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THEORETICAL EXPRESSION AND MONTE CARLO SIMULATION OF DIFFUSION BEHAVIORS IN NMR WITH NONLINEAR FIELD GRADIENTS

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Abstract: A propagator method was used to calculate diffusion attenuation of the NMR signal under general nonlinear field gradients. Theoretical expressions of the attenuation factor were obtained for free and restricted diffusion between two plates. Monte Carlo simulation was performed and the results were compared with the theory. It shows that the theoretical method is appropriate for the free diffusion, as well as the restricted diffusion under the short gradient pulse approximation. Monte Carlo simulation provides an alternate way to quantify the effects of inhomogeneous field gradients used in MRI and NMR.

Key words: NMR, Nonlinear gradient, Diffusion, Simulation, Theoretical expression

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INTRODUCTION

The use of magnetic field gradients is an integral part of MRI and has become indispensable for some new high-resolution NMR experiments in recent years. It is, however, not often realized that typical gradient experiments are designed based on a near-perfect performance of the gradients, i.e. minimal residual gradients after switching and perfect gradient linearity over the sample[1]. In diffusion-weighted imaging (DWI), for example, several factors including background and imaging gradients, and spatial gradient field distortions,

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lead to considerable deviations between the designed and the actually applied diffusion-weighting or spatial encoding. The precision and accuracy of experimentally measured translation diffusion coefficients are limited by the linearity of the gradient pulses over the sample volume[2]. The inhomogeneous broadening due to background gradients causes the angular frequency deviation from the resonance frequency[3]. Although the effect of residual gradients has been studied in some details[4], consequences of gradient non-linearity have not been fully appreciated. It is clear that the study of diffusion in arbitrary inhomogeneous field is important for a host of current applications[5].

In practice, the gradient may be nonlinear due to different experimental conditions. Even when the applied fields are homogeneous, the difference in susceptibility of the constituent materials gives rise to a microscopically inhomogeneous field[6,7]. For example the susceptibility contrast between pore space and grains in rocks or between tissue and fluid in biological samples poses serious problems in NMR imaging and relaxation. The non-linearity leads to a systematic deviation of the experimental data from the Stejskal-Tanner equation[2]. However, except the simplest nonlinear gradient, parabolic field, little theoretical work has been carried out on signal decay under nonlinear gradients[8,9]. In this work, diffusion attenuation under general nonlinear gradient fields was studied by the propagator formalism we reported recently[10] and Monte Carlo simulation. The results would be useful for correcting the systematic deviation due to the inhomogeneous fields.

1 NONLINEAR MAGNETIC FIELD

Assuming that a general nonlinear magnetic field, $B(z)$ is along the Z axis, the magnetic field can be unfolded by a Taylor expansion:

$$B(z)=\sum_{n=0}^{\infty}\frac{B^{n}(0)}{n\,!}z^{n}, \tag{1}$$

where z is the position coordinate in the Z direction, n is the order and $B^{n}(0)$ is the coefficient of the Taylor series. The gradient function can then be described as follows:

$$g(z)=\mathrm{d}B(z)/\mathrm{d}z=\sum_{n=1}^{\infty}\frac{B^{n}(0)}{(n-1)\,!}z^{n-1}. \tag{2}$$

The phase shift due to gradient after t' time is given

$$\varphi(z,t')=\int_{0}^{t'}\Big[\sum_{j}p_j(t'')\gamma_j\Big]B(z)\mathrm{d}t'', \tag{3}$$

where p_j and γ_j are the coherence order and the gyromagnetic ratio of the j-th type spin, respectively. Substituting Eq. (1) into Eq. (3), we obtain the phase difference of the spins at coordinates z and z':

$$\varphi(z',t')-\varphi(z,t')=\int_{0}^{t'}\Big[\sum_{j}p_j(t'')\gamma_j\Big]\Big[\sum_{n=0}^{\infty}\frac{B^{n}(0)}{n\,!}(z'^{n}-z^{n})\Big]\mathrm{d}t''. \tag{4}$$

Let $(\Delta z)=z'-z$, the z'^{n} term in Eq. (4) can be obtain from a Taylor expansion:

$$z'^{n}=z^{n}+\sum_{m=1}^{n}\frac{n\,!z^{(n-m)}}{(n-m)\,!m\,!}(\Delta z)^{m}. \tag{5}$$

In the case of $a \gg (\Delta z)$, where a is the length of the sample along the Z axis, the higher order terms, $(\Delta z)^m$ $(m \geqslant 2)$, can be neglected.

Substituting Eqs. (2) and (5) into Eq. (4), we have:

$$\varphi(z', t') - \varphi(z, t') = \int_0^{t'} [\sum_j p_j(t'')\gamma_j] [\sum_{m=0}^{\infty} \frac{g^m(z)(\Delta z)^{m+1}}{(m+1)!}] \mathrm{d}t''$$
$$\approx \int_0^{t'} [\sum_j p_j(t'')\gamma_j][g(z)\Delta z] \mathrm{d}t'', \tag{6}$$

where $g^m(z)$ represents the m order derivative of $g(z)$.

Using the method of the propagator[10] and the gradient pulse sequences shown in Fig. 1, we obtain the diffusion attenuation factor $E(\Delta, z)$ for free diffusion:

$$E(\Delta, z) = \exp[-D\gamma^2 g^2(z)\delta^2(\Delta - \delta/3)], \tag{7}$$

where D is diffusion coefficient, δ is the duration of the gradient pulse, and Δ is the time interval between the two gradient pulses. The total attenuation of the signal over the whole sample can be obtained as follows:

$$E(\Delta) = \frac{1}{a}\int_0^a \exp\{-D\gamma^2 g^2(z)\delta^2(\Delta - \delta/3)\} \mathrm{d}z \tag{8}$$

In the case of k-order nonlinear magnetic field, $B(z) = \sum_{i=1}^{k} g_i z^i + B_0$, the following expression can be got easily from Eq. (7):

$$E(\Delta, z) = \exp[-D\gamma^2(\sum_{i=1}^{k} i g_i z^{i-1})^2 \delta^2(\Delta - \delta/3)]. \tag{9}$$

When $k = 2$, the attenuation factor after the first gradient pulse is $E(\delta, z) = \exp[-D\gamma^2(g_1 + 2g_2 z)^2 \delta^3/3]$, which is the same as the result derived from the modified Bloch's equation[11]. It also agrees with the results reported by Bendel[9]. In the case of a parabolic magnetic field with $g_1 = 0$ and the minimal value at the center of the sample, Eq. (9) predicts the same curve as Fig. (6) in Ref. [11]. In the next section, we will discuss gradient fields with minimal field at the edge of the sample. In this case, the "edge enhancement effect" is very obvious. Now consider the restricted diffusion between two parallel reflecting plates separated by a distance $a = 2R$. In the case of $\Delta \gg \delta$, the probability equation[12] is:

$$P(z, z', t) = 1 + 2\sum_{n=1}^{\infty} \exp(-\frac{n^2\pi^2 Dt}{(2R)^2})\cos(\frac{n\pi z}{2R})\cos(\frac{(n\pi z')}{2R}), \tag{10}$$

where the $p(z, z', t)$ is the probability of a particle starting from z and moving to z' in time interval t. The attenuation factor is then deduced to be:

$$E(t, z) = \frac{\int_0^{2\pi}[1 + 2\sum_{n=1}^{\infty}\exp(-\frac{n^2\pi^2 Dt}{(2R)^2})\cos(\frac{n\pi z}{2R})\cos(\frac{n\pi z'}{2R})] \cos[\gamma\delta(B(z') - B(z))] \mathrm{d}z'}{\int_0^{2\pi}[1 + 2\sum_{n=1}^{\infty}\exp(-\frac{n^2\pi^2 Dt}{(2R)^2})\cos(\frac{n\pi z}{2R})\cos(\frac{n\pi z'}{2R})] \mathrm{d}z'}. \tag{11}$$

Although it is difficult to get a general analytical solution of Eq. (11), numerical solution is available. The method provided herein is simpler to that in Ref. [5]. It is worth mention that, unlike Eq. (9), in Eq. (11) doenot need to be expanded by Taylor expansion. Therefore, Eq. (11) does not require the condition of $a \gg \Delta z$. It means that Eq. (11) is still valid when the displacement of particle Δz reaches the order of magnitude of the sample size a . In the following section, Eq. (11) will be used to correct the boundary effect.

2 MONTE CARLO SIMULATION AND DISCUSSION

Brownian-dynamics computer simulation is a simple way to investigate how the deviation of a magnetic field from a perfectly constant gradient influences the attenuation of the signal[2] . If the model of diffusion simulation is correct, the simulated results should be reasonable (for a given field-gradient profile) and suffer only from statistical uncertainty. Therefore, computer simulation was used to study the effect of nonlinear magnetic field.

The diffusion of a particle is represented as a sequence of small random displacements. Since the magnetic gradient is applied along the Z direction in the pulse sequence (Fig. 1), only the displacements of the particles along the Z direction need to be considered. We have

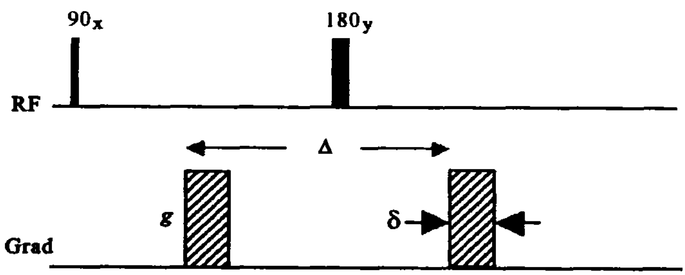

Fig. 1 PGSE pulse sequence

$$z(t+\Delta t) = z(t) + \Delta z, \qquad (12)$$

where $z(t)$ is the position of the particle at time t, $z(t+\Delta t)$, is the position of the particles at time $t+\Delta t$, and Δz is the random displacement of the particle in the time interval Δt. Since the walking of particles obeys the stochastic properties of Brownian particles, the random walk displacement Δz is given by:

$$\Delta z = \sqrt{2D\Delta t}\,\varepsilon\cos(\beta), \qquad (13)$$

where β is the angle between the z axis and the walking direction of the inspected particle, ε is a random number. The random numbers are totally uncorrelated, i.e., their distribution satisfies the free path distribution and their self—correlated coefficient is zero:

$$p(\varepsilon) = e^{-\varepsilon/\lambda}, \qquad (14)$$

where λ is the average free path which can be set as $\sqrt{2D\Delta t}$. Our simulation results showed that the sampling of free path distribution is better than that one of Gauss distribution which is usually used in the simulation of self—diffusion. We have

$$\varepsilon = -\ln(\varepsilon_1). \qquad (15)$$

Both ε_1 and β are distributed uniformly and can be produced by computer random function directly (ε_1 is limited to the range of 0 and 1, and β is limited to the range of 0 and 2π). To get reasonable simulation results, 450 000 particles were used and the random walk step was set to 100. The random function was produced by visual C++.

Firstly, the simplest nonlinear magnetic field, parabolic magnetic field, was simulated. The result was compared with the theoretical one. Let

$$B(z) = \frac{g_{max}}{2} z + \frac{g_{max}}{2R} z^2 - \frac{g_{max}}{6R^2} z^3 + B_0, \tag{16}$$

the gradient is given by:

$$g(z) = g_{max} - (z - R)^2 \times \frac{g_{max}}{2R^2}, \tag{17}$$

where $g_{max} = 2\pi q / \delta\gamma$ is the maximum gradient, and R is one half the length of the sample along the Z axis. The gradient value at $z = R$ is g_{max}. In our simulation, the length of the sample along the Z axis is set to 0.015 m. In such case, free diffusion can be assumed even if the diffusion time reaches the order of seconds. $q = \gamma g_{max} \delta / 2\pi$ is introduced to scale the gradient intensity for convenience.

Figure 2 shows the signal attenuation $E(z, \Delta)$ versus z for the free diffusion. The simulated results shown in Fig. 2(a) agree well with theoretical ones except when $z \to 0$ or $z \to 2R$. In the latter case, the simulated values are larger than the theoretical ones. The obvious derivation at the edge is called the "edge enhancement effect"[13]. The main reason may be due to the effect of boundary, which cannot be neglected when z is close to the boundary of the sample along the field gradient direction. For $\Delta \gg \delta$, Eq. (11) was used to correct the "edge enhancement effect". The corrected results near the boundary shown in Fig. 2(b) are improved and are more consistent with the theoretical values.

Secondly, we consider the NMR signal attenuation under the cosine-function magnetic field. The cosine field is of particular interest as it is taken as a crude model of microscopic inhomogeneous field originated from large difference in susceptibility near pore boundaries. Additionally, it is also a simple example of the field where the gradient at the walls vanishes. For a cosine field:

$$B(z) = B_1 \left(1 - \cos\left(\frac{\pi z}{2R}\right)\right) / 2 + B_0, \tag{18}$$

the magnetic gradient is:

$$g(z) = \frac{B_1 \pi}{4R} \sin\left(\frac{\pi z}{2R}\right), \tag{19}$$

where R and B_1 are constant. The attenuation factor can be written as:

$$E(\Delta, z) = \exp\left\{ - D\gamma^2 \left[\frac{B_1 \pi}{4R} \sin\left(\frac{\pi z}{2R}\right) \right]^2 \delta^2 (\Delta - \delta/3) \right\}, \tag{20}$$

In this case $q = \gamma g_{max} \delta / 2\pi = \gamma B_1 \delta / 8R$.

The simulated results are in good accord with the theoretical results in the whole z range (Fig. 2(c)) within the margin of the statistical error of Monte Carlo simulation. When $z \to 0$ or $z \to 2R$, the motion of the particles doesn't affect the NMR signal intensity due to the vanishing of field gradient. Therefore, the cosine filed has not "edge enhancement effect".

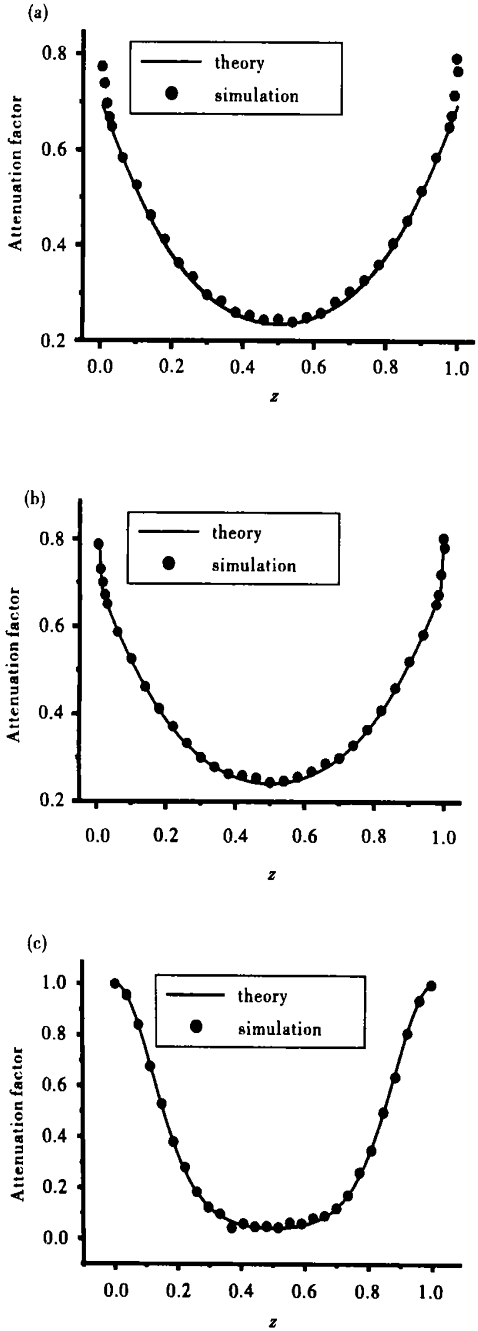

Fig. 2 Signal attenuation $E(z, \Delta)$ versus z for free diffusion, $D = 2.0 \times 10^{-9} m^2/s$. (a) The gradient field is a parabolic magnetic field, q = 3 000, a = 0.015 m, δ = 0.05 s, and Δ = 2.0 s. (b) The same as (a) with correction of the restricted effect near the edge. (c) The gradient field is a cosine magnetic field, q = 5 000, a = 0.015 m, δ = 0.2 s, and Δ = 1.5 s.

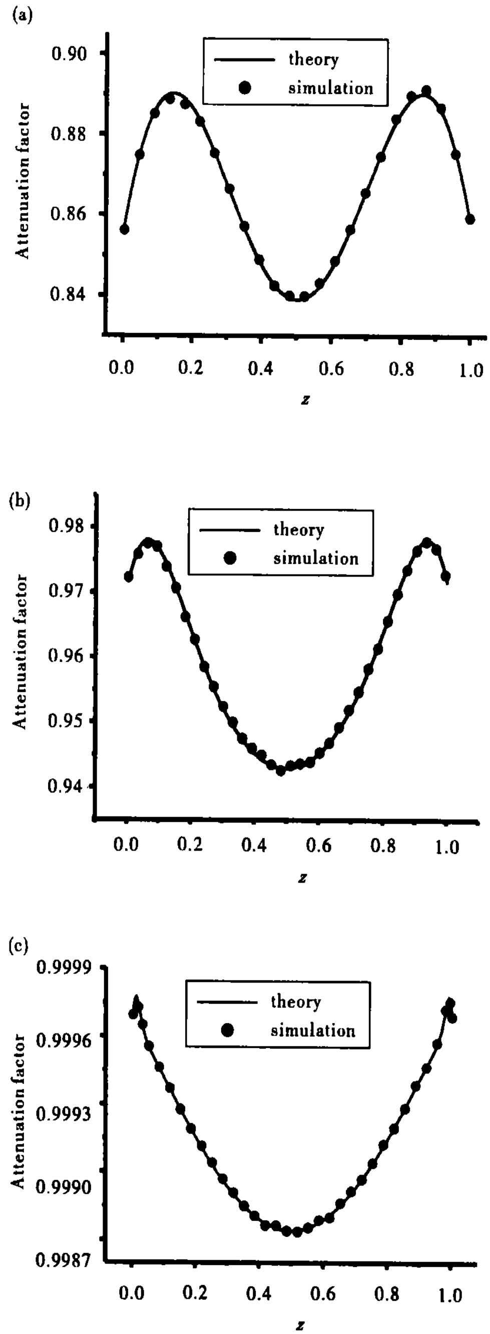

Fig. 3 Signal attenuation $E(z, \Delta)$ versus z for the restricted diffusion under parabolic magnetic field gradient with q = 8 000, $a = 5.2 \times 10^{-5}$ m, $\delta = 1.0 \times 10^{-8}$ s, and Δ = 0.05 s. (a) $D = 2.0 \times 10^{-9} m^2/s$; (b) $D = 5.0 \times 10^{-10} m^2/s$; and (c) $D = 1.0 \times 10^{-11} m^2/s$.

Now we discuss the signal attenuation of restricted diffusion between two plates. When the pulse width δ (see Fig. 1) is close to zero ($\delta \to 0$), the theoretical and simulated results with different diffusion rates were shown in Fig. 3. When $D=2.0\times 10^{-9}\ m^2/s$, the shape of the decaying curve shown in Fig. 3(a) is quite different from those of the free diffusion curves under the same gradient field (Fig. 2(a) and (b)). The maximum signal intensity doesn't occur near the walls where the gradient is the smallest due to the deviation of phase from the Gauss distribution caused by the boundary effect. These results showed that small diffusion rate decreases the boundary effect and makes the shape of the decaying curve more similar to those of free diffusion curves.

Similar analyses may provide information about the length scales of restricted diffusion, the character of self-diffusion, and the distribution of the magnetic field gradient. The information is useful for oil industry where porous materials are widely used in oil transportation. The different pore sizes, the heterogeneous pore distribution and the complicated pore connectivity make it difficult to determine by conventional techniques the characteristic pore—length scales that control fluid transport properties[14]. Exploiting the spatial variation of magnetic field inside the pore through NMR diffusion experiments, the primary pore-length scales can be deduced easily[15].

We also studied the precision of Monte Carlo simulation briefly. In general, increasing the number of particle and/or simulation step improves the precision of the simulation results, but it increases computational time in the meaning time. Therefore, it is necessary to find a balance between the precision and cost. Tables 1 and 2 listed the variation of root-mean-square deviation of the simulated results from the theoretical ones against the amount of simulation.

Table 1 Root-mean-square deviation σ of the simulated results from the theoretical ones against the number of simulated particle N

$N(\times 10^5)$	0.3	0.6	1.5	3.0	6.0	12	30	45
$\sigma(\times 10^{-2})$	5.6	3.8	2.6	1.9	1.3	0.96	0.72	0.50

Table 2 Root-mean-square deviation σ of the simulated results from the theoretical ones against the number of simulation step K with the simulated particle number 4.5×10^5

K	50	100	200	400	1 000	2 000	4 000	6 000
$\sigma(\times 10^{-2})$	1.8	1.5	1.5	1.6	1.6	1.5	1.6	1.6

Table 1 demonstrates that the deviation decreases with the increasing of the particle number. The selection of particle number depends on the precision required and the computational time affordable. When the particle number is 450 000, the deviation is smaller than 2%. Table 2 shows that the deviations hardly change when the step number exceeds 100, which was used in our simulations.

3 CONCLUSION

In this paper, a propagator method was used to describe the diffusion attenuation factor of NMR signal under general nonlinear field gradients. For the simplest nonlinear parabolic gradient field, the theoretical result agrees with the previous report. The results of Monte Carlo simulation under several gradient fields are consistent with the theoretical predictions for the free and restricted diffusion between two plates when $\Delta \gg \delta$. The effect of cosine field gradient is different from that of parabolic field gradient. The method discussed herein provides an easier way to quantify the effects of inhomogeneous field gradients used in MRI and NMR.

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NMR 中非线性梯度场下扩散行为的理论描述和蒙特卡罗模拟

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摘　要：利用传播子方法研究了在一般非线性场梯度下 NMR 信号的扩散衰减．在自由扩散和平板间的限制扩散情况下获得了扩散衰减因子的理论表达式．该表达式适用范围宽，且具有较简单的数学形式和明确的物理意义．文中还将理论预测与蒙特卡罗模拟结果进行了比较．结果表明：文中所采用的理论方法适合于表述自由扩散和短脉冲近似下的受限扩散；蒙特卡罗模拟提供了一种定性研究 MRI 和 NMR 中非均匀场梯度扩散衰减的方法．

关键词：核磁共振；非线性场梯度；扩散；模拟；理论表述

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