combines the average of time fluctuation with the ensemble average.

Herein, we aim to extend the previous analysis, in which the generalized GPA method is introduced [22], by showing relations between the APM and the GPA approach in the case of SPGSE sequence. In order to differentiate between both approaches, we study the convergence of cumulant expansion series beyond the GPA to test the convergence of cumulant series and to establish regimes of GPA validity for the gradient spin echo of restricted motion.

2. Spin echo of restricted diffusion

2.1. Propagator method

By neglecting spin relaxations, the normalized signal of the gradient spin echo appears as a sum of spin contributions

$$E(\tau) = \sum_i \left\langle e^{i\int_0^\tau \mathbf{q}(t)\cdot\mathbf{v}_i(t)\,dt} \right\rangle, \tag{1}$$

where the brackets $\langle \cdots \rangle$ denote the averaging over the fluctuation of spin velocity, $\mathbf{v}_i(t)$, in the magnetic field gradient, $\mathbf{G} = \nabla|\mathbf{B}(\mathbf{r})|$, while the factor of spin dephasing $\mathbf{q}(t) = \gamma\int_0^t \mathbf{G}^*(t')dt'$, which is zero at the time of signal refocusing, τ, is the time integral of the effective gradient.

In the case of two short gradient pulse sequence (SPGSE), the APM [11,3] is commonly used to solve the mean of spin echo phase fluctuations. With the gradient pulse duration, δ, much shorter than their separation, Δ, i.e., $\delta \ll \Delta$, $\mathbf{q}(t) \approx \mathbf{q} = \gamma\,\mathbf{G}\delta$ and Eq. (1) can be written as

$$E(\tau) = \sum_i \left\langle e^{i\mathbf{q}\cdot[\mathbf{r}_i(\tau)-\mathbf{r}_i(0)]} \right\rangle = \sum_i \int P(\mathbf{r}_i + \mathbf{R}, \tau|\mathbf{r}_i) e^{i\mathbf{q}\cdot\mathbf{R}}\, d\mathbf{R}. \tag{2}$$

Here, the function $P(\mathbf{r}_i + \mathbf{R}, \tau|\mathbf{r}_i)$ describes the probability that the spin at the location $\mathbf{r}_i$ is displaced for $\mathbf{R}$ in time τ.

In the case of unrestricted diffusion, the probability is independent of the spin position $P(\mathbf{r}_i + \mathbf{R}, \tau|\mathbf{r}_i) = P(\mathbf{R}, \tau)$ giving the spin echo as the Fourier transform of probability propagator

$$E(\tau, \mathbf{q}) \approx N \int P(\mathbf{R}, \tau) e^{i\mathbf{q}\cdot\mathbf{R}}\, d\mathbf{R}. \tag{3}$$

Thus, the inverse Fourier transform of $E(\mathbf{q}, \tau)$ with respect to $\mathbf{q}$ returns the probability function—the propagator, which is particularly useful to visualize the tracer spreading in a medium.

In the case of diffusion restricted by boundaries, the probability function depends not only on the spin displacement, but also on the location of spin. In order to write the spin echo in the form of Eq. (3), an averaged propagator has to be introduced

$$P(\mathbf{R},\tau) = \frac{1}{N}\sum_i P(\mathbf{r}_i + \mathbf{R},\tau|\mathbf{r}_i), \tag{4}$$

which brings in a kind of ensemble-average over the space of confinement. Thus, the Fourier transform of spin echo, according to Eq. (4), returns the probability function, the averaged propagator of restricted diffusion, in which certain local performances of spins could be average out.

From Ficks' diffusion equation follows the probability function of restricted diffusion

$$P(\mathbf{r},\tau|\mathbf{r}_i) = \sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}_i)\mathrm{e}^{-\mathbf{k}^2 D\tau}, \tag{5}$$

where an orthonormal set of solutions $\psi_{\mathbf{k}}(\mathbf{r})$ are parameterized by the eigenvalue $\mathbf{k}$ depending on the boundary condition. With Eq. (2), it gives the spin echo

$$E(\tau,\mathbf{q}) = \sum_k |S_{\mathbf{k}}(\mathbf{q})|^2 \mathrm{e}^{-\mathbf{k}^2 D\tau} \tag{6}$$

with $S_{\mathbf{k}}(\mathbf{q}) = \int_V \psi_{\mathbf{k}}(\mathbf{r})\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r}$.

2.2. Cumulant expansion and the Gaussian phase approximation

In the case of SPGSE, we can avoid the approach with the characteristic function, used in Ref. [22], by deriving the cumulant expansion of spin echo directly from expression (2). In this way, we can demonstrate the method in a manner, which is more common in this field of research, but it limits the study to the measurements by SPGSE sequence.

The Taylor expansion of Eq. (2) with respect to $q = |\mathbf{q}|$ gives the spin echo in a form of infinite series of moments:

$$\begin{aligned} E(\tau,\mathbf{q}) &= \sum_i \int P(\mathbf{r},\tau|\mathbf{r}_i)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}_i)}\mathrm{d}\mathbf{r} \\ &= \sum_i \int P(\mathbf{r},\tau|\mathbf{r}_i)\mathrm{e}^{\mathrm{i}q(z-z_i)}\,\mathrm{d}\mathbf{r} \\ &= \sum_i \sum_{n=1}^{\infty} \frac{(\mathrm{i}q)^n}{n!} M_{n,i}(\tau), \end{aligned} \tag{7}$$

which are the averaged powers of spin displacement at location $\mathbf{r}_i$ along the applied gradient as

$$\begin{aligned} \mathbf{M}_{n,i}(\tau) &= \int P(\mathbf{r},\tau|\mathbf{r}_i)(z-z_i)^n\,\mathrm{d}\mathbf{r} \\ &= \langle (z-z_i)^n \rangle = \langle Z_i^n \rangle. \end{aligned} \tag{8}$$

In the next step, we transform the series of moments into the series of cumulant by using the formula [13]

$$E(\tau,q) = \sum_i \mathrm{e}^{\sum_{n=1}^{\infty}((\mathrm{i}q)^n/n!)K_{n,i}(\tau)}. \tag{9}$$

Here, the cumulant relation to the moments is

$$\begin{aligned} K_{1,i} &= M_{1,i} = \langle Z_i \rangle, \\ K_{2,i} &= M_{2,i} - M_{1,i}^2 = \langle (Z_i - \langle Z_i \rangle)^2 \rangle = \langle \Delta Z_i^2 \rangle, \\ K_{3,i} &= M_{3,i} - 3M_{2,i}M_{1,i} + M_{1,i}^3 = \langle (Z_i - \langle Z_i \rangle)^3 \rangle \\ &= \langle \Delta Z_i^3 \rangle, \\ K_{4,i} &= M_{4,i} - 6M_{1,i}^4 + 12M_{1,i}^2 M_{2,i} \\ &\quad - 3M_{2,i}^2 - 4M_{1,i}M_{3,i} \end{aligned} \tag{10}$$

It shows that the first cumulant in Eq. (9) is in proportion to the mean displacement of spin at the location $\langle \mathbf{r}_i \rangle$ along the applied gradient, the second cumulant is in proportion to the mean squared deviation from the mean displacement, $\langle \Delta Z_i^2 \rangle = \langle (Z_i - \langle Z_i \rangle)^2 \rangle$, the third cumulant is in proportion to the mean of third power of displacement deviation, etc.

The resulting spin echo, Eq. (9) has the phase, which consists of an infinite sum of odd powers in q multiplied by odd cumulants, while the attenuation is a polynomial of even powers in q multiplied by even cumulants. The cumulant expansion to the second order involves a class of stochastic processes, named the Gaussian processes, and has many applications in physics. Just as a normal distribution is defined by the mean and the variance, the Gaussian phase approximation of the gradient spin echo neglects all terms beyond second one in Eq. (9) as

$$E(\tau,q) = \sum_i \mathrm{e}^{\mathrm{i}q\langle Z_i(\tau)\rangle - (1/2)q^2\langle \Delta Z_i^2(\tau)\rangle}. \tag{11}$$

It claims that the local spin echo phase shift is determined only by the first power in q multiplied by the mean local spin displacements, while the spin echo attenuations is the second power in q

multiplied by the mean squared deviations from the mean displacement.

2.3. Diffusive diffractions of spin echo

For given distributions of mean spin displacement and mean squared displacement, Eq. (11) provides the spin echo decay as function of time and q. Fig. 1a graphically visualizes it as a plot of $\mathrm{Log}(|E/E_0|)$ for the case of diffusion between parallel planes. Sharp minimum in the signal decay is considered as a diffraction-like effect. Contrary to the results of the propagator theory, Fig. 1b, which follows from Eq. (6) the GPA spin echo exhibits the diffraction dependence not only on the gradient magnitude, q, but also on the time. The diffraction minima appears at the values $qa \approx n2\pi$, where a is the pore size, like in the case of evaluation by APM only when the spin displacement is comparable to compartment size. While at early times, the diffraction minima are shifted toward larger q. This result throws a new light upon the diffusive diffraction phenomena, quite different from that of the APM. According to GPA approach [22], the diffraction like effect is a result of interference of signals induced by spins at different locations within the confinement. Namely, the mean spin displacement $\langle Z_i \rangle$, which depends on the time and spin proximity to the boundary, has the direction perpendicularly back from the boundary. Thus, the signals induced by spins close to the opposite boundaries have opposite phase shifts. Their interference brings about the diffraction effect when the mean displacement matches the spin phase grating.

Along the same reasoning, we can explain the second difference concerning the phase reversal at the diffraction minima point, where the APM spin echo exhibits a transition through minimum as seen in Fig. 2. It is clearly displayed in the

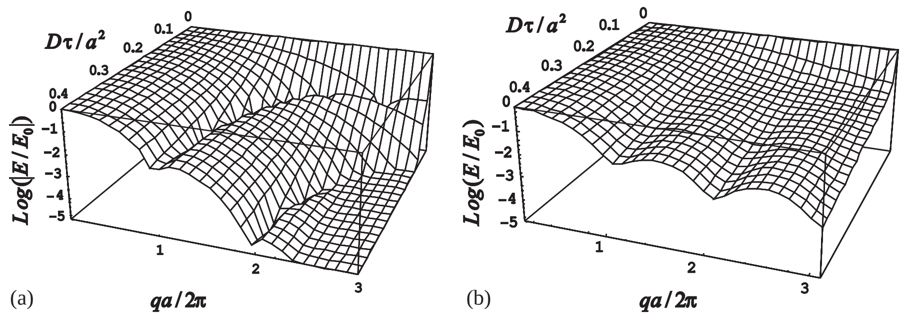

Fig. 1. Spin echo of diffusion between plan-parallel planes as function of time and spin dephasing q by different methods: (a) the GPA method, (b) the APM.

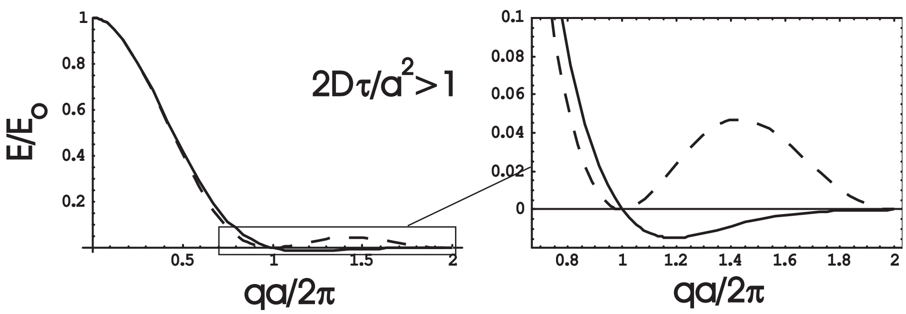

Fig. 2. Long-time limit of spin echo q dependence for the diffusion between plan-parallel planes by the GPA and by the APM (dotted curve).

long-time limit of the spin echo, when the phase shift distribution develops into almost linear dependence on position within the compartment, while the attenuation becomes almost uniform within a pore [22]. In this limit, the GPA spin echo gives from Eq. (11)

$$E(\tau, q) \approx e^{-(1/2)q^2(m_2 - m_1^2)} \int_V e^{iq(z-m_1)}\, dz, \tag{12}$$

where $m_1 = (1/V)\int_V z\, dz$ and $m_2 = (1/V)\int_V z^2\, dz$, while the APM gives from Eq. (6) the long time limit as

$$E(\tau, q) = |S_{\mathbf{o}}(q)|^2 = \left| \int_V e^{iq(z-m_1)}\, dz \right|^2. \tag{13}$$

In both cases, the factor $\int_V e^{iq(z-m_1)}\, dz$ is responsible for the diffraction-like patterns. However, in case of GPA Eq. (12), it reverses the spin phase at $qa = 2\pi$, while its squared absolute value, in the APM expression Eq. (13), provides the minimum at the same point.

2.4. Averaged propagator by GPA method

Gaussian form of spin echo in Eq. (11) permits to write the spin echo in the propagator form

$$E(\tau, \mathbf{q}) = \int P(\mathbf{R}, \tau) e^{i\mathbf{q}\cdot\mathbf{R}}\, d\mathbf{R} \tag{14}$$

with the averaged propagator defined as

$$P(\mathbf{R}, \tau) = \sum_i \frac{1}{\sqrt{2\pi \langle \Delta\mathbf{R}_i^2(\tau) \rangle}} e^{\frac{[\mathbf{R} - \langle \Delta\mathbf{R}_i(\tau) \rangle]^2}{2\langle \Delta\mathbf{R}_i^2(\tau) \rangle}}. \tag{15}$$

Thus, the inverse Fourier transformation of $E(\tau, \mathbf{q})$ with respect to $\mathbf{q}$ returns the propagator $P(\mathbf{R}, \tau)$, which is a distribution of normal probability functions of spins at different sites. The mean and the variance of these normal probability functions is the mean displacement $\langle \mathbf{R}_i(\tau) \rangle$ and the mean squared deviation of spin displacement $\langle (\Delta\mathbf{R}_i^2(\tau) \rangle$ at the location $\mathbf{r}_i$, respectively.

We can use the probability function from Fick's diffusion equation, Eq. (5), to evaluate the distributions of the mean spin displacement and the mean squared deviation of spin displacement within the space of confinement. While in the case of flow through porous medium, the Taylor's diffusion-dispersion equation is an option.

At least on the first sight, the averaged propagator of the GPA method, Eq. (15), looks quite different from that derived by the APM, due to differences in the form of Eq. (15) compared to Eq. (5) and theirs quite different dependence on q and time. In the case of diffusion between parallel planes with the inter-distance a, the long-time limit of the GPA spin echo follows from Eq. (12) as

$$E(\tau) \approx e^{-(1/24)(qa)^2} \frac{2\sin(qa/2)}{q}. \tag{16}$$

Its q-space Fourier transformation returns the average propagator

$$P(z) = \frac{1}{2a}\left[\mathrm{Erf}\left(\frac{\sqrt{\frac{3}{2}}(a - 2Z)}{a} \right) + \mathrm{Erf}\left(\frac{\sqrt{\frac{3}{2}}(a + 2Z)}{a} \right) \right]. \tag{17}$$

The Fourier transform of the long-time limit of APM spin echo in Eq. (13)

$$E(\tau) \approx \left(\frac{2\sin(qa/2)}{q} \right)^2 \tag{18}$$

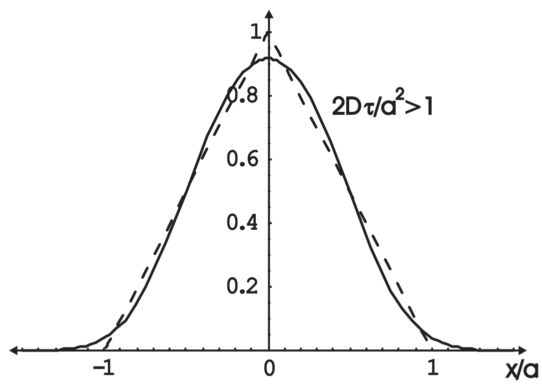

Fig. 3. Averaged propagator in the long-time limit of diffusion between parallel plates as obtained from the GPA spin echo and from the APM [3] (dotted lines).

results in the averaged propagator

$$P(Z) = \frac{1}{2a^2}[|a+Z| - 2|Z| + (a-Z)\,\mathrm{Sign}(a-Z)]. \qquad (19)$$

Plot of Eqs. (17) and (19) as function of spin setting in Fig. 3 shows the GPA propagator as a kind of round-off copy of the sharp-edged propagator of the APM. Thus, a closer inspection reveals much smaller differences between both propagators. It demonstrates that the propagator presentation conceal diversity of both approaches and perhaps confirms a statement from the statistical physics [26] that the description with the probability function sacrifices a part of information by some coarse graining procedure.

3. Corrections by higher orders of cumulant expansion

In the next step, we are trying to estimate corrections to the GPA by the terms of higher order of cumulant expansion in Eq. (9). In the continuum limit, we can write the cumulant expansion of spin echo as

$$E(\tau,q) \approx \int_V \rho(\mathbf{r})\, e^{\sum_{n=1}^{n_o} ((iq)^n/n!)K_n(\tau,\mathbf{r})}\,d\mathbf{r}. \qquad (20)$$

For the restricted diffusion between parallel planes with uniform spin distribution, the expansion to the fourth term gives the signal dependence on q at different times as shown in Fig. 4. At short time intervals, the first diffraction minimum of corrected spin echo exhibits even stronger time dependence than that of GPA. However, it also shows a disappearance of minimum at very short displacements, confirming the ascertainment that the diffraction effect is the phase interference of rebounding spins. Namely, the fraction of rebounding spins is very small at very short diffusion displacements.

Cumulant terms higher than the fourth one do not reverse the most distinct difference between the methods: the signal phase reversal at $qa = 2\pi$ as appears with the GPA method. Fig. 5 shows the spin echo dependence on q is changing with increasing correction by the third, the fourth, the fifth, the sixth, and the seventh order of cumulant expansion. Clearly, the corrections to the spin phase shift by the third, fifth and seventh cumulants have almost no effect on the q dependence, demonstrating the significance of the first-phase term, which is already included in the Gaussian phase approximation. The fourth and sixth cumulant terms, which represent correction to the attenuation, have noticeable but weak influence when $aq \leqslant 2\pi$, which cannot be totally neglected at $qa > 2\pi$.

Thus, the contributions of higher-order cumulants only slightly increase the spin echo attenuation at large q, but do not indicate that the corrected signal is converging into the result of APM as it occurs with the GPA-EA method. It means that, in addition to the time dependence of diffraction minima, the spin echo phase reversal at the diffraction point is a result of the cumulant expansion to any order.

Fig. 6 shows that the correction to the seventh order of cumulant expansion makes almost no difference to the shape of the averaged propagator, confirming a fast convergence of the cumulant series in the case of restricted diffusion.

4. Conclusion

The generalized GPA method, which accounts for the local distributions of spin phase and spin attenuation, enables the spin echo analysis in a broad range of decay. The method gives a new insight into the diffraction-like effect of spin echo, by explaining it as the phase interference of spins rebounding at the opposite walls. The most distinct difference compared to the APM results is the phase reversal at the point, where the APM gives the diffraction minimum as well as the dependence of diffraction minimum on time. The cumulant terms of higher order, beyond the second one, bring about only small corrections to the spin echo decay and to the form of averaged propagator, which does not reverse the basic points resulting from the GPA method.

Thus, the inclusion of local spin properties results in the GPA method, which is a fully satisfactory condition for the gradient spin echo

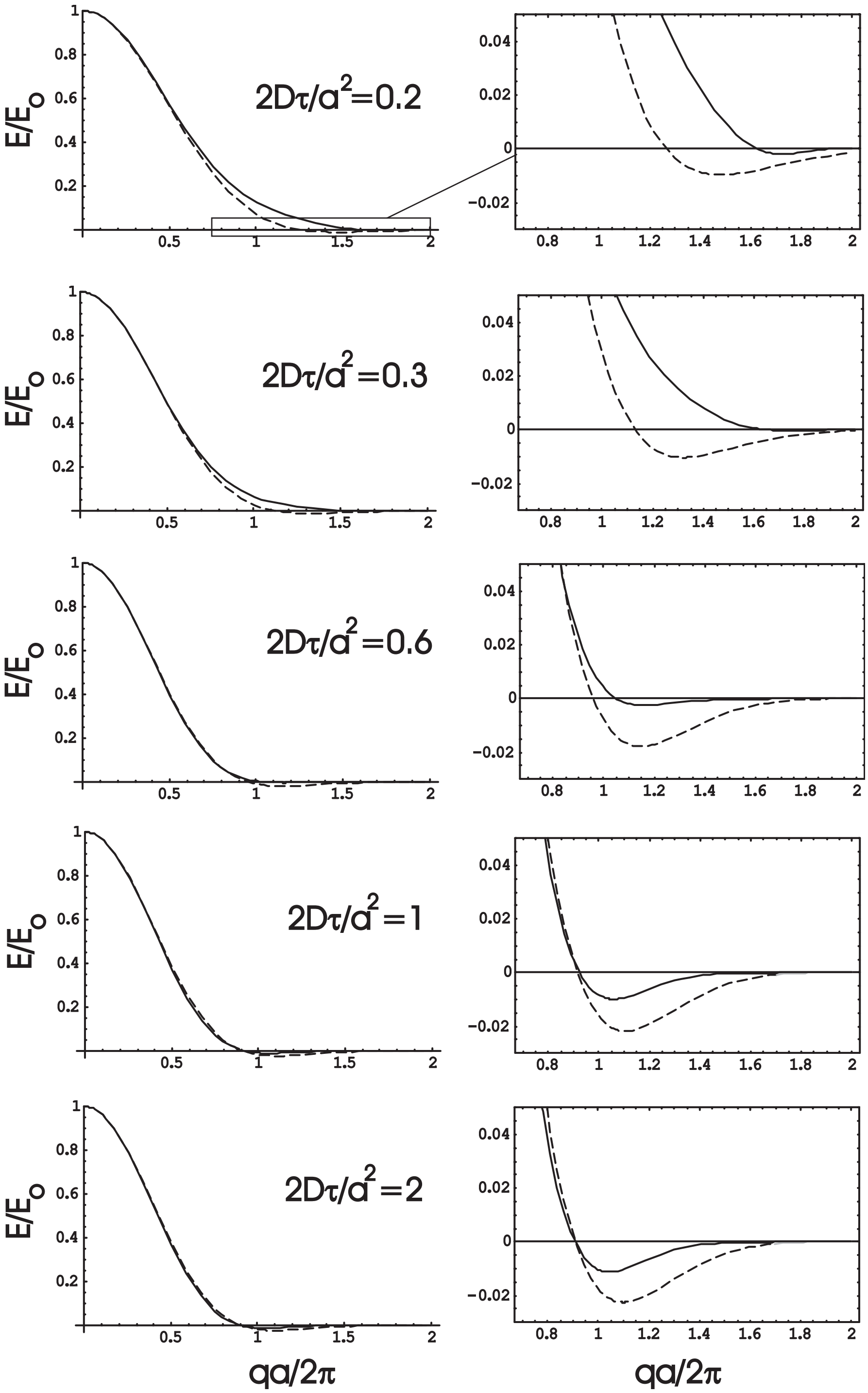

Fig. 4. Time dependence of spin echo q dependence with the correction to the fourth order of cumulant expansion and by the GPA method (dotted curve).

of restricted motion. Its averaged propagator is the distribution of normal probability functions of spins positioned at different sites in the medium. The spin displacement shifts the mean of each distribution along the local flow, while the variance of probability is the mean squared deviation from the mean spin displacement, which is associated with the diffusion or flow dispersion. This result can be applied very well to the measurement of diffusion and flow dispersion [27] as well as the result of simulations [28] in porous media.

The basic difference between both approaches seems to be in the fundamental of statistical physics. Namely, in order to reach the macroscopic of observation starting from the very microscopic level, we have to climb up successive levels of coarse graining. In going up each level of this staircase, a certain amount of information gets lost and a corresponding uncertainty is added to the probabilistic description [26]. The ensemble-average over the space of compartments with the average propagator method, as well as with the GPA-EA method, adds uncertainty about details of motion. By accounting for the local properties of correlation functions, the generalized GPA method of spin echo is atleast a stair step closer to the microscopic description.

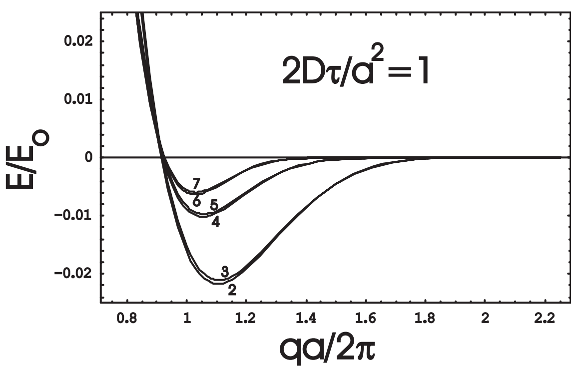

Fig. 5. Development of spin echo with the corrections from the second to the seventh order of cumulant expansion.

The GPA method makes possible to revive the old Hahn–Carr–Purcell approach to the effect of molecular diffusion and flow on the outcome of spin echo experiment, particularly when, instead of the simplest SPGSE case, the GPA is used for the spin echo of generalized gradient-RF sequence as shown in reference [22].

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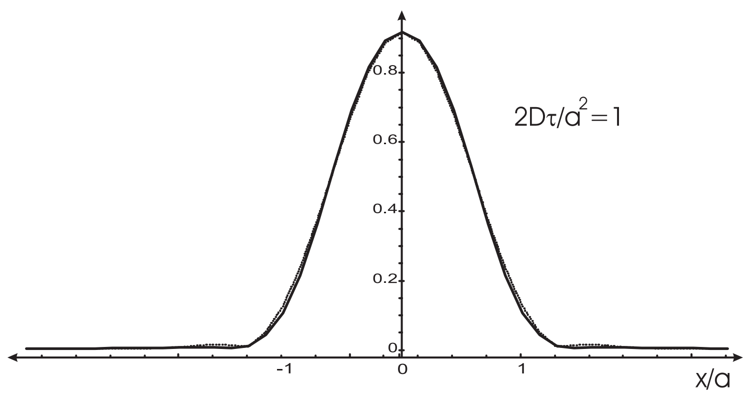

Fig. 6. Averaged propagator of diffusion between parallel plates as obtained from the GPA method and from the cumulant expansion to the seventh order (dotted curve).

Appendix A. Ensemble average of GPA spin echo

According to GPA method, the gradient spin echo consists of contributions, which have the phase and the attenuation dependent on the spin location as

$$E(\tau, q) = \sum_i e^{iq\langle Z_i(\tau)\rangle - (1/2)q^2\langle \Delta Z_i^2(\tau)\rangle} = \sum_i e^{iq\langle Z_i(\tau)\rangle - (q^2/2)(\langle Z_i^2(\tau)\rangle - \langle Z_i(\tau)\rangle^2)}. \quad (A.1)$$

In the case of diffusion in a polydispersive medium, the signal can be separated into contributions with index ij denoting spins within jth pore. The cumulant expansion with respect to the ensemble average of spins within a single pore gives the spin echo

$$E(\tau, q) = \sum_j E_{jo} e^{iq\overline{\langle Z_j(\tau)\rangle} - (q^2/2)\overline{\langle Z_j^2(\tau)\rangle} + q^4\Delta\beta_j^2(\tau) + \cdots}. \quad (A.2)$$

Here, E_{jo} determines a contribution of spins in the jth pore, with the phase shift averaged out because $\overline{\langle Z_j\rangle} = (1/N)\sum_i \langle Z_{ij}\rangle = 0$ in the case of diffusion, while the ensemble-averaged mean squared displacement $\overline{\langle Z_j^2\rangle} = (1/N)\sum_i \langle Z_{ij}^2\rangle$ brings about the signal attenuation. The correction to GPA-EA comes from the fourth order of cumulant expansion

$$\Delta\beta_j^2 = \frac{1}{4N}\sum_i \left[\frac{1}{2N}\sum_{i'} (\langle Z_{ij}^2\rangle - \langle Z_{i'j}^2\rangle)^2 - \frac{1}{3}\langle Z_{ij}\rangle^4\right], \quad (A.3)$$

which is an ensemble-averaged differences of the mean squared displacement within the single pore subtracted for the ensemble-averaged fourth power of the mean spin displacement.

As long the applied gradient is weak enough that $q^2\Delta\beta_j \ll \overline{\langle Z_j^2\rangle}/\Delta\beta_j$, the higher terms of cumulant expansion can be neglected. Clearly, the inhomogeneities of local spin properties multiplied by the spin dephasing determine the Gaussian approximation sufficiency. In order to break the GPA condition, we need to apply a gradient strong enough to enhance small differences in the local spin properties. In the case of restricted diffusion between parallel planes interspaced for a, it means that the gradients with $qa < \pi$ satisfy the Gaussian approximation in the long-time limit.

References

[1] E.L. Hahn, Phys. Rev. 80 (1950) 580.
[2] E.O. Stejskal, J.E. Tanner, J. Chem. Phys. 42 (1965) 288.
[3] P.T. Callaghan, Principles of Nuclear Magnetic Resonance Microscopy, University Press Oxford, Oxford, 1991.
[4] P.T. Callaghan, A. Coy, D. MacGowan, K.J. Packer, F.O. Zelaya, Nature 351 (1991) 467.
[5] A. Lennon, P. Kuchel, J. Magn. Reson. Ser. A 111 (1994) 208.
[6] J.D. Seymour, P.T. Callaghan, J. Magn. Reson. Ser. A 122 (1996) 90.
[7] C.D. Panfilis, K. Packer, Eur. Phys. J. Astro. Phys. 8 (1999) 77.
[8] H.Y. Carr, E.M. Purcell, Phys. Rev. 94 (1954) 630.
[9] J. Jeener, Concepts Magn. Reson. 14 (2002) 79.
[10] H.C. Torrey, Phys. Rev. 104 (1956) 563.
[11] J. Kärger, W. Heink, J. Magn. Reson. 51 (1983) 1.
[12] D.G. Cory, A.N. Garroway, Magnet. Reson. Med. 4 (1990) 435.
[13] N. van Kampen, Stochastic Processes in Physics and Chemistry, North-Holland, Amsterdam, 1981.
[14] P.D. Gennes, Phys. Lett. A 29 (1969) 20.
[15] J. Stepišnik, Physica B 104 (1981) 350.
[16] P. Callaghan, J. Stepišnik, J. Magn. Reson. Ser. A 117 (1995) 118.
[17] P. Callaghan, J. Stepišnik, Generalised analysis of motion using magnetic field gradients, in: W.S. Waren (Ed.), Advances in Magnetic and Optical Resonance, Vol. 19, Academic Press, San Diego, 1996, pp. 326–89.
[18] P.T. Callaghan, S.L. Codd, Phys. Fluids 13 (2002) 421.
[19] J. Stepišnik, P. Callaghan, Physica B 292 (2000) 296.
[20] D. Topgaard, C. Malmborg, O. Soederman, J. Magn. Reson. 156 (2002) 195.
[21] J. Stepišnik, J. Magn. Reson. 131 (1998) 339.
[22] J. Stepišnik, Europhys. Lett. 60 (2002) 453.
[23] A.M.J. Stepišnik, A. Duh, Physica B 307 (2001) 158.
[24] A. Duh, A. Mohorič, J. Stepišnik, J. Magn. Reson. 148 (2001) 257.
[25] A. Duh, Restricted self-diffusion and edge enhancement at NMR microscopy, Thesis, University of Ljubljana, Ljubljana, 1999.
[26] R. Kubo, Some Aspects of the Statistical–Mechanical Theory of Irreversible Processes, Lectures on Theoretical Physics, Interscience, New York, 1959.
[27] J.J. Tessier, K.J. Packer, Phys. Fluids 10 (1998) 75.
[28] S. Stapf, Phys. Fluids 12 (2000) 566.