# Kinetics of spin systems with three-spin interactions in a Lee–Goldburg experiment

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A theory is derived for the decays of free precession in the Lee–Goldburg experiment in the case in which the effective interactions of the spins are three-spin interactions. The theory is based on the analogy between the dynamics of the spin system of a solid described by an effective three-spin Hamiltonian and the dynamics of spins in liquids. Explanations are found for the asymmetry of the NMR line, the Gaussian nature of the free-precession decays at times $t\sqrt{M_2} \ll 1$, and the exponential nature of the decays for $t\sqrt{M_2} \gg 1$ ($M_2$ is the second moment of the central NMR line). Oscillations arise in the free-precession decays when there is a deviation from a magic angle. The results derived here agree qualitatively with experimental data found by Mefed *et al.* [JETP Lett. **55**, 418 (1992)].

The development of high-resolution NMR methods in solids (rotation of a sample at a magic angle,[1] the Lee-Goldburg experiment,[2] and multipulse methods[3]) has made it necessary to derive a theory for the corresponding spectra. This would provide a reliable theoretical foundation for extracting information on the structure and molecular mobility in solids by high-resolution NMR methods.

The spin dynamics in the experiments of Refs. 1–3 is distinguished by the circumstance that the nuclear spins involved are coupled with each other not by ordinary two-spin interactions but by effective three- and four-spin interactions. Multispin interactions arise in these experiments because the medium is acted upon by intense rf fields, which transform the anisotropic dipole-dipole interactions responsible for the broadening of observable lines into rapidly oscillating interactions. In experiments with a sample rotating at the magic angle, this transformation is caused by rapid rotation of the sample around the axis which makes the magic angle with the direction of the static magnetic field $H_0$ ("rapid" here means at a frequency of 10–15 kHz). In the Lee-Goldburg experiment, the corresponding transformation is achieved by creating a strong resonant field along the magic axis in the rotating coordinate system. In multipulse spectroscopy, this transformation is achieved through the simultaneous rotation of all the spins of the sample by specially designed periodic trains of resonant pulses. This rapid change in the sign of the dipole-dipole interaction produces a rapid change in the sign of the local field acting on each spin. This change leads in turn to partial or total averaging of the field and thus to weakening of the dipole-dipole interaction. The weakened effective dipole-dipole interactions which result from this averaging[4,5] are multispin interactions. For example, these are three-spin interactions in Lee–Goldburg experiments or when the sample is rotated at the magic angle, while they are four-spin interactions in the WHH-4 and MREV-8 experiments.[3]

The kinetics of systems with three- and four-spin interactions is of course considerably more complicated than the well-developed kinetics in ordinary NMR, in which two-spin interactions play a leading role.

As experimental data are accumulated by NMR spectroscopy in which the sample is rotated at the magic angle and on spectra obtained by the Lee–Goldburg method,[2] however, we are seeing more and more indications that the high-resolution NMR spectra of solids may reflect some behavior which is even simpler than in ordinary spectra. For example, in the WHH-4 multipulse experiment with resonant pulses[6] and in experiments in which the sample is rotated at the magic angle,[7] the decay of the magnetization due to four- and three-spin interactions, respectively, is a simple exponential decay. The shape of the free-precession-decay signals in the system of $^{19}F$ nuclear spins in a $CaF_2$ single crystal, on the other hand, is of a much more complex vibrational-decay nature.[8] Nevertheless, the theory of free-precession decay caused by two-spin interactions has been worked out quite well.[9] A simple explanation was also offered recently[7] for the exponential free-precession decays which are observed in experiments in which the sample is rotated at the magic angle. We will discuss this explanation in detail in Sec. 3 of this paper.

Our purpose here is to generalize the theory proposed in Refs. 7 and 9 for use in analyzing the free-precession decays observed in the Lee–Goldburg experiment.

It is convenient to begin this analysis with a brief derivation of the Hamiltonian for three-spin interactions in the Lee–Goldburg experiment. This derivation will clarify the subsequent discussion of the physical nature of three-spin interactions and the mechanisms by which these interactions affect the free-precession decays observed in the Lee–Goldburg experiment.

## 1. EFFECTIVE HAMILTONIAN

In the Lee–Goldburg experiment,[2] the system of spins coupled by the dipole-dipole interaction is subjected to an intense rf field $2H_1\cos(\omega t)$ whose frequency is shifted by an amount $\Delta$ from the Larmor precession frequency of the nuclear spins. In the rotating coordinate system, the spins experience an effective field

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$$H_e=(H_1^2+\Delta^2/\gamma^2)^{1/2}, \tag{1}$$

which makes an angle

$$\xi=\arctan(\omega_1/\Delta) \tag{2}$$

with the $z$ axis ($\omega_1=\gamma H_1$, where $\gamma$ is the gyromagnetic ratio of the nuclei). The equation for the system density matrix $\rho(t)$ in the rotating coordinate system can be written ($\hbar=1$)

$$i\frac{d\rho}{dt}=[\Delta S_z+\omega_1 S_x+\mathcal{H}_{dz},\rho(t)], \tag{3}$$

where $\mathcal{H}_{dz}$ is the Hamiltonian of the secular (with respect to the $z$ axis) part of the dipole-dipole interaction. This secular part is given by

$$\mathcal{H}_{dz}=\sum_{i<j} b_{ij}\{3S_{zi}S_{zj}-\mathbf{S}_i\cdot\mathbf{S}_j\}, \tag{4}$$

where the operator $S_{\alpha i}$ projects the spin of nuclear spin $i$ onto the $\alpha$ axis ($\alpha=x,y,z$), $S_\alpha=\Sigma_i S_{\alpha i}$, and $b_{ij}$ is the constant of the dipole-dipole interaction of nuclear spins $i$ and $j$. In a tilted rotating coordinate system defined by the transformation

$$\tilde{\rho}(t)=\exp(i\xi S_y)\rho(t)\exp(-i\xi S_y), \tag{5}$$

in which the effective field is directed along the $z$ axis, Eq. (3) becomes

$$i\frac{d\tilde{\rho}}{dt}=\left[\omega_e S_z+\sum_{m=-2}^{2}\mathcal{H}_m,\tilde{\rho}(t)\right], \tag{6}$$

where

$$\mathcal{H}_0=\frac{3\cos^2\xi-1}{2}\sum_{i<j} b_{ij}(3S_{zi}S_{zj}-\mathbf{S}_i\mathbf{S}_j), \tag{7}$$

$$\mathcal{H}_{\pm1}=-\tfrac{3}{4}\sin(2\xi)\sum_{i<j} b_{ij}(S_{zj}S_i^{\pm}+S_{zi}S_j^{\pm}), \tag{8}$$

$$\mathcal{H}_{\pm2}=\tfrac{3}{4}\sin^2\xi\sum_{i<j} b_{ij}S_i^{\pm}S_j^{\pm}, \tag{9}$$

and $S_j^{\pm}=S_{xj}\pm iS_{yj}$ ($S^{\pm}=\Sigma_j S_j^{\pm}$).

Switching to the effective-field picture of the interaction, i.e., carrying out the transformation

$$\tilde{\rho}(t)=\exp(-i\omega_e t S_z)\rho^*(t)\exp(i\omega_e t S_z), \tag{10}$$

we find that the density matrix $\rho^*(t)$ satisfies the equation

$$i\frac{d\rho^*(t)}{dt}=\left[\sum_{m=-2}^{2}\mathcal{H}_m\exp(im\omega_e t),\rho^*(t)\right]. \tag{11}$$

If the angle $\xi$ is equal to the magic angle $\xi_m$ ($\cos\xi_m=1/\sqrt{3}$), we have $\mathcal{H}_0=0$ according to (7), and the dipole-dipole interaction oscillates rapidly at $\omega_e\gg\omega_{loc}$, where $\omega_{loc}=(\mathrm{Sp}\mathcal{H}_{dz}^2/\mathrm{Sp}S_z^2)^{1/2}$. We restrict the discussion below to cases in which $\xi$ differs only slightly from $\xi_m$:

$$(|\Delta\xi|=|\xi-\xi_m|\ll 1).$$

This problem is thus one involving rapidly oscillating interactions. To solve such a problem we use the method of canonical transformations which has been developed previously.[4,5] This method makes it possible to find a representation in which the dynamics of the system is described by a time-independent Hamiltonian. In the problem at hand, the time-independent Hamiltonian $\mathcal{H}^{\text{eff}}$ can be written as follows, to within terms of order $\varepsilon=\omega_{loc}/\omega_e$ ($\varepsilon\ll 1$):

$$\mathcal{H}^{\text{eff}}=\mathcal{H}_0+\frac{1}{\omega_e}([\mathcal{H}_1,\mathcal{H}_{-1}]+\tfrac{1}{2}[\mathcal{H}_2,\mathcal{H}_{-2}]). \tag{12}$$

Since the operators $\mathcal{H}_i$ ($i=\pm1,\pm2$) are two-spin operators, the effective Hamiltonian in (12) contains a three-spin part. Terms of order $\varepsilon^2$, which are unimportant for the spin dynamics in the Lee–Goldburg experiment, are four-spin terms and play a governing role in multipulse NMR spectroscopy.[3] Using (8) and (9), we can write the part $\mathcal{H}^{(1)}$ of the effective Hamiltonian (12) which is of order $\varepsilon\omega_{loc}$ for spins $s=1/2$ as follows:

$$\mathcal{H}^{(1)}=\frac{9}{32\omega_e}(\sin^4\xi+\sin^2 2\xi)\sum_{i\neq j} b_{ij}^2 S_{iz}+\frac{9}{32\omega_e}\Big\{4\sin^2 2\xi \times\sum_{i\neq j\neq m} b_{ij}b_{jm}S_{iz}S_{jz}S_{mz}+\sum_{i\neq j\neq m}(b_{ij}\sin^4\xi -2b_{jm}\sin^2 2\xi)S_{iz}(S_j^+S_m^-+S_j^-S_m^+)\Big\}. \tag{13}$$

We wish to stress that the effective interaction in (12) is similar in structure and physical nature to the three-spin effective interactions which control free-precession decay in experiments in which the sample is rotating at the magic angle. In each case, the effective interaction is found by averaging the two-spin interactions over the rapidly oscillating trajectories of the individual spins. This oscillation is caused by the rotation of the sample or by the strong resonant rf field directed at the magic angle. The nature and mechanism of these effective interactions are completely similar to those for the occurrence of effective interactions in the Kapitsa problem[10] of the effect of a rapidly oscillating force on the motion of a particle in a static field.

When $\xi=\xi_m$ holds $\mathcal{H}^{(1)}$ is the same as the Hamiltonian derived in Refs. 11 and 12. If all the nuclei occupy equivalent sites in the crystal lattice, the one-spin part of $\mathcal{H}^{(1)}$ simply produces a shift of the NMR lines in the rotating coordinate system.[11] In the discussion below we accordingly focus on the three-spin part of (13), which governs the free-precession decays observed in the Lee–Goldburg experiment.

## 2. SHAPE OF A NMR LINE IN THE LEE–GOLDBURG EXPERIMENT

In order to observe NMR in the Lee–Goldburg experiment,[2] it is necessary to excite and measure a rotating component of the nuclear magnetization $\mathbf{M}_\perp$ which is directed perpendicular to the effective field $\mathbf{H}_e$. This was done in Ref. 13 by directly detecting the projection of $\mathbf{M}_\perp$ onto the $z$ axis of a rotating coordinate system; this projection was oscillating at a frequency $\omega_e$.

The time evolution of the polarization, which is proportional to $\mathbf{M}_\perp$, is described by

$$G(t)=\frac{\mathrm{Sp}\{\exp(-i\mathscr{H}^{\mathrm{eff}}t)S^{+}\exp(i\mathscr{H}^{\mathrm{eff}}t)S^{-}\}}{\mathrm{Sp}\{S^{+}S^{-}\}}, \quad (14)$$

since we have

$$G(t)=\frac{\mathrm{Sp}\{\exp(-i\mathscr{H}^{\mathrm{eff}}t)S_x\exp(i\mathscr{H}^{\mathrm{eff}}t)S_x\}}{\mathrm{Sp}S_x^2}$$
$$-i\frac{\mathrm{Sp}\{\exp(i\mathscr{H}^{\mathrm{eff}}t)S_x\exp(i\mathscr{H}^{\mathrm{eff}}t)S_y\}}{\mathrm{Sp}S_y^2}$$
$$=P_x-iP_y, \quad (15)$$

where $P_x$ and $P_y$ are components of the polarization along the $x$ and $y$ axes (in the plane perpendicular to $\mathbf{H}_e$) at the time $t$, under the condition that the polarization at $t=0$ was directed along the $x$ axis. Here we have

$$|G(t)|=\sqrt{P_x^2+P_y^2} \quad (16)$$

when the dynamics of the system is determined by the ordinary two-spin interactions, $\mathscr{H}^{\mathrm{eff}}$ in (14) must be replaced by $\mathscr{H}_{dz}$ [see (4)]. We then have $P_y(t)=0$ if the condition $P_y(0)=0$ held at the initial time. This result follows from the circumstance that when the spins are rotated 180° around the $x$ axis there is no change in $\mathscr{H}_{dz}$, but there is a change in the sign of $S_y$, which leads to $P_y=-P_y$; i.e., we have $P_y(t)\equiv 0$. In the case of two-spin interactions it follows that the resonant absorption line $g(\omega)$, which is the Fourier transformation of (14), is symmetric under a change in the sign of $\omega$.

On the other hand, the effective Hamiltonian $\mathscr{H}^{\mathrm{eff}}$ in (12) is not invariant under rotations of the spin through 180° around the $x$ and $y$ axes. In particular, in the case $\xi=\xi_m$ the effective Hamiltonian changes sign as the result of such rotations. The shape of the NMR line of a system of spins whose behavior is described by the effective Hamiltonian (12) is thus generally asymmetric.

A simple example helps clarify this important circumstance—a circumstance which substantially distinguishes the problem at hand from the usual problem, involving the dynamics of a system of spins which are interacting through $\mathscr{H}_{dz}$. Let us consider a system of four spins, 1, 2, 3, and 4, which are coupled by the interaction

$$\mathscr{H}_{zzz}=\frac{1}{\omega_e}\sum_{i\neq j\neq k}b_{ij}b_{kj}S_{iz}S_{kz}S_{jz}, \quad (17)$$

which is the $zzz$ part of the Hamiltonian (13), with $\xi=\xi_m=\arccos 1/\sqrt{3}$. In this case the field $h_{zz}^{(1)}$ created at spin 1 by spins 1, 3, and 4 is given by

$$h_{zz}^{(1)}=\frac{1}{\omega_e}\sum_{j=k\neq(1)}(2b_{kj}+b_{k1})b_{1j}S_{jz}S_{kz}. \quad (18)$$

To simplify the analysis we assume that the constants of the dipole-dipole interactions between all the spins are identical ($b_{kj}=b$). From (18) we then find

$$h_{zz}^{(1)}=\frac{6b^2}{\omega_e}(S_{2z}S_{3z}+S_{2z}S_{4z}+S_{3z}S_{4z}). \quad (19)$$

In six of the eight possible relative orientations of the spins which generate the field at spin 1, the value of this field is $3b^2/(2\omega_e)$. Only in the two orientations in which the $z$ projections of spins 2, 3, and 4 are identical does this field have the value $b^2/2\omega_e$. In this example, the lineshape function is therefore asymmetric.

The asymmetry of the line stems from the appearance of the polarization component $P_y$ in the free-precession decay. This circumstance in turn means that the phase of the magnetization $\mathbf{M}_\perp$ changes (as time elapses) in this experiment, in contrast with ordinary free-precession decays. In an $N$-spin system in which the spins are coupled by the interaction $\mathscr{H}_{zzz}$, the shape of the NMR line can be found through a numerical calculation.[14] This line is asymmetric, and its peak is shifted by an amount determined by the one-spin part of (13).

The decay of the magnetization $\mathbf{M}_\perp$ in a Lee–Goldburg experiment was studied experimentally in Ref. 15, with direct detection of the $z$ projection of $\mathbf{M}_\perp$. It was shown[15] that in the case $\xi=\xi_m$ the free-precession decays of the $^{19}F$ nuclear spins in a $CaF_2$ single crystal are attenuated monotonically, without oscillations, in contrast with the attenuation of the free-precession decays in $CaF_2$, which are caused by ordinary two-spin dipole-dipole interactions. The initial part of the decay (up to $\simeq 50\%$) is described by a Gaussian function, while the tail of the decay is described by a simple exponential function.[15] This circumstance means that the shape of the NMR line is approximately Lorentzian at frequencies near the center of the line and approximately Gaussian in the wings, as was pointed out in Ref. 13.

When there is a deviation from the magic angle, oscillations appear in the free-precession decays. These oscillations become more apparent as $\xi$ deviates further from $\xi_m$ (Ref. 15). This circumstance suggests that the oscillations observed in the free-precession decays are due to the binary Hamiltonian $\mathscr{H}_0$.

It is also important to note that in some similar experiments[16] carried out on samples in which intense molecular motions occur (solid benzene and a plastic) some monotonic free-precession decays (without oscillations) were observed at arbitrary values of the angle $\xi$.

These features of the attenuation of the transverse magnetization in the Lee–Goldburg experiment can be explained by the theory presented in the following sections of this paper.

### 3. KINETIC EQUATION

Let us discuss the important analogy between the dynamics of the spin system of a solid, described by the Hamiltonian $\mathscr{H}^{\mathrm{eff}}$, and the dynamics of spins in liquids. We first consider the system of spins in a liquid. We select some spin and call it spin 1. The constant of the spin-spin interaction of spin 1 with spin $j$ is denoted by $b_{1j}$, as before. The nearest neighborhood of spin 1 changes rapidly because of the arrival and departure of particles with opposite spin projections. The longitudinal local field at spin 1 changes rapidly in the process. This local field, which is parallel to the effective field $\mathbf{H}_e$, has the strongest effect on the observed spectra. The correlation time $\tau_c$ of the fluctuations of this field in liquids is much shorter than the time

scales determined by free-precession decays, with $b_{1j}\tau_c \ll 1$. The phase relaxation rate $1/T_2$ in a liquid can be found from[8]

$$\frac{1}{T_2}=\sum_{j\neq 1} b_{ij}^2\tau_c, \tag{20}$$

which describes the phase relaxation of spins in the fluctuating longitudinal local dipole fields. An important feature of (20) is that the phase relaxation rate of the spins is determined by the sum of the independent contributions generated by the interactions of spin 1 with its nearest neighborhood. Expression (20) also shows that the dipole-dipole interactions of nuclear spins have fluctuations due to the rapid relative motion of the molecules in the liquid, and the relaxation time is determined by the time-averaged dipole-dipole interactions, which are weaker than the original interactions by a factor of $1/(b_{1j}\tau_c)$.

Following Ref. 7, and working from the properties of effective interaction (13), which conserves $S_z$, we can now show that an expression analogous to (20) can be used for a qualitative description of free-precession decays in solids in the experiment in which the sample is rotating at the magic angle[1] and also in the Lee–Goldburg experiment.[2]

In the case $\xi=\xi_m$, the effective interaction in the spin system of a solid in the experiments of Refs. 1 and 2 is a three-spin interaction. Denoting by $b_0$ the constant of the dipole-dipole interaction between spin 1 and a nearly spin, we find that the field induced at spin 1 by any two spins of the nearest neighborhood is $b_0^2/\omega_e$ in order of magnitude, according to (13). Since there are $z\sim 10$ spins in the nearest neighborhood of spin 1, the average longitudinal local field $\omega_{av}$ at this spin is

$$\omega_{av}=\sqrt{\left(\frac{b_0^2}{\omega_e}\right)^2 z^2}=\frac{b_0^2}{\omega_e}z; \tag{21}$$

the reason is that this field is determined by $z^2$ independent contributions from various pairs of spins in the nearest neighborhood. The rate at which spin 1 processes in the local field is thus stronger by a factor of $z$ ($z\gg 1$) than each interaction of this spin with its neighbors. The three-spin interactions described by (13) in a solid are thus rapidly oscillating interactions, like the two-spin interactions in liquids. Consequently, there is a profound analogy between the spin system in a liquid and that in a solid in experiments in which the sample is rotating at the magic angle and in the Lee–Goldburg experiment. This analogy allows us to treat the latter spin system as a spin liquid. This analogy is seen in the circumstance that the free-precession decay in the experiments of Refs. 1 and 2 becomes exponential[7,15] after some initial attenuation of the signal.

These arguments are based on the circumstance that the dominant dynamic process in this system is the precession of spins in the local fields acting on them. This analogy also makes it possible to distinguish another elementary process which controls the spin dynamics. Here we need to bear in mind that in order to solve the problem of the shape of the NMR line in the Lee–Goldburg experiment and in many other cases it is not at all necessary to follow the time evolution of variables corresponding to a single spin. It is sufficient to introduce semimacroscopic variables which are smooth functions of the time. Although there is some loss of information in the switch to a semimacroscopic description, enough information is retained to describe the observable absorption lines. Since the dominant process in these problems is a precession of spins, it was proposed in Ref. 9 that kinetic equations be constructed with the help of the following variables: $\sigma_\alpha(h,t)$ ($\alpha=x,y,z$), which are the polarization densities of the spins which are in the longitudinal (i.e., parallel to the effective field $\mathbf{H}_e$) local field $h$ at the given time $t$. We need to stress that the complex polarization

$$F(h,t)=\sigma_x(h,t)+i\sigma_y(h,t)$$

precesses in the longitudinal field, which itself varies because of the relative flips of the spins due to the dipole-dipole interactions between these spins. This variation of the field can be described by means of spectral diffusion. The variation of $F(h,t)$ is thus governed by precession in the local field $h$, which depends on the time as a result of the spectral diffusion. The change in the polarization $F(h,t)$ due to these processes can be described by the equation

$$\frac{\partial F(h,t)}{\partial t}=ihF(h,t)+SF(h,t), \tag{22}$$

where the operator $S$ is responsible for the spectral diffusion. If the spectral diffusion can be described as a Markovian random process, we can write

$$SF(h,t)=\frac{F_0(t)-F(h,t)}{\tau}, \tag{23}$$

where $\tau^{-1}$ is the rate of spectral diffusion, and

$$F_0(t)=\int_{-\infty}^{\infty} g(h)F(h,t)dh, \tag{24}$$

where $g(h)$ is the normalized shape of the NMR line of the spins in longitudinal local field $h$.

## 4. THEORY OF FREE-PRECESSION DECAYS IN THE LEE-GOLDBURG EXPERIMENT

When the angle $\xi$ deviates from its magic value, oscillations appear in free-precession decays. These oscillations become progressively larger as the deviation increases.[15] Since the role of two-spin interactions $\mathscr{H}_0$ increases with increasing deviation from the magic angle, and since oscillations appear[8,9] in the free-precession decays which are determined by $\mathscr{H}_0$, it is natural to explain the oscillatory nature of the free-precession decays in the Lee–Goldburg experiment with $\xi\neq\xi_m$ on the basis of an effect of two-spin interactions on the dynamics of the system. In a study[9] of free-precession decays in the system of $^{19}F$ nuclei in $CaF_2$ it was found that the oscillations in the free-precession decays are caused by transverse local fields which arise because of the isotropic part of the dipole-dipole interaction. Taking into account (along with the longitudinal local field $h$, caused by the three-spin interaction) a local

TABLE I.

| Orientation | The angle $\xi$ | $M_2^{(3)}\cdot 10^5$, $\mu s^{-2}$ | $M_2^{(2)}\cdot 10^5$, $\mu s^{-2}$ | $M_3^{(3)}\cdot 10^7$, $\mu s^{-3}$ |
|---|---|---|---|---|
| [100] | 54,73° | 3,305 | 0 | −1,402 |
| [100] | 52,8° | 3,698 | 0,849 | −4,787 |
| [111] | 50° | 0,166 | 0,943 | −0,831 |
| [110] | 46° | 0,856 | 7,057 | −13,684 |

two-spin longitudinal field $h_2$, which is determined by the $zz$ part of $\mathscr{H}_0$, we rewrite Eq. (22) for a Markovian spectral diffusion as follows:

$$\frac{dF(h,h_2,t)}{dt}=i\left(h+\frac{3}{2}h_2\right)F(h,h_2,t)+i\left(\frac{3}{2}-\alpha\right)\times[-h_2F(h,h_2,t)+h_2F_0(t)+F_1^{(2)}(t)]+\frac{F_0(t)-F(h,h_2,t)}{\tau}, \quad (25)$$

where $\alpha$ is a parameter[1)] of order unity,

$$F_0(t)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\tilde{g}(h_2)g(h)F(h,h_2,t)dh_2dh, \quad (26)$$

and

$$F_1^{(2)}(t)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}h_2\tilde{g}(h_2)g(h)F(h,h_2,t)dh_2dh. \quad (27)$$

Here $g(h)$ is the distribution of the longitudinal (parallel to $\mathbf{H}_e$) local field determined by the three-spin interaction, and $\tilde{g}(h_2)$ is the NMR lineshape function, which is due to the $zz$ part of the two-spin dipole-dipole interactions and which is given by

$$\tilde{g}(h_2)=\frac{1}{\sqrt{2\pi M_2^{(2)}}}\exp\left(-\frac{h^2}{2M_2^{(2)}}\right), \quad (28)$$

where

$$M_2^{(2)}=\frac{1}{9}(1-3\cos^2\xi)^2M_2, \quad (29)$$

and $M_2$ is the second moment of the NMR absorption line, which is governed by two-spin dipole-dipole interactions. The expression in square brackets in (25) describes an exchange of polarization between layers,[9] i.e., between sets of spins which are in different fields $h$ and $h_2$ at the time $t$. This process is driven by the exchange part of the two-spin dipole-dipole interactions. This expression vanishes when we set $F=$const, in which case the exchange of polarization is halted because the polarizations in different layers become equal.[17] This expression also vanishes when it is multiplied by $g(h)\tilde{g}(h_2)$ and then integrated over $h$ and $h_2$ (Ref. 17). The latter circumstance is evidence that the resultant polarization is conserved in the course of spin exchange. A similar term does not arise in the three-spin kinetics because the Hamiltonian (13) has no interaction which conserves the resultant polarization.

We should stress that the two- and three-spin interactions are taken into account in Eq. (25) on the basis of the clearly defined one- and two-spin local fields, not by means of a memory function,[18] as in Ref. 15.

Integrating Eq. (25) with the initial condition $F(h,h_2,0)=1$, we find

$$F(h,h_2,t)=\int_0^t dt'\left\{\frac{F_0(t')}{\tau}+i\left(\frac{3}{2}-\alpha\right)[h_2F_0(t')+F_1^{(2)}\times(t')]\right\}\exp\left\{\left[i(h+\alpha h_2)-\frac{1}{\tau}\right](t-t')\right\}+\exp\left[i(h+\alpha h_2)t-\frac{t}{\tau}\right]. \quad (30)$$

To pursue the calculations we need the function $g(h)$, which can be written as follows:

$$g(h)=\int_{-\infty}^{\infty}G_3(t)\exp(-iht)dt, \quad (31)$$

where

$$G_3(t)=\frac{\mathrm{Sp}\{\exp(-i\mathscr{H}_3^{(1)}t)S^+\exp(i\mathscr{H}_3^{(1)}t)S^-\}}{\mathrm{Sp}\{S^+S^-\}}. \quad (32)$$

The quantity $\mathscr{H}_3^{(1)}$ is the three-spin part of Hamiltonian (13). A Gaussian function is a good approximation of the function $G_2(t)$, which is governed by the $zz$ part of the ordinary two-spin dipole-dipole interactions.[8] As we mentioned back in Sec. 2, we have $G_3(t)\neq G_3(-t)$. Making use of this circumstance, we find

$$G_3(t)=\exp\left(-\frac{M_2^{(3)}t^2}{2}\left(1-i\frac{M_3^{(3)}t^3}{6}\right)\right), \quad (33)$$

where $M_2^{(3)}$ and $M_3^{(3)}$ are respectively the second and third moments of $g(h)$. From (31) and (33) we find

$$g(h)=\frac{1}{\sqrt{2\pi M_2^{(3)}}}\left[1-\frac{M_3^{(3)}}{2(M_2^{(3)})^2}h+\frac{M_3^{(3)}}{6(M_2^{(3)})^3}h^3\right]\times\exp\left(-\frac{h^2}{2M_2^{(3)}}\right). \quad (34)$$

The function $g(h)$ satisfies the following relations:

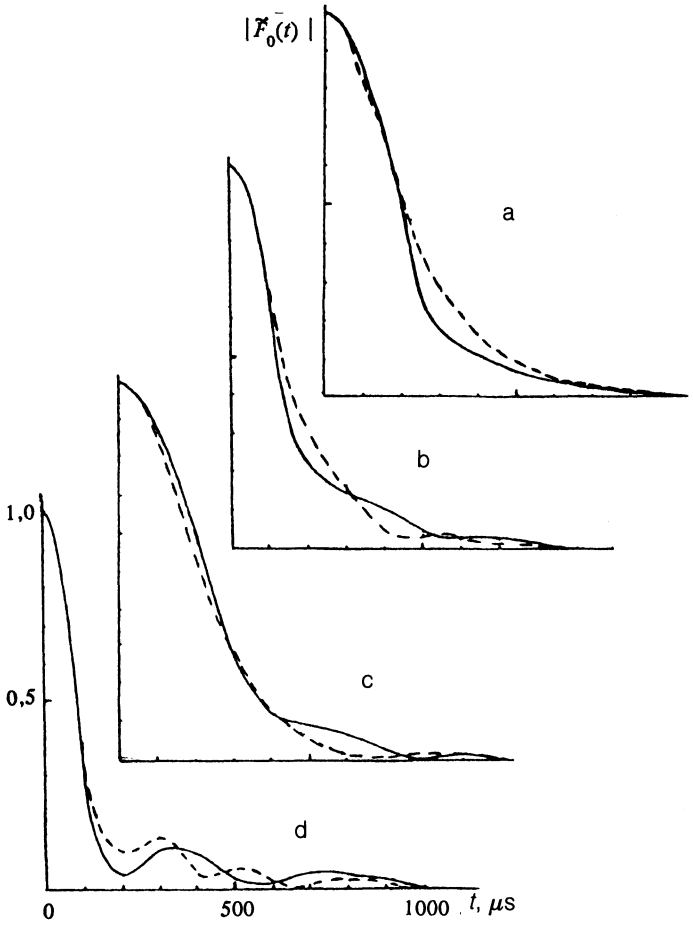


FIG. 1. Experimental and theoretical free-precession decays resulting from $^{19}F$ nuclear spins in a $CaF_2$ single crystal. Solid lines—Experimental free-precession decays.[15] Dashed lines—Theoretical values of $|\bar{F}_0(t)|$. a—[100]$\|\mathbf{H}_0$, $\xi=\xi_m=54.73°$, $\tau=300$ μs, b—[100]$\|\mathbf{H}_0$, $\xi\approx 52.8°$, $\tau=400$ μs, $\alpha=0.4$; c—[111] $\mathbf{H}_0$, $\tau=400$ μs, $\alpha=1.0$, $\xi=52°$ for the solid line and $\xi=50°$ for the dashed line; d—[110] $\mathbf{H}_0$, $\tau=300$ μs, $\alpha=0.9$, and $\xi=41.3°$ for the solid line and $\xi=46°$ for the dashed line. The values of the moments $M_2^{(2)}$, $M_2^{(3)}$, and $M_3^{(3)}$ and of the time $T^*$ are given in the text proper.

$$\int_{-\infty}^{\infty} g(h)dh=1, \quad \int_{-\infty}^{\infty} hg(h)dh=0,$$

$$\int_{-\infty}^{\infty} h^2 g(h)dh=M_2^{(3)}, \quad \int_{-\infty}^{\infty} h^3 g(h)dh=M_3^{(3)}. \tag{35}$$

The nonzero third moment $M_3^{(3)}$ arises because of the asymmetry of $g(h)$, which we mentioned back in Sec. 2.

Using Eq. (30) and definitions (26) and (27), we find a system of integral equations which completely govern the kinetics of the system of spins under consideration here:

$$F_0(t)=\frac{1}{\tau}\int_0^t dt' F_0(t-t')E(t')G(t')\left[1-\alpha\left(\frac{3}{2}-\alpha\right)\times M_2^{(2)}t'\tau\right]+i\left(\frac{3}{2}-\alpha\right)\int_0^t dt' F_1^{(2)}(t-t')\times E(t')G(t')+G(t)E(t), \tag{36}$$

where

$$F_1^{(2)}(t)=iM_2^{(2)}\int_0^t dt' F_0(t-t')E(t')G(t')\times\left[\frac{\alpha t'}{\tau}-\left(\frac{3}{2}-\alpha\right)(M_2^{(2)}\alpha^2 t'^2-1)\right]-M_2^{(2)}\alpha\left(\frac{3}{2}-\alpha\right)\int_0^t dt' F_1^{(2)}(t-t')t'E(t')G(t')+iM_2^{(2)}\alpha tE(t)G(t), \tag{37}$$

where

$$E(t)=\exp\left(-\frac{t}{\tau}-\frac{1}{2}M_2^{(2)}\alpha^2 t^2\right). \tag{38}$$

To find short-term solutions of (36) and (37), we set $F_0(t-t')\approx 1$, $F_1^{(2)}(t-t')\approx 0$ on the right side of (37). We then have

$$F_1^{(2)}(t)\simeq \tfrac{3}{2}iM_2^{(2)}t. \tag{39}$$

Using (39), and setting $F_0(t-t')\approx 1$ on the right side of (36), we find

$$F_0(t)=1-\tfrac{1}{2}(\tfrac{9}{4}M_2^{(2)}+M_2^{(3)})t^2. \tag{40}$$

To find a long-term solution of (36) and (37) we need to take Laplace transforms in system of integral equations (36) and (37). Omitting the details of the corresponding calculations, we find that the asymptotic long-term behavior of $F_0(t)$ is the exponential function

$$F_0(t) \approx ae^{-(b+ic)t}, \tag{41}$$

where $a$, $b$, and $c$ are functions of the parameters $M_2^{(2)}$, $M_2^{(3)}$, $M_3^{(3)}$, $\alpha$, and $\tau$. In particular, at the value $\xi=\xi_m$, in the limit of rapid spectral diffusion ($\tau\sqrt{M_2^{(3)}} \ll 1, \tau(|M_3^{(3)}|)^{1/3} \ll 1$), we find

$$F_0(t) \approx \exp[-(M_2^{(3)}+iM_3^{(3)}\tau)\tau t]. \tag{42}$$

Expression (42) shows that when the function $g(h)$ is asymmetric, under the condition $M_3^{(3)} \neq 0$, there is a change in the phase of the magnetization perpendicular to the effective field, as was pointed out in Ref. 15.

Analytic solutions can be found in only these two limiting cases. To compare this theory with the experimental data of Ref. 15, we have numerically solved the system of integral equations (36) and (37). The moments $M_2^{(3)}$ and $M_3^{(3)}$, required for the calculations, were furnished by Zobov and Popov;[19] the two-spin second moment $M_2^{(2)}$ was taken from (29). Table I shows values of the moments $M_2^{(2)}$, $M_2^{(3)}$, and $M_3^{(3)}$ for all values of the angle $\xi$ and for all orientations for which calculations were carried out.

Figure 1 shows the results of a numerical solution[2)] of (36), along with experimental data from Ref. 15. The nature of the free-precession decays according to our theory is in basic agreement with the experimental data.[15] The oscillations in the magnetization are completely absent at the magic angle (Fig. 1a). The asymptotic behavior of $|F_0(t)|$ at large and small values of $t$ [see (40) and (41)] agrees with the conclusion of Ref. 15 that the NMR lineshape is Lorentzian in the frequency region near the center of the line, while it is Gaussian in the wings. As the deviation from the magic angle increases (Fig. 1, b–d), the oscillations become progressively more prominent, due to the increasing contribution of the two-spin Hamiltonian $\mathscr{H}_0$ to the dynamics of the system. An important point is that the signal does not reach zero at the first few minima of the oscillations (Fig. 1d). As was mentioned above, the reason is the appearance of a magnetization component $M_y$, which does not vanish at the same time as $M_x$ in the course of the free-precession decay.

As the spectral diffusion accelerates, the oscillations disappear from the free-precession decay, and $|F_0(t)|$ is attenuated exponentially for $t \gg \tau$ [see (42)]. This agrees with the experimental results of Ref. 16, in which monotonic free-precession decays (without oscillations) were observed in samples with an intense molecular motion at arbitrary values of the angle $\xi$.

The values of $|F_0(t)|$ were measured in the experiments of Ref. 15. The numerical solution of (36) and (37), on the other hand, yields each of the polarization components $F_x(t)$ and $F_y(t)$. Figure 2, a and b, shows plots of $F_x(t)$ and $F_y(t)$ for the value $\xi=\xi_m$.

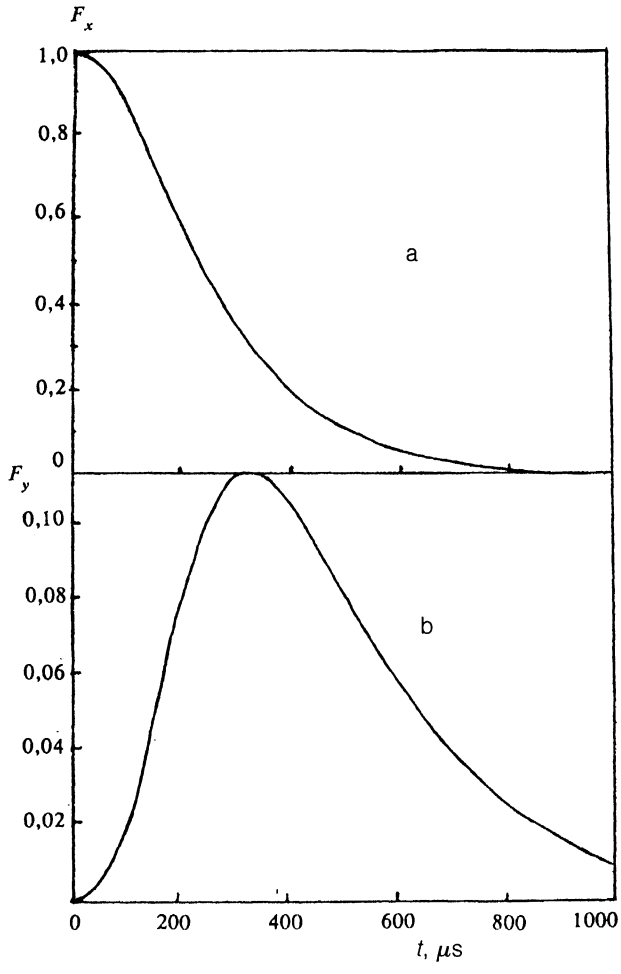


FIG. 2. Theoretical values of the polarization components of $^{19}F$ nuclear spins in a $CaF_2$ single crystal. a—$F_x(t)$; b—$F_y(t)$. $[100]\|\mathbf{H}_0$, $\xi=\xi_m=54.73°$, $\tau=300$ μs.

The theoretical free-precession decays agree qualitatively with the experimental data of Ref. 15, but there are some important quantitative discrepancies. The apparent reason is the approximate description of $g(h)$ in (34), which incorporates information[3)] on only the second and third moments of the line. We believe that a more detailed description of $g(h)$ is necessary; such a description may have an important effect on the theoretical free-precession decays at $\sqrt{M_2^{(3)}}t > 1$. Further progress in the theory could be made by incorporating the contributions of all the elementary spin processes to the dynamics of the system through analysis of the Hamiltonian (13).

On the other hand, the extent of the agreement between theory and experiment may be affected by some secondary factors associated with the experimental conditions of Ref. 15. To take account of effects of field variations, we compare the experimental data with the function $|\tilde{F}_0(t)|$ (Fig. 1), which is defined by

$$\tilde{F}_0(t) = F_0(t)e^{-t/T^*}. \tag{43}$$

The time $T^*$, governed by the field variations, was chosen to be 1000 μs, as in Ref. 15.

The approach proposed here can also be taken to analyze the kinetics of spin systems in multipulse experiments.

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[1)]It was shown in Ref. 9 that $\alpha$ is determined by the second and fourth moments of the absorption line.

[2)]The numerical solution of (36) was multiplied by an exponential function in order to deal with effects stemming from the variations in the field [see (43)]. In the [111] and [110] orientations, small changes (2–4°) in the angle from the experimental values considerably improved the quantitative agreement between theory and experiment (Fig. 1, c and d). Qualitative agreement is also reached at values of $\xi$ corresponding to the experimental values.

[3)]According to (35), the first moment of $g(h)$ is zero.

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