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Validity limits of Gaussian approximation in cumulant expansion for diffusion attenuation of spin echo

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Abstract

Cumulant expansion is a way to average out the spin frequency fluctuations, caused by molecular random migration in nonuniform magnetic field, in order to get spin echo attenuation. Since numerous spins have a share in NMR induction, the cumulative yield of frequency fluctuations features Gaussian randomness. Thus the cumulant expansion can be terminated by the second term giving the spin echo attenuation related to the time-correlation of molecular motion (Stepišnik, Physica B 104 (1981) 350) and to the time-space-correlation in the case of restricted self-diffusion. The validity limits of this approximation is tested by considering the convergence of the cumulant series. The estimate of high-order velocity correlations displays that the gap between the magnetization grating (spin-phase structure) caused by applied gradient field has to be much larger than the free path of moving spins. With the spins in confinement, the spin phase structure can be written as composition of plane waves (Stepišnik, J. Phys. 39 (1978) 689; Stepišnik, J. Magn. Res. 131 (1998) 339). The cumulant expansion in Gaussian approximation gives the spin echo attenuation as a discord of magnetization grating that can exhibit the diffusive diffraction patterns of porous structure (Coy, Callaghan, J. Chem. Phys. 101 (1994) 4599). Advantage of method is its ability to be implemented with any general gradient pulse sequence, i.e., the gradient pulses can violate the short pulse approximation that is required with the propagator method.

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1. Introduction

Processes in nature are often accompanied or even stipulated by molecular migration. Therefore, the investigation of diffusion phenomena has been important in both fundamental research and industrial applications. The scientific interest has focused on the development of efficient methods for their measurement. Among these techniques, the spin echo, which detects molecular displacements through precession of their atomic nuclear spins in non-uniform magnetic field, has gained most decisive role for measurement in fluids. It started at the beginning of NMR, when Hahn [5] pointed out that the Brownian motion would affect the spin echo amplitude in the presence of local magnetic

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field inhomogeneity. With the use of multiple pulse train, Carr and Purcell [6] developed formalism for relating the echo amplitude to the discrete hops of the spins, while Torrey [7] developed a continuum approach based on the magnetization diffusion equation, the so-called Bloch–Torrey equation. Stejskal and Tanner [8] initiated the methodology and theory of the pulsed gradient spin echo (PGSE) experiment. It was implemented to measure diffusion in systems for which restriction to motion caused a deviation from Fickian behavior. Based on the propagator method [9] and the Fourier q-space approach, Callaghan introduced spin echo diffusion diffraction [10]. It makes possible to extract information not only about the motion of molecules but also about the geometry of the boundaries and hence about the pore morphology of the surrounding medium.

The method has achieved a level of sophistication, which far exceeds those being reached by other methods. It provides new insight into transport phenomena on a microscopic level.

The signal of spin echo arises from the induction of immense number of spins $\gg 10^6$ where one cannot detect the magnetization of individual molecule undergoing Brownian motion but rather detects the induction signal created by innumerable spins, instead. In a non-uniform magnetic field, the molecular displacements cause many small perturbations of spin precession frequencies. The cumulative effect of a large number of small perturbations of spin precession frequency can be considered to be a Gaussian random process [1–3]. The bedrock of this method is the evaluation of the spin phase mean with the cumulant expansion in Gaussian approximation [11] (Appendix A), when all cumulants beyond the second order can be neglected. This approximation is often used to describe physical processes and can be justified in many processes in magnetic resonance as well.

Thus the ensemble average of spin phases with cumulant expansion directly provides diffusion attenuation of gradient spin echo [1,3]. It links the single-particle velocity correlation that contains details of motion and interaction on the molecular level to macroscopic variables. Thus the spin echo attenuation becomes a window looking into the world of molecular motion. Its opening is determined by form of gradient pulse sequence [12–15]. When sufficiently fast and properly shaped sequences are applied, it can be a tool to acquire information not only about macroscopic flow and diffusion but about the motion on a molecular level as well [16,17].

This method has been used to explain spin echo attenuation caused by restricted diffusion as well [18,3]. Owing to molecular confinements in the pore, the spin phase structure is composed of a series of plane waves with the wave vectors related to allowable momentum states of confined particles. Thus the ensemble average of the wave phase relates spin echo to the components of spin phase structure within the pore which are attenuated by a factor depending on the mean square displacement of particle in restricted geometry [3].

Although the method deepens insight into the phenomena of spin echoes and provides a simple derivation of spin echo attenuation for any gradient pulse sequence, questions have been raised, whether the Gaussian approximation can be justified for a molecular diffusion [19], or it is just an approximation with limited usefulness [20,21]. Our aim here is to clarify some details of the spin phase averaging with the cumulant expansion and point-out its successful application to free and restricted molecular self-diffusion.

2. Spin echo of moving particles

Free precession of the spin system is observed through voltage induced in a coil around the sample. Generally, in the case of quadrature detection where spin–spin relaxation is neglected, we can write the signal as [12,17]

$$E(t) = \sum_i M_i S(\boldsymbol{r}_i, t) \mathrm{e}^{\mathrm{i}\theta_i(t)}. \tag{1}$$

Migration of ith spin-bearing particles is encoded in the signal phase

$$\theta_i(t) = \gamma \int_0^t \boldsymbol{G}(t) \,.\, \boldsymbol{r}(t)\, \mathrm{d}t, \quad \boldsymbol{G}(t) = \mathrm{grad}|\boldsymbol{B}(\boldsymbol{r}, t)| \tag{2}$$

through the magnetic field inhomogeneity and in its amplitude through the spatial variation of transmitting magnetization M_i and receiving RF field sensitivity $S(\boldsymbol{r}_i)$. This means that various inhomogeneities can provide information about flow or diffusion. It is important to note that RF gradients also can be used for the measurement of the particle migration. It works not only as spin dephasing by RF inhomogeneity in the rotating frame but also to provide the correlation between the initial distribution of excited spins and the final one at the time of detection. In this study we will neglect the effect of RF inhomogeneity.

Brownian motion causes the fluctuation of $\theta_i(t)$ via its dependence on the location of spin in inhomogeneous magnetic field. After a stochastic displacement, the spin location changes as

$$\boldsymbol{r}_i(t) = \boldsymbol{r}_i + \partial\boldsymbol{r}_i(t) = \boldsymbol{r}_i(0) + \int_0^t \boldsymbol{v}_i(t')\,\mathrm{d}t', \tag{3}$$

where $\boldsymbol{v}_i(t)$ is a particle velocity. The normalized spin echo amplitude at the time t can be written as [17]

$$E(t) = \sum_i \mathrm{e}^{\mathrm{i}\gamma\int_0^t \boldsymbol{G}_i(t')\boldsymbol{r}_i(t')\,\mathrm{d}t'}$$

$$= \sum_i \mathrm{e}^{\mathrm{i}\boldsymbol{F}_i(t)\boldsymbol{r}_i(0) + \mathrm{i}\int_0^t [\boldsymbol{F}_i(t) - \boldsymbol{F}_i(t')]\boldsymbol{v}_i(t')\,\mathrm{d}t'}, \tag{4}$$

where

$$\boldsymbol{F}(t) = \gamma\int_0^t \boldsymbol{G}(t')\,\mathrm{d}t', \tag{5}$$

disappears at time of the spin refocusing, $t = \tau$, giving

$$E(\tau) = \sum_i \mathrm{e}^{\mathrm{i}\int_0^\tau \boldsymbol{F}_i(t)\boldsymbol{v}_i(t)\,\mathrm{d}t}. \tag{6}$$

Clearly, the sum over individual spins i means that the spin echo, Eq. (6), is a coherent superposition of signals from a very large number of spins. Because of this we need to introduce the ensemble-averaging and group spins into separate sub-ensembles for which the effect of applied fields is different but where particles exhibit similar motional behavior. For example, concerning their location in non-uniform magnetic field, one might distinguish groups of spins according to their precession frequency. For such grouping the averages within the sub-ensembles has to be performed. Thus the summation over individual spins in Eq. (6) is replaced by the summation over the sub-ensembles of spins as

$$E(\tau) = \sum_j E_{jo}\langle \mathrm{e}^{\mathrm{i}\int_0^\tau \boldsymbol{F}_j(t)\boldsymbol{v}_j(t)\,\mathrm{d}t}\rangle \tag{7}$$

but where $\langle\cdots\rangle$ means the ensemble average over the variable of particles in the jth sub-ensemble. E_{jo} is the resulting signal of all spins of the jth sub-ensemble.

We now turn our attention to general diffusion of molecules inside completely enclosing pores. We shall start with an ordinary PGSE sequence where two rectangular gradient pulses of duration δ separated by time Δ are applied. In the limit of very short gradient pulses, there is a simple relationship between the location of spin–particle and the spin phase

$$E(\Delta) = \sum_i \mathrm{e}^{\mathrm{i}\boldsymbol{F}\cdot[\boldsymbol{r}_i(\Delta) - \boldsymbol{r}_i(0)]}, \tag{8}$$

where $\boldsymbol{F} = \gamma\delta\boldsymbol{G}$. $\boldsymbol{r}_i(0)$ denotes the location of individual spin when the first gradient pulse is applied, while $\boldsymbol{r}_i(\Delta)$ is its location after the phase refocusing by the second gradient pulse. The first gradient pulse creates the spatial distribution of spin phases within the compartment as $\mathrm{e}^{-\mathrm{i}\boldsymbol{F}\cdot\boldsymbol{r}_i(0)}$. We call it *spin phase structure* instead of commonly used *magnetization grating* [10,22]. It seems to us that it better suits our explanation of this phenomena.

The spin phase structure is defined within a compartment, and depends on conditions at the boundaries. The confinement imposes constrains to the allowed states of spin-bearing particles resulting in the spin phase structure being expressed as a composite of plane waves

$$\mathrm{e}^{\mathrm{i}\boldsymbol{F}\cdot\boldsymbol{r}} = \sum_{\boldsymbol{k}} S_{\boldsymbol{k}}(\boldsymbol{F})\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{9}$$

Here the nonzero wave vectors $\boldsymbol{k}$ denote allowable momentum states of confined particles [3]. The

terms $S_k(\boldsymbol{F})$ are the components of spin phase structure in reciprocal space.

The spin phase coherence does not refocus completely after the second gradient pulse because migration of spin-bearing particles will cause changes in their locations as $\boldsymbol{r}_i(\tau) = \boldsymbol{r}_i(0) + \partial\boldsymbol{r}_i(\tau)$. With substitution of Eq. (9) in Eq. (8) the spin echo is

$$E(\Delta) = \sum_i \sum_k S_k(\boldsymbol{F}) e^{i(\boldsymbol{k}-\boldsymbol{F})\cdot\boldsymbol{r}_i(0)} e^{i\boldsymbol{k}\cdot\partial\boldsymbol{r}_i(\Delta)}. \tag{10}$$

Clearly, the spread in phase shifts made by particle displacement in time Δ reduces phase refocusing and can be considered as a measure of spin phase structure discord. Applying the average over the sub-ensemble like in the previous case, Eq. (10) becomes

$$E(\Delta) = \sum_j E_{oj} \sum_k S_k(\boldsymbol{F}) e^{i(\boldsymbol{k}-\boldsymbol{F})\cdot\boldsymbol{r}_j(0)} \langle e^{i\boldsymbol{k}\cdot\partial\boldsymbol{r}_j(\Delta)}\rangle. \tag{11}$$

Here, the summation over j means again the summation over the different spin sub-ensembles being formed of spins subjected to nearly the same magnetic fields.

When long gradient pulses or gradients of general modulated waveform are applied the spin phase structure is not created in a step, as in the case of short pulses, but is built up during extended gradient intervals. The formation of spin phase structure is accompanied by particle motion tending to destroy its build up. Therefore, we defined [3] a *mean spin dephasing* of moving spins, while the gradient is applied for duration τ, as

$$\boldsymbol{F}_a(\tau) = \frac{\boldsymbol{f}}{R_{gi}(\tau)} \sqrt{\int_0^\tau \int_0^\tau \boldsymbol{F}(t_1)\langle \boldsymbol{v}_i(t_1).\boldsymbol{v}_i(t_2)\rangle_c \boldsymbol{F}(t_2)\,dt_1\,dt_2}. \tag{12}$$

The unit vector $\boldsymbol{f}$ is aligned along the direction determined by cumulative effects of applied gradients. The mean square particle displacement of particles along the applied gradient, $R_g^2(\tau, \boldsymbol{r})$, depends on duration of applied gradients as well as on the location of particles in the confinement but, due to similar location dependence of correlation function, $F_a(\tau)$ is approximated as a homogeneous one within the volume of pore. These definitions are explained in more detail in Refs. [3,23].

As in the case of short gradient pulses, we can write the correlation between the non-uniform spin phase structure at different times as

$$E(\tau) = \sum_j E_{oj} \langle e^{i\int_0^\tau \boldsymbol{F}(t)\cdot\boldsymbol{v}_j(t)\,dt}\rangle = \sum_j E_{oj} \langle e^{i\boldsymbol{F}_a\boldsymbol{r}_j(0)} e^{-i\boldsymbol{F}_a[\boldsymbol{r}_j(0)+\partial\boldsymbol{r}'_j(\tau)]}\rangle, \tag{13}$$

but here $\boldsymbol{F}_a$ denotes the effect of applied finite or modulated gradient sequence that takes place during spin motion, and

$$\partial\boldsymbol{r}'_{gj}(\tau) = \int_0^\tau \frac{F(t)}{|F_a|}\boldsymbol{v}_{gj}(t)\,dt \tag{14}$$

denotes a virtual spin shift along an applied gradient as it is seen through an outlook of gradient dephasing. $\boldsymbol{v}_{gj}$ is velocity component along applied gradient. Following the line of the same procedure as before, we again expand the function of spin phase structure in a series of plane waves and rewrite the spin echo as

$$E(\tau) = \sum_j E_{oj} \sum_k S_k(\boldsymbol{F}_a) e^{i(\boldsymbol{k}-\boldsymbol{F}_a)\boldsymbol{r}_j(0)} \langle e^{i\boldsymbol{k}\partial\boldsymbol{r}'_j(\tau)}\rangle. \tag{15}$$

3. Gaussian approximation in cumulant expansion

To carry out the spin phase average, we use the method of characteristic functional, discussed in Appendix A. According to it, we assign in Eq. (32) $\boldsymbol{v}_j(t)$ as a stochastic variable and $\boldsymbol{F}_j(t)$ as the test function. The spin phase mean is

$$\langle e^{i\int_0^\tau \boldsymbol{F}_j(t)\boldsymbol{v}_j(t)\,dt}\rangle = e^{J_j(\tau)}, \tag{16}$$

where the cumulant function is defined as

$$\begin{aligned} J(\tau) = {} & i\int_0^\tau \langle \boldsymbol{F}(t_1)\boldsymbol{v}(t_1)\rangle\,dt' \\ & - \frac{1}{2}\int_0^\tau\int_0^\tau \langle \boldsymbol{F}(t_1)\boldsymbol{v}(t_1)\boldsymbol{F}(t_2)\boldsymbol{v}(t_2)\rangle_c\,dt_1\,dt_2 \\ & - i\frac{1}{6}\int_0^\tau\int_0^\tau\int_0^\tau \langle \boldsymbol{F}(t_1)\boldsymbol{v}(t_1)\boldsymbol{F}(t_2)\boldsymbol{v}(t_2) \\ & \times \boldsymbol{F}(t_3)\boldsymbol{v}(t_3)\rangle_c\,dt_1\,dt_2\,dt_3 + \cdots. \end{aligned} \tag{17}$$

For simple Brownian motion, the velocity autocorrelation function decays rapidly to zero over the correlation time, τ_c, corresponding to the average collision time. τ_c is exceedingly short for small molecules compared with the time regime accessible to spin echo sequence which is more than or about 10^{-5} s. Because the cumulant almost vanishes unless the time points in it are close together within of order τ_c, the entire contribution to the m-fold integral of series, Eq. (17), arises from the domain of order $t\tau_c^{m-1}$. One can estimate the convergence of cumulant series by denoting the magnitude of velocity fluctuation as (∂v) being related to the diffusion coefficient as

$$D = \frac{1}{3}\int_0^\infty \langle \boldsymbol{v}(t)\boldsymbol{v}(0)\rangle_c \, dt \approx (\partial v)^2\tau_c. \tag{18}$$

Approximating $\boldsymbol{F}(t) \approx F$, Eq. (17) is an expansion in powers of $F(\partial v)\tau_c$, with each term being roughly linear in time. The mth term of the cumulant series is of the order

$$F^2(\partial v)^2\tau_c[F(\partial v)\tau_c]^{m-2}t. \tag{19}$$

In the limit of

$$F(\partial v)\tau_c \ll 1, \quad \text{and} \quad F^2(\partial v)^2\tau_c t = \text{finite}, \tag{20}$$

all cumulants higher than the second order can be omitted and the fluctuations are considered as a Gaussian random process. It means that Gaussian approximation is valid as long as the gradient is weak enough so that $F(\partial v)\tau_c \approx F.l \ll 1$ where l denotes a molecular mean free path.

For gases at room temperature and atmospheric pressure, the mean free path is about 100 nm giving for 1 ms long gradient pulse its limiting value at about 40 T/m. While in liquids it is higher by about two orders of magnitude, what is above the practical attainability of gradients by the conventional coil. Their upper limit is on the order of 100 T/m.

Consequently, the approach with the Gaussian assumption in cumulant expansion is not an approximation with limited usefulness but the method relevant with nearly all NMR diffusion experiments.

3.1. Spin echo and velocity autocorrelation

For times $t > \tau_c$, when $\langle \boldsymbol{v}(t)\rangle = 0$, the spin echo signal of spin-bearing particle diffusing in a large container appears as

$$E(\tau) = \sum_j E_{jo} e^{-\frac{1}{2}[\int_0^\tau \boldsymbol{F}_j(t_1)\cdot\langle \boldsymbol{v}_j(t_1)\boldsymbol{v}_j(t_2)\rangle_c \cdot \boldsymbol{F}_j(t_2)\, dt_1\, dt_2}. \tag{21}$$

It contains features of particle motion in a single particle velocity correlation function and depends on the specific form of the applied gradient modulation $\boldsymbol{G}_j(t)$.

The self-diffusion tensor in general form [24,1] is the Fourier spectrum of translation motion velocity correlation function

$$\mathscr{D}(\omega) = 1/3\int_0^\infty \langle \boldsymbol{v}(t).\boldsymbol{v}(0)\rangle_c e^{i\omega t}\, dt. \tag{22}$$

With the Fourier transform of $F_j(t)$,

$$\boldsymbol{F}_j(\omega,\tau) = \int_0^\tau \boldsymbol{F}_j(t)e^{i\omega t}\, dt, \tag{23}$$

expression (21) changes into

$$E(\tau) = \sum_j E_{jo} e^{-\frac{1}{\pi}[\int_0^\infty \boldsymbol{F}_j(\omega,\tau)\cdot\mathscr{D}_j(\omega)\cdot\boldsymbol{F}_j(-\omega,\tau)\, d\omega}. \tag{24}$$

$\mathscr{D}_j(\omega)$ is the tensor representing the spectrum of auto-correlation between the velocity components of jth spin sub-ensemble. Its product with $\boldsymbol{F}_j(\omega)$ is the product between the spectrum of the velocity auto-correlation function and the squared spectrum of the gradient integral. Thus the spin echo attenuation exposes a part of diagonal correlation tensor components. When an appropriate form of the gradient modulation waveform is applied, the spin echo measurement of self-diffusion yields information about the velocity auto-correlation.

For simple fluids, the diffusion spectrum is relatively constant at low frequencies, and is declining at frequencies above $\omega \approx \tau_c^{-1}$. However, for motion in complex fluids there exists a number of characteristic time-scales, which correspond to frequencies in the regime accessible by NMR. These include a long tail decay of velocity correlation function in liquids [25,26], a characteristic negative

decay in confined fluid [27], tube disengagement times in entangled polymers [28] or wall collision times of molecules enclosed by porous solids [29]. Such times are more closely related to the structure dynamics of a liquid than to local particle motion, thus making this method sensitive to hydrodynamics effects, confinement and localization experienced by spins. For isotropic diffusion Eq. (24) has the form

$$E(\tau) = \sum_j E_{jo} \mathrm{e}^{-\frac{1}{\pi}\int_0^\infty D_j(\omega)|F_j(\omega,\tau)|^2\,\mathrm{d}\omega}. \tag{25}$$

This approach has led to a new NMR technique that directly probes the diffusion spectrum by appropriate choice of gradient modulation waveforms [16]. The method has been used to study complex motion in a turbulent liquid flow where spectrum below τ_c^{-1} contains structure related to the features of turbulent liquid motion. Thus whatever the complexity of spin motion, it is characterized by the velocity correlation function measured by this method up to a frequency limit dictated by the speed of applied gradient sequence. The only other experimental methods able to gain direct excess to the details of velocity correlation are incoherent polarized neutron scattering [30,31] and optical scattering [32,33].

If the molecular correlation rate, τ_c^{-1}, is much greater then the highest frequency component of the phase spectrum, $F_j(\omega,\tau)$, we can write

$$\begin{aligned} E(\tau) &= \sum_j E_{jo} \mathrm{e}^{-\frac{1}{\pi}D_j(0)\int_0^\infty |F_j(\omega,\tau)|^2\,\mathrm{d}\omega} \\ &= \sum_j E_{jo} \mathrm{e}^{-D_j(0)\int_0^\tau |F_j(t)|^2\,\mathrm{d}t}. \end{aligned} \tag{26}$$

Here the frequency plateau, $D_j(0)$, is self-diffusion coefficient at the location $\boldsymbol{r}_j$ in the sample. Given that the diffusion coefficient and the gradient are uniform within the sample, the subscript j may be dropped and Eq. (26) is identical to Torrey's formula [7].

3.2. Spin echo attenuation of restricted diffusion as a discord of spin phase structure

For the case of restricted diffusion the cumulant expansion method is employed to average out discord of spin phase structure caused by moving spins from Eq. (15). When the molecular mean free path is short compared to compartment size, Gaussian approximation gives the discord of spin phase structure as

$$\begin{aligned} \left\langle \mathrm{e}^{\mathrm{i}k\delta r_j'(\tau)} \right\rangle &= \left\langle \mathrm{e}^{\mathrm{i}k\int_0^\tau \frac{F(t)}{F_a} v_j(t)\,\mathrm{d}t} \right\rangle \\ &= \mathrm{e}^{-\frac{1}{2F_a^2}\int_0^\tau \mathrm{d}t_1 \int_0^\tau \mathrm{d}t_2 k\,F(t_1)\langle v_j(t_1), v_j(t_2)\rangle_c F(t_2)\,k} \\ &= \mathrm{e}^{-\frac{1}{2}k^2 R_{gj}^2(\tau)}. \end{aligned} \tag{27}$$

By definition, the particle mean square displacement along the applied gradient in time interval τ is

$$R_{gj}^2(\tau) = \int_0^\tau \int_0^\tau \langle v_{gj}(t_1)\, v_{gj}((t_2)\rangle_c\,\mathrm{d}t_1\,\mathrm{d}t_2 \tag{28}$$

with v_{gj} denoting the velocity component of jth particle along the directions of applied gradients. The substitution of Eq. (27) into Eq. (11) gives

$$E(\tau) = \sum_j E_{oj} \sum_{\boldsymbol{k}} S_{\boldsymbol{k}}(\boldsymbol{F}_a) \mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{F}_a)\boldsymbol{r}_j(0)} \mathrm{e}^{-\frac{1}{2}k^2 R_{gj}^2(\tau)} \tag{29}$$

with a corresponding continuum limit

$$\begin{aligned} E(\boldsymbol{F},\tau) = \sum_{\boldsymbol{k}} S_{\boldsymbol{k}}(\boldsymbol{F}) \int & E_o(\boldsymbol{r}) \mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{F}_a)\cdot\boldsymbol{r}} \\ & \times \mathrm{e}^{-\frac{1}{2}k^2 R_g^2(\tau,\boldsymbol{r})}\,\mathrm{d}\boldsymbol{r}, \end{aligned} \tag{30}$$

where the diffusion length, $R_g^2(\tau,\boldsymbol{r})$, depends on the time and on the particle position in the pore. For short time intervals it is longer for particles far from the compartment wall and shorter for those in its proximity [34,23], resulting in edge enhancement in images [35–38].

Neglecting the correlation dependence on position in the pore and replacing the corresponding dependence of the diffusion mean square displacement on wall proximity by its mean value, $\overline{R_g^2}$, the spin echo for restricted diffusion can be written as

$$E(\tau) \approx \sum_{\boldsymbol{k}} S_{\boldsymbol{k}}(\boldsymbol{F}_a) S_{\boldsymbol{k}}^+(\boldsymbol{F}_a) \mathrm{e}^{-\frac{1}{2}k^2 \overline{R_g^2}(\tau)}. \tag{31}$$

It is a result similar to that obtained in Refs. [4,10] by using the diffusion propagator method [9]. The results differ in the definition of $\boldsymbol{F}_a$ and $\overline{R_g^2}$ but become identical in the limit of short intervals when

$\overline{R_g^2}(\tau) \approx 2D\tau$ and when the short PGSE sequence is applied, giving $\boldsymbol{F}_a = \gamma G\delta$.

When treating restricted diffusion, people commonly use the propagators derived from Fick's equation. This type of propagator is applicable only to Markoffian types of diffusion. We believe restricted diffusion exhibits features [29,27] that only a more general probability propagator, that contains specificity of confined motion, can describe.

4. Conclusion

The validity of Gaussian approximation in cumulant expansion for NMR measurement of self-diffusion requires that the gap between the magnetization grating (spin phase structure) caused by applied gradient field has to be much larger than the free path of moving spins. Thus, the gradient must stay below a limit, which is higher than what is easily attainable with a conventional gradient coil. Thus the approach is not just an approximation with limited usefulness but the method that is relevant to most NMR diffusion experiments.

By relating the spin echo directly to the correlation of molecular motion, the method avoids an inquiry for proper probability propagator. Thus, the time dependence of velocity correlation function may include the features either of Markofian or of non-Markoffian types of diffusion. The method is relevant to diffusion in systems where the confinement of molecules undergoing Brownian motion is caused by some restoring forces. It is the case of Brownian movement in a periodic potential and particularly for the diffusion of macromolecules and their segments [39,40,14,41,25].

The method is also relevant to restricted diffusion where the boundaries impose constrains, and the behavior of systems is very different compared to unbounded self-diffusion. Here, the correlations over a much longer time scale, than those for local stochastic motion, become important, and the velocity correlation spectrum exhibits a weak but non-zero value beyond τ_c [29,27]. It gives a low-frequency part of the diffusion spectrum that depends on the nature of particle collision at boundaries. This approach [3] gives a new insight into the phenomena by displaying a nice interdependence of length and time scales.

Another advantage of the method is its ability to be implemented with any general gradient pulse sequence, i.e., the gradient pulses can violate the short pulse approximation [20,42] or can even be modulated with arbitrary waveforms. Thus it overcomes a drawback of the propagator method which is, in analytical form, useful only with short gradient pulses.

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Appendix A

From the theory of stochastic processes [11], the characteristic or moment generating functional of the stochastic variable $X(t)$ is defined as a function of the test function $k(t)$

$$E(k,t) = \int e^{i\int_0^t k(t')X(t')\,dt'} P[X(t)]\,dX = \left\langle \int e^{i\int_0^t k(t')X(t')\,dt'} \right\rangle, \tag{A.1}$$

where $P(X)$ is a probability distribution of X.

By expanding (A.1) in powers of k,

$$E(k,t) = \sum_{m=0}^{\infty} \frac{i^m}{m!} \int k(t_1)\ldots k(t_m) \times \langle X(t_1)\ldots X(t_m)\rangle\, dt_1 \ldots dt_m, \tag{A.2}$$

the moments of the joint distribution of $X(t_1), X(t_2)\ldots$ can be found as the coefficients of terms with $k(t_1)k(t_2)\ldots$. Similarly, the cumulants can be found from

$$\ln E(k,t) = \sum_{m=1}^{\infty} \frac{i^m}{m!}\int k(t_1)\ldots k(t_m) \times \langle X(t_1)\ldots X(t_m)\rangle_c \, dt_1 \ldots dt_m, \qquad (A.3)$$

where the autocorelation functions $\langle x\cdots x\rangle_c$ are combination of the moments, e.g.,

$$\langle x\rangle_c = \langle x\rangle$$

$$\langle xx\rangle_c = \langle xx\rangle - \langle x\rangle\langle x\rangle$$

$$\langle xxx\rangle_c = \langle xxx\rangle - 3\langle xx\rangle\langle x\rangle + 2\langle x\rangle\langle x\rangle\langle x\rangle$$

$$\langle xxxx\rangle_c = \langle xxxx\rangle - 4\langle xxx\rangle\langle x\rangle - 3\langle xx\rangle\langle xx\rangle + 12\langle xx\rangle\langle x\rangle\langle x\rangle - 6\langle x\rangle\langle x\rangle\langle x\rangle\langle x\rangle. \qquad (A.4)$$

A process is called a Gaussian process if all cumulants beyond $m = 2$ are zero and

$$\ln\Big\langle \int e^{i\int k(t')X(t')\,dt'}\Big\rangle = i\int_0^t k(t_1)\langle X(t_1)\rangle\, dt_1 \qquad (A.5)$$

$$+ \frac{1}{2}\int_0^t\int_0^t k(t_1)k(t_2)\langle X(t_1)X(t_2)\rangle_c \, dt_1\, dt_2. \qquad (A.6)$$

Thus, the process is fully specified by the average $\langle X(t)\rangle$ and its second moment $\langle X(t_1)X(t_2)\rangle_c$.

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