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Spin Echo Attenuation of Restricted Diffusion as a Discord of Spin Phase Structure

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By using the particle probability density we analyze the spin echo attenuation of particles, diffusing in a bounded region. It provides a means to expand a nonuniform spin phase distribution into a series of waves that characterize the geometry and boundary conditions of confinement. Random motion disrupts the initial phase structure created by applied gradients and consequently discords its structure waves. By assuming the spin phase fluctuation and/or the randomness of spin phase distribution in the subensemble as a Gaussian stochastic process, we derive a new analytical expression for the echo attenuation related to the particle velocity correlation. For a diffusion in porous structure we get the expression featuring the same "diffusive diffraction" patterns as those being found and explained by P. T. Callaghan and A. Coy ("Principles of Nuclear Magnetic Resonance Microscopy," Oxford Univ. Press, Oxford (1991); *J. Chem. Phys.* 101, 4599–4609 (1994)) with the use of propagator theory. With the new approach we cast a new light on the phenomena and derive analitically how the diffusive diffractions appear when the sequence of finite or even modulated gradients are applied. The method takes into account the non-Markovian character of restricted diffusion, and therefore the echo dependence on the diffusion lengths and on the strength of applied gradient differs from the results of authors assuming the Markovian diffusion either by dealing with the diffusion propagators or by the computer simulation of Fick's diffusion.

INTRODUCTION

The use of magnetic field gradients to detect the migration of nuclear spins is almost as old as NMR itself. In his paper Hahn (*2*) pointed out that the echo amplitude is affected by the Brownian motion in the presence of local magnetic field homogeneity. Stejskal and Tanner (*3*) initiated the methodology and theory of the pulsed gradient spin echo (PGSE) experiment and implemented it to measure diffusion in systems for which restriction to motion caused a deviation from Fickian behavior. Since then, the method has been extensively developed. Investigating molecular motions in confined geometry, Callaghan (*1*) has shown how the narrow pulse PGSE experiment can extract information about the geometry of the boundaries. Theory is based on the propagators obeying the Fick's law to obtain the average over the spin phase fluctuations because of stochastic particle migration in a nonuniform magnetic field

$$E(t) = \langle \sum_i e^{i\theta_i(t)} \rangle_L, \qquad [1]$$

where the phase term is given by

$$\theta_i(t) = \gamma \int_0^t \mathbf{G}(t')\mathbf{r}_i(t')dt', \qquad [2]$$

with $\mathbf{G}_i$ being the gradient of the magnetic field at the ith spin site. In the special case when two gradient pulses of duration δ separated by time Δ are very narrow, the average $\langle \cdots \rangle_L$, Eq. [1], can be evaluated by using the diffusion propagators (*4*). Denoting the positions of a particle at time 0 and Δ as $\mathbf{r}$ and $\mathbf{r}'$, it gives the normalized echo amplitude

$$E(q, \Delta) = \int d\mathbf{r}\varrho(\mathbf{r}) \int d\mathbf{r}' P(\mathbf{r}', \Delta|\mathbf{r}, 0) e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})}, \qquad [3]$$

where $q = \gamma G\delta$. This method has been successfully used for a restricted diffusion with the infinitely short gradient pulses (SGP approximation). However, it does not provide the general description of the effect when a finite or modulated magnetic field is applied. The results of a few previous attempts to unfold it (*5–7*) can be applied only in the regime of a weak gradient.

It has seemed hardly possible to get exact analytical results for restricted diffusion with the applied gradient pulses of finite duration, and therefore, only the numerical simulations have been done (*8–11*).

With the presumption of Gaussian randomness for the spin frequency fluctuations we derived, in 1981, a formula for the diffusive attenuation without any direct reliance on the Fick's diffusion law (*12*). It provides very general relationship between spin attenuation and the microscopic particle motion, i.e., its single-particle velocity correlation (*13*). This method shows that the spin echo can provide quite

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an extensive list of information about microscopic motion (*14, 15*).

Herein we are using a similar approach to study the spin echo with diffusion inside the bounded region. Our aim is to extend our previous theory and obtain the result that might surpasses a drawback of the propagator method being amenable only with SGP and to Markov processes.

The application of the method to a system where the compartment walls constrain the particle motion requires certain reconsideration of previous assumption (*12*), which states:

• The fluctuation of the spin echo frequency due to particle motion is supposed to behave as a stochastic Gaussian process.

In Ref. (*16*) we have supplemented it by the extension:

• When frequency fluctuations fail to behave in such a way, the Gaussian phases distribution within the ensemble can take this role.

With the motion restricted by the confinements, we must add the following presumptions:

• Spin variables as well as the probability density of moving particle determine the initial state of a system.
• Each particle is treated as a distinguished system being coupled to a bath of randomly colliding particles in which a density matrix in semi-quantum approximation describes its probability density within bounded region.

These assumptions are basic for the following theory of spin echo with restricted diffusion.

SPIN ECHO INDUCTION AND PARTICLE MIGRATION

A signal, induced by precessing magnetization in a coil, can be written either in terms of the changing magnetic flux or, following the reciprocity theorem, in terms of spin magnetization $\mathbf{M}(t)$ (*13*) as

$$E = -\sum_i \frac{d}{dt}[\mathbf{M}_i(t)\cdot\mathbf{R}(\mathbf{r}_i)], \qquad [4]$$

where the ratio, $\mathbf{R}(\mathbf{r}_i) = \mathbf{B}_r/I_c$ (of the virtual magnetic field $\mathbf{B}_r$ induced by the coil carrying virtual current I_c at the location of a magnetic dipole $\mathbf{M}_i$), describes the spin–coil interaction. For a long coil along the x axis the signal is given by

$$E = -\hbar\gamma \frac{d}{dt}\sum_i \langle I_{xi}R_{xr}(\mathbf{r}_i)\rangle, \qquad [5]$$

where the angle brackets $\langle\cdots\rangle$ denote an average over the spin variables and the variables associated with the particle motion. A microscopic nature of spin-bearing molecules requires a quantum mechanical evaluation of the expected values. It provides the induced voltage, Eq. [5], by knowing the state of the system via its density matrix $\rho(t)$ as

$$E(t) = -\hbar\gamma \frac{d}{dt}\sum_i Tr\rho(t) I_{xi}R(\mathbf{r}_i). \qquad [6]$$

The density matrix

$$\rho(t) = U(t)\rho(0)U^*(t) \qquad [7]$$

determines the spin evolution from the initial state $\rho(0)$ due to interaction with internal and applied fields, intermolecular interactions, and collisions with the boundaries. With respect to other interactions, the quantum state of the spin-bearing particles cannot be treated as a genuinely closed and isolated system. It is an open subsystem of a large, closed system in which there is a division into subsystem and environment. If the density operator ρ describes the state of the total system, then one obtains the state ρ_l of the subsystem by tracing it over the environment. One can treat each individual particle, closed within compartment boundaries, as a distinguished system being coupled to a bath of randomly colliding particles. To handle this complexity it is very helpful to consider separately variables associated with different kinds of interactions. Weak coupling of spin interaction to the variables associated with particle motion allows the detachment of spin interaction from intermolecular interaction and the interaction with confining barriers (*16*). Thus one can partition the time evolution operator into a product of the noncommutable terms

$$U(t) = U(t)_s U(t)_m. \qquad [8]$$

In general in magnetic resonance an initial spin state is determined by the spin evolution from a thermodynamic equilibrium after preparation by a selective or nonselective RF pulse sequence. We may presume the density matrix at $t = 0$ as having the form

$$\rho(0)_l = \hbar\omega_0 \sum_i \rho_m(0) \times (M_i\cos\phi I_{xi} + M_i\sin\phi I_{yi} + C_i I_{zi}), \qquad [9]$$

with M_i, ϕ, and C_i being constants denoting the state of spins after the preparation and with $\rho_m(0)$ as the remaining part of the density matrix truncated for the spin part.

The details, showing the manipulation of spin operators, are given elsewhere (*14, 16*). Here we are using the result that gives, in the case of quadrature detection, the normalized spin echo (*16*) as

$$E(t) = \mathrm{Tr}\sum_i \rho_m(t)e^{i\theta(t,\mathbf{r}_i)}M_i R[\mathbf{r}_i], \qquad [10]$$

with

$$\theta(t, \mathbf{r}_i) = \gamma \int_0^t \mathbf{G}(t')\mathbf{r}_i\, dt', \qquad [11]$$

where

$$\rho(t)_m = U(t)_m \rho(0)_m U^*(t)_m. \qquad [12]$$

The remaining part of the density matrix, being a function of particle coordinate, can be expanded as a sum

$$\rho(\mathbf{r}, \mathbf{r}', t)_m = \sum_{k,k'} \rho_{k,k'}(t)\psi_k(\mathbf{r})\psi_k(\mathbf{r}'), \qquad [13]$$

where the functions $\phi_k(\mathbf{r})$ form a complete orthonormal set of eigenfunctions of an operator acting upon the particle coordinate. This operator could be the Hamiltonian describing the particle confinement within the compartment boundaries. Thus, the eigenfunction, needed to expand the density matrix, results from a solution of the quantum mechanical problem of a particle closed in a potential well, where the potential well has the shape and strength of the walls constraining the particle motion. Thus, these eigenfunctions and eigenvalues characterize the compartment geometry and its boundaries, and denote the momentum states $\mathbf{k}$ of closed particle within the pore. In this way we have incorporated a particle confinement into our consideration. The eigenfunctions are standing waves that can always be expressed as a superposition of plane waves traveling in different directions but with the characteristic momentum. Their wave vectors are taken from the same characteristic set of momentum states above. Thus one can write the density matrix (or probability density of particle) as a sum of plane waves

$$\rho_m(\mathbf{r}, \mathbf{r}', t)_m = \sum_{\mathbf{k},\mathbf{k}'} \rho_m(\mathbf{k}, \mathbf{k}) e^{i(\mathbf{k}\mathbf{r} - \mathbf{k}'\mathbf{r}')}. \qquad [14]$$

The coupling to the environment is typically through position, and the density operator tends to become approximately diagonal in position very quickly. The emergence of classical behavior for the variables which have become definite can be seen by tracing the evolution of states initially localized in phase space. Such states tend to follow approximately classical trajectories. With the well-defined particle location at time t, the density matrix in a semi-classical approximation can be a probability function defined as

$$P[\mathbf{r}(t)] = \delta[\mathbf{r}_i(t) - \mathbf{r}], \qquad [15]$$

where a time dependence of particle coordinates $\mathbf{r}_i(t)$ comes from molecular collisions. Thus the trace in Eq. [10] becomes an integral

$$\mathrm{Tr}\ \rho_m(t)A(\mathbf{r}_i) \Rightarrow \left\langle \int P[\mathbf{r}_i(t)]A(\mathbf{r}_i)\, d\mathbf{r}_i \right\rangle_m.$$

$\int_v$ marks the integration over the compartment volume, while $\langle \cdots \rangle_m$ denotes the trace over the fluctuating variables associated with the intermolecular interactions.

Thus Eq. [10] gets the form

$$E(t) = \left\langle \sum_i \int_v d\mathbf{r}_i \delta[\mathbf{r}_i(t) - \mathbf{r}_i] e^{i\theta(t,\mathbf{r}_i)} M_i R[\mathbf{r}_i] \right\rangle_m. \qquad [16]$$

According to a previous definition, we can either expand the probability density, $\delta[\mathbf{r}_i(t) - \mathbf{r}]$, into a series of plane waves or write Eq. [16] as

$$E(t) = \langle \sum_i e^{i\theta[t,\mathbf{r}_i(t)]} M_i R[\mathbf{r}_i(t)] \rangle_m. \qquad [17]$$

In the last equation, we render the expansion into plane waves to the functions in brackets. Both the phase of spin echo, $\theta[t, \mathbf{r}_i(t)]$, and the parameter of spin–coil interaction, $R[\mathbf{r}_i(t)]$, contain information about the particle location at time t. We can convert dependence on the location into dependence on a particle velocity, $\mathbf{v}_i(t)$, by rewriting

$$\mathbf{r}_i(t) = \mathbf{r}_i(0) + \int_0^t \mathbf{v}_i(t')dt', \qquad [18]$$

where $\mathbf{r}_i(0)$ denotes the initial particle location. Integration of Eq. [2] gives

$$\theta(t) = \mathbf{F}(t)\mathbf{r}_i(0) + \int_0^t [\mathbf{F}(t) - \mathbf{F}(t')]\mathbf{v}_i(t')dt', \qquad [19]$$

with the phase factor,

$$\mathbf{F}(t) = \gamma \int_0^t \mathbf{G}(t')dt', \qquad [20]$$

being zero at the time of spin echo refocusing, $t = \tau$. These substitutions in Eq. [16] give

$$E(t) = \langle \sum_i e^{i\mathbf{F}(t)\mathbf{r}_i(0) - i\int_0^t [\mathbf{F}(t) - \mathbf{F}(t')]\mathbf{v}_i(t')dt'} M_i R[\mathbf{r}_i(t)] \rangle_m. \qquad [21]$$

A finite length coil always suffers a degree of RF inhomogeneity, and therefore the correlation of $R[\mathbf{r}_i(t)]$ with initial spin excitation M_i affects the NMR signal when liquid is not stationary. Thus, a signal attenuation occurs when diffusion length is comparable to the extension of the coil active zone. It explains unusual broadening of NMR lines in gaseous state (*17, 18*). In a porous system the particle motion is restricted within compartments of size much smaller than

that of a coil extension with nearly uniform $R[\mathbf{r}_i(t)]$ inside particle confinement.

The motional correlation, hidden in the phase term, becomes discernible by rewriting Eq. [21] as

$$E(\tau) = \sum_i \langle e^{i\mathbf{F}_a\mathbf{r}_i(0)} e^{-i\mathbf{F}_a[\mathbf{r}_i(0)+\delta\mathbf{r}_i'(\tau)]}\rangle_m], \qquad [22]$$

after neglecting spin-coil correlation. It describes the correlation between the nonuniform spin phase distributions at different moments. $\mathbf{F}_a$ is the spin dephasing when the gradient sequence is applied in the circumstance of moving spins. It gives to nonstationary particles the decreasing effect of spin dephasing when the width of the applied gradient pulse increases. We named it effective spin dephasing (ESD). Thus, the particle shift along the applied gradient seen from the viewpoint of spin dephasing is

$$\delta\mathbf{r}_{gi}'(t) = \int_0^t \frac{F(t')}{|\mathbf{F}_a|}\,\mathbf{v}_{gi}(t')dt'. \qquad [23]$$

Here $\mathbf{v}_{gi}$ is the velocity component along the applied gradient. It must be equal to the real particle shift when $\mathbf{F}_a$ is properly defined. In the following procedure of spin phase averaging we elucidate all details and meaning of these substitutions.

The phase term in Eq. [22] is a function of the particle coordinates. Similar to expansion with the probability function, Eq. [16], one can write it as a series of plane waves

$$e^{i\mathbf{F}_a\mathbf{r}} = \sum_k S_{\mathbf{k}}(\mathbf{F}_a)e^{i\mathbf{kr}}. \qquad [24]$$

The plane waves identify the shape and boundary conditions of compartments in the reciprocal space with the set of their wave vectors, $\mathbf{k}$. They are different for planar, cylindrical, or spherical geometry and also depend on the interconnectivity of the compartment walls. With these substitutions, one can rewrite the spin echo as

$$E(\tau) = \sum_i \sum_{\mathbf{k},\mathbf{k}'} S_{\mathbf{k}}(\mathbf{F}_a)S_{\mathbf{k}'}^{+}(\mathbf{F}_a)e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}_i(0)}\langle e^{i\mathbf{k}'\delta\mathbf{r}_i'(\tau)}\rangle_m. \qquad [25]$$

PHASE AVERAGING AND SPIN ECHO ATTENUATION WITH RESTRICTED DIFFUSION

The signal echo arises from the induction of the immense number of spins $>10^6$, where one cannot detect the displacements from the individual molecular collisions, but rather from average long range displacements, where each particle shift arises from innumerable molecular collisions.

There is also another in which one may reasonably group spins into separate subensembles for which the dynamic behavior may be different. For such a grouping the averages within subensembles may be handled.

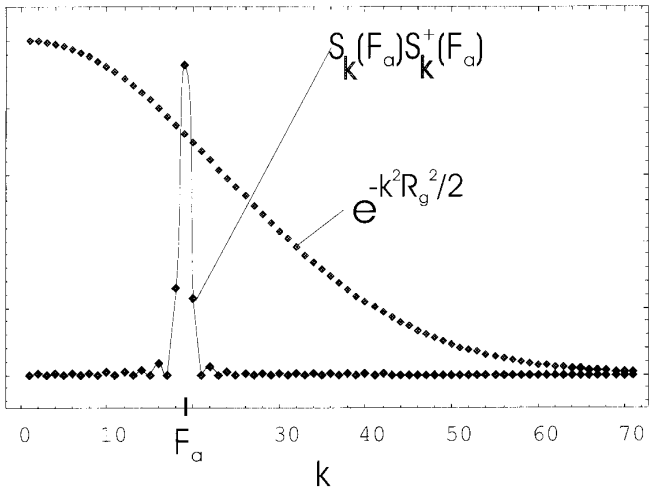

FIG. 1. The damping and the structure terms from the expression of spin echo in the case of short diffusion length—a free diffusion.

By performing the continuum limit, we can transform the sum on the subensemble into the mean value of the subensemble variables in which one can also incorporate the average motion of a particular spin. Thus we can join both time and ensemble averages into common brackets as

$$\langle \sum_i \cdots \rangle_m \Rightarrow \left\langle \int \cdots d\mathbf{r} \right\rangle. \qquad [26]$$

Furthermore, we can assume a stochastic process where the fluctuating deviations of spin frequency $\omega(t)$ from the mean value have a Gaussian distribution. In Refs. (*12–14, 16*) we used the method of exponential expansion (cummulant expansion) in order to find a mean value of the phase term. This method transforms the average of randomly distributed oscillators into an exponential series with an average phase (see Appendix I).

During the spin echo evolution, we observe the cumulative effect of a large number of small but random perturbations of spin frequency. It is typical for the Gaussian process. In such a case one can truncate all but the first two terms in Eq. [45]. In the description below we have applied the method only to the frequency fluctuations. The same can be done with respect to the randomness of spin phase distribution within a subensemble. Namely, the particles that exercise almost simultaneous random walks in different directions bring about a random distribution of spin phase at any instant. Their shifts are proportional to the length of the particle drift along the applied gradient. For small phase deviations, it can be regarded as a Gaussian process, and we can approximate it by the spin phase expansion to the second order again. Thus both the time and the subensemble average lead to the same approximation. Furthermore, it is beneficial

when the frequency fluctuations do not behave as a Gaussian process, and we rely on the Gaussianity of the spin phase distribution within a subensemble. Thus, one can always derive the spin echo diffusive attenuation from the commulant expansion which relates spin attentuation directly to microscopic values.

The details, showing the procedure of phase averaging by cummulant expansion in Eq. [25], are given elsewhere (*16*). Here we are using the result that gives, in the case of stationary liquid, $\langle \mathbf{v}_g(t) \rangle = 0$, and assumptions of isotropic restricted self-diffusion in a pore, averaged as

$$\langle e^{i\mathbf{k}\delta\mathbf{r}'_{gi}(\tau)} \rangle = \langle e^{i\mathbf{k}\int_0^\tau \frac{F(t)}{F_a}\mathbf{v}_{gi}(t)\,dt} \rangle = e^{-\frac{1}{2F_a^2}\int_0^\tau dt_1 \int_0^\tau dt_2 F(t_1)\mathbf{k}\langle \mathbf{v}_{gi}(t_1)\cdot\mathbf{v}_{gi}(t_2)\rangle \mathbf{k}F(t_2)}. \quad [27]$$

The diffusion constant is equal to the time integral of the tagged particle velocity autocorrelation function

$$D = \tfrac{1}{6}\lim_{\tau\to\infty}\int_0^\tau \langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle\, dt, \quad [28]$$

and the diffusion length in the time interval τ along the applied gradient is

$$R_g(\tau)^2 = \int_0^\tau dt' \int_0^\tau dt'' \langle \mathbf{v}_g(t')\cdot\mathbf{v}_g((t'')\rangle. \quad [29]$$

For an infinite system the velocity correlation is positive and falls off exponentially with time. In this case the diffusion constant and the diffusion length are related as

$$R_g(\tau)^2 = 2D\tau. \quad [30]$$

In a confined system the effect of the walls sets up a small negative velocity correlation which persists for a long time. It gives the diffusion constant D which decreases with time and R_g which cannot be larger than the dimensions of the cell. The works of others (*19–21*) indicate that the shape of the long time tail depends on the nature of the molecular scattering on the walls. The velocity correlation for a perfectly reflecting wall in a one-dimensional cell is derived in Ref. (*22*). It gives a long time tail for velocity correlation with a maximal diffusion length equal to $d^2/12$ with d being the cell width.

It was shown (*23*) that the velocity correlation function changes only at wall proximity on a distance of a few mean-free paths. For a much larger cell we can approximate the velocity correlation as an almost uniform function inside the pore. For a finite or modulated gradient it turns out that the natural description of ESD via the velocity autocorrelation function and via the particle displacement in Eq. [22] is

$$F_a(\tau) = \frac{\mathbf{f}}{R_g(\tau)} \times \sqrt{\int_0^\tau dt' \int_0^\tau dt''\, \mathbf{F}(t')\,\langle \mathbf{v}(t')\cdot\mathbf{v}(t'')\rangle\, \mathbf{F}(t'')}, \quad [31]$$

where $\mathbf{f}$ is a unit vector aligned along the gradient. Its substitution in Eq. [25] gives the spin echo of restricted diffusion in isotropic fluid as

$$E(\tau) = \sum_{\mathbf{k}} S_{\mathbf{k}}(\mathbf{F}_a) S^+_{\mathbf{k}}(\mathbf{F}_a) e^{-\frac{1}{2}\mathbf{k}^2 R_g^2(\tau)}. \quad [32]$$

The first factor in the sum of Eq. [32], $S_{\mathbf{k}}S^+_{\mathbf{k}}$, is the component of the spin phase structure within a pore set up by gradient spin dephasing F_a. The second one, $e^{-\frac{1}{2}\mathbf{k}^2 R_g^2(\tau)}$, denotes the damping due to diffusion and depends only on the length of particle diffusion R_g. For a diffusion length much shorter than the compartment size, the structure component is a narrow function settled in the region around the point $\mathbf{k} = \mathbf{F}_a$ (Fig. 1). By using the identity

$$\sum_{\mathbf{k}} S_{\mathbf{k}}(\mathbf{F}_a)\, S^+_{\mathbf{k}}(\mathbf{F}_a) = 1, \quad [33]$$

and neglecting the long time tail for velocity correlation, the well-known expression for spin echo attenuation appears as

$$E(\tau) = e^{-\frac{1}{2}\mathbf{F}_a^2 R_g^2(\tau)} = e^{-\mathbf{F}_a^2(\tau)D\tau}. \quad [34]$$

The damping due to diffusion is greater for the components with the highest values of k. Figure 2 shows the spin

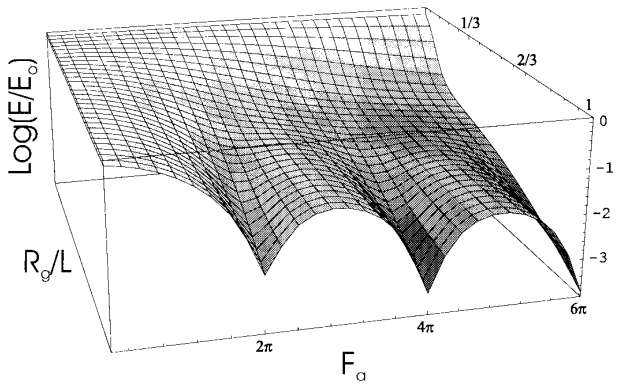

FIG. 2. The spin echo of particles diffusing between the parallel planes as a function of diffusion length and mean gradient dephasing.

echo as a function of diffusion length and gradient strength, $|\mathbf{F}_a|$. Clearly, the diffraction-like pattern, which appears along the gradient axis, becomes more distinct with increased diffusion length which is limited above by the pore dimension.

For a diffusion length about the size of the pore, all components, except those with $\mathbf{k} = 0$, vanish, and the spin echo becomes

$$E(\tau) \approx |S_0(\mathbf{F}_a)|^2 \approx |\int_V e^{-\mathbf{F}_a\mathbf{r}}\, d\mathbf{r}|^2. \quad [35]$$

It is similar either to the cross-section formula of neutron scattering or to the Fraunhofer diffraction formula in optics. $|S_0(\mathbf{F}_a)|^2$ describes the diffraction pattern of the pore found first by Coy and Callaghan (*9*) who named it the *diffusive diffraction* and explained it by the propagator theory (*4*) in the case of a sequence with two very short gradients. Our result becomes identical to theirs when $|\mathbf{F}_a|$ is replaced in Eq. [32] by $q' = \gamma\delta G$. It means that we ignore the effects of reduced dephasing for finite pulses. On the other hand Eq. [32] follows from the propagator method when q' in formula [3] (*9*) is replaced by ESD parameter $\mathbf{F}_a$ as

$$E(\mathbf{F}_a, \tau) = \int d\mathbf{r}\, \varrho(\mathbf{r}) \int d\mathbf{r}'\, P(\mathbf{r}', \tau\,|\,\mathbf{r}, 0) e^{i\mathbf{F}_a\cdot(\mathbf{r}'-\mathbf{r})}. \quad [36]$$

In this case we assert that the propagator evolution rate depends on the time-dependent diffusion constant defined as $D(\tau) = \frac{1}{2}R_g^2(\tau)/\tau$ (*22*).

In the real analysis information about the compartment shape, the boundary conditions, and perhaps something about the size distribution must be available. In the following we demonstrate the method on a simple case of diffusion restricted inside a box of reflecting plan-parallel walls.

SELF-DIFFUSION RESTRICTED WITHIN PLAN-PARALLEL PLANES

Here we are concerned with the molecular diffusion restricted by a rectangular box with sides d_x, d_y, and d_z. The classic quantum solution of a particle closed within a rectangular box, with walls of infinite potential, gives the set of wave vectors

$$\mathbf{k} = \left[\frac{n_x\pi}{d_x}, \frac{n_y\pi}{d_y}, \frac{n_z\pi}{d_z}\right], \quad [37]$$

with $n_{x,y,z} = 1, 2, 3, \ldots$. The plane wave expansion of probability density, Eq. [13], adds to it the component with $n_{x,y,z} = 0$. Thus, the components of reciprocal phase structure

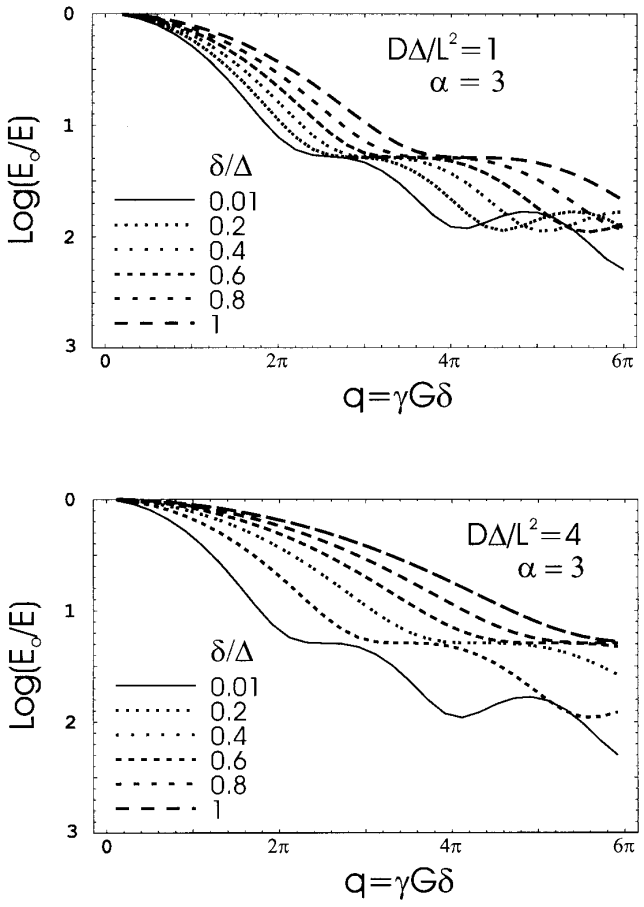

FIG. 3. The spin echo as a function of q for different widths of gradient pulse at the diffusion lengths $D\Delta/L^2 = 1$ and 4.

for the effective gradient along an arbitrary direction, $\mathbf{F}_a = F_{ax}, F_{ay}, F_{az}$, are

$$S_{\mathbf{k}}(\mathbf{F}_a)S_{\mathbf{k}}^+(\mathbf{F}_a) = \left[\frac{\sin((k_x - F_{ax}d_x)/2)}{(k_x - F_{ax})} \times \frac{\sin((k_y - F_{ay}d_y)/2)}{(k_y - F_{ay})} \frac{\sin((k_z - F_{az}d_z)/2)}{(k_z - F_{az})}\right]^2, \quad [38]$$

when all $n_{x,y,z} \neq 0$. For each $n_{x,y,z}$ equal to zero, the above expression is multiplied by 2.

For the gradient applied only along the x axis, the structure factors in Eq. [32] are

$$S_k(F_a)S_k^+(F_a) = \left[\frac{\sin((k - F_a d)/2)}{(k - F_a)}\right]^2, \quad [39]$$

when $n \neq 0$, and

$$S_0(F_a)S_0^+(F_a) = 2\left[\frac{\sin(F_a d/2)}{(F_a)}\right]^2, \qquad [40]$$

for $n = 0$.

The velocity correlation of a particle enclosed in a one-dimensional box has been derived (*22*). For the sake of simplicity here we approximate it by the expression

$$\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle = D(\beta e^{-\beta t} - \kappa e^{-\kappa t}), \qquad [41]$$

where $1/\beta$ is molecular correlation time and $\kappa = D\alpha/d_x^2$ describes the rate of particle collision with walls. α is a parameter describing the nature of scattering.

Equation [41] gives the diffusion length in time τ

$$R_g^2(\tau) = \frac{D}{\kappa}(1 - e^{-\kappa\tau}). \qquad [42]$$

According to this, the mean squared shift the particle reaches at long times $\tau \gg d^2/D$ is about

$$R_g^2(\tau) = \frac{d^2}{\alpha}, \qquad [43]$$

where α is 12 for a perfectly reflecting wall and around 3 for a rough surface.

In the special case when two gradient pulses of duration δ separated by time Δ are applied, the spin dephasing is

$$F_a^2(\Delta, \delta) = \frac{2(\gamma G)^2 D}{\kappa^3 R_g^2(\Delta + \delta)}(\kappa\delta - 1 + e^{-\kappa\delta} + e^{-\kappa\Delta}(1 - \cosh(\kappa\delta))). \qquad [44]$$

With these substitutions in Eq. [32] we get the spin echo as a function of the diffusion length $R_g(\tau)$ and the mean gradient dephasing, F_a. Figure 2 shows distinctive diffraction patterns for long diffusion lengths. The dales of pattern are placed at points where F_a equals a multiple of 2π.

CONCLUSION

With the new approach to the spin echo of restricted self-diffusion, we express the nonuniform spin phase distribution in a pore as a series of waves with wave vectors characterizing the geometry and boundaries of confinement. The Gaussian assumption about the stochastic spin phase fluctuation and/or the random spin phase distribution provides the analytical expression for the echo attenuation of restricted self-diffusion, Eq. [32], without a reference to the Fick's diffusion law. When the diffusion length is about the size of the pore, it features a diffusive diffraction dependence on $\gamma G\delta$, the effect observed in experiments of Callaghan (*24–26*) and others (*27*). This new result follows right from spin phase average, giving the direct reliance on the molecular correlation. Thus, it surpasses a drawback of the propagator method being amenable only with short gradient pulses and to the Markov processes. Using the propagator formalism, a relationship between the structure parameters restricting the migration and the spin echo can be determined when a complete knowledge of the diffusion propagator is available. However, people usually rely on the propagators derived from the Fick's equation that are amenable only for the Markovian diffusion.

There are also numerical simulations of spin echo with gradient pulses of finite width in Refs. (*8–11*). The authors have simulated the spin echo of particles diffusing in a confinement between reflecting walls, using various numeric methods but assuming it is a Fick's diffusion, i.e., as a Markov stochastic process. By comparing our results derived from Eq. [32] in Fig. 3 and those in Refs. (*8–11*) we see a resemblance but the diffraction dales are much shallower in our case. We believe that the deep minimum in their cases follows from the assumption of unlimited diffusion length when Fick's propagators are supposed to govern restricted self-diffusion. For a Markov process, the correlation function fulfills the functional equation with the solution of a simple one-exponential function (*28*). It is shown that the correlation function of bounded diffusion is a nonexponential function and certainly must be considered as a non-Markovian process. In such a case only solutions of more complex Fokker–Planck's equations provide appropriate propagators. In our method, we can avoid this procedure but we must have knowledge about the velocity correlation function. Figure 3 also shows that the position of the minimum as a function of $\gamma G\delta$ moves with changing δ/Δ. The shift depends on $D\Delta/L^2$ as well as on the scattering parameter α. For the gradient pulses of maximal widths, $\delta/\Delta = 1$, the first minimum should be between $qa = \sqrt{32}\pi$ and about $qa = \sqrt{152}\pi$, depending on the above estimates for α.

Our new approach is useful for any sequence of finite or modulated gradients and has no limit on the width of pulses. In our next paper, we'll provide very coexistent experimental verification of a new approach applying the modulated gradient method to the study of diffusion in a porous structure. It provides a new means to resolve the microscopic structure that limits the migration of molecules.

APPENDIX I

The oscillator with the fluctuating frequency $\omega(t)$ can be expanded into an infinite exponential series as

$$\langle e^{i\int_0^t \omega(t')dt'}\rangle = e^{g_0(t)+g_1(t)+g_2(t)+\cdots}, \qquad [45]$$

where

$$g_0(t) = i < \omega > t, \qquad [46]$$

$$g_1(t) = -\int_0^t dt_1 \int_0^{t_1} dt_2 < \omega(t_1)\omega(t_2) >_c, \qquad [47]$$

and so on.

APPENDIX II

The velocity correlation for plan-parallel planes with perfectly reflecting walls (*22*) is

$$\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle = D(\beta e^{-\beta t} - \frac{4D}{d_x^2}\sum_{k=-\infty}^{\infty} e^{-b_k t}), \qquad [48]$$

with $b_k = (2k+1)^2 D/d_x^2$. It gives the diffusion length in time τ

$$R_g^2(\tau) = \frac{8D^2}{d_x^2}\sum_{k=-\infty}^{\infty}\frac{(1-e^{-b_k\tau}}{b_k^2}. \qquad [49]$$

According to this, the mean squared shift the particle reaches at long times $\tau \gg d^2/D$ is not larger than

$$R_g^2(\tau) = \frac{d^2}{12}. \qquad [50]$$

In the special case when two gradient pulses of duration δ separated by time Δ are applied, the spin dephasing is

$$F_a^2(\Delta,\delta) = \frac{16(\gamma G)^2 D^2}{d_x^2} \times \sum_{k=-\infty}^{\infty}\frac{(b_k\delta - 1 + e^{-b_k\delta} + e^{-b_k\Delta}(1-\cosh(b_k\delta))}{b_k^4 R_g^2(\Delta+\delta)}. \qquad [51]$$

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