JOURNAL OF MAGNETIC RESONANCE, Series A 107, 167–172 (1994)

Strong Nonuniform Magnetic Field for Self-Diffusion Measurement by NMR in the Earth's Magnetic Field

JANEZ STEPIŠNIK, MIHA KOS, GORAZD PLANINŠIČ, AND VITAL ERŽEN

Physics Department, University of Ljubljana, and J. Stefan Institute, Jadranska 19, 61 111 Ljubljana, Slovenia

Received June 14, 1993; revised August 2, 1993

Self-diffusion measurement by NMR requires a magnetic-field gradient that is strong enough to cause sufficient dephasing of the signal of migrating spins in the time of its application. The spin-relaxation mechanism limits the duration of the gradient field, and whenever particle migration is slow, the strength of the required inhomogeneous magnetic field may exceed that of the main magnetic field. In this case, the definition of the magnetic-field gradient fails and the usual formula for self-diffusion attenuation of spin echoes is no longer valid. This always happens with NMR in the earth's weak magnetic field. In the paper an expression for the self-diffusion attenuation of the spin echo is derived that is valid for a strong nonuniform magnetic field, and it is shown that the nonuniform magnetic field must have the appropriate spatial symmetry and that only isotropic self-diffusion can be measured with the new method. NMR measurement in the earth's magnetic field of the self-diffusion constants in some liquids confirms these results.

INTRODUCTION

The determination of molecular migration with nuclear magnetic resonance has a long history (*1–5*). Being nondestructive and noninvasive, the method is attractive for the study of random molecular migration in various systems. It uses labeling of molecules by changing the phase of spin precession. A nonuniform magnetic field, $\mathbf{B}_g(\mathbf{r}_i, t)$, creates a nonuniform precession of spins. Particle migration across the inhomogeneous magnetic field causes a dephasing of the spin induction, which leads to an attenuation of the spin signal. The attenuation depends on the strength of the nonuniform magnetic field, its duration, and the rate of the particle migration. The spin relaxation limits the time of gradient application in the spin-echo experiment, and in circumstances of slow migration, a strong inhomogeneous magnetic field must be applied.

The usual technique uses the spin-echo RF sequence with pulses of the magnetic-field gradient. In NMR "the magnetic-field gradient" is called a nonuniform magnetic field only when it is weaker than the main magnetic field, B_{z0}. According to Maxwell's equations, the direction of a nonuniform magnetic field is always changing. This means that there is always more than one component of the field different from zero. The inhomogeneous magnetic field at a point shifted from the initial position for $d\mathbf{r}$ can be written

$$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_g(\mathbf{r}, t) \quad [1]$$

$$= \mathbf{B}_0 + \mathcal{G}(t)d\mathbf{r}, \quad [2]$$

with $\mathcal{G}$ being a tensor. In the case of $\mathbf{B}_g(\mathbf{r}_i, t) \ll B_{z0}$ the magnetic-field components perpendicular to the static magnetic field are neglected. The magnetic-field gradients are the remaining components of the tensor. This approximation has no meaning whenever the applied nonuniform magnetic field is of the order of or larger than the main magnetic field.

Herein, we consider this problem in order to find a way to measure diffusion by NMR in a weak magnetic field such as the earth's magnetic field. In a weak main magnetic field, we can only employ a weak magnetic-field gradient, and the spins may not accumulate measurable signal dephasing in the interval between the gradient pulses. Therefore a stronger nonuniform magnetic field is needed to replace the magnetic-field gradient. Its strength may be greater than that of the main magnetic field. In this case, the perpendicular components of the nonuniform magnetic field also become important and the usual formula that uses approximation with a magnetic-field gradient must be carefully reconsidered.

MIGRATING SPINS IN AN INHOMOGENEOUS MAGNETIC FIELD

The spin-precession properties of the system in a spin-echo experiment are governed by the Hamiltonian

$$\mathcal{H} = -\hbar\omega_0\mathcal{I}_z - \hbar\gamma \sum_i \mathbf{B}_g(\mathbf{r}_i, t)\boldsymbol{\mathcal{I}}_i + \mathcal{H}_{RF}, \quad [3]$$

with $\gamma B_{z0} = \omega_0$ and with $\mathcal{H}_{RF}$ describing the effect of the RF pulses. The frequency of spin precession depends upon the location of a molecule $\mathbf{r}_i$ and changes with migration. The

1064-1858/94 $6.00

RF pulses and other magnetic fields affect spin dynamics. The time-evolution operator of the system is

$$\mathcal{U}(t) = \exp\left[-\frac{i}{\hbar}\int_0^t \mathcal{H}(t')dt'\right], \qquad [4]$$

$$\mathcal{U}(t) = \mathcal{U}_{m2}(t)\mathcal{U}_{\pi}\mathcal{U}_{m1}(t)\mathcal{U}_{\pi/2}, \qquad [5]$$

where $\mathcal{U}_{\pi}$ and $\mathcal{U}_{\pi/2}$ are the operators of the $\pi/2$ and π RF pulses, respectively. $\mathcal{U}_{m1}$ and $\mathcal{U}_{m2}$ describe the spin precession in the static and the nonuniform magnetic fields before and after the π RF pulse. They are responsible for the effects of spin dephasing resulting from the particle migration. With the factoring theorem (*6*) we can transform

$$\mathcal{U}_m = \exp\left[i\int_0^t \omega_0\mathcal{I}_z - \gamma\sum_i \mathbf{B}_g(\mathbf{r}_i, t')\boldsymbol{\mathcal{I}}_i dt'\right] \qquad [6]$$

into

$$\mathcal{U}_m(t) = \mathcal{T}\exp\left[i\sum_i\int_0^t [\dot{\boldsymbol{\varphi}}(\mathbf{r}_i, t')\boldsymbol{\mathcal{I}}_i + \omega_{\text{eff}}(\mathbf{r}_i, t')\mathcal{I}_{zi}dt'\right]\mathcal{R}(t), \qquad [7]$$

where

$$\mathcal{R}(t) = \exp\left[-i\sum_i\int_0^t \dot{\boldsymbol{\varphi}}(\mathbf{r}_i, t')\boldsymbol{\mathcal{I}}_i dt'\right]. \qquad [8]$$

The operator $\mathcal{R}(t)$ represents rotation around the direction of the vector $\boldsymbol{\varphi}(\mathbf{r}_i, t)$, which is perpendicular to the plane lying on the z axis and the line along $\mathbf{B}_g(\mathbf{r}_i, t)$ (see the Appendix). The effective precession frequency is

$$\omega_{\text{eff}}(\mathbf{r}_i, t) = \sqrt{[\omega_0 + \gamma B_{gz}(\mathbf{r}_i, t)]^2 + \gamma^2 B_{gy}(\mathbf{r}_i, t)^2 + \gamma^2 B_{gx}(\mathbf{r}_i, t)^2}. \qquad [9]$$

According to Eq. [7], the rate of magnetic-field variation determines the spin response. In the case of slow field variation

$$|\dot{\boldsymbol{\varphi}}(\mathbf{r}_i, t)| \ll \omega_{\text{eff}}(\mathbf{r}_i, t), \qquad [10]$$

one can neglect the angular velocity $|\dot{\boldsymbol{\varphi}}(\mathbf{r}_i, t)|$ in the first term of Eq. [7].

The time-evolution operator, Eq. [7], is reduced to

$$\mathcal{U}_m(t) = \exp\left[i\sum_i\int_0^t \omega_{\text{eff}}(\mathbf{r}_i, t')\mathcal{I}_{zi}dt'\right]. \qquad [11]$$

The spin-echo induction in the coil follows from

$$S(t) = -\frac{\hbar\gamma}{i_c}\frac{d}{dt}\sum_j \langle \mathcal{I}_{xj}(t)B_{x1}(\mathbf{r}_j)\rangle \qquad [12]$$

and the use of Eqs. [5] and [11] gives the signal (*7*) as the sum of the contributions from all spins inside the coil:

$$S(t) = S_0\langle \sum_i e^{i\theta(\mathbf{r}_i, t)}\rangle. \qquad [13]$$

The average over the remaining degree of freedom $\langle\ \rangle$ also includes the effects of molecular migration. The spin phase appears as

$$\theta(\mathbf{r}_i, t) = \int_0^t \omega_{\text{eff}}^{\pi}[\mathbf{r}_i(t'), t']dt', \qquad [14]$$

with the tilted precession frequency (*7*) defined as

$$\omega_{\text{eff}}^{\pi}(\mathbf{r}_i, t) = \begin{cases} \omega_{\text{eff}}[\mathbf{r}_i(t), t], & 0 < t < \tau, \\ -\omega_{\text{eff}}[\mathbf{r}_i(t), t], & \tau < t < 2\tau, \end{cases} \qquad [15]$$

if we assume that the π RF pulse acts at time τ and that at this time the nonuniform magnetic field is zero. We can write a shift of the particle from an initial position as $\mathbf{r}_i(t') = \mathbf{r}_{i0} + \Delta\mathbf{r}_i(t')$, and the frequency of spin precession becomes

$$\omega_{\text{eff}}^{\pi}[\mathbf{r}_i(t'), t'] = \omega_{\text{eff}}^{\pi}(\mathbf{r}_{i0}, t') + \Delta\mathbf{r}_i(t)\text{grad}[\omega_{\text{eff}}^{\pi}(\mathbf{r}_{i0}, t')]. \qquad [16]$$

With use of Eq. [16], the integration by parts of Eq. [14] gives the phase of spins at the peak of the spin-echo signal (*7*),

$$\theta(\mathbf{r}_i, 2\tau) = -\int_0^{2\tau} \mathbf{F}_i(\mathbf{r}_{i0}, t)\mathbf{v}_i(t)dt, \qquad [17]$$

where $\mathbf{v}_i$ is particle velocity and with

$$\mathbf{F}(\mathbf{r}_{i0}, t) = \int_0^t \text{grad}[\omega_{\text{eff}}^{\pi}(\mathbf{r}_{i0}, t)]dt. \qquad [18]$$

In Eq. [17] we assume that the applied sequence of inhomogeneous magnetic field and π RF pulses brings about a refocusing of the spin phase at time 2τ, so that

$$\int_0^{2\tau} \omega_{\text{eff}}^{\pi}(\mathbf{r}_{i0}, t)dt = 0, \qquad [19]$$

and according to the definition in Eq. [18] also

$$\mathbf{F}(\mathbf{r}_{i0}, 2\tau) = 0. \quad [20]$$

The last reference of (7) shows the details of this calculation.

SELF-DIFFUSION WITH A STRONG INHOMOGENEOUS MAGNETIC FIELD

Random migration of particles brings about a dephasing of the signal, which results in its attenuation. By using the transformation of the average over the exponent in Eq. [13] into the averages over the exponential terms (8, 7), Eq. [17] becomes

$$S(t) = S_0 \sum_i e^{-\beta_i(t)}, \quad [21]$$

with the attenuation term

$$\beta_i(t) = \frac{1}{2}\int_0^t dt_1 \int_0^t dt_2 \mathbf{F}(\mathbf{r}_{i0}, t_1)\cdot \langle \mathbf{v}(t_1)\mathbf{v}(t_2)\rangle \cdot \mathbf{F}(\mathbf{r}_{i0}, t_2). \quad [22]$$

In general form the time correlation between the components of particle velocity represents a tensor,

$$\mathcal{D}(t_1, t_2) = \frac{1}{2}\begin{bmatrix} \langle v_x(t_1)v_x(t_2)\rangle & \langle v_x(t_1)v_y(t_2)\rangle & \langle v_x(t_1)v_z(t_2)\rangle \\ \langle v_y(t_1)v_x(t_2)\rangle & \langle v_y(t_1)v_y(t_2)\rangle & \langle v_y(t_1)v_z(t_2)\rangle \\ \langle v_z(t_1)v_x(t_2)\rangle & \langle v_z(t_1)v_y(t_2)\rangle & \langle v_z(t_1)v_z(t_2)\rangle \end{bmatrix}, \quad [23]$$

so that the damping term (Eq. [22]) can be written as

$$\beta_i(t) = \int_0^t dt_1 \int_0^t dt_2 \mathbf{F}(\mathbf{r}_{i0}, t_1)\mathcal{D}(t_1, t_2)\mathbf{F}(\mathbf{r}_{i0}, t_2). \quad [24]$$

We will limit further consideration to the case of an isotropic molecular random walk where the tensor has the form

$$\mathcal{D}(t_1 - t_2) = D\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\delta(t_1 - t_2), \quad [25]$$

with D being the self-diffusion coefficient. Thus Eq. [22] is simplified to

$$\beta_i(t) = D\int_0^t |\mathbf{F}(\mathbf{r}_{i0}, t')|^2 dt'. \quad [26]$$

At first sight this resembles Torrey's well-known expression (5) but there are notable distinctions. In the classical technique, the perpendicular components of the magnetic field are neglected, and migration along the gradient of the component parallel to the main field is responsible for the signal attenuation. In our case all the components of the magnetic field play a part. Thus $\mathbf{F}(\mathbf{r}_{i0}, t)$ includes the gradient of Larmor frequency $\omega_{\mathrm{eff}}[\mathbf{r}_i(t), t]$, which is related to the magnetic field as

$$\operatorname{grad}\omega = \gamma\frac{B_x \operatorname{grad} B_x + B_y \operatorname{grad} B_y + B_z \operatorname{grad} B_z}{|\mathbf{B}|}. \quad [27]$$

By taking into account the equation rot $\mathbf{B} = 0$, this expression becomes

$$\operatorname{grad}\omega = \gamma\frac{(\mathbf{B}\boldsymbol{\Delta})\mathbf{B}}{|\mathbf{B}|}. \quad [28]$$

Thus the gradient of the effective Larmor frequency is proportional to the change of the magnetic field along its direction. We can call it the line gradient of the magnetic field (LGMF). The main difference from Torrey's approximation is that spin dephasing results from the molecular motion along the gradient of lines of the total magnetic field.

For quadrupolar gradient coils with the axis perpendicular to the main field B_0, the sum of both fields can be approximated as $\mathbf{B} = (-Gz, 0, -Gx + B_0)$ in a wide region between the coils. Here G is the first derivative of the nonuniform magnetic field at the point where the coordinates x, y, and z are zero. The gradient of the field magnitude is

$$\operatorname{grad}|\mathbf{B}| = G\frac{Gx - B_0, 0, Gz}{|\mathbf{B}|} \quad [29]$$

with the absolute value

$$|\operatorname{grad}|\mathbf{B}||^2 = G^2. \quad [30]$$

The self-diffusion attenuation follows from Eq. [26] as

$$\ln\frac{S(t)}{S_0} = \gamma^2 D\int_0^t \left|\int_0^u G(t')dt'\right|^2 du. \quad [31]$$

By chance this formula is identical to Torrey's well-known result but it does not occur for an inhomogeneous magnetic field created by the reversed Helmoltz coil. We show results of this calculation in the Appendix and there we have proved that it is unsuitable for self-diffusion measurement when $|\mathbf{B}_g(\mathbf{r}_i, t)| \geqslant B_{z0}$. There results a rule that the method works only if nonzero components of a strong nonuniform magnetic field have the same first derivative. Thus, the technique

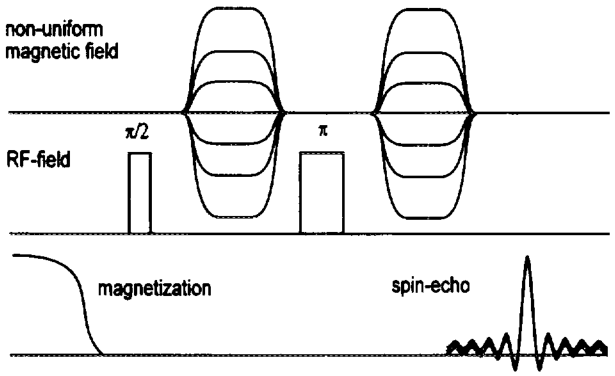

FIG. 1. The pulse sequence used for self-diffusion measurement by NMR in the earth's magnetic field.

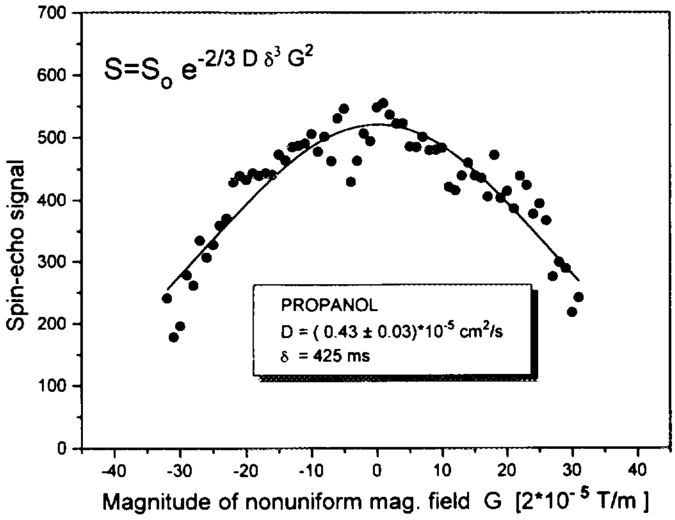

FIG. 3. The spin-echo signal as a function of the amplitude of a nonuniform magnetic field in propanol and fitting to the Gaussian-shaped function.

imposes certain requirements regarding the symmetry of the applied nonuniform magnetic field.

We have not considered the details of the self-diffusion in anisotropic liquids by this technique. But it seems to us that the method can be developed with the appropriate combination of two or three nonuniform fields of different symmetry to determine all components of the self-diffusion tensor.

EXPERIMENTAL RESULTS

We have tested the new technique on a homemade setup for NMR in the earth's magnetic field (Fig. 1). The method uses a combination of the Varian–Packard prepolarizing method and the technique with RF pulses to manipulate the spins. After prepolarization in a field of 50 mT, the ordinary sequence for the spin echo with the inhomogeneous magnetic field (IMF) is applied. The sequence consists of a RF $\pi/2$ pulse and two identical IMF pulses with an intermediate RF π pulse.

The method was tested by measuring the self-diffusion constant of water (Fig. 2), of propanol (Fig. 3), and of ethanol (Fig. 4). In our experiments, we use quadrupolar gradient coils with the axis perpendicular to the earth's mag-

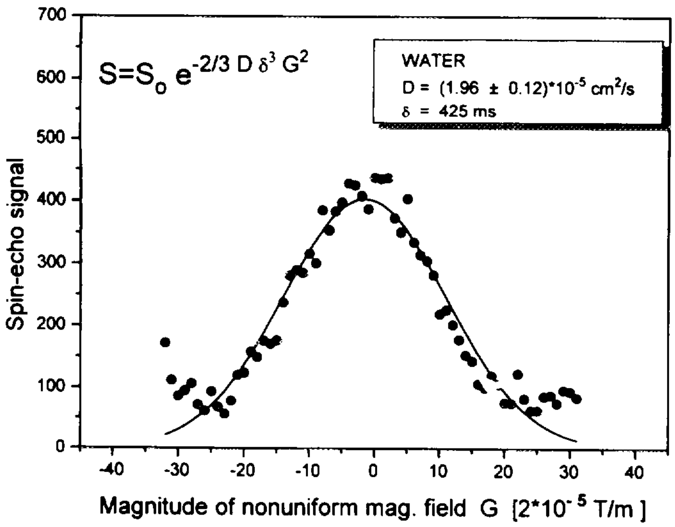

FIG. 2. The spin-echo amplitude as a function of the magnitude of the applied nonuniform magnetic field in water and fitting to the Gaussian-shaped function.

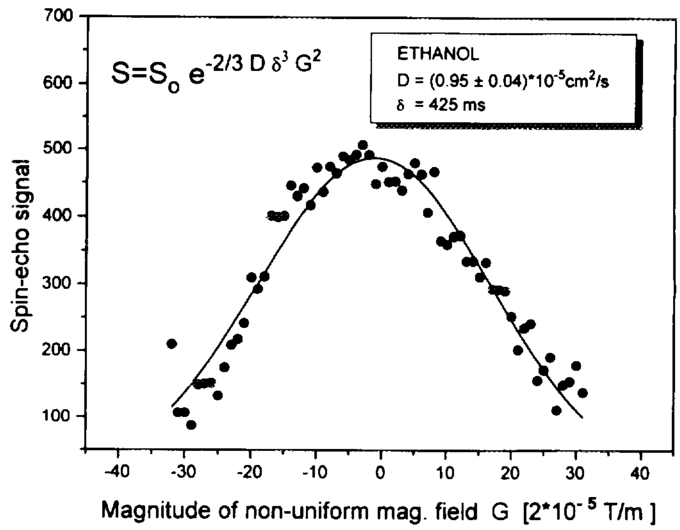

FIG. 4. The spin-echo amplitude as a function of the magnitude of the applied nonuniform magnetic field in ethanol and fitting with the Gaussian-shaped function.

netic field and the spin-echo attenuation follows from Eq. [31] as

$$\beta(2\tau) = G^2\delta^2 D\left(\tau - \frac{\delta}{3}\right). \quad [32]$$

During the experiments we had $\delta = \tau$ and we changed the amplitude G in 64 steps from a negative to a positive value. At its maximum, when G was about 60×10^{-5} T/m, IMF exceeded the density of the earth's magnetic field at the edges of the sample. Thus the results cannot be treated with the gradient approximation.

The experimental results of the spin-echo amplitude as a function of the amplitude of IMF, G (Figs. 2, 3, and 4) were fitted to the Gaussian curves. The results gives expected values for the self-diffusion coefficients of these liquids. The temperature dependences of the self-diffusion coefficient of tap water are 1.50×10^{-5}, 1.96×10^{-5}, and 2.30×10^{-5} cm^2/s at 11, 20, and 24°C, respectively, with an experimental error of 8%. The values for ethanol and propanol at T = 20°C are $D_{Et} = 0.95 \times 10^{-5}$ (1 ± 0.06) cm^2/s and $D_{Pr} = 0.43 \times 10^{-5}$ (1 ± 0.06) cm^2/s.

References (*9*, *10*) show the results for the same quantities measured at the same temperature by NMR in high field. The diffusion constants are $D_{Et} = 0.93 \times 10^{-5}$ cm^2/s and $D_{Pr} = 0.51 \times 10^{-5}$ cm^2/s with an error 3%.

Despite the very low magnetic field (0.05 mT) in our measurements, the experimental error is comparable to that obtained in a high magnetic field (0.1 T). This is due to the extremely good homogeneity of the earth's magnetic field that allows very efficient refocusing of the spin phase and thus the accumulation of sampling points in a wide interval of spin relaxation.

CONCLUSION

In self-diffusion measurement by NMR there are no severe limitations with respect to the strength of the inhomogeneous magnetic field. It can be even stronger than the main field. The new technique permits the measurement of molecular migration by NMR in an extremely low magnetic field such as the earth's magnetic field. It is useful also in other cases where a low magnetic field or a short spin relaxation limits the application of the standard methods. We suggest its application to self-diffusion measurements in solids. It may be used also with EPR spin echoes for migration measurement. A very short spin-relaxation time is the main restriction in both cases.

APPENDIX

Vector Rotation

The rotation of the coordinate system around the unit vector $\mathbf{n}$ by an angle ϕ transforms a vector $\mathbf{B}$ into

$$\mathbf{B}' = \mathbf{B}\cos\phi + \mathbf{n}(\mathbf{n}\cdot\mathbf{B})(1 - \cos\phi) + (\mathbf{n}\times\mathbf{B})\sin\phi. \quad [33]$$

This expression can be used for the rotation of the vector sum $\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1$, with $\mathbf{B}_0 = (0, 0, b_0)$ and $\mathbf{B}_1 = (b_{1x}, b_{1y}, b_{1z})$ aligned along the z axis:

$$\mathbf{n} = \frac{\mathbf{B}_1 \times \mathbf{B}_0}{|\mathbf{B}_1 \times \mathbf{B}_0|} = \frac{(b_{1y}, -b_{1x}, 0)}{\sqrt{b_{1x}^2 + b_{1y}^2}} \quad [34]$$

$$\sin\phi = \frac{|(\mathbf{B}_0 + \mathbf{B}_1)\times\mathbf{B}_0|}{|\mathbf{B}_0 + \mathbf{B}_1|\cdot|\mathbf{B}_0|} = \sqrt{\frac{b_{1x}^2 + b_{1y}^2}{b_{1x}^2 + b_{1y}^2 + (b_{1z} + b_0)^2}} \quad [35]$$

$$\cos\phi = \frac{(\mathbf{B}_0 + \mathbf{B}_1)\cdot\mathbf{B}_0}{|\mathbf{B}_0 + \mathbf{B}_1||\mathbf{B}_0|} = \frac{b_{1z} + b_0}{\sqrt{b_{1x}^2 + b_{1y}^2 + (b_{1z} + b_0)^2}}. \quad [36]$$

The rotation vector that transforms $\mathbf{B}$ into

$$\mathbf{B}' = \left(0, 0, \sqrt{b_{1x}^2 + b_{1y}^2 + (b_{1z} + b_0)^2}\right) \quad [37]$$

is defined as

$$\boldsymbol{\phi} = \mathbf{n}\phi = \frac{(b_{1y}, -b_{1x}, 0)}{\sqrt{b_{1x}^2 + b_{1y}^2}} \arctan\frac{\sqrt{b_{1x}^2 + b_{1y}^2}}{b_{1z} + b_0}.$$

Reversed Helmholtz Coil

The reversed Helmholtz creates, with the main magnetic field which is pointing parallel to the coil axes, nonuniform magnetic fields $\mathbf{B} = (Gx, Gy, 2G(z - z_0) + B_0)$ in a wide region between the coils. The gradient of the field magnitude is

$$\text{grad}|\mathbf{B}| = G\frac{[Gx, Gy, 2[2G(z - z_0) + B_0]]}{\sqrt{(Gx)^2 + (Gy)^2 + [2G(z - z_0) + B_0]^2}} \quad [38]$$

$$= \mathbf{f}(x, y, z, t), \quad [39]$$

if the magnitude of the nonuniform magnetic field G is time dependent. The spin-echo signal appears from Eq. [21] and Eq. [26] in a sophisticated form as

$$S(2\tau) = S_0 \sum_i \exp\left[-D\int_0^{2\tau}\int_0^{t}\mathbf{f}(x, y, z, t_1)dt_1 \times \int_0^{t}\mathbf{f}(x, y, z, t_2)dt_2 dt\right]. \quad [40]$$

The attenuation depends upon the spin location in the sample and the extraction of the self-diffusion constant from Eq. [40] might be a very complex problem.

Only when $\mathbf{B}_g(\mathbf{r}_i, t) \ll B_{z0}$ can Eq. [39] be approximated as

$$(\mathrm{grad}|\mathbf{B}|)^2 = 4G^2 \quad [41]$$

and we can use the usual expression for the spin-echo attenuation.

REFERENCES

1. N. Blombergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
2. E. L. Hahn, *Phys. Rev.* **80**, 580 (1950).
3. E. O. Steyskal and J. E. Tanner, *J. Chem. Phys.* **42**, 288 (1965); E. O. Stejskal, *J. Chem. Phys.* **43**, 359 (1965).
4. H. Y. Carr and E. M. Purcell, *Phys. Rev.* **94**, 630 (1954).
5. H. C. Torrey, *Phys. Rev.* **76**, 1095 (1946); **104**, 563 (1956).
6. W. A. B. Evans and J. G. Powles, *Proc. Phys. Soc.* **92**, 1046 (1967); R. M. Wilcox, *J. Math. Phys.* **8**, 962 (1967).
7. J. Stepišnik, *Physica B* **104**, 350 (1981); J. Stepišnik, *Prog. NMR Spectrosc.* **17**, 187 (1985); J. Stepišnik, *Physica B* **183**, 343 (1994).
8. R. Kubo, *in* "Some Aspects of the Statistical-Mechanical Theory of Irreversible Processes: Lecture on Theoretical Physics" (Brittin and Dunham, Eds.), Vol. 1, p. 181, Interscience, New York, 1959.
9. S. Meckl and M. D. Zeidler, *Mol. Phys.* **63**(1), 85 (1988).
10. J. Jonas and J. A. Akai, *J. Chem. Phys.* **66**, 4946 (1977).