Spin relaxation and diffusional damping of the spin-echo amplitude of a particle moving in a random Gaussian magnetic field

N. F. Fatkullin

Kazan State University

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The interaction of a spin with the random magnetic field created by the difference of the magnetic susceptibilities of the components of spatially inhomogeneous media leads to a number of radio-frequency spectroscopic effects: distortion of the measured diffusion coefficient, and new mechanisms of spin-spin and spin-lattice relaxation. The case of a spin diffusing freely in a random Gaussian magnetic field is considered. Analytical expressions are obtained for the measured diffusion coefficient, the free-induction decay, and the spin-lattice relaxation time. It is shown that the manifestations of the effects of the interaction with a random magnetic field can differ substantially for different relative magnitudes of the characteristic parameters.

1. INTRODUCTION

In spatially inhomogeneous systems, such as porous media and micellar and colloidal solutions, the magnetic susceptibility is different at different points in space. If the characteristic linear sizes of the inhomogeneities are greater than the interatomic spacings, the susceptibility can be regarded as a certain function $\chi(\mathbf{r})$ of the spatial coordinates.

After an external constant magnetic field $\mathbf{H}_0$ along the z axis has been switched on, a spatially nonuniform magnetic induction is induced in the system:

$$\mathbf{B}(\mathbf{r})=(1+4\pi\chi(\mathbf{r}))\mathbf{H}_0. \tag{1}$$

Because of this, the magnetic field $\mathbf{B}(\mathbf{r})$ naturally has internal gradients of the order of $4\pi\delta\chi H_0/\xi$, where $\delta\chi$ is the characteristic amplitude of the variation of the magnetic susceptibility and ξ is the correlation length of the induced nonuniform magnetic field $4\pi\chi(\mathbf{r})\mathbf{H}_0$.

One of the widely used methods for investigating heterogeneous media is NMR spectroscopy (see, e.g., Ref. 1). Naturally, in view of this, the need arises for a theory that takes account of the effect of the nonuniform magnetic field $4\pi\chi(\mathbf{r})\mathbf{H}_0$ on various radiospectroscopic phenomena, such as diffusional damping of the spin-echo signal and spin-spin and spin-lattice relaxation processes.

In the papers known to the author that are related to this effect (Refs. 2–4), the first of these problems has been discussed. However, it has been possible to obtain concrete results for just one of the limiting cases: $Dt_D \ll \xi^2$, where D is the self-diffusion coefficient of the molecules that contribute to the NMR signal and t_D is the time for which a molecule is observed (the so-called "diffusion" time). In this limit the spatial displacements of molecules are small. Therefore, for each of the molecules the magnetic field $\mathbf{B}(\mathbf{r})$ and its spatial derivatives $\partial B_\alpha/\partial x_\beta$ (in accordance with established tradition,[2–4] the full set of the latter will be called the magnetic-field gradient) can reasonably be regarded as constant over the time t_D. By assuming next for these quantities a distribution that is convenient for analytical calculations, it is possible to obtain useful analytical results.

Any attempt to analyze this problem in a more general situation comes up against the following two fundamental questions in the physics of disordered media:

The first is related to the fact that the field $\delta\mathbf{B}(\mathbf{r})=4\pi\chi(\mathbf{r})\mathbf{H}_0$ is not a random quantity but a random field. Therefore, averaging over all random realizations of $\delta\mathbf{B}(\mathbf{r})$ reduces to the operation of functional integration. The second is the problem of the diffusion of a particle in an inhomogeneous medium.

In this general formulation the problem turns out to be extremely complicated. Therefore, it is natural to attempt to take both these aspects into account in isolation from each other. Problems associated with diffusional damping of the amplitude of the spin echo of a particle moving in a random external field have been discussed in a paper by the author.[5] In the present paper we attempt to discuss the influence of the random magnetic field $\delta\mathbf{B}(\mathbf{r})$ on the amplitude of the diffusional damping and on the spin-relaxation processes. But we shall neglect completely the effect of the spatial inhomogeneities of the system on the character of the displacements of the molecules, assuming that the latter are normal and in no way slowed down by self-diffusion.

We note that even after this simplification the problem remains hopelessly complicated for the derivation of any analytical results, since the operation of functional integration can only be effectively applied to Gauss-distributed fields. Therefore, below, the random field $\delta\mathbf{B}(\mathbf{r})$ will be regarded as a Gaussian random field.

2. DESCRIPTION OF THE MODEL

We note, first of all, that the quantity $\chi(\mathbf{r})$ in the relation (1) is, generally speaking, not a scalar but a rank-2 tensor. Therefore, the operation $\chi(\mathbf{r})\mathbf{H}_0$ should be understood as the contraction of a tensor and a vector to give a vector.

The magnetic susceptibility in diamagnetic and paramagnetic media is a small quantity ($|\chi|\ll 1$). This enables us to neglect the difference between the average value of the magnetic induction $\mathbf{B}(\mathbf{r})$ and the field $\mathbf{H}_0$:

$$\langle\mathbf{B}(\mathbf{r})\rangle=(1+4\pi\langle\chi(\mathbf{r})\rangle)\mathbf{H}_0\sim\mathbf{H}_0. \tag{1'}$$

For brevity, we shall denote the fluctuating part of the magnetic field $\mathbf{B}(\mathbf{r})$ as

$$\mathbf{B}^*=4\pi\delta\chi(\mathbf{r})\mathbf{H}_0, \tag{2}$$

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where $\delta\chi(\mathbf{r}) = \chi(\mathbf{r}) - \langle\chi(\mathbf{r})\rangle$ is the fluctuation of the magnetic-susceptibility tensor.

Next, for greater coherence of our account, we shall give certain necessary properties of a three-dimensional Gaussian random field (see, e.g., Refs. 6–8).

The distribution functional of a random vector field has the form

$$\rho\{\mathbf{B}^*(\mathbf{r})\} = W(0)\exp\left\{-\frac{1}{2}\int d^3\mathbf{r}\sum_{k=1}^{3}\left[\alpha B_k^{*2}(\mathbf{r}) + \beta\left(\frac{\partial B_k^*(\mathbf{r})}{\partial \mathbf{r}}\right)^2\right]\right\}. \quad (3)$$

where α and β are parameters describing the random field, $B_k^*(\mathbf{r})$ are the Cartesian components of the random field, and $W(0)$ is a normalizing factor.

We note that we have assumed for simplicity that the parameters α and β of the distribution are the same for all components of the field $\mathbf{B}^*(\mathbf{r})$.

In what follows, a central role for us will be played by the binary correlation function $\langle B_k^*(\mathbf{r}_1)B_m^*(\mathbf{r}_2)\rangle_B$, which in the case of a Gaussian random field is known exactly:

$$\langle B_k^*(\mathbf{r}_1)B_m^*(\mathbf{r}_2)\rangle_B = \frac{1}{4\pi}\frac{1}{\beta|\mathbf{r}_1-\mathbf{r}_2|}\exp\left\{\frac{-|\mathbf{r}_1-\mathbf{r}_2|}{\xi}\right\}\delta_{km}, \quad (4)$$

where $\xi = (\beta/\alpha)^{1/2}$ is the correlation length of the random field, δ_{km} is the Kronecker delta symbol, and $\langle\ldots\rangle_B$ denotes averaging over all realizations of the random field.

For greater clarity we represent the parameter $(4\pi\beta)^{-1}$ in the relation (4) in the form

$$(4\pi\beta)^{-1} = {}^1/_3\langle B^{*2}\rangle a_0,$$

where a_0 is the characteristic minimum length scale of the problem and $\langle B^{*2}\rangle$ can be regarded as the mean square fluctuation of the random field over the spatial scale a_0.

In this notation, the relation (4) can be rewritten as follows:

$$\langle B_k^*(\mathbf{r}_1)B_m^*(\mathbf{r}_2)\rangle_B = \frac{1}{3}\frac{\langle B^{*2}\rangle a_0}{|\mathbf{r}_1-\mathbf{r}_2|}\exp\left\{\frac{-|\mathbf{r}_1-\mathbf{r}_2|}{\xi}\right\}. \quad (5)$$

3. AMPLITUDE OF THE DIFFUSIONAL DAMPING OF THE STIMULATED-ECHO SIGNAL WITH A PULSED MAGNETIC-FIELD GRADIENT

The technique discussed here is a traditional way of investigating the translational mobility of molecules with magnetic nuclei and has been described repeatedly in the literature (see, e.g., Refs. 9–12). In the present section we completely neglect spin-lattice and spin-spin relaxation effects, which are unimportant for the spin-echo phenomenon.

The amplitude of the diffusional damping of the spin-echo signal is related to the spin dephasing induced by the action of the gradient magnetic-field pulses that are switched on after the first and third radiofrequency (RF) pulses and by the action of the random magnetic field $\mathbf{B}^*(\mathbf{r})$ during the period between the first and second RF pulses and after the third RF pulse.

The spin-dephasing angle between the first two RF pulses is the sum:

$$\varphi_1 = \varphi_1' + \varphi_1'', \quad (6)$$

where

$$\varphi_1' = \gamma\int_0^{\delta}\mathbf{r}(t)\,\mathbf{g}\,dt \approx \gamma\delta\mathbf{g}\mathbf{r}(0)$$

is the dephasing, of a spin with position vector $\mathbf{r}(t)$, induced by the interaction with the gradient $\mathbf{g}$ of the external magnetic field directed along the z axis and acting for a short time δ, and $\varphi_1'' = \gamma\int_0^{\tau_1}B_z^*(\mathbf{r}(t))dt$ is the dephasing induced by the interaction with the random magnetic field.

An analogous relation can be written for the spin-dephasing angle after the action of the third RF pulse:

$$\varphi_2 = \varphi_2' + \varphi_2'', \quad (7)$$

where

$$\varphi_2' = \gamma\int_0^{\delta}\mathbf{g}\mathbf{r}(t_D+t)\,dt \approx \gamma\delta\mathbf{g}\mathbf{r}(t_D),$$

in which t_D is the "diffusion" time, i.e., the time between the first and third RF pulses.

The spin-echo amplitude is expressed in terms of the quantities φ_1 and φ_2 by the relation

$$A(g^2) = \langle\exp\{-i(\varphi_2-\varphi_1)\}\rangle, \quad (8)$$

where $\langle\ldots\rangle$ denotes averaging over all random realizations of the field $\mathbf{B}^*(\mathbf{r})$ and random trajectories of the spin.

The amplitude of the diffusional damping of the spin-echo signal is defined as the ratio

$$\tilde{A}(g^2) = \frac{A(g^2)}{A(0)}. \quad (9)$$

It can be seen from the relations (7) and (8) that the phases φ_1' and φ_2' do not depend on the random magnetic field $\mathbf{B}^*(\mathbf{r})$. Therefore, in the calculation of the amplitude $A(g^2)$ it is convenient to average first over all realizations of the random fields:

$$A(g^2) = \langle\exp\{-i(\varphi_2'-\varphi_1')\}\langle\exp\{-i(\varphi_2''-\varphi_1'')\}\rangle_B\rangle_r, \quad (10)$$

where $\langle\ldots\rangle_r$ denotes averaging over realizations of the random trajectories; obviously, $\langle\ldots\rangle = \langle\ldots\rangle_{B,r}$.

Taking the relations (6) and (7) into account, we transform the factor associated with the influence of the random fields in the expression (10) to the form

$$A\{B^*\} \equiv \langle\exp\{-i(\varphi_2''-\varphi_1'')\}\rangle_B = \left\langle\exp\left\{-i\gamma\int_0^{\tau_1}(B_z^*(\mathbf{r}(t_D+t))-B_z^*(\mathbf{r}(t)))\,dt\right\}\right\rangle_B. \quad (11)$$

A Gaussian random field possesses the properties of a normal distribution, and this makes it possible to express the amplitude $A\{B^*\}$ in terms of binary correlation functions of the field $\mathbf{B}^*(\mathbf{r})$:

$$A\{B^*\} = \exp\left\{\gamma^2\iint_0^{\tau_1}dt_2\,dt_1 F(t_D;t_2;t_1)\right\}. \quad (12)$$

where

$$F(t_D; t_2; t_1)=2\langle B_z^*(\mathbf{r}(t_D+t_1)-\mathbf{r}(t_1))B_z^*(r(0))\rangle_B$$
$$-\langle B_z^*(\mathbf{r}(t_D+t_2)-\mathbf{r}(t_D+t_1))B_z^*(\mathbf{r}(0))\rangle_B$$
$$-\langle B_z^*(\mathbf{r}(t_2)-\mathbf{r}(t_1))B_z^*(\mathbf{r}(0))\rangle_B.$$

It can be seen from (10) and (12) that the spin-echo amplitude $A(g^2)$ has the structure

$$A(g^2)=\langle\exp\{\hat{\alpha}(t_D)+\hat{\beta}(t_D)\}\rangle_r. \tag{13}$$

where $\hat{\alpha}(t_D)$ and $\hat{\beta}(t_D)$ are random functionals of the particle trajectories, specified by the relations

$$\hat{\alpha}(t_D)=-i\gamma\delta g(\mathbf{r}(t_D)-\mathbf{r}(0)),$$
$$\hat{\beta}(t_D)=\gamma^2\int_0^{\tau_1}\int dt_2\,dt_1 F(t_D; t_2; t_1). \tag{13a}$$

The main difficulty in the calculation of the spin-echo amplitude $A(g^2)$ is associated with the averaging over the random trajectories of the particles. In the general situation this difficulty seems to us to be insuperable. Therefore, we shall make use of the approximation mentioned in the Introduction, i.e., we shall neglect the influence of the inhomogeneities of the system on the character of the translational displacements of the particles. The bracket $\langle\ldots\rangle_r$, which denotes averaging over random trajectories, will imply averaging over trajectories of a particle that executes random walks with self-diffusion coefficient D.

Even in this approximation, the expression for the amplitude $A(g^2)$ is not simple enough to enable us to obtain some reasonable closed analytical expression. We confine ourselves, therefore, to the cumulant expansion of the spin-echo amplitude, taking the first nonvanishing terms into account. Fortunately, for most real experimental situations this turns out to be entirely adequate.

The point is that the term proportional to g^2 in the expansion

$$\ln\tilde{A}(g^2)=-\gamma^2g^2\delta^2t_DD^*(t_D)+\ldots. \tag{14}$$

determines the quantity $D^*(t_D)$, which is experimentally measurable from the initial slope of $\ln\tilde{A}(g^2)$ and is called the apparent, or effective, diffusion coefficient.

In the situation that we are studying, the quantity $D^*(t_D)$ differs from the true self-diffusion coefficient D, since it contains contributions from the random field $\mathbf{B}^*(\mathbf{r})$. One of the principal problems in experimental investigations of spatially inhomogeneous media by the spin-echo method is the determination of the quantity D on the basis of measured values of $D^*(t_D)$ and the elucidation of the nature of this correction.

In macroscopic isotropic systems, as can be seen from the relations (13) and (13a), in the cumulant expansion of the amplitude $\tilde{A}(g^2)$ [see the expression (10)] all the terms proportional to odd powers of $\hat{\alpha}(t_D)$ vanish after averaging over random trajectories of the spins. Furthermore, in diamagnetic and paramagnetic systems we have $|\delta\chi|\ll 1$. Therefore, in calculating the apparent diffusion coefficient $D^*(t_D)$ it is reasonable to confine oneself to terms linear in $\hat{\beta}(t_D)$. Taking this into account, we easily obtain

$$\ln\tilde{A}(g^2)=\frac{\ln\langle\exp\{\hat{\alpha}(t_D)+\hat{\beta}(t_D)\}\rangle_r}{\ln\langle\exp\{\hat{\beta}(t_D)\}\rangle_r}$$
$$=\frac{1}{2}\langle\hat{\alpha}^2(t_D)\rangle_r+\frac{1}{2}[\langle\hat{\alpha}^2(t_D)\hat{\beta}(t_D)\rangle_r$$
$$-\langle\hat{\alpha}^2(t_D)\rangle_r\langle\hat{\beta}(t_D)\rangle_r]+\ldots. \tag{15}$$

Using the relation (13a) and the Markovian character of the random walks of the spins, we can transform the expression (15) to the form

$$\ln\tilde{A}(g^2)=-\gamma^2g^2\delta^2t_DD-\frac{\gamma^4g^2\delta^2}{3}\left\{\tau_1^2X(t_D)\right.$$
$$\left.-2\int_0^{\tau_1}(\tau_1-t)X(t)\,dt\right\}, \tag{16}$$

where

$$X(t)=\langle\langle B_z^*(\mathbf{r}(t)-\mathbf{r}(0))B_z^*(\mathbf{r}(0))\,(\mathbf{r}(t_D)-\mathbf{r}(0))^2\rangle_r$$
$$-\langle B_z^*(\mathbf{r}(t)-\mathbf{r}(0))B_z^*(\mathbf{r}(0))\rangle\langle(\mathbf{r}(t)-\mathbf{r}(0))^2\rangle$$

and it has been taken into account that, as a rule, $t_D\gg\tau_1$.

The term proportional to $X(t_D)$ in (16) is related to the influence of correlations between values of the random field $B^*(\mathbf{r}(t))$ that affected the kinetics of the spin system after the first and third RF pulses. The other term reflects the action of the field $B(\mathbf{r}(t))$ between the first and second RF pulses.

The analogous contributions from the actions of the field $B^*(\mathbf{r})$ between the second and third RF pulses and after the third RF pulse are equal to zero: In the former case this is due to the fact that the spins were oriented along the z axis, while in the latter case it is due to the absence of correlations in the motions of the particles in the time intervals from 0 to t_D and after the time t_D.

We turn now to the calculation of the quantity $X(t)$. Using the relation (5), we obtain

$$X(t)=\frac{\langle B^{*2}\rangle a_0}{3}\int\frac{d^3\mathbf{r}}{(4\pi Dt)^{3/2}}\frac{r^2-6Dt}{r}\exp\left\{-\frac{r^2}{4Dt}-\frac{r}{\xi}\right\}. \tag{17}$$

After transformations, the right-hand side of the relation (17) can be expressed in terms of the complementary error integral:

$$X(t)=\frac{2\langle B^{*2}\rangle a_0(Dt)^{1/2}}{3\pi^{1/2}}\left\{2\frac{Dt}{\xi^2}-1\right.$$
$$\left.+2\pi^{1/2}\exp\left(\frac{Dt}{\xi^2}\right)\left(\frac{Dt}{\xi^2}\right)^{1/2}\operatorname{erfc}\left(\left(\frac{Dt}{\xi^2}\right)^{1/2}\right)\right\}, \tag{18}$$

where

$$\operatorname{erfc}(x)=\frac{2}{\pi^{1/2}}\int_x^\infty e^{-x^2}\,dx.$$

We shall write out the easily derived asymptotic relations for the quantity

$$X(t)=\frac{\langle B^{*2}\rangle a_0}{3}\begin{cases}-2\left(\dfrac{Dt}{\pi}\right)^{1/2}, & Dt\ll\xi^2,\\ -\dfrac{3}{\pi^{1/2}}\dfrac{\xi^2}{(Dt)^{1/2}}, & Dt\gg\xi^2.\end{cases}\tag{19}$$

Using the definition (14) and the expansion (16), we obtain a relation for the apparent diffusion coefficient:

$$D^*(t_D)=D+\frac{\gamma^2}{3t_D}\left\{\tau_1^2X(t_D)-\int_0^{\tau_1}(\tau_1-t)X(t)\,dt\right\}.\tag{20}$$

In the problem that we are considering, it is natural to distinguish three characteristic times: the correlation time $\tau_c=\xi^2/D$ of a particle moving in the random magnetic field $\mathbf{B}^*(\mathbf{r})$, the time interval τ_1 between the first and second RF pulses, and the "diffusion" time t_D. Depending on the relative magnitudes of these, three regimes of motion can be distinguished.

A. Long correlation times ($\tau_1\ll t_D\ll\tau_c$)

From the relations (19) and (20) it is easy to find that the apparent diffusion coefficient is equal to

$$D^*(t_D)=D\left(1-\frac{2}{9\pi^{1/2}}\frac{\gamma^2\langle B^{*2}\rangle a_0\tau_1^2}{(Dt_D)^{1/2}}\right).\tag{20a}$$

In a certain sense this case is analogous to the limit (considered in Ref. 4) of large correlation lengths of the random magnetic field. The apparent diffusion coefficient D^* is slightly smaller than the true diffusion coefficient D. The difference between them decreases with increase of the time t_D. This has a simple physical meaning: With increase of the time t_D the random trajectories encompass ever greater regions of space. This leads to averaging of the action of the random field $\mathbf{B}^*(\mathbf{r}(t))$ on a particle, and its influence on the coefficient $D^*(t_D)$ tends to zero.

In Ref. 4, as in our paper, the result $D^*(t_D)<D$ was obtained. However, the behavior of the relative correction $\delta D/D=(D^*(t_D)-D)/D$ as a function of the molecular self-diffusion coefficient is qualitatively different: $|\delta D/D|\sim D$, whereas in our case $|\delta D/D|\sim D^{-1/2}$. It is easily understood that the decrease of the relative correction with increase of the coefficient D is natural, since it is one of the manifestations of the averaging of the random internal fields by the molecular motion.

We turn now to a discussion of the other two cases.

B. Intermediate correlation times ($t_D\gg\tau_c\gg\tau_1$)

Proceeding in the same way as above, we obtain

$$D^*(t_D)=D\left[1+\frac{8}{135\pi^{1/2}}\frac{\gamma^2\langle B^{*2}\rangle a_0\tau_1^{3/2}}{D^{1/2}t_D}\left\{1-\frac{45}{8}\frac{\xi^2}{D(t_D\tau_1)^{1/2}}\right\}\right].\tag{20b}$$

When the diffusion time is equal to $t_D^*=(\frac{45}{8})^2(\xi^4/D^2\tau_1)$ the sign of the correction δD changes. For times $t_D<t_D^*$, as in the case of long correlation times, we have $D^*<D$, although the dependence on the experimental parameters is different. For times $t_D>t_D^*$, on the other hand, $D^*>D$. Furthermore, at the time $t_D^{**}=(\frac{135}{32})^2(\xi^4/D^2\tau_1)$ the correction δD as a function of the time t_D reaches a maximum.

C. Short correlation times, i.e., $t_D\gg\tau_1\gg\tau_c$

The apparent self-diffusion coefficient turns out to be equal to

$$D^*(t_D)=D\left(1+\frac{4}{9\pi^{1/2}}\frac{\gamma^2\langle B^{*2}\rangle a_0\tau_1^{3/2}\xi^2}{D^{3/2}t_D}\right).\tag{20c}$$

As in the case of intermediate correlation times, the sign of the correction δD is positive for $t_D\gg t_D^{**}$. The behavior of the relative correction $\delta D/D$ as $t_D\to\infty$ and $D\to\infty$ is physically reasonable in all three cases.

4. SPIN RELAXATION OF A PARTICLE MOVING IN A RANDOM GAUSSIAN MAGNETIC FIELD

Spin-spin relaxation

Spin-spin relaxation determines the decay of the free-induction signal $G(t)$. Neglecting all the relaxation mechanisms except for the mechanism associated with the interaction with the random field $\mathbf{B}^*(\mathbf{r})$, we can write the following expression for the free-induction decay (see, e.g., Refs. 9, 10, and 13):

$$G(t)=\left\langle\exp\left\{i\gamma\int_0^t B_z^*(\mathbf{r}(t))\,dt\right\}\right\rangle.\tag{21}$$

For a Gaussian random field the functional integration that appears in the averaging operation can be implemented trivially and the expression (21) can be represented in the form

$$G(t)=\left\langle\exp\left\{-\gamma^2\int_0^t(t-\tau)\langle B_z^*(\mathbf{r}(\tau))B_z^*(\mathbf{r}(0))\rangle_B\,d\tau\right\}\right\rangle_r.\tag{22}$$

The expression (22) is still rather complicated for the derivation of analytical results. We shall turn, therefore, to the cumulant expansion, confining ourselves to the first nonvanishing term:

$$G(t)=\exp\left\{-\gamma^2\int_0^t(t-\tau)\langle B_z^*(\mathbf{r}(\tau))B_z^*(\mathbf{r}(0))\rangle d\tau\right\}.\tag{23}$$

The correlation function $\langle B_z^*(\mathbf{r}(t))B_z^*(\mathbf{r}(0))\rangle$ is found by simple integration:

$$\begin{aligned}\langle B_z^*(\mathbf{r}(t))B_z^*(\mathbf{r}(0))\rangle&=\int\frac{d^3\mathbf{r}}{(4\pi Dt)^{3/2}}\frac{\langle B^{*2}\rangle a_0}{3\tau}\\&\times\exp\left\{-\frac{r^2}{4Dt}-\frac{r}{\xi}\right\}=\frac{1}{3}\frac{\langle B^{*2}\rangle a_0}{(\pi Dt)^{1/2}}\\&\times\left\{1-\frac{(Dt)^{1/2}}{\xi}\pi^{1/2}\operatorname{erfc}\left(\frac{(Dt)^{1/2}}{\xi}\right)\exp\left\{\frac{Dt}{\xi^2}\right\}\right\}.\end{aligned}\tag{24}$$

Below, we write out the easily obtained asymptotic values of the expression (24):

$$\langle B_z^*(\mathbf{r}(t))B_z^*(\mathbf{r}(0))\rangle=\begin{cases}\dfrac{1}{3}\dfrac{\langle B^{*2}\rangle a_0}{(\pi Dt)^{1/2}}, & Dt\ll\xi^2,\\ \dfrac{1}{6\pi^{1/2}}\dfrac{\langle B^{*2}\rangle a_0\xi^2}{(Dt)^{3/2}}, & Dt\gg\xi^2.\end{cases}$$

Substituting these values into the relation (23), we obtain the following expression for the free-induction decay:

$$G(t)=\begin{cases}\exp\left\{-\left(\frac{t}{T_2'}\right)^{3/2}\right\}, & DT_2'\ll\xi^2, \quad (23a)\\ \exp\left\{-\frac{t}{T_2''}\right\}, & DT_2''\gg\xi^2. \quad (23b)\end{cases}$$

where the spin-spin relaxation times are given by the relations

$$T_2'=\left(\frac{9\pi^{1/2}}{4}\right)^{2/3}\frac{D^{1/3}}{(\gamma^2\langle B^{*2}\rangle a_0)^{2/3}},$$

$$T_2''\approx T_2'\frac{D^{1/2}}{\xi}\approx\frac{D}{\gamma^2\langle B^{*2}\rangle a_0\xi}.$$

The limit (23a) describes the kinetics of the spin-spin relaxation in the limit of long correlation times. Attention is drawn to the non-Gaussian character of the decay, i.e., the power of the time in the exponential is equal to 3/2, and not 2. This is due to the partial averaging of the random field $\mathbf{B}^*(\mathbf{r})$ by the molecular motion. The other limit (23b) corresponds to the limit of short correlation times. Therefore, as follows from general considerations (see, e.g., Refs. 9, 10, and 13), the kinetics of the decay is Lorentzian. We note that, in contrast to the case of the dipole-dipole mechanism of relaxation, the relaxation times T_2^* and T_2^{**} depend through the field B^* on the NMR frequency: $T_2^*\sim\omega^{-4/3}$ and $T_2^{**}\sim\omega^{-2}$ [see the relation (2)], while in the case of long correlation times they depend on the temperature.

Spin-lattice relaxation

Spatial displacements of the particle in a random magnetic field give rise to modulation of the energy of the interaction of the spin with this field. Fluctuations of the x and y components of the random field $\mathbf{B}^*(\mathbf{r}(t))$ lead to spin-lattice relaxation.

The spin-lattice relaxation time is conveniently calculated from the general formula (see, e.g., Ref. 13)

$$\frac{1}{T_1}=\int_0^\infty\frac{\mathrm{Sp}([\hat I_z;\hat H_{sl}(t)][\hat H_{sl}(0);\hat I_z])dt}{4\hbar^2\,\mathrm{Sp}\,\hat I_z^2}, \quad (25)$$

where the operators appearing in the commutators have the standard meanings: $\hat I_z$ is the operator of the z component of the spin, and $\hat H_{sl}(t)=-\gamma\hbar\hat{\mathbf{I}}(t)\mathbf{B}^*(\mathbf{r}(t))$ is the operator of the Zeeman interaction of the spin with the random magnetic field in the interaction picture.

By performing the standard operations of commutation of operators and calculation of traces, we transform (25) to the form

$$\frac{1}{T_1}=2\gamma^2\int_0^\infty\langle B_x^*(r(t))B_x^*(r(0))\rangle\cos\omega t\,dt. \quad (26)$$

In our chosen model the autocorrelation functions of the various components of the field $\mathbf{B}^*(\mathbf{r}(t))$ are equal to each other:

$$\langle B_x^*(\mathbf{r}(t))B_x^*(\mathbf{r}(0))\rangle=\langle B_z^*(\mathbf{r}(t))B_z^*(\mathbf{r}(0))\rangle.$$

Substituting the expression (24) into the relation (26), after integrating we find

$$\frac{1}{T_1}=\frac{2^{1/2}\gamma^2\langle B^{*2}\rangle a_0\xi}{3D^{1/2}}\frac{\omega^{1/2}\xi+D^{1/2}}{2\omega\xi^2+2(D\omega)^{1/2}\xi+D}. \quad (27)$$

We shall consider the limiting values of this expression:

$$\frac{1}{T_1}=\begin{cases}\frac{2^{1/2}}{3}\frac{\gamma^2\langle B^{*2}\rangle a_0\xi}{D}, & \omega\xi^2\ll D, \quad (27a)\\ \frac{2^{1/2}}{3}\frac{\gamma^2\langle B^{*2}\rangle a_0}{D^{1/2}\omega^{1/2}}, & \omega\xi^2\gg D. \quad (27b)\end{cases}$$

We note that, in accordance with Bloembergen–Purcell–Pound theory, the frequency and temperature dependences of the spin-lattice relaxation time for relaxation induced by modulation of the dipole-dipole interactions by thermal motion of a liquid are substantially different from these (see, e.g., Refs. 9, 10, and 13). In the low-frequency limit the time T_1 does not depend on the frequency, while in the high-frequency limit it increases as $T_1\propto\omega^2$. A characteristic feature of the temperature dependence of the time T_1 is the presence of a minimum when the condition $\omega\tau_c=1$ is fulfilled.

In the case that we are analyzing, the spin-lattice relaxation time T_1 becomes shorter with increase of the resonance frequency: $T_1\propto\omega^{-2}$ in the low-frequency limit, and $T_1\propto\omega^{-3/2}$ in the high-frequency limit. The temperature dependence of the time T_1 is characterized by a monotonic increase with increase of the temperature. When the condition $\omega\tau_c=1$ is fulfilled, instead of a minimum there is only a weakening of the temperature dependence: $T_1\sim D$ at low temperatures, and $T_1\sim D^{1/2}$ at high temperatures.

As the temperature tends formally to absolute zero, the diffusion coefficient $D\to0$; consequently, the time $T_1\to0$ also. This conclusion, of course, is not physical, but is an artifice of the model of the Gaussian random field. The point is that the binary correlation function of a Gaussian random field [see relations (4) and (5)] at short distances possesses singular behavior:

$$\lim_{r\to0}\langle\mathbf{B}^*(\mathbf{r})\mathbf{B}(0)\rangle=\infty.$$

Therefore, there should exist some smallest length scale a_0 (evidently of the order of the interatomic spacings) that determines the lower spatial boundary of the range of applicability of the model. From this it is clear that all the results of this paper are valid when the condition $D\omega^{-1}\gg a_0^2$ is fulfilled.

5. CONCLUSION

We shall summarize briefly the principal results:

1. The measured (by the method of stimulated spin echo) self-diffusion coefficient D^* of a particle moving in a random Gaussian field can be either greater or smaller than the true self-diffusion coefficient D [see relations (20a,b,c)]. A decisive role is played by the relative magnitudes of the characteristic times of the experiment (the time τ_1 between the first and second RF pulses and the "diffusion" time t_D) and the correlation time $\tau_c=\xi^2/D$ of the motion of the spin in the random magnetic field. When these parameters have a certain relative magnitude the difference between D and D^* reaches a maximum and tends to zero as $t_D\to\infty$.

2. The kinetics of the spin-spin relaxation in the limit of long correlation times [see (23a)] has a non-Gaussian character with exponent equal to 3/2. The characteristic damping time T_2^* of the free-induction decay in this limit has an

anomalous (in comparison with the dipole-dipole mechanism of relaxation) temperature and frequency dependence $T_2^* \propto D^{1/3}\omega^{-4/3}$. In the limit of short correlation times [see (23b)] the spin-spin relaxation time $T_2^{**} \propto D\omega^{-2}$.

3. The spin-lattice relaxation time T_1 [see (27), (27a), and (27b)] does not have the minimum that is typical for dipole-dipole relaxation, and increases monotonically with temperature. When we go from low to high temperatures in the vicinity of the temperature satisfying the condition $\omega\tau_c = 1$, a strengthening of the temperature and frequency dependences, from $T_1 \propto D^{1/2}\omega^{-3/2}$ to $T_1 \propto D\omega^{-2}$, occurs.

In conclusion, we shall give estimates of the orders of magnitude of the possible values of the spin-spin and spin-lattice relaxation times associated with the interaction of the spin with the random magnetic field. We set $D \sim 10^{-6}$ cm^2/sec, $\omega \sim 10^8$ sec^{-1}, $B^* \sim 4\pi|\delta\chi|H_0 = 4\pi|\delta\chi|\omega/\gamma$, $a_0 = 5$ Å, and $\delta\chi \sim 10^{-6}$; then $T_2 \sim 10^{-2}$ sec and $T_1 \sim 1$ sec. From this it can be seen that the spin-spin and spin-lattice relaxation mechanism that we have discussed may turn out to be fully effective and accessible to experimental investigations. In our view, it is especially necessary to pay attention to the kinetics of spin-spin relaxation in porous media with sufficiently large pore diameters $\sim 10^4$–10^5 Å at sufficiently high resonance frequencies $\omega \simeq 10^{-8}$–10^9 sec^{-1}.

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[1]V. Mank and N. I. Lebovka, *NMR Spectroscopy of Water in Heterogeneous Systems* [in Russian], Naukova Dumka, Kiev (1986).
[2]K. A. Valiev and M. M. Bil'danov, Zh. Strukt. Khim. **7**, 834 (1966).
[3]I. Zupancic, Solid State Commun. **65**, 199 (1988).
[4]S. Majumdar and J. C. Gore, J. Magn. Reson. **78**, 41 (1988).
[5]N. F. Fatkullin, Zh. Eksp. Teor. Fiz. **98**, 2030 (1990) [Sov. Phys. JETP **71**, 1141 (1990)].
[6]A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, *Fluctuation Theory of Phase Transitions*, Pergamon, Oxford (1979).
[7]V. I. Klyaukin, *Stochastic Equations and Waves in Randomly Inhomogeneous Media* [in Russian], Nauka, Moscow (1986).
[8]P. Ramond, *Field Theory: A Modern Primer*, Benjamin/Cummings, Reading, Mass. (1981).
[9]C. P. Slichter, *Principles of Magnetic Resonance with Examples from Solid State Physics*, Harper and Row, New York (1963).
[10]K. M. Salikhov, A. G. Semenov, and Yu. D. Tsvetkov, *Electron Spin Echo and its Application* [in Russian], Nauka, Moscow (1976).
[11]A. I. Maklakov, V. D. Skirda, and N. F. Fatkullin, *Self-diffusion in Polymer Solutions and Melts* [in Russian], Kazan State University, Kazan (1987).
[12]A. I. Maklakov, V. D. Skirda, and N. F. Fatkullin, "Self-diffusion in Polymer Systems," in *Encyclopedia of Fluid Mechanics, Vol. 9, Polymer Flow Engineering*, edited by N. P. Cheremisinoff, Gulf Publishing Company (1990), Chapter 22, p. 705.
[13]I. V. Aleksandrov, *Theory of Magnetic Relaxation* [in Russian], Nauka, Moscow (1975).

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