Asymptotic similarity of temporal correlation functions and the problem of NMR lineshape in solids

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The problem of the shape of the free-induction decay signal in a solid is solved analytically, on the basis of the hypothesis advanced here that a similarity exists between the temporal correlation functions arising in an infinite chain of coupled differential equations for the NMR free-induction decay signal and the temporal correlation functions which are associated with this signal, for crystals with a large number of equivalent nearest neighbors surrounding any spin in the lattice. It is demonstrated that the similarity law is a consequence of definite symmetry relations between the coefficients appearing in the chain of equations for the temporal correlation functions. Moreover, the proposed similarity law is confirmed for the first two temporal correlation functions by a direct numerical calculation for fragments of a simple cubic lattice with periodic boundary conditions and linear crystalline polyethylene. © *1996 American Institute of Physics.* [S1063-7761(96)01610-1]

1. INTRODUCTION

Oscillations in the free-induction NMR decay signals in a solid were first observed experimentally in 1957 by Lowe and Norberg.[1] Since the free-induction decay signal is the Fourier transform of the absorption spectrum, the results obtained were fundamentally at variance with the beliefs which were widely held at that time and which go back to the first works on the observation of NMR:[2] The absorption lineshape must be close either to a Lorentzian or a Gaussian curve. The Gaussian spectra were associated with a quasistatic distribution of the local fields, which was assumed to arise in ordinary solids. The Lorentzian spectra, however, were associated with, e.g., for example, liquids and solids with a strong exchange interaction, i.e., substances in which rapid fluctuations of the local magnetic field are present.

The presence of oscillations in the free-induction decay signals of a CaF_2 single crystal—a classic test object for investigating NMR spin dynamics—gave rise to many theoretical and experimental works (for example, Refs. 3–10), and their number is still increasing. There is great interest in this problem, on the one hand, as a specific example of the central problem of nonequilibrium statistical mechanics—the problem of the establishment of equilibrium in systems of many interacting bodies. On the other hand, the shape of the magnetic-resonance spectra contains information about the crystal and electronic structure of the sample and about the mobility of atoms and atomic groups, i.e., it contains a substantial fraction of the information accessible to the method, and in solids part of this information is, as a rule, masked by the main broadening mechanism (the dipole–dipole interaction of the nuclear spins). Finally, we note that the NMR lineshape problem is related to spin-diffusion problems,[11] the problem of calculating the magnetic part of neutron scattering by paramagnets,[12] and the spectrum of Raman scattering from quadrupole solids[13] and it has deep analogies with many other problems in the statistical physics of condensed media. At the same time, the obvious advantages of nuclear spin systems, which make them, in the words of Bloembergen, an "excellent laboratory of statistical physics," are the relative simplicity of the well-known spin–spin interaction laws, the weak coupling of the spins with the crystal lattice, and the possibility of making precise measurements by NMR methods.

The objective of the present paper is to seek and to investigate similarity laws and their consequences for the temporal correlation functions arising in an infinite hierarchy of coupled differential equations, the first of which is the equation for the free-induction decay signal, and to construct on this basis an analytical solution of the problem of the shape of magnetic-resonance spectra for crystals with a large number of spins in a cell.[14]

2. FREE-INDUCTION DECAY IN NONMETALLIC DIAMAGNETIC CRYSTALS

As is well known,[15] the free-induction decay signal appearing after a $\pi/2$ pulse is applied to an equilibrium nuclear spin system in a strong constant magnetic field H_0 is proportional to the temporal correlation function determined in a coordinate system rotating with the Larmor frequency by the relation

$$\Gamma(t)=\frac{1}{\mathrm{Tr}(S_x^2)}\mathrm{Tr}(S_x(t)S_x)=\frac{1}{\mathrm{Tr}(S^+S^-)}\mathrm{Tr}(S^+(t)S^-), \tag{1}$$

where

$$S_x=\sum_{i=1}^{N} S_{xi}$$

is the total x-component of the spin of the system, satisfying the Heisenberg equation of motion

$$dS_x/dt=i[H,S_x]. \tag{2}$$

In Eq. (2) and below, energy is measured in frequency units; H is the secular part of the dipole–dipole interaction,[15] which is mainly responsible for the broadening of the NMR spectra in nonmetallic diamagnetic crystals,

$$H=\frac{1}{2}\left(\sum_{i\neq j} b_{ij}S_{zi}S_{zj}+\sum_{i\neq j}\alpha_{ij}S_i^+S_j^-\right)=H_{zz}+H_{ff},$$

$$\alpha_{ij}=-\frac{1}{2}b_{ij},\quad b_{ij}=\frac{\gamma^2\hbar}{r_{ij}^3}(1-3\cos^2\theta_{ij}),\tag{3}$$

the vector $\mathbf{r}_{ij}$ connects the spins i and j, θ_{ij} is the angle made by the vector $\mathbf{r}_{ij}$ and an external magnetic field, and γ is the gyromagnetic ratio.

At the beginning of the 1960s, Abragam[15] found empirically that the free-induction decay signal in a CaF_2 single crystal at not too long times is described, with reasonable accuracy (different for different orientations of the external magnetic field with respect to the crystallographic axes), by the expression

$$\Gamma(t)=\exp\left(-\frac{a^2t^2}{2}\right)\frac{\sin(bt)}{bt}=\exp\left(-\frac{a^2t^2}{2}\right)\Gamma_0(t).\tag{4}$$

The quantities a and b were chosen so as to obtain the correct second and fourth moments of the absorption line. Later, it was shown experimentally[16] that for $t\geqslant 3T_2$ the Gaussian component of the free-induction decay signal (4) transforms into an exponential

$$\Gamma(t)=\exp(-ct)\sin(bt)/bt=\exp(-ct)\Gamma_0(t).\tag{5}$$

The first attempt to explain these simple and surprisingly "physical" results was the model proposed in Ref. 14. It was noted there that the entire crystal can be divided with respect to a distinguished (arbitrary) spin with the label 0 into two regions, in one of which the motion of the spins is correlated with the distinguished spin and in the other it is not. The region with the correlated motion was termed a cell. Here, of course, the discussion concerned exclusively the temporal correlations—the temperature of the nuclear spin system is essentially infinite. It was determined[14,17,18] that the Gaussian–exponential contribution in the trial functions (4) and (5) is due to spins which are located outside the cell. The shape and parameters of this component of the free-induction decay signal were completely calculated in the same treatments. Later, it was shown in Refs. 17 and 18 that in crystals with a large number of spins in a cell the flip–flop process described by the term H_{ff} in the Hamiltonian (3) occurs for each pair of spins independently of the flip–flop process in all other pairs. This made it possible to construct a simple and convenient "pair-interaction model" which gives for the free-induction decay signal $\Gamma_0(t)$ of a cell an integral equation whose numerical solution satisfactorily describes the experiment. At the same time, the simplicity and "physicality" of the trial function $\Gamma_0(t)=\sin(bt)/bt$, pertaining in accordance with the results of Refs. 14, 17, and 18 to the free-induction decay signal of the spins in a cell, undoubtedly makes it necessary to construct a theory which could give an analytical (and not numerical) description of the component $\Gamma_0(t)$. This is especially true, since, as has been demonstrated experimentally, the trial functions (4) and (5) describe very well the experimental free-induction decay signals not only for different orientations of the external magnetic field in CaF_2 but also for a wide class of crystals (see, for example, Refs. 19 and 20) in which a spin in the lattice is surrounded by a large number of neighbors. Therefore the other objective of the present work is to construct a theory that demonstrates the well-known universality of functions of the form (4) and (5) for solids of this kind.

3. SIMILARITY OF TEMPORAL CORRELATION FUNCTIONS

In Ref. 21 it was shown that the problem of calculating the free-induction decay signal (1) is completely equivalent to solving an infinite (dimension 10^{23}) system of differential equations

$$\begin{gathered}\dot A_0(t)=i\nu_0^2A_1(t),\\ \dot A_1(t)=i[A_0(t)+\nu_1^2A_2(t)],\\ \vdots\\ \dot A_n(t)=i(A_{n-1}(t)+\nu_{n+1}^2A_{n+1}(t)),\end{gathered}\tag{6}$$

with the initial conditions $A_0(0)=1$ and $A_n(0)=0$ for $n\geqslant 1$. Here $A_0(t)\equiv\Gamma(t)$ is the total free-induction decay signal. The functions $\{A_i(t)\}$ are "multicommutator" (multiparticle) temporal correlation functions, since each differentiation of the free-induction decay signal (1) adds a commutation relation and thereby adds another lattice summation index. For example, the temporal correlation function $A_1(t)$ $\propto$ $\mathrm{Tr}[S_{zi}(t)S_0^+(t)S^-]$ describes pair processes, the function $A_2(t)$ describes three-particle processes, and so on. The parameters $\{\nu_i^2\}$, whose values determine the solution of the system, are related to the moments of the absorption line

$$\nu_n^2=D_{n-1}D_{n+1}/D_n^2,\tag{7}$$

where $\{D_n\}$ are determinants which have the form

$$D_n=\begin{vmatrix}1 & M_1 & \dots & M_n\\ M_1 & M_2 & \dots & M_{n+1}\\ \vdots & & & \\ M_n & M_{n+1} & \dots & M_{2n}\end{vmatrix}.\tag{8}$$

Here the moments $\{M_i\}$ are the coefficients of the series expansion of the free-induction decay signal in powers of the time:

$$A_0(t)=\Gamma(t)=\sum_{n=0}^{\infty} i^{2n}\frac{M_{2n}}{(2n)!}t^{2n}.\tag{9}$$

As a result of the high temperatures, only the even-order moments in Eqs. (8) and (9) are different from zero. For convenience, we present expressions for the first few coefficients:

$$\begin{gathered}D_{-1}=D_0=1,\quad D_1=M_2,\quad D_2=M_2(M_4-M_2^2),\\ D_3=(M_4-M_2^2)(M_2M_6-M_4^2),\quad \nu_0^2=M_2,\\ \nu_1^2=(M_4-M_2^2)/M_2,\quad \nu_2^2=(M_2M_6-M_4^2)/M_2(M_4-M_2^2).\end{gathered}\tag{10}$$

We note that, in accordance with the result of Ref. 22, the relations (6)–(10), which are, in principle, determined for the entire crystal, can be related only to the component of the free-induction decay signal that is due to the spins in a cell, since the behavior of the solution of the system is completely determined by the coefficients $\{\nu_n^2\}$.

In the language of multiple-quantum NMR, developed over the last 15 years and now widely recognized and used,[23] the system of equations (6) reflects the transfer of one-spin one-quantum coherence $A_0(t)$ to multispin one-quantum coherences (the functions $\{A_i(t)\}$) or, in other words,[23,24] the flow of a gas of correlations through the one-dimensional Liouville space whose points are the indices of the corresponding coherences (temporal correlation functions). Indeed, the initial order transferred to the spin system in the form of a magnetization directed along the x axis flows along the higher-order temporal correlation functions and is redistributed among them.

In Ref. 24 an attempt was made to investigate this flow process with the aid of a numerical experiment performed on a finite cluster of a simple cubic lattice. Since from the standpoint of Ref. 24 the system (6) is too complicated (indeed, to find the coefficient ν_n^2 it is necessary to know the moment M_{2n}), in Ref. 24 it is replaced by a simpler, Markovian-type system. The main objective of Ref. 24 was to investigate the final state of the spin system (distribution of the populations (statistical weight) of different coherences at long times). From the standpoint of the present work, however, the most important fact is the mutual and virtually complete similarity of the temporal behavior, neglecting effects associated with the finiteness of the cluster, of different temporal correlation functions of the system[24] which are presented in the figures displayed there.

The fundamental possibility of expressing the higher-order temporal correlation functions in terms of the lower-order functions goes back to the well-known ideas advanced in Bogolyubov's work. On the other hand, the success of the pair-interaction model[17,18] in describing free-induction decay signals of crystals with a large number Z of spins per cell can be attributed to the fact that the higher-order temporal correlation functions of the system (6) decompose into one-spin and pair coherences, which is why there is hope of reconstructing the higher-order coherences in terms of the set of the lower order coherences mentioned above. Therefore there is hope that the time dependence of the relaxation of the higher-order temporal correlation functions will be of a form that is close to the time dependences of the lower-order functions. This gives a basis for advancing the hypothesis that the flow of the gas of correlations which are described by the system of equations (6) in nuclear spin systems with large numbers Z exhibits similarity. A more solid motivation for this hypothesis will be presented below.

Let $A_2(t)$ from the system (6) satisfy the condition

$$A_2(t)=\alpha A_0(t)+\alpha\dot{A}_0(t)\tau(t), \tag{11}$$

where α is a number to be determined below and the function $\tau(t)$ satisfies the condition $\tau(t)\rightarrow 0$ as $t\rightarrow\infty$. We thereby assume that the temporal correlation function $A_2(t)$ is completely similar to the free-induction decay signal at long times and possibly somewhat different at short times. The latter circumstance is associated, in an obvious way, with the different initial conditions for the functions $A_0(t)$ and $A_2(t)$ of the system (6), and Figs. 3 and 4 from Ref. 24 can serve as an illustration of this difference. The spike in the amplitude $A_2(t)$ from 0 up to a finite value is delayed somewhat relative to the time $t=0$ and, taking account of this delay, we find that the Markovian functions $A_0(t)$ and $A_2(t)$ from Ref. 24 similar. Therefore for short $\tau(t)$ we obtain from Eq. (11) the relation

$$A_2(t)\approx\alpha A_0(t+\tau(t)), \tag{12}$$

reflecting the mutual similarity of the temporal correlation functions with the delay $\tau(t)$.

Using the system (6) and comparing directly the series expansions of the functions $A_0(t)$, $A_1(t)$, and $A_2(t)$ in powers of t, it is easy to verify that the first term of the expansion in the power series of the function $A_2(t)$ equals $-t^2/2$, which, on account of the relation (11), uniquely determines the choice of the function $\tau(t)$:

$$\tau(t)=1/\nu_0^2 t. \tag{13}$$

At the same time, the relation (13) also ensures that the second moment of the spectrum (the first sum rule) is correct. Next, let $\alpha=\beta/\nu_1^2$. Then the similarity law (12) transforms the system (6) into the closed equation

$$\ddot{A}_0+(\beta/t)\dot{A}_0+(\beta+1)\nu_0^2A_0,\quad A_0(0)=1. \tag{14}$$

In accordance with Ref. 25 the solution of Eq. (14) has the form

$$A_0(t)=\frac{J_\lambda(\sqrt{\beta+1}\,\nu_0t)}{(\sqrt{\beta+1}\,\nu_0t)^\lambda}=\frac{CJ_\lambda(bt)}{(bt)^\lambda}, \tag{15}$$

where $\lambda=|\beta-1|/2$, J_λ is a Bessel function of order λ, and C is a normalization constant, which gives the initial conditions (14). The frequency Fourier spectrum of the function (15) is described by the expression

$$g_0(\omega)=\frac{\Gamma(\lambda+1)}{b\sqrt{\pi}\Gamma(\lambda+1/2)}\left(1-\frac{\omega^2}{b^2}\right)^{(2\lambda-1)/2} \tag{16}$$

for $|\omega|<b$ and $g_0(\omega)\ =0$ for $|\omega|>b$. Here $\Gamma(x)$ is the gamma function, and the spectral component (16) is normalized to unity

$$\int_{-\infty}^{\infty}g_0(\omega)d\omega=1.$$

The moments of the function (16) are determined from the formula

$$M'_{2n}=(2n-1)b^{2n}\left[2n\prod_{i=1}^{n}(i+\lambda)\right]^{-1}. \tag{17}$$

The order λ of the Bessel function (and therefore the value of β) can easily be related to the excess ε (the ratio of the fourth moment of the spectrum to the square of the second moment) of the component of the free-induction decay signal produced by the spins in a cell:

$$\lambda=(2\varepsilon-3)/(3-\varepsilon).$$

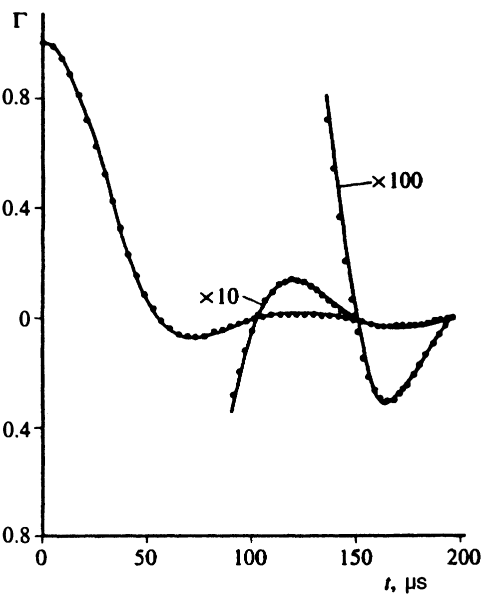

FIG. 1. Free-induction decay signal for a CaF_2 single crystal with the external field in the [111] direction. Solid curves—experiment of Ref. 16. Dots—proposed theory (the function Eq. (15) with $\lambda=1$, premultiplied by the "Gaussian-exponential contribution" from distant spins[14,16–18]).

For field orientations in the [100] and [110] directions in CaF_2, the values of ε for a cell, equal to 1.75 and 1.88, respectively, can be rounded off to 1.8, which gives $\lambda=0.5$ and $\beta=2$. Therefore, for these orientations, in exact agreement with the trial functions (4) and (5), we obtain from Eq. (15)

$$A_0(t)=\Gamma_0(t)=\frac{J_{1/2}(\sqrt{3}\nu_0 t)}{(\sqrt{3}\nu_0 t)^{1/2}}=\frac{\sin(\sqrt{3}\nu_0 t)}{\sqrt{3}\nu_0 t}, \qquad (18)$$

where the value of the parameter b, calculated in accordance with what was said above as $\sqrt{3}\nu_0=\sqrt{3M_2'}$, where M_2' is the contribution of the spins in a cell to the second moment of the spectrum, agrees very well with all existing experimental results.[14,17,20,26] For the spins of a cell in polyethylene and field orientation along the axis of the molecule, the computed value[19] $\varepsilon=1.83$ can also be rounded off to 1.8. For a field orientation in the [111] direction in CaF_2, the value $\varepsilon=2.2$ can be rounded off to $\varepsilon\approx 2$, giving $\lambda=1$ and, corresponding, $\beta=3$. The function $J_1(2\nu_0 t)/(\nu_0 t)$ arising here describes very well the oscillatory component of the free-induction decay signal observed experimentally for this orientation (see Fig. 1). Since Bessel functions are entire functions of their order λ for every fixed value of their argument, it can be assumed that round-off does not affect the computational results much. At the same time, the rounding off makes it possible to work with the simplest Bessel functions, those of integer and half-integer order.

We note that for the free-induction decay signal $A_0(t)$ given by the expression (18) the function $A_2(t)$ from the system (6) is

$$A_2(t)=15\left(1-\frac{3}{b^2t^2}\right)\frac{\sin(bt)}{2b^3t}+\frac{45\cos(bt)}{2b^4t^2}. \qquad (19)$$

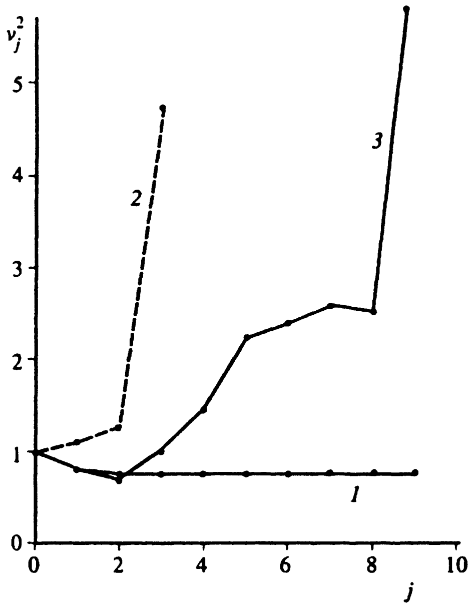

FIG. 2. Parameters $\{\nu_j^2\}$ versus j. The curve *1* corresponds to crystals with a large number of spins per cell. The parameters were calculated numerically for the cell. It was assumed that the moments of the free-induction decay of a cell satisfy the relation $N_{2n}'=b^{2n}/(2n+1)$. The curve *2* corresponds to the parameters calculated according to the moments of the total spectrum of a CaF_2 single crystal (the theoretical values of the moments are available only up to the eighth moment inclusively). The curve *3* corresponds to the spectrum of a quasi-one-dimensional system of ^{19}F nuclei in fluoroapatite. The lines connecting the dots were drawn as a visual aid.

The expression obtained for $A_2(t)$ by substituting the function (18) into the similarity law (11) is identical to the formula (19).

The similarity hypothesis (11) and (12) can also be regarded as being a consequence of some exact results. In Ref. 22 it was shown that in crystals with large Z and an interaction described by the Hamiltonian (3), i.e., in crystals in which the form of the contribution of the spins in a cell to the spectrum is close to that of the spectra given by the Fourier transform of the component $\Gamma_0(t)$ from Eqs. (4) and (5), the constants $\{\nu_j^2\}$ of the system (6) for the temporal correlation functions of a cell quickly "freeze" (see Fig. 2), i.e., they virtually cease to depend on j and assume a constant value. At the same time, both the curve *2* in Fig. 2, calculated from the theoretical values of the total moments (M_2-M_8) calculated for CaF_2,[27] and the curve *3*, calculated according to the theoretical values of the moments of the spectrum of the one-dimensional system of fluoroapatite,[28] show an absence of "freezing," thereby attesting to the fact that the investigation performed is admissible only for the spins of a cell and in crystals with large numbers Z.

In Ref. 22 several theorems concerning the system (6) were also proved and a number of exact results was obtained. Specifically, when the constants are frozen the system (6) can be solved in quadratures:

$$\Gamma_0(t)=A_0(t)=\frac{\gamma_0}{\pi}\int_{-2}^{2}dp\,\frac{\cos(p\nu_m t)}{Q_{2m}(p^2)}\sqrt{1-\frac{p^2}{4}}+A_0^{\rm dis}(t). \qquad (20)$$

The second term in Eq. (20) corresponds to a discrete spectrum and appears only in special situations, which will not of interest below; Q_{2m} are polynomials in p^2 of degree $2m$, where m is the number of the equation starting with which all constants are assumed to be frozen: $\nu_l=\nu_m$ for all $l\geqslant m$. For convenience we give explicit expressions for the free-induction decay signals in the lowest-order approximations following from Eq. (16). For $m=0$

$$A_0^0(t)=\Gamma_0^0(t)=\frac{1}{\pi}\int_{-2}^{2}dp\,\cos(p\nu_0 t)\sqrt{1-\frac{p^2}{4}}. \tag{21}$$

For $m=1$

$$A_0^1(t)=\Gamma_0^1(t)=\frac{\gamma_0}{\pi}\int_{-2}^{2}dp\,\cos(p\nu_1 t)\frac{\sqrt{1-p^2/4}}{p^2(1-\gamma_0)+\gamma_0^2}, \tag{21a}$$

where $\gamma_0=\nu_0^2/\nu_1^2$. For $m=2$

$$A_0^2(t)=\Gamma_0^2(t)=\frac{\gamma_0}{\pi}\int_{-2}^{2}dp\frac{\cos(p\nu_2 t)}{Q_4(p^2)}\sqrt{1-\frac{p^2}{4}}, \tag{22}$$

where

$$Q_4(p^2)=p^4\nu_2^2(\nu_2^2-\nu_1^2)\nu_1^4+\left(1-\frac{2\nu_0^2\nu_2^2}{\nu_1^4}+\frac{\nu_0^2}{\nu_1^2}\right)p^2+\frac{\nu_0^4}{\nu_1^4}.$$

The solutions (20)–(22) make it possible to check the validity of the similarity laws (11) and (12) by means of direct calculations. For this, the solution with the number m corresponding to the equation for which the constants are first frozen must be substituted into the system (6), the differentiation with respect to time must be performed, and then, as a simplification, the remaining integral over p must be integrated by parts. Then

1) for $m=0$, i.e., $\nu_j^2=\nu_0^2$ for $j\geqslant 0$,

$$A_2(t)\equiv\frac{3}{\nu_0^2}\left[A_0(t)+\frac{1}{\nu_0^2 t}\dot{A}_0(t)\right]\approx\frac{3}{\nu_0^2}A_0\left(t+\frac{1}{\nu_0^2 t}\right); \tag{23}$$

2) for $m=1$, i.e., $\nu_j^2=\nu_1^2$ for $j\geqslant 1$,

$$A_2(t)\approx\frac{1}{\nu_1^2}\left[\frac{4-\gamma_0}{\gamma_0}A_0(t)+\left(3-\frac{8\zeta}{\gamma_0^2}\right)\frac{1}{\nu_0^2 t}\dot{A}_0(t)\right]$$

$$\equiv\frac{1}{\nu_1^2}\left[2.2A_0(t)+\frac{1.72}{\nu_0^2 t}\dot{A}_0(t)\right], \tag{24}$$

where $\zeta=1-\gamma_0=-0.25$. The similarity laws (23) and (24) lead, respectively, to equations for the free-induction decay signals

$$\ddot{A}_0(t)+(3/t)\dot{A}_0(t)+4\nu_0^2A_0(t)=0, \tag{25}$$

$$\ddot{A}_0(t)+(1.72/t)\dot{A}_0(t)+3.2\nu_0^2A_0(t)=0. \tag{26}$$

The equation (25) corresponds to the lowest approximation of the theory. It corresponds to the value $\beta=3$ and thereby the [111] orientation in CaF_2, for which the number of spins in the cell is characteristically largest among the three principal orientations. In Eq. (26), however, corresponding to the first approximation of the theory, the value of β lies much closer to the number 2, corresponding to the Abragam trial function, which best describes the free-induction decay signals for orientations with a smaller number of spins in a cell (for example, [100]) and thereby allows, to a greater degree, for the finiteness of the number Z of spins in a cell.

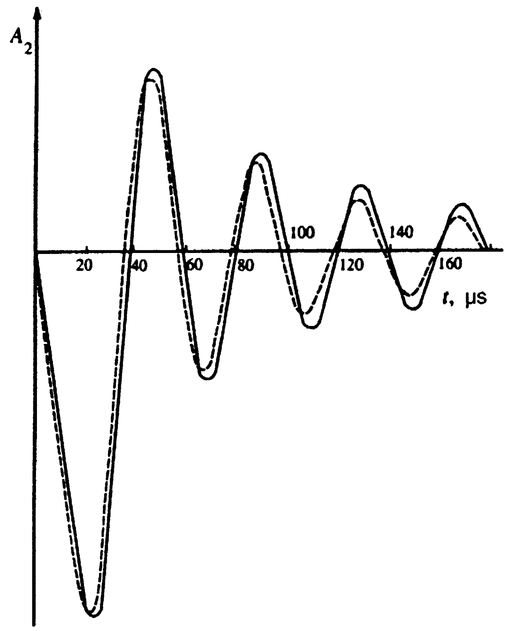

FIG. 3. $A_2(t)$ calculated for a cell of a CaF_2 single crystal with periodic boundary conditions with the external magnetic field in [100] direction. Dashed line—direct numerical calculation; solid curve — approximation by the similarity law (11). In the calculations, the function $A_0(t)$ was normalized to unity.

Finally, the similarity law (11) and (12) was subjected to an experimental–numerical check: The temporal correlation function $A_2(t)$ was calculated numerically for a cluster of a simple cubic lattice with periodic boundary conditions, which models a cell in CaF_2 with the external field oriented in the [100] direction, and for a cell of extended single-crystal polyethylene in the trans–zigzag conformation with the external field oriented along the axis of the molecule. In the calculations the matrix of the Hamiltonian (3), corresponding to a cell with periodic boundary conditions, was diagonalized numerically and its eigenfunctions and eigenvalues were determined. Next, the trace corresponding to the required temporal correlation function was calculated in this representation. The method for performing such calculations is described in greater detail in Ref. 26. In both cases the computed curve agreed well with the similarity law (11) and (12) (see Figs. 3 and 4).

Let us now discuss some qualitative features of the behavior of the solution of Eq. (14) as a function of the parameter β. The parameter β can be related via the excess to the ratio of the interaction constants in the spin Hamiltonian. For this, we employ the corresponding expressions for M_2 and M_4 from Ref. 29. Then

$$\beta=-\frac{6\xi^2+3}{\xi^2+2\xi}, \tag{27}$$

where ξ is the ratio of the "transverse" and "longitudinal" interaction constants in the Hamiltonian (3). For example, in

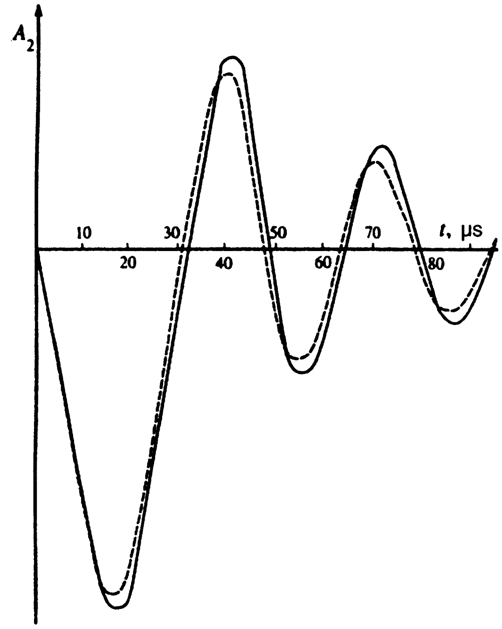

FIG. 4. $A_2(t)$ calculated for the cell of single-crystal, extended polyethylene. The external magnetic field is directed along the axis of the molecule. The notation is the same as in Fig. 3.

the case of the secular part of the dipole–dipole interaction $\xi=-1/2$ holds. We note that, on account of the approximations made in Ref. 29 in the derivation of Eq. (27) (the number of nearest neighbors satisfies $Z\rightarrow\infty$ and $d\rightarrow\infty$, where d is the dimension of the space), this formula gives too high a value for the excess. The passage to the limit[29] itself could require additional discussion. For example, for the secular part of the dipole–dipole interaction $\varepsilon\approx 2.3$ (Ref. 29), irrespective of orientation and crystal structure. Of course, the smaller the value of Z, the larger the error. In addition, the cell is not distinguished in Eq. (27); this also introduces an error, though it is smaller than the main approximation. In principle, it is not difficult to take account of the required corrections, but this would make the discussion excessively complicated without introducing anything qualitatively new. It is easily found that we have $\beta>0$ for $\xi\subset(-2,\,0)$ and $\beta<0$ for $\xi\subset(-\infty,\,-2)\cup(0,\,\infty)$. As $\xi\rightarrow 0^-$ (from the left) we have $\beta\rightarrow\infty$. At the same time, in crystals with large Z the free-induction decay signal (and hence the spectrum also) produced by the H_{zz} interaction is nearly Gaussian.[30] But this is what happens as β (and hence also λ) increases with the expressions (15) and (16). Even for $\lambda=8$ the spectrum (16) is approximated well by a Gaussian function, at least for not too high frequencies.[31] In general, for large λ it can be assumed for the spectrum (16)

$$g_0(\omega)\propto\exp\left[-\frac{\omega^2}{(b/\sqrt{\lambda})^2}\right].$$

Let us now consider the case $\xi\subset(0,\,\infty)$. Here $\beta<0$ holds and both parts of the Hamiltonian (3) have the same sign. We thereby move in the direction of systems with a strong indirect exchange interaction, for which the shape of the NMR spectra merits at least a brief discussion here.

In crystals with strong electronic paramagnetism, such as Tl_2O_3, $KMnF_3$, $RbMnF_3$, and so on, which at low temperatures transform into a magnetically ordered state, there exists a strong indirect (via the electronic shells) exchange interaction between the nuclear spins. It is described by an additional term[15] in the Hamiltonian (3) (or by a corresponding renormalization of the constants in the Hamiltonian (3))

$$H_{\mathrm{ex}}=\sum_{i\neq j}A_{ij}\mathbf{S}_i\cdot\mathbf{S}_j. \tag{28}$$

We note that, in addition, the interaction of the form (28) between electronic spins almost always plays a large role in the ESR spin dynamics, determining at sufficiently high densities of the paramagnetic centers the shape of the absorption line.

The exchange interaction constants A_{ij} are much larger than the dipole–dipole interaction constants b_{ij}, as a result of which the signs of the coefficients b_{ij} and α_{ij} (i.e., signs of the terms H_{zz} and H_{ff}), which are different in the Hamiltonian (3), become the same in the complete (total) Hamiltonian. Now Eq. (14) can be rewritten in the form

$$\ddot{A}_0(t)-(\beta/t)\dot{A}_0(t)-(\beta-1)\nu_0^2A_0(t)=0,\quad \beta>0 \tag{29}$$

(the minus sign of the parameter β is written out explicitly in Eq. (29), so that here and below β is itself positive). Substituting $A_0(t)=w(t)y(t)$ (Ref. 32) with

$$w(t)=\exp\left(\int_{t_0}^{t}\frac{\beta}{2}\frac{dt_1}{t_1}\right) \tag{30}$$

gives

$$\ddot{z}+q(t)z=0,\quad q(t)=-\left[(\beta-1)\nu_0^2+\frac{\beta}{2t^2}+\frac{\beta^2}{4t^2}\right]. \tag{31}$$

The presence or absence of oscillations in the solutions of Eqs. (14), (29), and (31) is determined exclusively by the sign of the function $q(t)$.[32] For $q(t)>0$ the solutions oscillate. In the opposite case ($q(t)<0$), the oscillations vanish. Therefore the solutions of Eqs. (29) and (31) for appropriate values of β can be expressed in terms of modified Bessel functions,[25] and for long times they are described by the expression

$$A_0(t)=\Gamma_0(t)\propto\ \exp(-\sqrt{\beta-1}\,\nu_0t). \tag{32}$$

For example, the solution of Eq. (29) for $\beta=2$ (correspondingly, $\lambda=3/2$) has a quite simple form, since all cylinder functions of half-integral order can be expressed in terms of elementary functions:

$$A_0(t)=K_{3/2}(\sqrt{\beta-1}\,\nu_0t)(\sqrt{\beta-1}\,\nu_0t)^{3/2}=(\nu_0t)^{3/2}$$
$$\times\exp(-\nu_0t)[(\nu_0t)^{-3/2}+(\nu_0t)^{1/2}], \tag{33}$$

which is qualitatively in complete agreement with the experimental data on both NMR and ESR (see, for example, Ref. 33). Quantitative agreement can be achieved, however, with an appropriate choice of the parameters. It should be noted that for a Lorentzian spectrum, which appears when the temporal correlation functions (32) and (33) are Fourier-transformed, it is not at all easy to choose these parameters from first principles (for example, with the aid of sum rules):

The moments of the Lorentz function diverge, and specialized and quite extensive work must be performed in order to compare correctly the theoretical results (32) and (33) with the experimental data. Nonetheless, in the simplest variant the value of β can be chosen using the half-width of the experimental spectrum.

4. DISCUSSION

The similarity law (11) and (12) leads (in the limit $Z\rightarrow\infty$) to a universal form of the free-induction decay signal from a cell in crystals with different types of crystal lattices: The shape of the free-induction decay signal depends only on the ratio of the interaction constants in the Hamiltonian (3) and not on the details of the internal structure. For finite values of Z, however, the shape of the free-induction decay signal varies slightly in the direction of the Abragam trial function, continuing to depend slightly on the structure. The only element which is common to different crystals is the large (though finite) number Z of spins in a cell. Therefore, in a certain sense, it can be asserted that the interaction H_{ff} transforms the universal Gaussian spectrum, produced on these lattices by the H_{zz} interaction,[30] into a spectrum which is also universal, possessing a characteristic limiting frequency and described by the function (16) for values of the parameter λ lying in the interval [0.5, 1] (taking account of roundoff). Generally speaking, it is impossible to indicate exactly in advance the number Z of spins per cell that can be regarded as being large. However, the function (4) describes very well the free-induction decay signal in polyethylene, where we have $Z=3$, with the field oriented along the axis of a molecule,[19,20] while for the quasi-one-dimensional fluoroapatite crystal, where we have $Z=2$, this trial function is completely useless, as are the similarity law (12) and the solution in quadratures (20) in the lowest approximations. This has been checked.

Of course, the qualitative considerations presented above by no means comprise a rigorous theorem. Moreover, it can be assumed in advance that an ample number of objects with an intermediate structure does exist, for example, two spins which are strongly coupled with a distinguished spin and a third spin whose interaction with the distinguished spin is much weaker than with the first two spins but, at the same time, much stronger than its interaction with ''distant spins.'' This situation is characteristic for polyethylene[19,20] and $Ca(OH)_2$ (Ref. 34) crystals for some orientations of the external magnetic field.

In the light of what has been said above, it is nonetheless possible that similarity, together with the rapid ''freezing'' of the constants in the system (6), are reflections of a hidden symmetry of the system, somewhat reminiscent of the physics of critical phenomena. For the systems considered above, however, different regions of the Liouville space behave identically in time.

Finally, we note that Eqs. (14), (29), and (31) are particular variants of the equation

$$\ddot{A}_0(t)+a(t)\dot{A}_0(t)+b(t)A_0(t)=0, \qquad (34)$$

which in the theory of differential equations is a very popular object of investigation as a function of the behavior of the coefficients $a(t)$ and $b(t)$[32] because of the great diversity of solutions obtained by choosing different functions as $a(t)$ and $b(t)$. This feature of Eq. (14) was employed in Refs. 31 and 35 to construct empirical trial functions in different objects: aluminum powders, aluminum alloys with copper, PbF_2 crystals, characterized by a high mobility, and so on. We emphasize that equations of the form (14) were used in Refs. 31 and 35 for the sole purpose of constructing empirical trial functions which approximate the entire diversity of observed spectra in a unified manner so as to facilitate analysis of an experiment. The choice of this equation in Refs. 31 and 35 was determined by the diversity of the possibilities provided.

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