Statistical theory of the NMR absorption line shape

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The Anderson-Weiss statistical NMR absorption-line-shape theory, which takes into account only the longitudinal local fields, is generalized to the case of arbitrary local fields produced by dipole-dipole interactions. We calculate the free-induction drop and the NMR absorption line shape which is connected with it through a Fourier transformation, for arbitrary correlation times for the molecular motions. We show that the oscillations observed in the drop for not too fast molecular motions are caused by the effect of transverse local fields. We compare the experimental decrease with the theoretical results in a wide range of variation of the time correlation of the molecular motions. The comparison shows good agreement.

1. INTRODUCTION

When studying a substance by spectroscopic methods (in the NMR, NQR, ESR, optical, IR, and UV bands) important information about its properties, structure, and composition can be obtained from the absorption line shape $g(\omega)$.[1–3] Of course, one needs for this a theory which connects in a simple way the absorption line shape with the properties of the substance—a theory of the absorption line shape of a macroscopic system of interacting particles which participate in the thermal motion. In first instance the interactions and the dynamics of the (magnetic or electric) dipole moments considered are important whereas the thermal motions may be taken into account to a good degree of accuracy using statistical methods.[1]

In the present paper we restrict ourselves to constructing a theory of the line shape in the case of NMR where the temperature and other dependences of $g(\omega)$ are very completely studied. The proposed theory can easily be generalized to the optical case as the pseudo-dipole moments of molecular spectroscopic transitions rotate in local electric fields in the same way as magnetic moments in local magnetic fields.[3]

In the NMR case the dipole-dipole interactions (DDI) are the most important ones for the dynamics of the dipole moments (nuclear magnetic dipole moments). The part of the DDI Hamiltonian $\hat{H}_d^z$ which is diagonal with respect to the z axis which is the direction of the magnetic field in which the system is placed has the form[1]

$$\hat{H}_d^z = 3\hat{H}^z - \hat{H}^0, \tag{1}$$

$$\hat{H}^0 = \hat{H}^x + \hat{H}^y + \hat{H}^z, \tag{2}$$

$$\hat{H}^q = \sum_{i<j} b_{ij} \hat{S}_i^q \hat{S}_j^q = \sum_{i<j} \hat{H}_{ij}^q, \quad q = x, y, z, \tag{3}$$

$$b_{ij} = \mu^2 \hbar^{-1} |\mathbf{r}_{ij}|^{-3} (3\cos^2\theta_{ij} - 1), \tag{4}$$

where μ is the magnetic moment of the nuclei studied, $\mathbf{r}_{ij}$ a vector connecting the ith and the jth spins, θ_{ij} the angle which $\mathbf{r}_{ij}$ makes with the z axis, and $\hat{S}_i^q$ the operator of the spin component of the ith nucleus along the $q = x,y,z$ axis.

It is well known that $g(\omega)$ is connected through a Fourier transformation with the autocorrelation function of the orthogonal z-component of the total spin of the system[1] which describes the free induction signal (FIS) $G(t)$:

$$g(\omega) = (2\pi)^{-1} \int \exp(-i\omega t) G(t)\, dt, \tag{5}$$

$$G(t) = \mathrm{Sp}\,\{\rho(t)\hat{S}^x\}/\mathrm{Sp}\,\{\rho(0)\hat{S}^x\}, \tag{6}$$

where

$$\hat{S}^x = \sum_i \hat{S}_i^x,$$

$\rho(t)$ is the density matrix of the spin system with a time dependence determined by the evolution equation[1]

$$\frac{d}{dt}\rho(t) = -i[\hat{H}_d^z, \rho], \tag{7}$$

which has the solution

$$\rho(t) = \exp(-it\hat{H}_d^z)\rho(0)\exp(it\hat{H}_d^z), \tag{8}$$

where $\rho(0)$ is the density matrix at the initial time,

$$\rho(0) = (2S+1)^{-N}(1 - \beta\hat{S}^x), \tag{9}$$

and N is the number of spins in the system.

The problem of the absorption line shape thus reduces to evaluating $G(t)$ in a system of strongly interacting particles with Hamiltonian (1).

Both the FIS and $g(\omega)$ in NMR have by now been well studied experimentally for many substances.[1,4] We note here two cases of often-observed characteristics.

In systems with strong thermal motions, i.e., when $\omega_l \tau_c \ll 1$, where $\omega_l^2 = M_2$ (M_2 is the second moment of the spectral line), τ_c is the correlation time of the molecular motions, $G(t)$ is monotonically damped and is well approximated by an exponential[1,5,6]

$$G(t) = \exp(-\omega_l^2 \tau_c t). \tag{10}$$

In systems without thermal motion, i.e., formally as $\tau_c \to \infty$, oscillating drops are observed which are well described by the empirical formula proposed by Abragam[1]:

$$G(t) = (bt)^{-1} \sin(bt) \exp(-a^2 t^2/2). \tag{11}$$

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A theoretical analysis of the case as $\omega_l \tau_c \ll 1$ was given in Ref. 1 on the basis of a statistical perturbation theory where $\omega_l \tau_c$ played the role of a small parameter, and in the papers by Anderson and Weiss[5,6] who used a statistical theory in the framework of which only the rotation of the spins in logitudinal (parallel to the z axis), local fields described by the terms $3\hat{H}^z$ in the Hamiltonian was taken into account. The isotropic interaction $\hat{H}^0$ which includes not only longitudinal but also transverse local fields, perpendicular to the z axis, are taken into account only as a source for fluctuations in the longitudinal local fields. Although this way of describing the FIS gives a physically clear picture of the spin dynamics and is formally applicable for any value of τ_c, it always leads[5,6] to a monotonically damped decrease which, as is clear from (11), disagrees with the experimental data as $\tau_c \to \infty$. This is connected with the fact that in that case taking $\hat{H}^0$ into account merely through the fluctuations of the longitudinal local fields is insufficient and one must also take into account directly the effect of the isotropic interaction on the spin-polarization rotation itself.

We note that there occurs in the isotropic interaction not only the interaction of the spins with the transverse fields, $\hat{H}^x + \hat{H}^y$, but also $\hat{H}^z$. It will become clear in what follows that it is by far simplest to take into account the contribution from the transverse local fields to the dynamics of the spin polarization in a compound with an isotropic interaction $\hat{H}^0$ which commutes with the total spin operator of the system.

A number of explanations of (11) were proposed in Refs. 7 to 16, where good agreement was obtained with the experimental data of Refs. 1 and 4, thanks to taking into account both the longitudinal and transverse local fields. However, the theories of Refs. 7 to 16 have a very formal character and use a number of not fully justified assumptions, and most importantly are inapplicable for the case when there are thermal motions present.

There is thus so far no theory which would describe the FIS for the whole range of τ_c, notwithstanding the urgent need for a development of methods for studying experimentally the properties and structure of substances at different temperatures.

The development of such a theory of the FIS and hence also of a theory of the absorption line shape on the basis of an analysis of the mechanisms for forming the FIS in a wide range of τ_c values is the aim of the present paper.

2. LAYER-POLARIZATION METHOD AND THE ANDERSON-WEISS THEORY

To construct a consistent theory of the FIS it is important to select correctly the variables in terms of which one can describe the spin dynamics in a macroscopic system of strongly interacting spins (the number of spins in the sample is $N \sim 10^{23}$). The FIS signal itself which is the response of the system to a pulse of the radio-frequency field is a particularly macroscopic characteristic and is equal to the total polarization of the sample, knowledge of which is insufficient to explain the mechanism of the observed oscillations and dampings. On the other hand, the polarizations of separate spins can also not be fixed as the basis of the analysis, as they move in too complicated a manner. It is important to select for the description of the spin dynamics variables which, while possessing a rather smooth time dependence, nevertheless would enable us to describe the elementary spin processes. We shall choose as such variables the components $G^q(h,t)$ of the polarizations of the layers h, where $q = x,y,z$. By the layer h we mean the set of spins in the sample which at a given time are in the longitudinal field h. The advantage of such variables is that using them one can not only duplicate the phenomenological Anderson-Weiss results but there is also a consistent solution of the FIS problem starting from the evolution equations for the density matrix (7), which enables us to take into account rather rigorously the effect of $\hat{H}^0$ on $g(\omega)$ and on the FIS.

Generally speaking, the variables introduced here are essentially analogous to those introduced when the problem of the destruction of the hyperfine structure was considered in Ch. X of Ref. 1, in which for the complex layer polarization

$$G^+(h,t) = G^x(h,t) + iG^y(h,t),$$

which characterizes the polarization of all spins of the sample in a given hyperfine field h at time t, a phenomenological equation was obtained for a discrete set of h. This equation, rewritten for a continuous h distribution has the form

$$\frac{d}{dt} G^+(h,t) = ihG^+(h,t) - \Omega(h) G^+(h,t) + \Omega(h) \times \int g(h') P(h,h') G^+(h',t)\, dh',$$

$$g(h) = (2\pi M)^{-1/2} \exp(-h^2/2M), \tag{12}$$

$g(h)$ is the density of layers, $\Omega(h)$ is the probability that h changes to another value in a unit time, and $P(h,h')$ is the probability that this other value is equal to h'.

The total polarization $G(t)$ which is measured in NMR equals

$$G(t) = \int dh\, g(h) G^+(h,t). \tag{13}$$

We note that Eq. (12) and the Anderson-Weiss theory[5,6] give physically similar results: a Gaussian decrease in the case of large correlation times and an exponential one in the case of short correlation times. One can easily check the latter by putting $\Omega(h) = 1/\tau_0$ $P(h,h') = 1$ and use a Laplace transformation to solve (12). Both the theory of Refs. 5 and 6 and Eq. (12) thus correctly describe the change from the broad lines of a solid to the narrow Lorentz lines of a fluid when the temperature is raised. However, in neither theory are there for any τ_c oscillations such as (11). To explain these oscillations one needs to take into account the contribution of the transverse local fields not only to the spectral diffusion but also to the rotation of the polarization of the layers, for which it is sufficient to add to the right-hand side of (12) a term taking into account the rotation of the polarization of the layers under the influence of the isotropic interaction.

3. EFFECTIVE ISOTROPIC INTERACTION AND TRANSVERSE LOCAL FIELDS OF FAR AND NEAR SPINS

Before finding the contribution of $\hat{H}^0$ to Eq. (12) we show that for each pair of spins i,k one can consider $\hat{H}_{ik}^0$ as a fast oscillating interaction, i.e., an interaction such that its oscillation frequency is much larger than its amplitude. This enables us to determine the contribution from $\hat{H}_{ik}^0$ to (12) using simple and well known methods to take into account fast oscillating interactions[17–19] which consist in changing from fast oscillating interactions to effective interactions which are time averaged.

We restrict ourselves to developing an FIS theory for the case of a CaF_2 single crystal. The translational symmetry of the cubic lattice formed by the magnetic ^{19}F ($S=\frac{1}{2}$) nuclei simplifies the calculations considerably. A generalization of the theory to amorphous substances and to other kinds of lattices does not meet with any difficulties of principle.

It is important to emphasize that in a condensed paramagnetic substance each spin is surrounded by a large number ($Z \sim 10$) of independently oriented near spins. Each spin rotates therefore in a mean square local field with a frequency ω_l:

$$\omega_l = M_2^{1/2} \approx {}^3/_2 \max_k |b_{ik}| Z^{1/2}. \tag{14}$$

As the local fields at the ith and k th spins are directed arbitrarily, the rotation of these spins in different local fields causes the interaction $\hat{H}_{ik}^0 \sim (\hat{\mathbf{S}}_i \hat{\mathbf{S}}_k)$ to oscillate with a frequency ω_l and

$$\frac{\|b_{ik}(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_k)\|}{\omega_l} \approx |b_{ik}|/6Z^{1/2} \max_k |b_{ik}| \leqslant 1/6Z^{1/2}. \tag{15}$$

We now show that the whole interaction $\hat{H}_{ik}^0$ and not some part of it oscillates around zero. To do this we consider the time variation of the x-component of the polarization of the ith spin under the influence of $\hat{H}_{ik}^0$:

$$\frac{d}{dt}\hat{s}_i^x = -ib_{ik}[(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_k), \hat{s}_i^x] = b_{ik}(\hat{s}_i^z\hat{s}_k^y - \hat{s}_i^y\hat{s}_k^z). \tag{16}$$

Hence it follows that

$$\frac{d}{dt}\mathrm{Sp}(\rho(t)\hat{s}_i^x\} = b_{ik}[\mathrm{Sp}\{\rho\hat{s}_i^z\hat{s}_k^y\} - \mathrm{Sp}\{\rho\hat{s}_i^y\hat{s}_k^z\}] = 0, \tag{17}$$

as the difference within the square brackets vanishes due to the translational invariance of the cubic lattice of CaF_2. The equation obtained means that the ensemble-averaged and hence also time-averaged[20] effect of the isotropic interaction on the x-component of the polarization vanishes. One can also easily prove this for the y- and z-components. Therefore, the time-averaged $\hat{H}_{ik}^0$ vanishes.

The amplitude of the effective isotropic interaction $\overline{H}_{ik}^0$ averaged over the oscillations about zero is, according to Refs. 17 and 18 of order of the quantity b_{ik}^2/ω_l. Moreover, we note that since the oscillating isotropic interaction $\hat{H}_{ik}^0$ at any time conserves the total spin $\hat{\mathbf{S}}_i + \hat{\mathbf{S}}_k$, $\overline{H}_{ik}^0$ clearly has the same property. Bearing in mind that the only two-particle interaction satisfying this is an interaction proportional to $(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_k)$, we find

$$\hat{\overline{H}}_{ik}^0 = a_{ik}(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_k), \tag{18}$$

$$a_{ik} = cb_{ik}^2/\omega_l, \quad c \sim 1. \tag{19}$$

The problem then reduces to finding the dynamics of the layer polarization governed by the evolution equation for the density matrix $\bar{\rho}$:

$$\frac{d}{dt}\bar{\rho} = -i[3\hat{H}^z - \hat{\overline{H}}^0, \bar{\rho}], \tag{20}$$

where

$$\hat{\overline{H}}^0 = \sum_{i<k} a_{ik}(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_k), \tag{21}$$

characterizing the trajectories of the rotation of the spins in the local fields, smoothed by averaging over a time interval $\tau \sim 1/\omega_l$. It is just these trajectories which determine the evolution of the polarizations of the layers for times $t > T_2$.[17,18]

The small oscillations of real trajectories about the smoothed ones, which are characterized by a small ($\sim Z^{-1/2}$) amplitude, practically vanish when one averages the polarizations over the layers when changing to the observed total magnetization of the sample, because the number of layers is $n \sim 2^Z$ and the fast oscillating components of the polarizations of different layers are incoherent because the fluctuations of the local fields which generate them at the different spins can be assumed to be statistically independent.

It is clear from Eqs. (19) and (4) that the effective isotropic interaction $\overline{H}_{ik}^0$ depends on the distance $|\mathbf{r}_{ik}|$ between the spins like $|\mathbf{r}_{ik}|^{-6}$. This means that one must take this interaction into account only for the nearest spins, and the interaction between all other pairs of spins which depends on $|\mathbf{r}_{ik}|$ like $|\mathbf{r}_{ik}|^{-3}$ may be assumed to equal $3\hat{H}_{ik}^z$. It will become clear in what follows that the contribution from the transverse local fields of the near spins can be expressed simply in terms of the longitudinal local fields produced by those spins, and it is therefore convenient for taking into account the transverse fields to include in our considerations two local longitudinal fields, h_c and h_f:

$$h_c = 2\sum_\alpha b_{i\alpha}S_\alpha^z, \quad h_f = 2\sum_\beta b_{i\beta}S_\beta^z, \quad h = h_c + h_f, \tag{22}$$

generated by near and far spins which are numbered by the indexes α and β. Following Ref. 13 we call the near spins a cell and include in the cell of the ith spin all spins satisfying the relation

$$b_{i\alpha}^2 > 0.1 \max_k |b_{ik}^2|. \tag{23}$$

For the far spins we have

$$b_{i\beta}^2 \leqslant 0.1 \max_k |b_{ik}^2|. \tag{24}$$

The parameter 0.1 occurring in (23) and (24) is selected such[13] that the spins of a cell would contribute to the second moment of the absorption line $b^2/3$ and the far spins a^2, where a and b are the parameters occurring in (11).

We now define a layer as the collection of spins in the sample at which at a given time the z-components of the local fields produced by the spins in a cell and the far spins are equal to h_c and h_f [in what follows $\{h_c, h_f\} = \mathbf{h}$]. The quantum-mechanical operators of the components of the layer polarization corresponding to the given definition have the form

$$\hat{S}^q(\mathbf{h}) = \sum_i \hat{S}_i^q(\mathbf{h}) = \sum_i \hat{S}_i^q \hat{P}_i(\mathbf{h}), \tag{25}$$

$$\hat{P}_i(\mathbf{h}) = \delta\Big(h_c - 2\sum_\alpha b_{i\alpha}\hat{S}_\alpha^z\Big)\delta\Big(h_f - 2\sum_\beta b_{i\beta}\hat{S}_\beta^z\Big). \tag{26}$$

For the operators $\hat{S}^0(\mathbf{h}) = \hat{S}^z(\mathbf{h})$, $\hat{S}^\pm(\mathbf{h}) = \hat{S}^x(\mathbf{h}) \pm i\hat{S}^y(\mathbf{h})$, which are the most convenient to use, we have relations (see the Appendix)

$$\mathrm{Sp}\,\{\hat{S}^m(\mathbf{h})\hat{S}^{m'}(\mathbf{h}')\} = N2^{N-2}\delta_{m,-m'}R(\mathbf{h})\delta(\mathbf{h}-\mathbf{h}'), \tag{27}$$

$$R(\mathbf{h}) = R_c(h_c)R_f(h_f), \tag{28}$$

$$R_c(h_c) = (2\pi)^{-1}\int dt\,\exp(ih_ct)\prod_\alpha \cos b_{i\alpha}t, \tag{29}$$

$$R_f(h_f) = (2\pi)^{-1}\int dt\,\exp(ih_ft)\prod_\beta \cos b_{i\beta}t. \tag{30}$$

The components $G^q(\mathbf{h},t)$ of the polarizations of the layers are connected with $\bar{\rho}(t)$ through the relation

$$G^q(\mathbf{h},t) = \beta\frac{N}{4}R^{-1}(\mathbf{h})\,\mathrm{Sp}\{\bar{\rho}(t)\hat{S}^q(\mathbf{h})\}. \tag{31}$$

It is convenient to assume in what follows that $G^x(\mathbf{h},0) = 1$, for which it is sufficient to put formally $\beta = 4/N$. We note the identity, which is important for the problem we are considering,

$$G^0(\mathbf{h},t) = \mathrm{Sp}\{\hat{S}^0(\mathbf{h})\exp(-it\hat{H}_d^z)\bar{\rho}(0)\exp(it\hat{H}_d^z)\} = 0. \tag{32}$$

To prove (32) we act on the operators which occur under the trace by the operator producing a rotation of 180° around the z axis: $\exp(-i\pi\hat{S}^z)$. Such a transformation does not change the value of the trace, as it is unitary. On the other hand, the operators $\hat{H}_d^z$ and $\hat{S}^0(\mathbf{h})$ are invariant under a rotation and the initial condition (9) changes its sign. Therefore, $G^0(\mathbf{h},t)$ turns out to equal itself with opposite sign, which proves (32).

To write down the time evolution of the quantities $G^x(\mathbf{h},t)$ and $G^y(\mathbf{h},t)$ and thereby also of the quantity $G(t)$ which is the total polarization and which equals

$$G(t) = \iint dh_c\,dh_f\,R(\mathbf{h})G^x(\mathbf{h},t),$$

it is convenient to introduce, as in section 2, a complex polarization of the layers

$$G^\pm(\mathbf{h},t) = G^x(\mathbf{h},t) \pm iG^y(\mathbf{h},t) \tag{33}$$

and to obtain for it an equation like (12), which describes the motion of the complex layer polarization taking into account the dipole terms on the right-hand side, which reflect the effect of the isotropic interactions on the spin motion.

4. CALCULATION OF THE CONTRIBUTION OF THE ISOTROPIC INTERACTIONS TO THE EQUATION FOR THE LAYER POLARIZATIONS

To evaluate this contribution it is convenient to rewrite (7) in a more compact form

$$\frac{d}{dt}\bar{\rho}(t) = -i[(\hat{h}_z + \hat{h}_\perp), \bar{\rho}], \tag{34}$$

where

$$\hat{h}_z = 3\hat{H}^z - \sum_{i<k} a_{ik}\hat{S}_i^z\hat{S}_k^z, \tag{35}$$

$$\hat{h}_\perp = -\sum_{i<k} a_{ik}(\hat{S}_i^x\hat{S}_k^x + \hat{S}_i^y\hat{S}_k^y) = -\sum_{i<k} a_{ik}\hat{H}_\perp^{ik}. \tag{36}$$

Equations for the layer polarizations, defined by a set of orthogonal operators $\hat{S}^+(\bar{h})$ and by a density matrix $\bar{\rho}(t)$ satisfying an equation like (34), were derived in Ref. 11. It is then convenient to look for the solution of Eq. (34) in the form

$$\bar{\rho}(t) = \bar{\rho}_0(t) + \bar{\rho}_1(t), \tag{37}$$

where

$$\bar{\rho}_0(t) = 2^{-N}\Big\{1 + \frac{4}{N}\int d\mathbf{h}[\hat{S}^+(\mathbf{h})G^+(\mathbf{h},t) + \text{c.c.}]\Big\}, \tag{38}$$

and $\bar{\rho}(t)$ does not contribute to the layer polarization and is a linear combination of operators orthogonal to the operators $\hat{S}^\pm(\bar{h})$. In the equations obtained in Ref. 11 there occur coefficients which are very complex to evaluate and which are expressed in terms of memory functions. To evaluate these coefficients we therefore use below the solution of. Eq. (34) in the form of an iteration series in the small parameter $\varepsilon = \|\hat{h}_\perp\|/\|\hat{h}_z\| \sim 1/3Z^{1/2}$. To construct this series we change in Eq. (34) to the interaction representation in $\hat{h}_z$:

$$\bar{\rho}'(t) = \exp(-it\hat{h}_z)\bar{\rho}(t)\exp(it\hat{h}_z). \tag{39}$$

The equation for $\bar{\rho}'(t)$ has the form

$$\frac{d}{dt}\bar{\rho}' = -i[\hat{\tilde{h}}_\perp(t), \bar{\rho}'], \tag{40}$$

$$\hat{\tilde{h}}_\perp(t) = \exp(it\hat{h}_z)\hat{h}_\perp\exp(-it\hat{h}_z). \tag{41}$$

Using the definition (38) we get[11,21]

$$\bar{\rho}'(t) = \bar{\rho}_0'(t) + \bar{\rho}_1'(t) = \hat{P}\bar{\rho}'(t) + (1-\hat{P})\bar{\rho}'(t), \tag{42}$$

where $\hat{P}$ is the projection operator which separates from $\bar{\rho}'(t)$ a part like (38). Moreover, using a relation given in Ref. 11 which connects $\bar{\rho}_0(t)$ with $\bar{\rho}_1(t)$ we find

$$\bar{\rho}'(t) = \bar{\rho}_0'(t) - i(1-\hat{P})\int_0^t dt'[\hat{\tilde{h}}_\perp(t'), \bar{\rho}_0'(t')] + O(\varepsilon^2) \tag{43}$$

or, with allowance for (39),

$$\bar{\rho}(t) = \bar{\rho}_0(t) - i(1-\hat{P})\int_0^t [\hat{\tilde{h}}_\perp(t'-t), \bar{\rho}_0(t)]\,dt' + O(\varepsilon^2). \tag{44}$$

In going from (43) to (44) we replace in the integrand

$\bar{\rho}_0'(t')$ by $\bar{\rho}_0'(t')$, which is fully legitimate as $\hat{h}_\perp(t'-t)$ oscillates with a frequency $\sim\|\hat{h}_z\|$, $\bar{\rho}_0(t)$ changes with a frequency $\sim\|\hat{h}_\perp\|$ and the ratio $\|\hat{h}_\perp\|/\|\hat{h}_z\|=\varepsilon$ is much less than unity.

We note that at $t=0$ (44) is the same as (9) with $\beta=4/N$. To find the required equations for the layer polarizations $G^+(\mathbf{h},t)$ we multiply both sides of (34) by $\hat{S}^-(\mathbf{h})$, substituting into the right-hand side of the equation the approximate expression (44) for $\bar{\rho}(t)$, and take the trace of both sides:

$$\frac{d}{dt}G^+(\mathbf{h},t)=-iR^{-1}(\mathbf{h})\,\mathrm{Sp}\{\hat{s}^-(\mathbf{h})[(\hat{h}_z+\hat{h}_\perp),(\bar{\rho}_0+\bar{\rho}_1)]\}. \tag{45}$$

The evaluation of the trace (see the Appendix) gives

$$\frac{d}{dt}G^+(\mathbf{h},t)=-i\left(\frac{3}{2}h_f+\delta h_c\right)G^+(\mathbf{h},t)$$
$$-i\left(\frac{3}{2}-\delta\right)\{G_{1c}(h_f,t)+h_cG_{0c}(h_f,t)\}$$
$$+\int d\mathbf{h}'\,W(\mathbf{h},\bar{\mathbf{h}}')G^+(\mathbf{h}',t), \tag{46}$$

where

$$G_{mc}(h_f,t)=\int dh_c\,h_c^mR_c(h_c)G^+(\mathbf{h},t), \tag{47}$$

$$\delta=1+{}^1/_2\sum_\alpha a_{i\alpha}^2/\omega_i^2. \tag{48}$$

The function $W(\mathbf{h},\mathbf{h}')$ is the sum of terms of the kind [see (91)]

$$R^{-1}(\mathbf{h})\,\mathrm{Sp}\,\{\bar{\rho}(t)[\hat{s}_i^-(\mathbf{h}),\hat{H}_\perp^{pq}]\}, \tag{49}$$

where $p,q\neq i$ which are connected with the flip-flop of the pth and qth spins and the change in the field at the ith spin corresponding to it, i.e., with the spectral diffusion process. We note the important relation

$$\int d\mathbf{h}\,W(\mathbf{h},\mathbf{h}')=0 \tag{50}$$

following directly from (49). Any kernel satisfying this condition will qualitatively correctly describe the effect of spectral diffusion on the FIS.

The simple generalization of (12) to the case when the layer polarizations depend on two uncorrelated local fields h_c,h_f, with account taken of the immediate motion of the spins under the action of the transverse part of the DDI, therefore gives the equation

$$\frac{d}{dt}G^+(\mathbf{h},t)=-i\left(\frac{3}{2}h_f+\delta h_c\right)G^+(\mathbf{h},t)$$
$$-i\left(\frac{3}{2}-\delta\right)(G_{1c}(h_f,t)+h_cG_{0c}(h_f,t))+W_c+W_f, \tag{51}$$

$$W_q=-\Omega_q(h_q)G^+(\mathbf{h},t)+\Omega_q(h_q)$$
$$\times\int R_q(h_q')P_q(h_q,h_q')G^+(h_q',h_{q'},t)\,dh_q',$$
$$q=c,f,\qquad q'=f,c. \tag{52}$$

We note that the first and the two last terms on the right-hand side of (51) correspond to the analogous terms in (12) while the term $(\frac{3}{2}-\delta)$ is a new one in principle and corresponds to the contribution of the transverse local fields to the rotation of the layer polarizations.

5. SOLUTION OF THE KINETIC EQUATION AND COMPARISON OF THEORY WITH EXPERIMENT

The substitution

$$G^+(\mathbf{h},t)=F_c(h_c,t)F_f(h_f,t) \tag{53}$$

gives

$$\frac{d}{dt}F_c(h_c,t)=-i\delta h_cF_c(h_c,t)$$
$$-i\left(\frac{3}{2}-\delta\right)(h_cF_{0c}(t)+F_{1c}(t))+W_c, \tag{54}$$

$$\frac{d}{dt}F_f(h_f,t)=-\frac{3}{2}ih_fF_f(h_f,t)+W_f, \tag{55}$$

where

$$F_{mq}(t)=\int dh_q\,h_q^mF_q(h_q,t),\quad q=c,f, \tag{56}$$

while

$$G(t)=F_{0c}(t)F_{0f}(t), \tag{57}$$

$$F_{0c}(0)=F_{0f}(0)=1. \tag{58}$$

The existence of independent equations for $F_c(h_c,t)$ and $F_f(h_f,t)$ is a consequence of the fact that the fields h_c and h_f are uncorrelated.

It is convenient to look for the solutions of Eqs. (54) and (55) by putting first $W_c=W_f=0$ introducing the spectral diffusion into the solution, as shall be done in what follows.

Multiplying (54) by $\exp(i\delta h_ct)$ and integrating both sides from zero to t we find

$$F_c(h_c,t)=\exp(i\delta h_ct)$$
$$-i\left(\frac{3}{2}-\delta\right)\int_0^t dt'\exp[-i\delta(t-t')h_c]\{h_cF_{0c}(t')+F_{1c}(t')\}. \tag{59}$$

Multiplying both sides of (59) by $R_c(h_c)$ and afterwards by $h_cR_c(h_c)$ and integrating over h_c we get a set of two equations for $F_{0c}(t)$ and $F_{1c}(t)$, solving which we find an integral equation for $F_{0c}(t)$:

$$F_{0c}(t)=\tilde{R}_c(t)+\left(\frac{9}{4\delta^2}-1\right)\int_0^t F_{0c}(t')\frac{d\tilde{R}_c(t-t')}{d(t-t')}dt' \tag{60}$$

A similar equation was obtained in Ref. (12) for $G(t)$, but not for $F_{0c}(t)$ in the limit as $\tau_c\to\infty$.

One can easily find directly from (55) an expression for $F_{0f}(t)$ when $W_f=0$:

$$F_{0f}(t)=\tilde{R}_f(t). \tag{61}$$

In the above

$$\tilde{R}_q(t)=\int\exp(i\gamma_qh_qt)R_q(h_q)\,dh_q, \tag{62}$$

where $\gamma_c = \delta$, $\gamma_f = 3/2$. Taking into account the discrete local field distribution, we have

$$\tilde{R}_c(t) = \prod_\alpha \cos(\gamma_c b_{i\alpha} t), \tag{63}$$

$$\tilde{R}_f(t) = \prod_\beta \cos(\gamma_f b_{i\beta} t). \tag{64}$$

We note that using a Laplace transformation to solve (59) and putting in the solution obtained the Laplace variable $P = i\omega$ we find easily

$$g_c(\omega) = 4\delta^2 H'/9\pi[1 + 2\omega(1 - 4\delta^2/9)H'' + \omega^2(1 - 4\delta^2/9)((H')^2 + (H'')^2)], \tag{65}$$

$$H(\omega) = H' - iH'' = \int_0^\infty \exp(-i\omega t)\tilde{R}_c(t)\,dt, \tag{66}$$

$$g_c(\omega) = \int \exp(i\omega t) F_{0c}(t)\,dt.$$

Using (57), (62), and (5), Eqs. (65) and (66) enable us as $\tau_c \to \infty$ to obtain for the function $g(\omega)$ an analytical expression

$$g(\omega) = \int d\omega' (3\pi M_f)^{-1/2} \exp(-{}^3/_4 M_f \omega'^2) g_c(\omega - \omega'). \tag{67}$$

To take into account molecular motions and flip-flop processes which lead to spectral diffusion, we assume that as a result of the action of these two processes the quantities b_{ij} become random functions $b_{ij}^{\varkappa_{ij}}(t)$ of the time, and rewrite (63), (64) in the form[1,5,6]

$$\tilde{R}_c(t) = \left\langle \prod_\alpha \cos\left\{\gamma_c \int_0^t b_{i\alpha}^{\varkappa_{i\alpha}}(t')\,dt'\right\}\right\rangle, \tag{68}$$

$$\tilde{R}_f(t) = \left\langle \prod_\beta \cos\left\{\gamma_f \int_0^t b_{i\beta}^{\varkappa_{i\beta}}(t')\,dt'\right\}\right\rangle, \tag{69}$$

where the angle brackets indicate averaging over all possible trajectories $\varkappa_{ij}$ of the changes $b_{ij}^{\varkappa_{ij}}(t)$. In the case of a condensed substance, when the local field distribution to a good approximation is described by the normal law, the evaluation of (69) is given in Refs. 5 and 6:

$$\tilde{R}_q(t) = \exp\left\{-\frac{4}{9}\gamma_q^2 M_{2q} \int_0^t (t - t') k_q(t')\,dt'\right\}, \tag{70}$$

where

$$k_q(t) = \langle h_q(t) h_q(0)\rangle / \langle h_q^2(0)\rangle \tag{71}$$

are the local field correlation functions

$$h_c(t) = 2\sum_\alpha b_{i\alpha}^{\varkappa_{i\alpha}}(t) S_\alpha^z(t), \quad S_\alpha^z(t) = \pm{}^1/_2, \tag{72}$$

$$h_f(t) = 2\sum_\beta b_{i\beta}^{\varkappa_{i\beta}}(t) S_\beta^z(t), \quad S_\beta^z(t) = \pm{}^1/_2, \tag{73}$$

which are below approximated by the expression

$$k_q(t) = \exp(-t^2/\tau_q^2). \tag{74}$$

The correlation times τ_c and τ_f are defined by the relation

$$\tau_q^{-1} = 1/3T_2 + (\tau_q^*)^{-1}, \tag{75}$$

where $1/3T_2$, $1/\tau_q^*$ are the contributions to the damping of the correlation function of the flip-flop processes and the molecular motions, respectively.

The equations obtained were used to evaluate the FIS both in the case of a single crystal without molecular motions and when the latter are present. In both cases $F_{0f}(t)$ was calculated using (70) with $\tau_c = T_2/3 = (1/3M_2)^{1/2}$. The function $F_{0c}(t)$ was found through a numerical solution of (60) while we used in the presence of molecular motions Eq. (70) for $\tilde{R}_c(t)$ and when they are absent Eq. (63). The latter was justified by a direct calculation computer showing that the effect of the flip-flop on $\tilde{R}_c(t)$ is quite negligible when there are no molecular motions.

To determine the parameter δ in (60) we used (63) to find the quantity $d^4F_{0c}(t)/dt^4$ which afterwards for $t = 0$ was equated to the exact fourth moment M_4 of the absorption line which gives the following equation:

$$M_4/M_2^2 = \left[1 + {}^8/_9\delta^2\left(1 - \left(\sum_j b_{ij}^4\right)\Big/_i M^2\right)\right]. \tag{76}$$

A similar procedure enables us to use the information included in M_4 to find more accurately the degree, determined by the quantity δ, of averaging of the isotropic interactions taking place at small times $t \sim \omega_l^{-1}$. The value of δ calculated using (76) for the three orientations of the CaF_2 single crystal considered turned out to be very close to $(\frac{3}{2})^{1/2}$, which agrees with the result obtained in Ref. 12. We performed the actual calculations of the FIS, for all orientations considered, for $\delta = (\frac{3}{2})^{1/2}$.

The calculations of the FIS were performed for a CaF_2 single crystal in the orientations $H_0 \| [100]$, $H_0 \| [110]$, $H_0 \| [111]$. A comparison of the results with the experimental data of Ref. 4 showed excellent agreement. The case of the orientation $H_0 \| [100]$ is shown in Fig. 1.

The results show that the FIS of a CaF_2 single crystal are, indeed, the product of an oscillating and a monotonical-

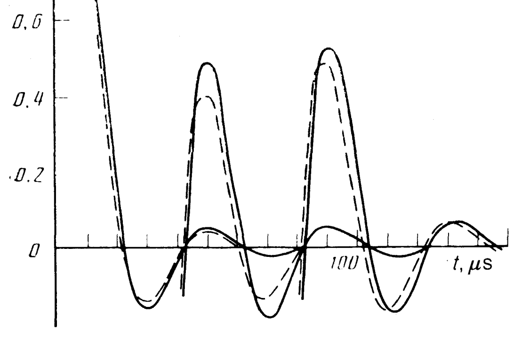

FIG. 1. Free induction signal in a CaF_2 single crystal with the orientation $H_0 \| [100]$. The solid lines are the results of the theory and the dashed ones the experimental data of Ref. 4 (between the second and fourth and between the fourth and the seventh zeroes we have also shown the FIS multiplied, respectively, by 10 and 100).

ly damped component [see (11)] which are connected with the interactions with, respectively, the spins from the cell and the far spins. The possibility to identify $F_{0c}(t)$ and $F_{0f}(t)$ with the oscillating and the monotonically damped factors in (11) also confirms that, as was shown in Ref. 13, the quantities a and b in (11) with a good accuracy can be found by summing over the spins of the cell and over the far spins:

$$a^2=\frac{9}{4}\sum_{\beta} b_{i\beta}^2, \quad b^2=\frac{3}{4}\sum_{\alpha} b_{i\alpha}^2. \tag{77}$$

The results of the calculation of the FIS when molecular motions are present for several values of $\tau_c = \tau_f$ are shown in Fig. 2. It is clear from Fig. 2 that in accordance with the experimental data for $\tau_c = \tau_f \to 0$ the FIS becomes exponential, which corresponds to the transformation of the broad lines of a condensed substance into the narrow Lorentz lines of a fluid.[1] The last result can also be obtained in analytical form. Indeed, when $\tau_c = \tau_f \ll M_c^{-1/2}$

$$\tilde{R}_q(t)=\exp(-{}^4/_9\gamma_q^2M_{2q}\tau_qt). \tag{78}$$

Substituting (78) for $q=c$ into (60) we find by solving (6) using a Laplace transform

$$F_{0c}(t)=\exp(-M_{2c}\tau_ct). \tag{79}$$

Finally

$$G(t)=\exp[-(M_{2c}+M_{2f})\tau_ct). \tag{80}$$

The approach developed here enables us thus to give a description of the FIS both in a fluid and in the condensed phase, i.e., over a broad range of temperatures.

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APPENDIX

To prove (27) to (30) we rewrite them using the integral representation of the δ-function

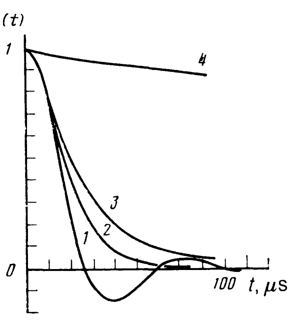

FIG. 2. Free induction signal taking into account molecular motions (theoretical results): 1: $\tau_c = 3T_2$, 2: $\tau_c = 0.33\ T_2$, 3: $\tau_c = 0.25\ T_2$, 4: $\tau_c = 10^{-2}\ T_2$.

$$\mathrm{Sp}\{\hat{s}^+(\mathbf{h})\,\hat{s}^-(\mathbf{h}')\}=(2\pi)^{-4}\int\int\int\int d\mathbf{x}\,d\mathbf{x}'\sum_{i}\mathrm{Sp}$$
$$\times\Big\{\hat{s}_i^+\hat{s}_i^-\exp\Big[-i\Big(x_ch_c+x_fh_f+x_c'h_c'+x_f'h_f'$$
$$-2(x_c+x_c')\sum_{\alpha}b_{i\alpha}\hat{s}_\alpha^z-2(x_f+x_f')\sum_{\beta}b_{i\beta}\hat{s}_\beta^z\Big)\Big]\Big\}. \tag{81}$$

Straightforward calculations give

$$\mathrm{Sp}\{\hat{s}^+(\mathbf{h})\,\hat{s}^-(\mathbf{h}')\}$$
$$=2^{N-2}N\delta(\mathbf{h}-\mathbf{h}')\left[\frac{1}{2\pi}\int dx_c\exp(-ix_ch_c)\prod_{\alpha}\cos(b_{i\alpha}x_c)\right]$$
$$\times\left[\frac{1}{2\pi}\int dx_f\exp(-ix_fh_f)\prod_{\beta}\cos(b_{i\beta}t)\right]. \tag{82}$$

Replacing x_q by t we have from this

$$R(\mathbf{h})=R_c(h_c)R_f(h_f), \tag{83}$$

where

$$R_c(h_c)=\frac{1}{2\pi}\int dt\exp(-ih_ct)\prod_{\alpha}\cos(b_{i\alpha}t),$$
$$R_f(h_f)=\frac{1}{2\pi}\int dt\exp(-ih_ft)\prod_{\beta}\cos(b_{i\beta}t). \tag{84}$$

Neglecting the discrete distribution of the fields h_c, h_f

$$R_q(h_q)=(2\pi M_q)^{-1/2}\exp(-h_q^2/2M_q), \tag{85}$$

$$M_c=\sum_{\alpha}b_{i\alpha}^2=\frac{4}{9}M_{2c}, \tag{86}$$

$$M_f=\sum_{\beta}b_{i\beta}^2=\frac{4}{9}M_{2f}. \tag{87}$$

To calculate

$$Q=-i\,\mathrm{Sp}\{\hat{s}^-(\mathbf{h})[(\hat{h}_z+\hat{h}_\perp),\ (\bar{\rho}_0+\bar{\rho}_1)]\}/R(\mathbf{h}) \tag{88}$$

we substitute into the trace Eq. (36) for $\hat{h}_\perp$, (35) for $\hat{h}_z$, and (44) for $\bar{\rho}_0+\bar{\rho}_1$. We use Eq. (38) for $\bar{\rho}_0(t)$. Applying now the integral representation for the δ-function we find

$$Q=\int d\mathbf{h}'[K(\mathbf{h},\mathbf{h}')-W(\mathbf{h},\mathbf{h}')]G^+(\mathbf{h}',t), \tag{89}$$

$$K(\mathbf{h},\mathbf{h}')=-\frac{3}{2}ih_f\delta(\mathbf{h}-\mathbf{h}')-i\delta h_c\delta(\mathbf{h}-\mathbf{h}')$$
$$-i\left(\frac{3}{2}-\delta\right)R_c(h_c')\delta(h_f-h_f')$$
$$\times\sum_{\alpha}(b_{i\alpha}^2/2M_{c\alpha}')\frac{h_c+h_c'}{1+C_{i\alpha}}\exp[-(h_c'-C_{i\alpha}h_c)^2/2M_{c\alpha}'(1-C_{i\alpha}^2)], \tag{90}$$

$$W(\mathbf{h},\mathbf{h}')=\int_0^t dt'\,R^{-1}(\mathbf{h})\,\mathrm{Sp}\{\hat{s}^-(\mathbf{h})[\hat{h}_\perp,[\hat{\tilde{h}}_\perp(t'-t),\hat{s}^+(\mathbf{h}')]]\}, \tag{91}$$

$$C_{i\alpha}=\sum_{\alpha'}b_{i\alpha}b_{\alpha\alpha'}/M_{c\alpha}', \qquad M_{c\alpha}'=M_c-b_{i\alpha}^2, \tag{92}$$

$$\delta=1+\sum_{\alpha}a_{i\alpha}^2/2M_c. \tag{93}$$

The index α' in (92) is taken over the spins which simultaneously belong to the cells of the ith and the αth spins. As their number is very small even for neighboring spins we can put $C_{i\alpha} = 0$, which gives

$$K(\mathbf{h},\mathbf{h}') = -\frac{3}{2} i h_f \delta(\mathbf{h}-\mathbf{h}') - i\delta h_c \delta(\mathbf{h}-\mathbf{h}') - i\left(\frac{3}{2}-\delta\right) R_c(h_c) \frac{h_c+h_c'}{2} \delta(h_f-h_f'). \qquad (94)$$

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