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Violation of the Gradient Approximation in NMR Self-Diffusion Measurements

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Dedicated to Prof. Dr. Dr. H. Pfeifer on the occasion of his 65th birthday

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The gradient approximation of magnetic field fails at NMR self-diffusion measurement with a very strong nonuniform magnetic field. The standard formula for self-diffusion attenuation of the spin-echoes has to be replaced by a new one where the role of the gradient of one field component ist taken over by the gradient of the magnitude of the total magnetic field. It leads to a distribution of the spin-echo attenuation in specimens, and to a nonexponential relation between the spin-echo signal and parameters of the applied nonuniform magnetic field. The anisotropy of particle migrations furthermore enlarges the nonuniformity of the attenuation distribution.

Die Gradientennäherung des magnetischen Feldes versagt bei NMR-Selbstdiffusionsmessungen mit einem starken inhomogenen Magnetfeld. Der Standardausdruck für die Selbstdiffusionsdämpfung des Spinechos muß durch einen neuen Ausdruck ersetzt werden, in dem die Rolle des Gradienten einer Feldkomponente vom Gradienten des Betrags des Magnetfeldes übernommen wird. Dies führt zu einer Verteilung der Spinechodämpfung in der Probe und zu Abweichungen vom exponentiellen Zusammenhang zwischen der Intensität des Spinechos und den Parametern des angelegten inhomogenen Magnetfeldes. Eine Anisotropie der Teilchenwanderung vergrößert die Ungleichmäßigkeit der Echodämpfung über der Probe.

1. Introduction

NMR self-diffusion measurement requires a magnetic field gradient that is strong enough to cause sufficient dephasing of the signal of migrating spins [1–3]. With very slow molecular migrations (10^{-14} m^2/s) one needs to apply extremely strong magnetic field gradient [3, 4]. There are reports of

NMR self-diffusion measurements in the fringe field of superconducting magnets [5]. They have realised magnetic field gradients of 10−100 T/m. The other limit is represented by NMR self-diffusion measurements in a weak earth's magnetic field [8]. Here, the necessary spin dephasing is brought about by the nonuniform magnetic field that is comparable to or larger than the weak homogeneous B_{zo}. Hence, both NMR self-diffusion measurements in a weak homogeneous magnetic field (the geomagnetic field) and in an extremely strong nonuniform magnetic field (the fringe field of the magnet) are at the margin of the magnetic field gradient approximation. In both cases, the inhomogeneous component of the field is of the same order of magnitude as the homogeneous one.

The spin precession is controlled by the magnitude and direction of the total magnetic field. Hence, migration along directions with a varying magnetic field leads to a spin dephasing and therefore to a spin-echo attenuation. Large inhomogeneous fields imply deviations from a simple linear relation between the intensity of the magnetic field and one space coordinate (the direction of the field gradient in the conventional magnetic field gradient representation), which leads to a non-uniform spin-echo attenuation. Diffusion anisotropy, involving unlike diffusion rates in different directions, leads to an additional nonuniformity of the attenuation. In specific experimental situations we can use NMR imaging to visualize the planar distribution of the spin-echo attenuation to determine the diffusion rates. From the nonexponential decay of the signal of a bulk sample, one can correctly evaluate the self-diffusion coefficient by knowing the geometry of the field, and the dimensions of a sample or a selected slice.

The term "magnetic field gradient" for a non-uniform magnetic field is only appropriate if it is much weaker than the main magnetic field, B_{zo}. Namely, according to Maxwell's equations the direction of a non-uniform magnetic field is changing along its line, and there must be always more than one component of the field different from zero. The inhomogeneous magnetic field at a point, shifted from the initial position by $\Delta\mathbf{r}$, can be written as:

$$\mathbf{B} = \mathbf{B}_o + \mathbf{B}_g\,(\Delta\mathbf{r},t) \tag{1}$$

$$\mathbf{B} = \mathbf{B}_o + \mathcal{G}(t)\,\Delta\mathbf{r} \tag{2}$$

with $\mathcal{G}$ being a tensor. In the case of $\mathbf{B}_g(\Delta\mathbf{r},t) \ll B_{zo}$, we may neglect the magnetic field component perpendicular to the static main magnetic field, and the magnetic field gradients are the remaining components of the tensor. With a strong nonuniform component of the magnetic field the definition of the magnetic field gradient fails, and the usual formula for the self-diffusion attenuation of the spin-echo is no longer valid. In the following, we shall recapitulate the basic idea of the NMR self-diffusion measurement in a strong inhomogeneous magnetic field, in order to precisely reveal the problems that can appear during measurements in a fringe field of magnets, and by other techniques with relatively large gradients.

2. Spin-Echo attenuation

All spins inside the coil contribute to the spin-echo, yielding [9]:

$$S(t) = S_o \left\langle \sum_i e^{i\theta(\mathbf{r}_i,t)} \right\rangle . \tag{3}$$

The average $\langle\rangle$ is to be taken over the remaining degrees of freedom including the effect of molecular migration. The spin phase appears as

$$\theta(\mathbf{r}_i,t) = \int_0^t \omega_{\text{eff}}^{\pi}[\mathbf{r}_i(t'),t']dt' , \tag{4}$$

with the tilted precession frequency [9] defined as

$$\omega_{\text{eff}}^{\pi}(\mathbf{r}_i,t)=\begin{cases} \omega_{\text{eff}}[\mathbf{r}_i(t),t], & 0 < t < \tau \\ -\omega_{\text{eff}}[\mathbf{r}_i(t),t], & \tau < t < 2\,\tau \end{cases} \tag{5}$$

if we assume that the π RF pulse acts at time τ. The effective frequency of the spin precession is

$$\omega_{\text{eff}}(\vec{r}_i, t) = \sqrt{(\omega_o + \gamma B_{gz}(\vec{r}_i, t))^2 + \gamma^2 B_{gy}(\vec{r}_i, t)^2 + \gamma^2 B_{gx}(\vec{r}_i, t)^2} \ . \tag{6}$$

Spin-echo sequences involving different RF and magnetic field gradient pulse program require an appropriate redefinition of $\omega_{\text{eff}}^{\pi}(\mathbf{r}_i,t)$.

A small shift of the particle from an initial position $\mathbf{r}_{io}$ to $\mathbf{r}_i(t) = \mathbf{r}_{io} + \Delta\,\mathbf{r}_i(t)$ changes the frequency of spin precession as

$$\omega_{\text{eff}}^{\pi}(\mathbf{r}_i(t),t) = \omega_{\text{eff}}^{\pi}(\mathbf{r}_{io},t) + \Delta\,\mathbf{r}_i(t)\ \text{grad}\ [\omega_{\text{eff}}^{\pi}(\mathbf{r}_{io},t)]. \tag{7}$$

By taking into account the rephasing of stationary spins at the time of the spin echo, $2\,\tau$

$$\int_0^{2\tau} \omega_{\text{eff}}^{\pi}(\mathbf{r}_{io},t)dt = 0, \tag{8}$$

the integration of Eq. (4) gives the phase shifts due to the particle velocity $\mathbf{v}_i$ [9] as

$$\theta(\mathbf{r}_i,2\,\tau) = -\int_0^{2\tau} \mathbf{F}_i(\mathbf{r}_{io},t)\mathbf{v}_i(t)dt, \tag{9}$$

with

$$\mathbf{F}(\mathbf{r}_{io},t) = \int_0^t grad\ [\omega_{\text{eff}}^{\pi}(\mathbf{r}_{io},t)]dt. \tag{10}$$

Ref. [8] shows the details of this calculation.

Random migration of the particles brings about a dephasing of the signal that results in an attentuation of the spin-echo signal. By replacing the average over the exponential terms in Eq. (3) by the average over the exponent [6, 9], with Eq. (9), one obtains

$$S(t) = S_o \sum_i e^{i\langle\theta_i(t)\rangle - \beta_i(t)}, \tag{11}$$

with the attenuation term

$$\beta_i(t) = \frac{1}{2}\int_0^t dt_1 \int_0^t dt_2\, \mathbf{F}(\mathbf{r}_{io},t_1)\cdot\langle\mathbf{v}(t_1)\,\mathbf{v}(t_2)\rangle\cdot\mathbf{F}(\mathbf{r}_{io},t_2). \tag{12}$$

In its most general form, the time correlation between the compontents of particle velocity represents a tensor [7]:

$$\mathcal{D}(t_1, t_2) = \frac{1}{2}\begin{bmatrix} \langle v_x(t_1)v_x(t_2)\rangle & \langle v_x(t_1)v_y(t_2)\rangle & \langle v_x(t_1)v_z(t_2)\rangle \\ \langle v_y(t_1)v_x(t_2)\rangle & \langle v_y(t_1)v_y(t_2)\rangle & \langle v_y(t_1)v_z(t_2)\rangle \\ \langle v_z(t_1)v_x(t_2)\rangle & \langle v_z(t_1)v_y(t_2)\rangle & \langle v_z(t_1)v_z(t_2)\rangle \end{bmatrix}, \tag{13}$$

so that the damping term [Eq. (12)] can be written as

$$\beta_i(t) = \int_0^t dt_1 \int_0^t dt_2\, \mathbf{F}(\mathbf{r}_{io},t_1)\,\mathcal{D}(t_1,t_2)\,\mathbf{F}(\mathbf{r}_{io},t_2). \tag{14}$$

In the case of isotropic molecular random walk, it is the unity tensor multiplied by the self-diffusion coefficient D. The resulting spin-echo attenuation is

$$\beta_i(t) = D\int_0^t |\mathbf{F}(\mathbf{r}_{io},t')|^2\, dt'. \tag{15}$$

At first sight, Eq. (15) resembles Torrey's well-known expression [2]. But there is a significant difference: The dependence of the phase term, $\mathbf{F}(\mathbf{r}_{io},t)$, on the spin location results in a spatial dependence of the spin-echo attenuation in the examined samples. In the following, we shall see how it depends on the geometry of the applied nonuniform magnetic field, and on the anisotropy of particle migration. In Bloch-Torrey's expression, one neglects the transverse component of the magnetic field, and the signal attenuation results from the migration along the gradient of the main field. In the following, we shall consider the influence of strong magnetic field gradients on the spin-echo attenuation brought about by the spatial dependence of the magnetic field in all dimensions.

3. Line gradient of the magnetic field

3.1 General relationship

In a strong inhomogeneous magnetic field all components are of relevance. By taking into account the Maxwell equations for the magnetic field inside the gradient coils, $rot\mathbf{B} = 0$, the gradient of the Larmor frequency in Eq. (10) may be transformed into

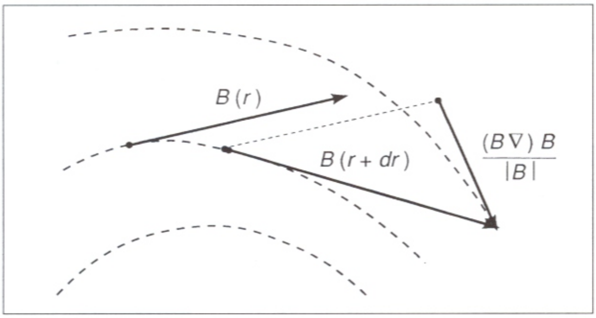

Fig. 1. The variation of the magnetic field along its line (the "line gradient of magnetic field").

$$grad\,\omega = \gamma \frac{(\mathbf{B}\ \nabla)\mathbf{B}}{|\mathbf{B}|}. \tag{16}$$

The right side of the expression is the derivative of the magnetic field along the magnetic field vector. It means that the vector *grad* ω is pointing in the direction of the magnetic field variation along its line, $(\mathbf{B}\ \nabla)\mathbf{B}$ (Fig. 1), and only migration along this direction effects a spin-echo attenuation. Thus, the former role of the gradient of only one component of the weak gradient magnetic field is now assumed by the variation of the magnetic field along its line. We call it "the line gradient of the magnetic field" (LGMF). Let us in the following consider the effect of isotropic and anisotropic self-diffusion on the spin-echo attenuation in the inhomogeneous magnetic field created by different coils.

3.2 Quadrupolar coils

Near the centre of the coils, the total magnetic field of quadrupolar gradient coils and of the main field B_0, which is perpendicular to the coil axis, can be approximated by

$$\mathbf{B} = (-Gz, 0, -Gx + B_o). \tag{17}$$

G is the first derivative of the nonuniform magnetic field at the cylinder axis. The gradient of the field magnitude is

$$grad|\mathbf{B}| = G \frac{(-Gx + B_0, 0, -Gz)}{|\mathbf{B}|} \tag{18}$$

with the absolute value

$$|grad|\mathbf{B}||^2 = G^2. \tag{19}$$

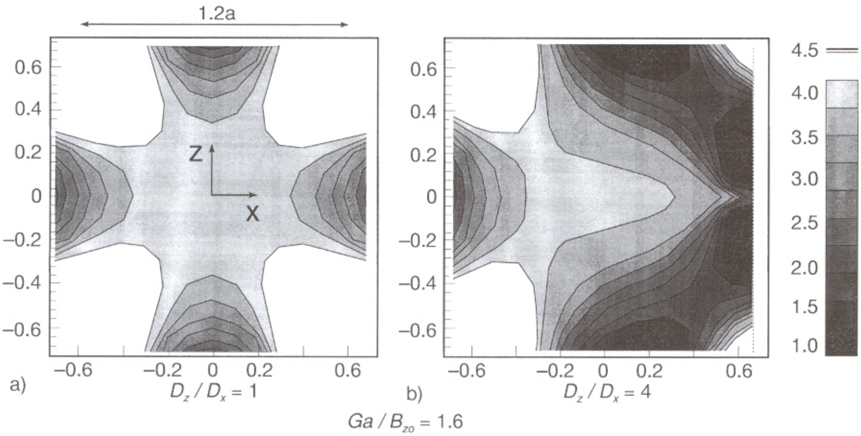

Fig. 2. The planar distribution of the spin-echo attenuation, $\log[S_o/S(2\,\tau)]$, for a.) isotropic and b.) anisotropic self-diffusion in the quadrupolar coils, with $\gamma^2\, G^2\, g(\tau)\, D_x$ equal to 4 in the center of the coils.

The absolute value of the line gradient is constant, and the resulting spin-echo attenuation is uniform in the sample. Fig. 2 shows the distribution of the square of the line gradient for the real quadrupolar coil, where the main field is directed along the z-axis. It turns out that the approximation Eq. (17) is correct in a very broad region around the coil axis. The spin-echo intensity results from

$$\ln \frac{S(t)}{S_0} = \gamma^2 D \int_0^t \Big| \int_0^u G^{\pi}(t')dt' \Big|^2 du, \tag{20}$$

which is identical to Torrey's expression. The anisotropy of diffusion leads to a nonuniform distribution of the spin-echo attenuation, Fig. 2 b. With the main axes of the diffusion tensor oriented along the coordinate axes one has

$$\mathcal{D}(t_1-t_2) = \begin{bmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{bmatrix} \delta(t_1 - t_2), \tag{21}$$

and the spin echo attenuation becomes

$$S(2\,\tau) = S_0 \int\int e^{-\gamma^2 G^2 g(\tau) \frac{D_1(-Bo + Gx)^2 + D_3 G^2 z^2}{(-Bo + Gx)^2 + G^2 z^2}} dx\, dy\, dz \tag{22}$$

with $g(\tau) = \delta^2\,(\tau - \delta/3)$. The anisotropic migration of a particle causes a nonuniform distribution of the spin-echo attenuation. It depends on the sample dimensions and on the degree of anisotropy. Fig. 2 b shows the distribution of the attenuation along the sample if the diffusion rate in one

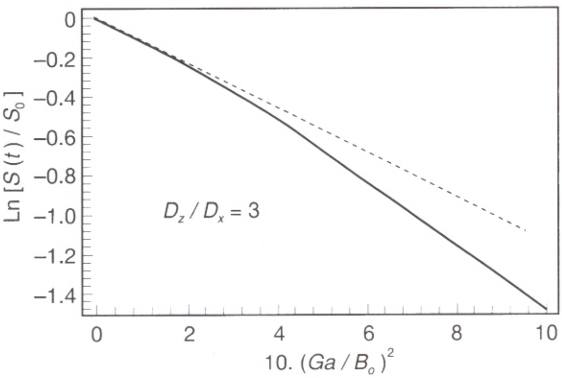

Fig. 3. The spin-echo intensity as a function of the square of the gradient amplitude for anisotropic self-diffusion in quadrupolar coils.

direction is four times faster than along the other one. In Fig. 2 b the inhomogenous component of the field at the figures edges is equal to the main field B_o.

The nonuniform distribution of the attenuation leads to a spin-echo intensity [Eq. (11)], which does not follow the usual dependence on the gradient amplitude and its duration. The calculation with Eq. (11) and Eq. (17) gives

$$S(2\tau) = S_o e^{-\gamma^2 G^2 D_1 g(\tau)} \left[\frac{1 + \gamma^2 G^2 (D_1 - D_2)}{3} g(\tau) \left[\frac{G^2 l_z^2}{B_o^2} + \frac{G^3 l_x^3}{B_o^3} + \ldots \right] \right] \tag{23}$$

when Gl_x and $Gl_z \ll B_o \cdot l_x$ and l_z denote the sample dimensions. It discloses that the signal digresses from the usual exponential dependence on G^2 and $g(\tau)$. Fig. 3 shows the result of the exact calculation where the deviation from the linear relation between the logarithm of the signal and G^2 becomes visible when the inhomogeneous field is about half of the homogeneous one. In this example, the diffusion rate along the z-direction is three times faster than the rate along the x-axis.

3.3 The Maxwell pair coils

In the center of a Maxwell pair of coils the radial component of the magnetic field is only half of the longitudinal one. With the main magnetic field pointing parallel to the coil axis the total magnetic field is

$$\mathbf{B} = (Gx/2, Gy/2, Gz + B_o) \tag{24}$$

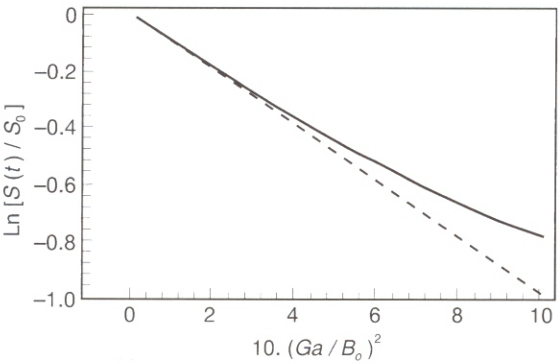

Fig. 4. The spin-echo intensity as a function of the magnetic field gradient for isotropic self-diffusion in the Maxwell pair coils.

and the gradient of the field magnitude is

$$grad|\mathbf{B}| = G\,\frac{[Gx/4,\, Gy/4,\, [Gz + B_o]]}{|\mathbf{B}|} \tag{25}$$

The square of the line gradient is not constant. Therefore, the spin-echo attenuation depends upon the spin location in the sample even for an isotropic self-diffusion. Fig. 4 shows the result of the exact numerical calculation that proves that the spin-echo attenuation does not follow the exponential law when the strenght of the inhomogeneous field Ga reaches about half of B_o. With the condition $\mathbf{B}_g(\mathbf{r}_i,t) \leqslant B_{zo}$ the solution of Eq. (11) and Eq. (15) for isotropic diffusion is

$$S(2\,\tau) = S_o\, e^{-\gamma^2 D\, G^2 g(\tau)} \left[1 - \gamma^2\, D\, G^2\, g(\tau) \frac{G^2(l_x^2 + l_y^2)}{B_o^2} + \ldots \right]. \tag{26}$$

l_x and l_y denote the sample dimensions.

3.4 Fringe field of a magnet, simple coils as a model

There are reports on using the fringe field of superconducting magnets for the measurement of very slow diffusion processes [5]. By this means, they provide a very strong nonuniform magnetic field with gradients of 10−100 T/m. Therefore, the ratio of the nonuniform field component versus the uniform cannot be a small number. On interpretating these results, one hence has to consider a possible violation of the gradient approximation. The fringe field of magnet may not be so well defined as that produced by the quadrupolar coils and Maxwell pair coils. As a model system, in the

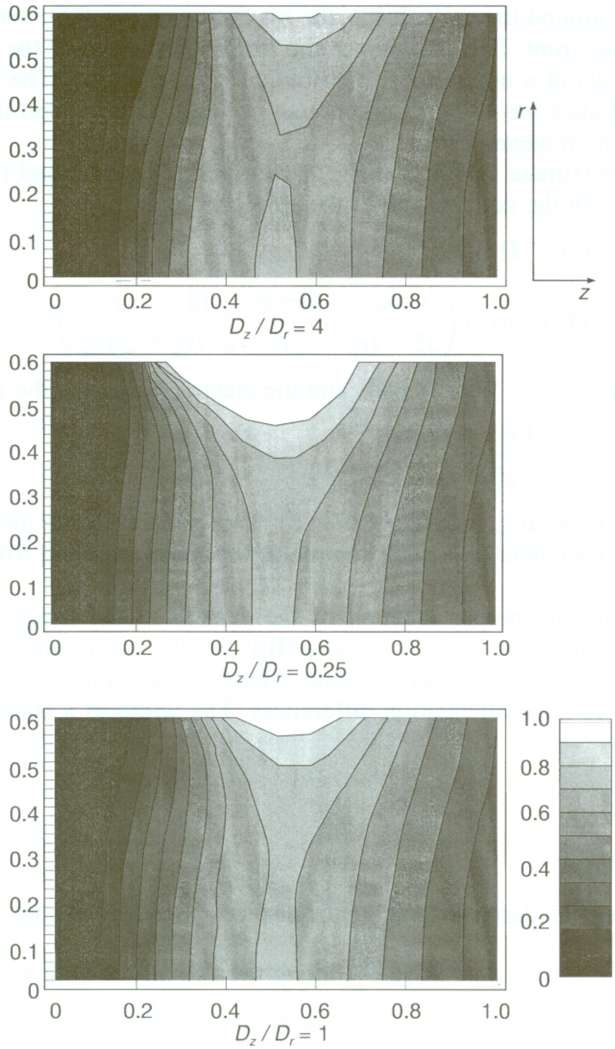

Fig. 5. The planar distribution of the spin-echo attenuation, $\log[S_o/S(2\,\tau)]$ in arbitrary units for anisotropic and isotropic diffusion in the near field of the coil at a fixed value of $\gamma^2\ G^2\ g(\tau)\ D_z$. The dimension is in units of the coil radius.

following we shall consider the magnetic field distribution created by simple coils of radius r_o. We have obtained the spatial distribution of the spin-echo damping from Eq. [12] by numerical evaluation of the magnetic field around the coil axis. Fig. 5 shows that the square of the line gradient is changing around the coils. It has the maximum at $z = 0.5\, r$ with a broad homogeneous front. This is a proper site for the placement of the specimen, in order to avoid a nonuniform distribution of attenuation. The sample or the selected slice has to be small enough not to extend beyond the regions of gradient homogeneity.

The approximate calculation for the sample of radius r and thickness z located at z_o on the coil axis gives the spin-echo intensity

$$S(2\,\tau) = S_o\, e^{-\gamma^2\, D\, G^{2(z_o)} g(\tau)} \tag{27}$$
$$\left[1 - \gamma^2\, D\, G^2(z_o) k(\tau) \left(\frac{3}{32}\, \frac{(8r_o^2 - 23z_o^2)r^2}{(r_o^2 + z_o^2)^2} + \frac{(4\, z_o^2 - r_o^2)\, z}{(r_o^2 + z_o^2)\, z_o}\right) + \ldots\right]$$

if $r \ll r_o$ and $z \ll z_o$. With N coils and the electric current I, the gradient

$$G(z_o) = \frac{\mu_o\, N\, I\, r_o^2\, z_o}{2\, (r_o^2 + z_o^2)^{5/2}} \tag{28}$$

has its maximum at $z_o = r_o/2$ (cf. Fig. 5). This position is the most suitable site for the placement of a small sample or for a slice selected from a larger specimen.

Therefore, the proper location of the sample in the fringe field of a magnet is at the point where $g = |grad|\mathbf{B}||^2$ has the maximum. But outside of it one has to take precautions with regard to the sample dimension, in order to avoid large attenuation differences. The width of a slice, z, should be

$$z \ll \frac{g}{\frac{dg}{dz}}, \tag{29}$$

with $\frac{dg}{dz}$ being the derivative perpendicular to a slice. Fig. 6 shows the variation of $g(z)$, and its derivative, $\frac{dg}{dz}$, along the axis of the simple coil.

Fig. 5 also shows how the attenuation distribution changes with varying degree of diffusion anisotropy.

4. Conclusion

When the inhomogeneous magnetic field in spin-echo self-diffusion measurements becomes comparable with the homogeneous component of the field, the usual dependence of the signal intensity on the gradient parameters must be replaced by a new relation. Otherwise, incorrect conclusions about the microscopic processes leading to the observed spin-echo attenuation

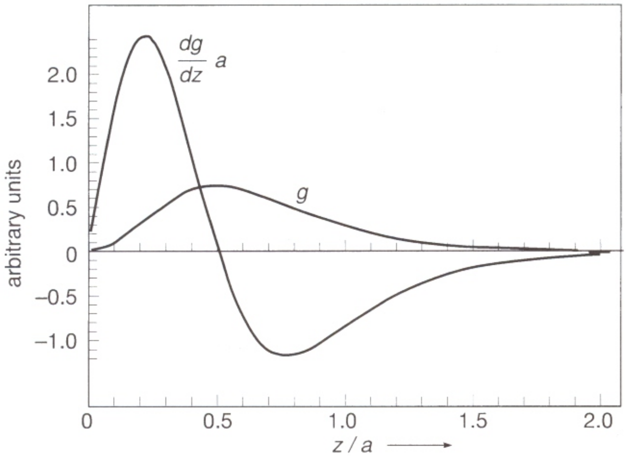

Fig. 6. The variation of the gradient, g, and its derivative, $\frac{dg}{dh}$, along the axis of the coil.

may be drawn. The method offers a new technique to determine the self-diffusion tensor from the NMR image of the spin-echo attenuation distribution.

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