Time correlation during anomalous diffusion in fractal systems and signal attenuation in NMR field-gradient spectroscopy

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(Received 21 December 1987)

Analytical expressions for the correlation of subsequent molecular displacements during diffusion along fractal networks are derived. On the basis of these relations, the NMR spin-echo attenuation due to anomalous diffusion in both constant and pulsed field-gradient experiments is determined.

I. INTRODUCTION

The bulk mean-square distance $\langle r(t)^2 \rangle$ traveled by a molecule (random walker) in time t represents a most informative quantity characterizing the time dependence of molecular propagation. In many cases this quantity may be shown to follow the scaling law[1-3]

$$\langle r(t)^2 \rangle = \alpha t^\kappa , \tag{1}$$

including the cases of both ordinary diffusion ($\kappa = 1$) and anomalous diffusion along a fractal network ($\kappa < 1$). α denotes a time-independent proportionality constant. For ordinary diffusion in three dimensions one has

$$\alpha = 6D , \tag{2}$$

with D denoting the self-diffusion coefficient.

Information on the correlation between subsequent increments of molecular migration may be deduced from Eq. (1) by representing the particle displacement $r(t + \Delta t)$ during the time interval $0 \cdots t + \Delta t$ with $\Delta t > 0$ as a vector sum of the displacements $r(t)$ and $r(t + \Delta t) - r(t)$ during the time intervals $0 \cdots t$ and $t \cdots t + \Delta t$, respectively.[4] Taking the mean square of the vector sum, one obtains

$$\langle r(t + \Delta t)^2 \rangle = \langle r(t)^2 \rangle + \langle [r(t + \Delta t) - r(t)]^2 \rangle$$
$$+ 2\langle r(t)[r(t + \Delta t) - r(t)] \rangle . \tag{3}$$

It is evident that for a linear relation between the mean-square displacement and the observation time, i.e., for ordinary diffusion, the last term on the right-hand side of Eq. (3) must be zero. This clearly indicates that the increments during ordinary diffusion are uncorrelated and hence independent of each other. For anomalous diffusion, however, the mean-square displacement increases less than linearly with the observation time, and one has

$$\langle r(t)[r(t + \Delta t) - r(t)] \rangle < 0 . \tag{4}$$

This relation indicates that subsequent displacements during molecular migration along fractal networks are negatively correlated.[5]

In the following, Eq. (1) will be transferred into an analytical expression for this correlation. As an example,

this expression is used to treat analytically NMR field-gradient experiments in the case of anomalous diffusion.

II. CORRELATION BETWEEN SUBSEQUENT DISPLACEMENTS

Rearranging Eq. (3) and replacing the mean-square displacements in Eq. (3) by Eq. (1), one obtains

$$\langle r(t)[r(t + \Delta t) - r(t)] \rangle = \frac{\alpha}{2}[(t + \Delta t)^\kappa - t^\kappa - (\Delta t)^\kappa] . \tag{5}$$

By replacing the different mean-square displacements on the right-hand side of Eq. (3) by Eq. (1), we have implied that the considered transport phenomena are time invariant.

Introducing the ratio $x = \Delta t / t$ between the duration of subsequent time intervals, Eq. (5) may be transferred into the dimensionless representation

$$\frac{\langle r(t)[r(t + \Delta t) - r(t)] \rangle}{\langle r(t)^2 \rangle} \equiv f(x) = \frac{(1+x)^\kappa - 1 - x^\kappa}{2} ,$$
$$\tag{6}$$

with $f(x)$ denoting the reduced correlation function. Figure 1 shows the plots of the reduced correlation func-
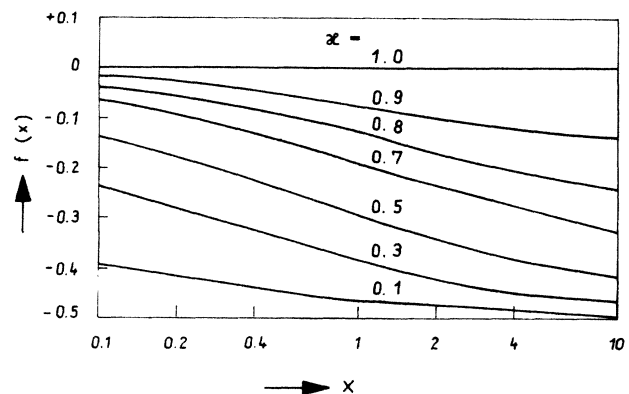

FIG. 1. Representation of the reduced correlation function $f(x)$ [cf. Eq. (6)], describing the correlation of molecular displacements in subsequent time intervals t and Δt in terms of the ratio $x = \Delta t / t$.

tion f versus the ratio x between the subsequent time intervals for different scaling exponents κ. Clearly, for κ approaching the value of 1 for ordinary diffusion, the reduced correlation function becomes zero. Equation (5) will be applied in the Sec. III for the calculation of the NMR signal intensity.

The main features of the correlation of molecular mean displacements, however, are more clearly visualized upon considering the displacements during two time intervals of identical duration with starting points separated from each other by the time interval t_1. The calculation of the corresponding correlation function $\langle \mathbf{r}(t)[\mathbf{r}(t_1+t)-\mathbf{r}(t_1)]\rangle$ requires a separate consideration of the cases $t_1 \leq t$ and $t_1 \geq t$: In the former case we use the identities

$$\langle \mathbf{r}(t)\mathbf{r}(t+t_1)\rangle = \langle \mathbf{r}(t)\{[\mathbf{r}(t+t_1)-\mathbf{r}(t)]+\mathbf{r}(t)\}\rangle \tag{7}$$

and

$$\langle \mathbf{r}(t)\mathbf{r}(t_1)\rangle = \langle \mathbf{r}(t_1)\{[\mathbf{r}(t)-\mathbf{r}(t_1)]+\mathbf{r}(t_1)\}\rangle . \tag{8}$$

By applying Eqs. (1) and (6), the difference between these equations may easily be shown to lead to the normalized correlation function

$$\frac{\langle \mathbf{r}(t)[\mathbf{r}(t_1+t)-\mathbf{r}(t_1)]\rangle}{\langle \mathbf{r}(t)^2\rangle}$$

$$\equiv g(y)=\tfrac{1}{2}[(1+y)^\kappa+(1-y)^\kappa-2y^\kappa] \tag{9}$$

for $y=t_1/t \leq 1$.

For ordinary diffusion ($\kappa=1$), Eq. (9) reduces to $g(y)=1-y$ as a straightforward consequence of the fact that there is complete correlation during the overlap of the two intervals and none outside. When considering separation times t_1 exceeding the interval length t (i.e., for time intervals without any overlap), Eq. (8) has to be replaced by the equivalent identity

$$\langle \mathbf{r}(t)\mathbf{r}(t_1)\rangle = \langle \mathbf{r}(t)\{[\mathbf{r}(t_1)-\mathbf{r}(t)]+\mathbf{r}(t)\}\rangle , \tag{10}$$

and instead of Eq. (9) one obtains

$$g(y)=\tfrac{1}{2}[(y+1)^\kappa+(y-1)^\kappa-2y^\kappa] , \tag{11}$$

with $y \geq 1$. Corresponding to the fact that there is no overlap of the considered time intervals any more, in the case of ordinary diffusion $g(y)$ becomes identical to zero for all $y \geq 1$. Figure 2 shows the complete dependence of the correlation function $g(y)$ on y for different scaling factors κ. As an asymptotic representation of Eq. (11) for $y \gg 1$, i.e., for sufficiently large spacings between the two time intervals, one obtains

$$\lim_{y\to\infty} g(y)=-\tfrac{1}{2}(1-\kappa)\kappa y^{\kappa-2} . \tag{12}$$

III. NMR FIELD-GRADIENT EXPERIMENTS UNDER THE INFLUENCE OF ANOMALOUS DIFFUSION

The NMR field-gradient spectroscopy allows an *in situ* measurement of molecular displacements from several hundred nanometers up to hundreds of micrometers.[6−8]
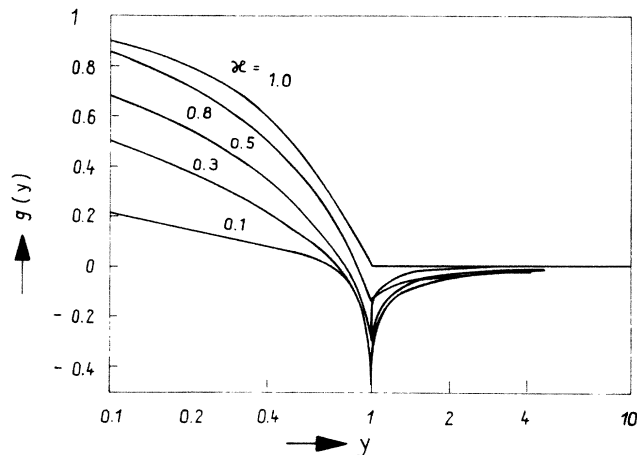

FIG. 2. Representation of the reduced correlation function $g(y)$ [cf. Eqs. (9) and (11)], describing the correlation of molecular displacements in the intervals of identical duration t shifted against each other by the time interval t_1, in terms of the ratio $y=t_1/t$.

Due to this fact, this method has been successfully applied to the investigation of both homogeneous[9] and heterogeneous[10] systems, and a series of papers can be found in the literature dealing with the theoretical analysis of NMR diffusion measurements in heterogeneous systems (cf., e.g., Refs. 11–15). As yet, however, all these considerations have been based on the assumption that in the individual subregions molecular diffusion is following the ordinary law of Fickian diffusion.

A first attempt of an analytical treatment of field-gradient experiments to study diffusion in fractal networks has been based on the phenomenological equations of motion of nuclear magnetism (Bloch equations). For this purpose, the decay rate of nuclear magnetization $\mathbf{M}(\mathbf{r})$ at position $\mathbf{r}$ due to anomalous diffusion was represented by an expression of the type

$$d\mathbf{M}(\mathbf{r})/dt \propto t^{-\beta}\nabla^2\mathbf{M}(\mathbf{r}) , \tag{13}$$

with $\beta>0$ denoting an appropriately chosen constant.[16] However, the general validity of such a procedure is questionable, and the analytical form of the distribution function for diffusing particles is an open problem.[17−19] In Ref. 4 it can be shown that the proposed way to determine the NMR signal attenuation may lead to incorrect results.

In the present Brief Report, the time dependence of nuclear magnetization is considered within the concept of accumulating phases[11] which has been successfully applied to the analysis of a series of NMR diffusion studies in heterogeneous systems.[12,13,15] In this procedure the attenuation of the transverse nuclear magnetization is represented by the relation

$$\Psi=\langle \cos\varphi\rangle , \tag{14}$$

with φ denoting the deviation of the precessional phase of an individual spin from the average value. With the Larmor condition

$$\omega = \gamma B \tag{15}$$

relating the precessional frequency ω to the applied magnetic field B, the phase deviation $\varphi(t)$ at time t may be easily shown to be

$$\varphi(t) = -\gamma \int_0^t [B(z(t')) - \langle B \rangle] dt'$$

$$= -\gamma \int_0^t g z(t') dt' . \tag{16}$$

In these equations, g denotes the gradient of the magnetic field, which has been assumed to determine the direction of the z axis. γ is the gyromagnetic ratio of the resonating nuclei and $z(t')$ denotes the z coordinate of the spin under consideration at time t'. In the following we shall consider two different experimental conditions: a time-independent field gradient (constant-field-gradient method) and a sequence of two identical field-gradient pulses (pulsed-field-gradient method).

In both cases the calculation is based on the assumption that the phase distribution can be approximated by a Gaussian function[10,11,13,15] so that one obtains

$$\Psi = \int_{-\infty}^{\infty} \cos\varphi \, \frac{1}{\sqrt{2\pi\langle\varphi^2\rangle}} \exp\left[-\frac{\varphi^2}{2\langle\varphi^2\rangle}\right] d\varphi$$

$$= \exp(-\langle\varphi^2\rangle/2) . \tag{17}$$

Hence the problem is reduced to the determination of the mean-square value of φ.

NMR field-gradient self-diffusion measurements are commonly carried out by applying a sequence of two rf pulses in addition to the magnetic field gradient. While the first rf pulse ($\pi/2$ pulse) defines the initial value of φ (for a constant field gradient), the second one (π pulse), applied at time τ, affects a change of the sign of φ. At time $t = 2\tau$, the mean-square value of φ passes through a minimum, thus giving rise to the formation of an NMR signal, the so-called spin echo. Hence, in order to determine the attenuation of the spin echo, we have to calculate the mean-square value of

$$\varphi(t = 2\tau) = \gamma \left[\int_0^\tau g(t')z(t')dt' - \int_\tau^{2\tau} g(t')z(t')dt' \right] . \tag{18}$$

This calculation must be based on the relations obtained for the correlation between subsequent molecular displacements.

A. Constant field-gradient experiments

Under the influence of a constant field gradient g_0, the mean-square value of φ according to Eq. (18) is given by the relation

$$\langle \varphi(t = 2\tau)^2 \rangle = \gamma^2 g_0^2 \left[\int_0^\tau \int_0^\tau \langle z(t')z(t'') \rangle dt'dt'' + \int_0^\tau \int_0^\tau \langle z(t')z(t'') \rangle dt'dt'' - 2 \int_0^\tau \int_\tau^{2\tau} \langle z(t')z(t'') \rangle dt'dt'' \right] , \tag{19}$$

which may be transferred into the following form:

$$\langle \varphi(t = 2\tau)^2 \rangle = \gamma^2 g_0^2 \left[\int_{t'=0}^\tau \int_{\theta=0}^{\tau-t'} \langle z(t')z(t'+\theta) \rangle d\theta \, dt' + \int_{t'=0}^\tau \int_{\theta=0}^{t'} \langle z(t')z(t'-\theta) \rangle d\theta \, dt' \right.$$

$$+ \int_{t'=\tau}^{2\tau} \int_{\theta=0}^{2\tau-t'} \langle z(t')z(t'+\theta) \rangle d\theta \, dt' + \int_{t'+\tau}^{2\tau} \int_{\theta=0}^{t'-\tau} \langle z(t')z(t'-\theta) \rangle d\theta \, dt$$

$$\left. - 2 \int_{t'=0}^\tau \int_{\theta=\tau-t'}^{2\tau-t'} \langle z(t')z(t'+\theta) \rangle d\theta \, dt' \right] . \tag{20}$$

If one assumes isotropy of space, i.e., the validity of the equation

$$\langle z(t')z(t'+\theta) \rangle = \tfrac{1}{3} \langle \mathbf{r}(t')\mathbf{r}(t'+\theta) \rangle , \tag{21}$$

one can easily show by means of the identity

$$\langle z(t')z(t'+\theta) \rangle \equiv \langle z(t')z(t') \rangle$$

$$+ \langle z(t')[z(t'+\theta) - z(t')] \rangle \tag{22}$$

and using Eqs. (1) and (5) that the integrands of Eq. (20) are equal to

$$\langle z(t')z(t'+\theta) \rangle = \frac{\alpha}{6} [(t'+\theta)^\kappa + t'^\kappa - \theta^\kappa] \tag{23}$$

and

$$\langle z(t')z(t'-\theta) \rangle = \frac{\alpha}{6} [(t'-\theta)^\kappa + t'^\kappa - \theta^\kappa] . \tag{24}$$

With Eqs. (23) and (24), in a straightforward but tedious procedure, the right-hand side of Eq. (19) may be integrated, and one obtains

$$\langle \varphi(t = 2\tau)^2 \rangle = \frac{(1 - 1/2^\kappa)}{3(\kappa+1)(\kappa+2)} \gamma^2 g^2 \alpha t^{\kappa+2} . \tag{25}$$

Inserting this expression into Eq. (17), the echo attenuation due to diffusion on fractal networks is found to be given by the relation

$$\Psi(t = 2\tau) = \exp\left[-\frac{(1 - 1/2^\kappa)}{6(\kappa+1)(\kappa+2)} \gamma^2 g^2 \alpha t^{\kappa+2}\right] . \tag{26}$$

It may be easily shown that in the limiting case of ordinary diffusion ($\kappa = 1$, $\alpha = 6D$) Eq. (26) coincides with the corresponding, familiar expression[8,9]

$$\Psi(t = 2\tau) = \exp(-\tfrac{1}{12} \gamma^2 g^2 D t^3) . \tag{27}$$

B. Pulsed-field-gradient experiments

In this case the field gradient is applied not permanently but in the form of two short pulses of length δ, intensity g, and separation Δ. If the first field-gradient pulse is between the $\pi/2$ pulse and the π pulse and the second one is between the π pulse and the spin echo, instead of Eq. (19) one has

$$\langle \varphi(t=2\tau)^2 \rangle = \gamma^2 g^2 \left[\int_{t'=t_1}^{t_1+\delta} \int_{\theta=t_1-t'}^{t_1+\delta-t'} \langle z(t')z(t'+\theta)\rangle d\theta \, dt' + \int_{t'=t_1+\Delta}^{t_1+\Delta+\delta} \int_{\theta=t_1+\Delta-t}^{t_1+\Delta+\delta-t'} \langle z(t')z(t'+\theta)\rangle d\theta \, dt' \right.$$
$$\left. -2\int_{t'=t_1}^{t_1+\delta} \int_{\theta=-t'}^{\delta-t'} \langle z(t')z(t_1+\Delta+t'+\theta)\rangle d\theta \, dt' \right] , \tag{28}$$

with $t_1 < \tau$ denoting the time interval between the $\pi/2$ pulse and the first-gradient pulse. Following the above outlined procedure, the attenuation of the spin echo is found to be

$$\Psi(t=2\tau)=\exp\left[-\frac{\gamma^2 g^2 \alpha}{3(\kappa+1)(\kappa+2)}[\tfrac{1}{2}(\Delta+\delta)^{\kappa+2}+\tfrac{1}{2}(\Delta-\delta)^{\kappa+2}-\Delta^{\kappa+2}-\delta^{\kappa+2}] \right] . \tag{29}$$

The fact that this result does not depend on the time t_1 of the insertion of the first field-gradient pulse may be understood as follows: In the present experiment the molecules are labeled by the first gradient pulse. Therefore t_1 does only notate the starting point of the diffusion process, and any dependence of the result on t_1 would violate the time invariance of the observed transport phenomena.

For field gradient pulses of short duration ($\delta \ll \Delta$), Eq. (29) reduces to

$$\Psi(t=2\tau)=\exp\left[-\gamma^2 g^2 \delta^2 \frac{\alpha}{6} \Delta^\kappa \right] , \tag{30}$$

which by means of Eq. (1) may be written as

$$\Psi(t=2\tau)=\exp[-\gamma^2 g^2 \delta^2 \langle r(\Delta)^2 \rangle /6] . \tag{31}$$

This equation, which is formally identical with the corresponding expression for ordinary diffusion, coincides with the expression predicted on the basis of the propagator concept of NMR pulses field-gradient spectroscopy.[4]

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