Cross-relaxation rate

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A dynamical theory of a heteronuclear magnetic spin system on a large lattice is developed. Nonlinear integral equations are derived for the time-dependent spin autocorrelation functions. The closest singularities of these functions on the imaginary time axis are studied, and it is shown that their parameters depend on the ratio of the homo- and heteronuclear contributions to the dipole–dipole interaction, which is a function of the orientation of the crystal in a magnetic field. Simple analytic expressions are derived both for the rate of different cross-relaxation processes as functions of the detuning, for large detunings, and for the wings of the spectra of other correlation functions. The theoretical results are in good agreement with the published experimental results. © *1994 American Institute of Physics.*

1. INTRODUCTION

Since the publication of the first work on cross relaxation by Bloembergen, Shapiro, *et al.*,[1] a great deal of attention has been devoted to the problem of energy transfer between subsystems in magnetic spin systems consisting of different types of nuclei. On the one hand, cross relaxation is of great interest as a particular manifestation of the central problem of nonequilibrium statistical physics—the establishment of equilibrium in systems of many interacting bodies. The advantages of nuclear spin systems are that the well-known interaction laws in the system are simple, the coupling with the crystal lattice is weak, and accurate measurements can be performed by the methods of nuclear magnetic resonance. On the other hand, cross-relaxation processes form the foundation of the nuclear double resonance method, which is a uniquely sensitive method for studying the local properties of solids.

The basic laws of cross-relaxation processes have been explained within the thermodynamic theory.[2–4] Kinetic equations have been derived, in which the kinetic coefficients are actually empirical constants for the temperatures of different reservoirs. The problem of calculating the rates of different cross-relaxation processes has still not been solved satisfactorily.

In the present work our objective is to construct a theory that makes it possible to find quite simply the dependences of different cross relaxation processes on the energy unbalance or detuning of the processes for large detunings—the range of greatest interest. The theory is constructed in the approximation of a Gaussian self-consistent fluctuating local field, an elaboration of the well-known Anderson–Weiss approximation.[5] The crux of the Anderson–Weiss approach is that the real motion of a spin interacting with many surrounding spins is replaced by the rotation of the spin in a fluctuating, one-component, local magnetic field described by a Gaussian random process. The approach proposed initially to explain the exchange-narrowing of the magnetic-resonance line was very fruitful, and it was later used successfully to describe many effects in spin dynamics. The important role played by the fluctuating local field in cross-relaxation processes was pointed out in Ref. 6. For an elementary cross-relaxation event between spins in a Gaussian local field, the high-frequency asymptotic behavior of the cross-relaxation rate is exponential, which agrees with experiment.[7] Application of this popular approach are limited by the fact that the Gaussian random field was introduced phenomenologically. In the present paper, the conditions[8,9] that lead to such a field are imposed on the motion of the spins themselves, and a microscopic model theory of heteronuclear spin systems is constructed on this basis.

2. CROSS-RELAXATION RATE

Consider a system consisting of nuclei of different types distinguished by their gyromagnetic ratios (γ_p) and, therefore, by their precession frequencies in a constant magnetic field H_0. For clarity, we consider a system with two types of nuclei with spins I and S. The extension to the case of a large number of subsystems is obvious. In the thermodynamic theory,[2–4] the cross-relaxation rate obtained by means of perturbation theory, whose applicability improves with increasing detuning, is

$$I/T_{IS}=Af(\omega), \tag{1}$$

where

$$f(\omega)=\frac{1}{\pi}\int_0^\infty F(t)\cos(\omega t)dt, \tag{2}$$

$$F(t)=\mathrm{Sp}\{\exp(i\mathscr{H}t)V^+\exp(-i\mathscr{H}t)V^-\}/\mathrm{Sp}(V^+V^-). \tag{3}$$

The secular part of the dipole–dipole interaction Hamiltonian

$$\mathscr{H}=\mathscr{H}_{II}+\mathscr{H}_{SS}+\mathscr{H}_{IS} \tag{4}$$

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consists of the homonuclear parts $\mathscr{H}_{II}$ and $\mathscr{H}_{SS}$ and the heteronuclear part $\mathscr{H}_{IS}$, consisting of the interactions between the projections of the spins on the field H_0. The coefficients in these three parts are b_{ij}, $b_{\alpha\beta}$, and $b_{i\alpha}$, respectively, where the Roman subscripts refer to the lattice sites occupied by the I spins and the Greek subscripts refer to the lattice sites occupied by S spins. The perturbation $V=V^{+}+V^{-}$ flips the spins. For one-, two-, and three-spin cross-relaxation, V can be written in the following forms:

$$V_1^{\pm}=\sum_{i,\alpha} A_{i\alpha}I_i^{\pm}S_\alpha^z, \quad \omega=\gamma_I H_0, \tag{5}$$

$$V_2^{\pm}=\sum_{i,\alpha} B_{i\alpha}I_i^{\pm}S_\alpha^{\mp}, \quad \omega=(\gamma_I-\gamma_S)H_0, \tag{6}$$

$$V_3^{\pm}=\sum_{i,\alpha} C_{ij\alpha}I_i^{\pm}I_j^{\pm}S_\alpha^{\mp}, \quad \omega=(2\gamma_I-\gamma_S)H_0. \tag{7}$$

The right-hand column gives the detuning corresponding to a given process. Expressions for the coefficients in Eqs. (1)–(7) are given in the literature cited below for each specific case. The shape function $f(\omega)$ is normalized so that the area under the curve equals 1; it reflects the capability of the spin system to emit or absorb energy ω ($\hbar=1$). The form of this function is determined by the interactions of the spins participating in an elementary event and all other spins in the system, as a result of which the calculation of this function is a very difficult problem.

We begin our analysis with two-spin cross-relaxation. Substituting Eq. (6) into Eq. (3) we obtain

$$F_2(t)=\Gamma_{xI}(t)\Gamma_{xS}(t)+\frac{1}{4}\sum_{i,j,\alpha,\beta}{}' B_{i\alpha}B_{j\beta}\Gamma_{xij}(t)\Gamma_{x\alpha\beta}(t)\Big/\sum_{i,\alpha} B_{i\alpha}^2, \tag{8}$$

where in the residual sum at least one pair of site indices is different. Here and below $\Gamma_{mij}(t)$ and $\Gamma_{m\alpha\beta}(t)$, where $m=x$, y, and z, are the two-spin correlation functions, which are determined by the expression (3) after the operators of the corresponding spin components (S_α^m, S_β^m or I_i^m, I_j^m) are substituted for $V^{\pm}$. On account of the axial symmetry of the Hamiltonian (4), $\Gamma_{xkl}(t)=\Gamma_{ykl}(t)=\Gamma_{+-kl}(t)$. The functions $\Gamma_{mI}(t)=\Gamma_{mii}(t)$ and $\Gamma_{mS}(t)=\Gamma_{m\alpha\alpha}(t)$ are autocorrelation functions (ACFs).

We now compare the two parts of Eq. (8). For this, we consider their power series as functions of the time. The zeroth term equals 1 for the first part and 0 for the second part. The ratio of the quadratic terms is determined by the ratio of the lattice sums of the following form[10]

$$\varepsilon=\sum_{i,j,\alpha} B_{i\alpha}B_{j\alpha}b_{ij}^2\Big/\left(\sum_{i,j,\alpha} B_{i\alpha}^2 b_{ij}^2\right). \tag{9}$$

For NaF and LiF lattices and a constant magnetic field oriented along the crystallographic axes [100], [110], and [111] this ratio is 0.069, 0.085, and 0.28, respectively.[10] In higher orders, the lattice sums are more complicated. The structure of the second part of Eq. (8) is such that the lattice sums of its series necessarily contain loops from the couplings, while the lattice sums of the first part of Eq. (8) contain sums with a tree structure and no loops. Numerical calculations of lattice sums which are more complicated than in Eq. (9)[11,12] and the estimates made in Appendix A show that as the size of a loop or the number of loops increases, the differences of the magnitudes of these two classes of lattice sums increase.

The smallness of the lattice sums containing loops suggests that discarding these sums does not change the shape function $f(\omega)$. Without such sums, however, the theory is much simpler. First, the second term in Eq. (8) vanishes, so that

$$F_2(t)=\Gamma_{xI}(t)\Gamma_{xS}(t). \tag{10}$$

In the same fashion, in the case of one-spin cross-relaxation we find, after substituting Eq. (5) into Eq. (3) and dropping terms containing lattice sums with loops, that

$$F_1(t)=\Gamma_{xI}(t)\Gamma_{zS}(t). \tag{11}$$

Similarly, even in more complicated cases the correlation function $F(t)$ can be expressed in terms of a product of the autocorrelation functions of the spins participating in an elementary cross-relaxation event.

3. EQUATIONS FOR THE AUTOCORRELATION FUNCTIONS

The autocorrelation function can be determined by averaging the rotation of a spin in the local field generated by the surrounding spins.[8,9,13] The transverse components of the local field are determined by the interaction with spins of the same type

$$h_i^{x(y)}=-\frac{1}{2}\sum_j b_{ij}I_j^{x(y)}, \tag{12}$$

while the longitudinal components acquire a contribution from the interaction $\mathscr{H}_{IS}$ with spins of different type

$$h_i^z=\sum_j b_{ij}I_j^z+\sum_\alpha b_{i\alpha}S_\alpha^z. \tag{13}$$

We shall now find the correlation functions of the field components. Just as in the case of Eq. (8), after dropping terms containing lattice sums with loops, we obtain

$$g_{xI}(t)=\mathrm{Sp}\{h_i^x(t)h_i^x\}/\mathrm{Sp}\,1=\tfrac{1}{4}\,\Delta_{II}^2\Gamma_{xI}(t),$$

$$g_{yI}(t)=g_{xI}(t), \tag{14}$$

$$g_{zI}(t)=\mathrm{Sp}\{h_i^z(t)h_i^z\}/\mathrm{Sp}\,1=\Delta_{II}^2\Gamma_{zI}(t)+\Delta_{IS}^2\Gamma_{zS}(t), \tag{15}$$

where

$$\Delta_{II}^2=I(I+1)\,\frac{1}{3}\sum_j b_{ij}^2, \quad \Delta_{IS}^2=S(S+1)\,\frac{1}{3}\sum_\alpha b_{i\alpha}^2 \tag{16}$$

are the mean squares of the two contributions to the longitudinal local field at an I spin. (Similar formulas are obtained for the field at the S spins by interchanging the indices (i,j) and (α,β).) Moreover, just as in the homonuclear case,[8,9] the average of the product of a large number of variables $h_i^m(t)$ decomposes into a sum of products of all possible pair averages (14) and (15).

The latter property is a definition of a Gaussian random process.[14] Therefore, in the approximation under consideration, the local field is a three-dimensional (three-component) Gaussian random field. It should be noted that the large number of contributions to Eqs. (12) and (13) is in itself not sufficient for this. The contributions must vary in time independently of one another. Under conditions when the temporal fluctuations are caused by spin–spin interactions, independence requires that an additional condition be imposed on the motion of the spins. The terms containing lattice sums with loops from the couplings must be dropped. As shown in Appendix A, in model spin systems on infinite lattices the required condition is satisfied automatically, while increasing the interaction radius does not in itself ensure satisfaction of the condition. In Refs. 5, 13, and 15 a Gaussian random field was introduced on the basis of the fact that the number of neighbors is large, irrespective of the independence condition. On the other hand, the condition derived above implies that Eqs. (14) and (15) are self-consistent, which in the previous works Refs. 13 and 16–18 had to be introduced explicitly.

The equations for the autocorrelation functions of a spin rotating in a general Gaussian random field were derived in Ref. 9. In the heteronuclear case these equations must be written out for each type of spin, and we obtain the system of integral equations

$$\frac{d}{dt}\Gamma_{mp}(t)=-\int_0^t G_{mp}(t-t')\Gamma_{mp}(t')dt', \tag{17}$$

where the index m enumerates the spin projections x, y, and z and the index p enumerates the spin subsystems I and S. The memory function $G_{mp}(t)$ is expressed as an infinite series. These terms are described in Appendix B. The heteronuclear function $G_{mp}(t)$ is different from the homonuclear case in that the form of the correlation function (15) of the longitudinal component of the local field changes. This component of the field couples the spins of the subsystems, and as a result of this coupling, a coupled system of equations is obtained instead of independent equations for nuclei of different types.

Equations of the general form (17) are intended for Hamiltonians with arbitrary magnetic anisotropy. In our case of an axisymmetric Hamiltonian, the longitudinal and transverse components of the spin vary differently,[19,20] the longitudinal local fields (13) being mainly responsible for the change in the transverse spin components.

After transforming the equations for the transverse spin components (see Appendix B), the point of the transformation being to take into account predominantly the longitudinal local fields, we obtain integral equations in a different form

$$\Gamma_{xp}(t)=\Gamma_{0p}(t)-\int_0^t \Gamma_{0p}(t-t')\int_0^{t'}[G_{xp}(t'') -G_{0p}(t'')]\Gamma_{xp}(t-t')dt'dt'', \tag{18}$$

where

$$\Gamma_{0p}(t)=\exp\left\{-\sum_q \Delta_{pq}^2\int_0^t\int_0^{t'}\Gamma_{zp}(t'')dt'dt''\right\} \tag{19}$$

is the autocorrelation function for a spin rotating in a longitudinal local field, and which can be obtained from the Anderson–Weiss formula[5] for the case of the resonance frequency, described by a Gaussian random process, by substituting Eq. (15) into it; $G_{0p}(t)$ is the memory function of an integral equation of the form (17) for $\Gamma_{0p}(t)$. We leave the equations for $\Gamma_{zp}(t)$ unchanged.

Retaining only the leading terms of the series for the memory functions, we obtain

$$\Gamma_{xp}(t)=\Gamma_{0p}(t)-\frac{1}{4}\Delta_{pp}^2\int_0^t\Gamma_{0p} \times(t-t')\int_0^{t'}\Gamma_{xp}(t'')\Gamma_{zp}(t'')\Gamma_{xp}(t'-t'')dt'dt'', \tag{20}$$

$$\frac{d}{dt}\Gamma_{zp}(t)=-\frac{1}{2}\Delta_{pp}^2\int_0^t\Gamma_{xp}^2(t-t')\Gamma_{zp}(t')dt', \tag{21}$$

which together with Eq. (19) form a closed system.

4. SINGULARITIES OF THE CORRELATION FUNCTIONS ON THE IMAGINARY TIME AXIS

A complicated system of nonlinear integral equations that is difficult to solve is obtained even in the lowest-order approximation for the memory function. Fortunately, large detunings are most important for describing cross-relaxation processes. According to the well-known property of the Fourier transform,[21] the function $f(\omega)$ in this region will be determined by the form of $F(t)$ near the singularities closest to the real axis in the plane of the complex time variable. If the principal part of $F(t)$ in this neighborhood has the form

$$F(t)\approx C(\tau_0+it)^{-\beta}+C(\tau_0-it)^{-\beta}, \tag{22}$$

then for the Fourier components in the wings we have

$$f(\omega)\approx C|\omega|^{\beta-1}\exp(-\tau_0|\omega|)/\Gamma(\beta), \tag{23}$$

where $\Gamma(\beta)$ is the gamma function. To determine the parameters in Eq. (22) it is sufficient to find the form of the solution of the system of equations (19)–(21) near the closest singularities. The existence of singularities in the nonlinear integral equations (17) on the imaginary axis at a finite distance was proved in Refs. 8 and 9 for the homonuclear case, i.e., for $p=I$. This property of the equations under study remains as the number of equations increases, though the characteristics of the singularities will change, as we shall now show.

Let the principal parts of the ACFs near the singularity closest to the origin have the forms

TABLE I. Mean-squared homo- and heteronuclear contributions to the longitudinal local fields in LiF.

Quantity	$\mathbf{H}_0 \parallel [111]$	$\mathbf{H}_0 \parallel [110]$	$\mathbf{H}_0 \parallel [100]$
Δ^2_{FF},(рад/с)^2	$2838 \cdot 10^6$	$2581 \cdot 10^6$	$1809 \cdot 10^6$
$\Delta^2_{\mathrm{FLi}}/\Delta^2_{\mathrm{FF}}$	0.3065	1.9559	9.7209
$\Delta^2_{\mathrm{LiF}}/\Delta^2_{\mathrm{FF}}$	0.0613	0.3912	1.9442
$\Delta^2_{\mathrm{LiLi}}/\Delta^2_{\mathrm{FF}}$	0.1455	0.1455	0.1455

$$\Gamma_{zp}(t) \approx \frac{C_{zp}}{(\tau_0 + it)^{\zeta_p}}, \quad \Gamma_{xp}(t) \approx \frac{C_{xp}}{(\tau_0 + it)^{\chi_p}},$$

$$\Gamma_{0p}(t) \approx \frac{C_{0p}}{(\tau_0 + it)^{\delta_p}}. \tag{24}$$

We call attention to the fact that in Eq. (24) we assumed that the singularities for all types of spins occur at the same point. This result is a consequence of the existence of a coupling, realized in Eqs. (20) and (21) through $\Gamma_{0p}(t)$, between the spin subsystems. In the opposite case, when $\Delta^2_{pq} = 0$, the coordinates of the singularities of the different subsystems would be different. We shall seek the parameters in Eq. (24) by the same method as in the homonuclear case,[8,9,20] similar to the Painlevé analysis[22] of moving singularities of nonlinear differential equations. To this end, we substitute Eq. (24) into Eqs. (19)–(21) and equate the most highly divergent terms of both parts of each equation. From the equations for $\Gamma_{zp}(t)$ and $\Gamma_{xp}(t)$ we obtain the simple relations

$$C_{zp}\zeta_p(\zeta_p + 1) = \tfrac{1}{2}\Delta^2_{pp}C^2_{xp}, \quad 2\chi_p = \zeta_p + 2,$$

$$C_{xp}\chi_p(\chi_p + 1) = C_{0p}\delta_p(\delta_p + 1) \quad \text{for } \chi_p = \delta_p > \chi_p + \zeta_p - 2,$$

$$C_{xp}\chi_p(\chi_p + 1) = C_{0p}\delta_p(\delta_p + 1) + \tfrac{1}{4}\Delta^2_{pp}C_{xp}C_{zp}$$

$$\text{for } \chi_p = \delta_p = \chi_p + \zeta_p - 2. \tag{25}$$

In the equations for $\Gamma_{0p}(t)$, obtained by differentiating Eq. (19) with respect to the time, the terms containing the square of the small quantity should be retained in the denominator. We obtain for the coefficients of these terms a system of algebraic equations that can be written in the conventional form

$$\delta_p = \sum_q \Delta^2_{pq}C_{zq}(\tau_0 + it)^{2-\zeta_q}/(\zeta_q - 1), \tag{26}$$

anticipating that the term with $\zeta_q < 2$ vanishes in the limit $t \to i\tau_0$.

As a specific example, we consider an LiF crystal, in which the shape functions of interest to us were measured for large detunings.[23–27] The quantities Δ^2_{pq} (16), where p and q denote the ^{7}Li or ^{19}F nuclei, were calculated for three orientations of the constant magnetic field relative to the crystallographic axes on the basis of the lattice sums from Ref. 25; the results are presented in Table I. The calculation was performed neglecting the rare isotopes ^{6}Li.[28]

The system (26) with $t = i\tau_0$ has a solution in two cases:

1) If $\zeta_{\mathrm{F}} = \zeta_{\mathrm{Li}} = 2$, then

$$C_{z\mathrm{F}} = 2\,\frac{\Delta^2_{\mathrm{FLi}} - \Delta^2_{\mathrm{LiLi}}}{\Delta^2_{\mathrm{FLi}}\Delta^2_{\mathrm{LiF}} - \Delta^2_{\mathrm{FF}}\Delta^2_{\mathrm{LiLi}}},$$

$$C_{z\mathrm{Li}} = 2\,\frac{\Delta^2_{\mathrm{LiF}} - \Delta^2_{\mathrm{FF}}}{\Delta^2_{\mathrm{FLi}}\Delta^2_{\mathrm{LiF}} - \Delta^2_{\mathrm{FF}}\Delta^2_{\mathrm{LiLi}}}. \tag{27}$$

2) If $\zeta_{\mathrm{F}} = 2$, $\zeta_{\mathrm{Li}} < 2$, then

$$C_{z\mathrm{F}} = 2/\Delta^2_{\mathrm{FF}}, \quad \delta_{\mathrm{Li}} = 2\Delta^2_{\mathrm{LiF}}/\Delta^2_{\mathrm{FF}}. \tag{28}$$

The choice between these two cases is determined by the ratio of the mean squared fields Δ^2_{LiF}. The first case obtains when

$$\begin{cases} \Delta^2_{\mathrm{FF}} > \Delta^2_{\mathrm{LiF}} \\ \Delta^2_{\mathrm{LiLi}} > \Delta^2_{\mathrm{FLi}} \end{cases} \text{or} \quad \begin{cases} \Delta^2_{\mathrm{FF}} < \Delta^2_{\mathrm{LiF}} \\ \Delta^2_{\mathrm{LiLi}} < \Delta^2_{\mathrm{FLi}} \end{cases}.$$

According to the data in Table I, this case is realized in LiF for the [100] orientation of the crystal. For other ratios of Δ^2_{pq}, for example, in LiF with [110] and [111] orientations, the second case is realized. The difference of the formulas (27) and (28) is a consequence of the fact that the lithium spins play different roles in the spin dynamics. In the second case the interaction of the fluorine spins with one another is stronger than all other interactions. It is the fluorine spin subsystem that plays the leading role (driving spins) in the dynamics, while the lithium spins play a secondary role (driven spins). In the first case this is not so and both spin systems play an equivalent role: both are driving spins.

Substituting Eq. (27) or (28) into Eq. (25) we find for the driving spins

$$\chi_p = \delta_p = 2, \quad C_{xp} = \sqrt{12C_{zp}/\Delta^2_{pp}},$$

$$C_{0p} = C_{xp}(1 - C_{zp}\Delta^2_{pp}/24). \tag{29}$$

For the driven spins only the exponents can be found from the relations (28) and (25):

$$\chi_{\mathrm{Li}} = \delta_{\mathrm{Li}}, \quad \zeta_{\mathrm{Li}} = 2\delta_{\mathrm{Li}} - 2. \tag{30}$$

The foregoing analysis says nothing about the coordinate τ_0 of the singularity. It can be found from the power series for the AFC:

$$\Gamma_{mp}(t) = \sum_{n=0}^{\infty} M^{mp}_{2n}\,\frac{(-1)^n t^{2n}}{(2n)!} \quad (m = 0,x,y,z;\ p = I,S) \tag{31}$$

TABLE II. Computed values of the parameters determining the form of the principal parts of the correlation functions (24) for LiF.

Parameter	$H_0 \parallel [111]$		$H_0 \parallel [110]$		$H_0 \parallel [100]$	
	F	Li	F	Li	F	Li
$\chi_p = \delta_p$	2	0.1226	2	0.7838	2	2
ζ_p	2	-1.7548	2	-0.4324	2	2
$C_{0p}(\Delta_{FF})^{\delta_p}$	$11/\sqrt{6}$	1.637	$11/\sqrt{6}$	0.6198	3.3516	2.8811
$C_{xp}(\Delta_{FF})^{\chi_p}$	$2\sqrt{6}$	1.638	$2\sqrt{6}$	0.6195	3.5006	2.8818
$C_{zp}(\Delta_{FF})^{\zeta_p}$	2	0.157	2	-0.1205	1.0212	0.1007
$\tau_0^2\Delta_{FF}^2$	5.626		3.397		1.27	
τ_0, MKC	45		36		27	

whose convergence radius is τ_0. This approach is used in the physics of critical phenomena for determining the critical exponents from high-temperature expansions.[29] We shall employ the formulas for the convergence radius with known exponent α of the singularity (in Eq. (24) $\alpha=\zeta_{I(S)},\chi_{I(S)}$)

$$\tau_0=\left[\frac{M_{2n-2}\Gamma(2n+\alpha)}{M_{2n}\Gamma(2n-2+\alpha)}\right]^{1/2},$$
$$\tau_0=\left[\frac{2C\Gamma(2n+\alpha)}{M_{2n}\Gamma(\alpha)}\right]^{1/(2n+\alpha)}. \tag{32}$$

The series (31) can be used to find the missing coefficients for the driven nuclei, using the formula

$$C=M_{2n}\tau_0^{2n+\alpha}\Gamma(\alpha)/[2\Gamma(2n+\alpha)]. \tag{33}$$

We obtain a system of recurrence relations for the coefficients of the series (31) (moments) by substituting the series into the system (19)–(21) and equating coefficients with like powers of the time:

$$M^{0p}_{2n+2}=\sum_{k=0}^{n} M^{0p}_{2n-2k}\binom{2n+1}{2k}(\Delta^2_{pI}M^{zI}_{2k}+\Delta^2_{pS}M^{zS}_{2k}),$$

$$M^{zp}_{2n+2}=\frac{1}{2}\Delta^2_{pp}\sum_{k=0}^{n} M^{zp}_{2n-2k}\sum_{l=0}^{k}\binom{2k}{2l}M^{xp}_{2l}M^{xp}_{2k-2l},$$

$$M^{xp}_{2n+2}=M^{0p}_{2n+2}+\frac{1}{4}\Delta^2_{pp}\sum_{k=0}^{n} M^{0p}_{2n-2k}\sum_{l=0}^{k} M^{xp}_{2k-2l}$$
$$\times\sum_{f=0}^{l}\binom{2l}{2f}M^{zp}_{2f}M^{xp}_{2l-2f}. \tag{34}$$

Moments up to 50th order were calculated, and the parameters τ_0 and $C_{m\mathrm{Li}}$ were calculated from the moments using Eqs. (32) and (33). The values of these and other parameters, determined above by Eqs. (27)–(30), are presented in Table II.

We now estimate by how much the parameters of the principal parts of the ACFs change when the terms in the series for $G_{mp}(t)$ which were dropped in Eqs. (20) and (21) are taken into account. Consider $G^z_{z\mathrm{Li}}(t)$ (Appendix B). Substituting into its integrand the expression for the principal parts (24) of the ACFs we obtain

$$G^{(4)}_{z\mathrm{Li}}(t)=\frac{\Delta^4_{\mathrm{LiLi}}}{8}C^2_{x\mathrm{Li}}C_{z\mathrm{Li}}\int_0^t dt'\int_0^{t'}dt''[\tau_0+i$$
$$\times(t'-t'')]^{-\zeta_{\mathrm{Li}}}(\tau_0+it')^{-\chi_{\mathrm{Li}}}[\tau_0+i(t-t'')]^{-\chi_{\mathrm{Li}}}. \tag{35}$$

For the [111] and [110] orientations, the exponent of the small quantity in Eq. (35), after the double integration is performed and taking into account Eq. (30), will be $4\chi_{\mathrm{Li}}-2$. The first term retained in Eq. (21), $G^{(2)}_{z\mathrm{Li}}(t)$, will have the larger exponent $2\chi_{\mathrm{Li}}+2$, since $\chi_{\mathrm{Li}}<2$ in these orientations. In each successive term in the series $G_{z\mathrm{Li}}(t)$ two additional time integrations and a factor $(\tau_0+it_n)^{-\zeta_{\mathrm{Li}}}$ or $(\tau_0+it_n)^{-\chi_{\mathrm{Li}}}$ appear in the integrand. As a result, premultiplication by a small quantity raised to a positive power appears. All terms beyond the first term in the series for $G_{z\mathrm{Li}}(t)$ can therefore be dropped near the singularity. The same result is also obtained in these orientations for the series $G_{x\mathrm{Li}}(t) - G_{0\mathrm{Li}}(t)$.

For the [100] orientation $\chi_{\mathrm{Li}}=\zeta_{\mathrm{Li}}=2$, and we find for the principal part of the integral (35)

$$G^{(4)}_{z\mathrm{Li}}(t)=\xi_{z\mathrm{Li}}G^{(2)}_{z\mathrm{Li}}(t),\quad \xi_{z\mathrm{Li}}=(10-\pi^2)C_{z\mathrm{Li}}\Delta^2_{\mathrm{LiLi}}/4. \tag{36}$$

Substituting numerical values we obtain $\xi_{z\mathrm{Li}}\approx5\cdot10^{-4}$. For $G^{(4)}_{x\mathrm{Li}}(t) - G^{(4)}_{0\mathrm{Li}}(t)$ we find

$$\xi_{x\mathrm{Li}}=(10-\pi^2)\Delta^2_{\mathrm{LiLi}}C^2_{x\mathrm{Li}}/C_{z\mathrm{Li}}\approx0.39.$$

For the fluorine ACF the singularity exponents equal 2 in all orientations, and for this reason $G^{(4)}_{m\mathrm{F}}(t)$ near a singularity is determined by the relation (36) with the coefficients $\xi_{z\mathrm{F}}$ and $\xi_{x\mathrm{F}}$, where $\xi_{z\mathrm{F}}=0.033$ in the [100] orientation and 0.065 in the other two orientations, and $\xi_{x\mathrm{F}} = 0.39$ in all three orientations.

It is not so obvious that the terms omitted from the series for $G_{xp}(t)$ are small. The subsequent terms in the series must indeed be taken into account when equations of the form (17) are used. Switching to the form (18), however, we already took into account via $G_{0p}(t)$ a large part of the series for $G_{xp}(t)$, associated with the zz interaction. For example, in the homonuclear case[8,9,20] an estimate gives a 2.5% change in τ_0 after such terms are dropped in Eq. (18), as opposed to a 15% change in the case of Eq. (17). In the heteronuclear case, the interaction $\mathcal{H}_{IS}$ enhances the role of the zz interaction, increasing the accuracy of the first-approximation equations (19)–(21).

5. HIGH-FREQUENCY ASYMPTOTIC BEHAVIOR OF THE SHAPE FUNCTION $f(\omega)$

We are now in a position to determine the form of the desired function $f(\omega)$ for the rates of different cross-relaxation processes for large detunings. Since the coordinates of the singularities are the same in all correlation functions, in Eqs. (22) and (23) β is the sum of the exponents of the singularities, and C is the product of the coefficients of the principal parts (24) for the ACFs of the spins participating in an elementary event of the corresponding cross-relaxation process. For two-spin cross-relaxation (10)

$$\beta_2=\chi_I+\chi_S,\quad C_2=C_{xI}C_{xS}, \tag{37}$$

and for one-spin cross-relaxation (11)

$$\beta_1=\chi_I+\zeta_S,\quad C_1=C_{xI}C_{zS}. \tag{38}$$

Two-spin cross-relaxation is more difficult to observe experimentally than one-spin relaxation. For this reason, one-spin relaxation, usually termed cross-polarization, has been studied in greatest detail.[11,24,25,30–32] To observe it, a strong rf field at the resonant frequency of the I spins is applied to the system and the rate of change of the temperature of the Zeeman reservoir, which is produced by the rf field in a rotating coordinate system, and the temperature of the dipole–dipole-interaction reservoir are measured. The I subsystem consists of the nuclei of the rare isotopes[11,24,25,30] or nuclei with a small gyromagnetic ratio.[31,32] In either case the interaction $\mathscr{H}_{II}$ can be neglected, compared to the interaction $\mathscr{H}_{SS}$. After this, we return to the dynamics of the homonuclear system[20] in all of the cases listed above, except Ref. 24. In Ref. 24 the rf field also acts on the nuclei of the rare isotopes ^{6}Li, but in the LiF crystal under study, cross-polarization now occurs in a system which consists of two types of nuclei—^{7}Li and ^{19}F—and is described by Eqs. (19)–(20). In this case we find

$$F_1(t)=(\Delta^2_{\mathrm{LiF}}\Gamma_{z\mathrm{F}}(t)+\Delta^2_{\mathrm{LiLi}}\Gamma_{z\mathrm{Li}}(t))/(\Delta^2_{\mathrm{LiF}}+\Delta^2_{\mathrm{LiLi}}). \tag{39}$$

In Eq. (39) we replaced Δ^2_{pq} for ^{6}Li nuclei with ^{7}Li, and ^{19}F nuclei by the expressions for ^{7}Li nuclei, since both nuclei occupy the same sites and the differences Δ^2_{pq} reduce to premultiplication by the constant $\gamma^2_{^6\mathrm{Li}}/\gamma^2_{^7\mathrm{Li}}$. The shape function $f(\omega)$ will consist of two terms of the form (23) with the parameters ζ_F, $C_{z\mathrm{F}}$ and ζ_{Li}, $C_{z\mathrm{Li}}$ presented in Table II for three orientations of the field. In particular, in the [111] orientation chosen for the experiment, we have

$$f_1(\nu)\simeq(8.24\cdot10^{-3}|\nu|+1.68|\nu|^{-2.75})$$
$$\times\exp(-\tau_0|\nu|2\pi\cdot10^3). \tag{40}$$

In Eq. (40) and in the similar formulas (44) and (46) the frequency ν is given in kHz. As a result of this substitution, $f(\nu)=2\pi\cdot10^3 f(\omega)$.

As a more complicated example, we consider three-spin cross-relaxation in LiF between the Zeeman reservoirs of the ^{7}Li and ^{19}F nuclei in a constant field H_0. Pershan[23] measured the field dependence of this relaxation rate. In an elementary event, the z projections of two lithium spins and one fluorine spin undergo changes of opposite sign. The effective perturbation operator (7) for such harmonic cross-relaxation is obtained in second-order perturbation theory.[3,23] We now substitute Eq. (7) into Eq. (3). First, we drop terms containing lattice sums with loops from the couplings. Second, the term with $j=1$, responsible for the change in the projection of one lithium spin by two units, is dropped, since the summation over the lattice indices in this term is smaller than in the retained term, and its value will be Z times smaller (Z is the number of neighbors).

The result is obtained in the form of a series. This series appears as a result of the presence of two lithium spin operators in the perturbation for the same reasons as the series for the kernel of the memory function of the integral equation (17). The first term in the series has the simple form

$$F_3^{(1)}(t)=\Gamma_{x\mathrm{F}}(t)\Gamma^2_{x\mathrm{Li}}(t). \tag{41}$$

The second term in the series is

$$F_3^{(2)}(t)=2k\Gamma_{x\mathrm{F}}(t)G^{(4)}_{z\mathrm{Li}}(t)/\Delta^2_{\mathrm{LiLi}}. \tag{42}$$

Here we have introduced a coefficient $k<1$. The point is that the perturbation $V_3^{\mp}$ contains terms in which two lithium nuclei interact only with a fluorine nucleus. Their contribution to the terms (42) contains a loop from the couplings, which is why the coefficient in front of the formula decreases. For high-order terms in the series, the factor in front of $\Gamma_{z\mathrm{F}}(t)$ in Eq. (42) has the same structure as $G^{(2n)}_{z\mathrm{Li}}(t)$, but it is not identical. From the fact, proved above, that for $G^{(2n)}_{z\mathrm{Li}}(t)$ is smaller than $G^{(2)(t)}_{z\mathrm{Li}}$ $n>1$, it follows that the correction terms to the leading contribution $F_3^{(1)}(t)$ (41) are small, so that in subsequent calculations we retain only this contribution.

Substituting into Eq. (41) the principal parts of the AFC (24) which were determined above, we find in Eq. (22) and (23)

$$\beta_3=2\chi_{\mathrm{Li}}+\chi_\mathrm{F},\quad C_3=C^2_{x\mathrm{Li}}C_{x\mathrm{F}}. \tag{43}$$

In particular, from Table II we find for the [111] orientation

$$f_3(\nu)\simeq9.59\cdot10^{-2}|\nu|^{1.25}\exp(-\tau_0|\nu|2\pi\cdot10^3). \tag{44}$$

Finally, we consider the results of the interesting experiment of Refs. (26) and (27), performed in the same heteronuclear system of a LiF crystal. In these papers it is not the cross-relaxation rate that is studied, but rather the AFCs which according to the theory developed here, determine these rates. The spectrum of the AFC (19) of the ^{8}Li nuclei was determined from the dependence of the asymmetry of the β-emission from these nuclei on the frequency of the rf field. The ^{8}Li nuclei occupy the same lattice sites as the ^{7}Li nuclei, and for this reason the ratios of the quantities Δ^2_{pq} (16) for them is

$$\mu=\gamma^2_{^8\mathrm{Li}}/\gamma^2_{^7\mathrm{Li}}=0.14.$$

The ratio of the exponents of the AFCs (19) of these nuclei will be equal to the same number. Hence there follows a simple relation between the functions themselves:

$$\Gamma_{0^8\mathrm{Li}}(t)=[\Gamma_{0^7\mathrm{Li}}(t)]^{\mu}. \tag{45}$$

Substituting Eq. (24) into Eq. (45), we obtain the principal part and the wings of the spectrum in the form (22) and (23) with the parameters

$$\beta=\mu\chi_{\mathrm{Li}},\quad C=(C_{x\mathrm{Li}})^{\mu}.$$

In particular, for the [111] orientation

$$f_{^8\mathrm{Li}}(\nu)\simeq1.85\cdot10^{-2}|\nu|^{-0.98}\exp(-\tau_0|\nu|2\pi\cdot10^3). \tag{46}$$

6. DISCUSSION AND COMPARISON WITH EXPERIMENT

The theoretical frequency dependences, calculated using the formulas (40), (44), and (46), for the three cases considered are displayed in Fig. 1 together with the corresponding experimental data from Refs. 23–27.

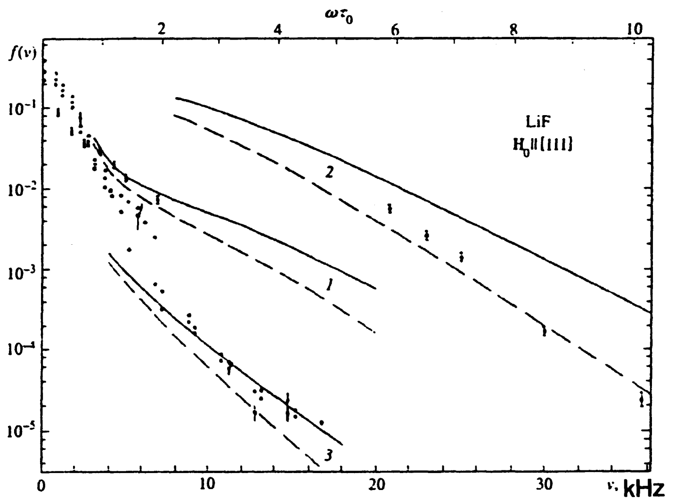


FIG. 1. Normalized shape functions of the frequency dependences of the cross-polarization rate of ^{6}Li nuclei (*1*), the three-spin cross-relaxation rate (*2*), and the spectrum of the autocorrelation function of ^{8}Li nuclei (*3*) in a LiF crystal with $\mathbf{H}_0$||[111]. The dots represent the experimental results of Refs. 24, 23, and 26, respectively. The solid lines represent the theoretical curves with $\tau_0=45$ μs and the dashed curves represent the theoretical curves for $\tau_0=55$ μs. The frequencies on the frequency scale at the top are multiples of τ_0^{-1} with $\tau_0=45$ μs.

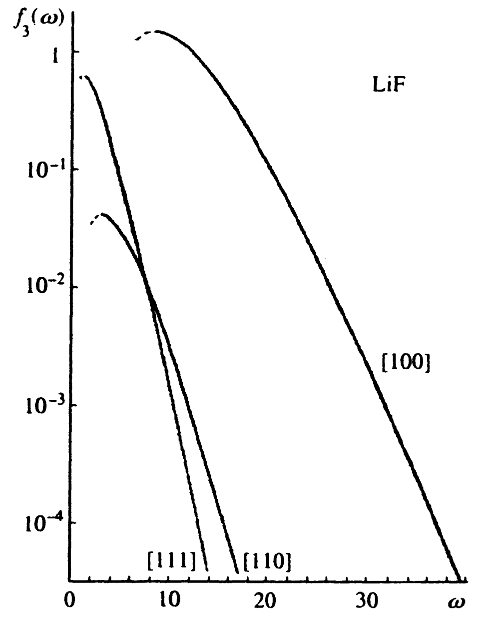


FIG. 2. Normalized shape function of the frequency dependence of three-spin cross-relaxation for a LiF crystal for three orientations of the field $\mathbf{H}_0$. The frequencies are multiples of $1/\tau_0$ with $\mathbf{H}_0$||[111].

The theory correctly conveys the relationship among the shape functions observed in the three different experiments. This also confirms the important result of the theory that the high-frequency asymptotic behavior is universal. According to this result, the rates of any cross-relaxation processes with large detunings and the wings of the spectra of other correlation functions, referring to different spins of the same spin system, have the same exponential factor, and the diversity of shapes is determined completely by the difference of the preexponential factors in Eq. (23). For $\beta=1$ the plot of $f(\omega)$ in semilogarithmic coordinates will be a straight line, for $\beta>1$ the plot bends and shifts upward relative to the straight line, and for $\beta<1$ it shifts downward, becoming, correspondingly, "Gaussian-like" or "Lorentz-like."

As another illustration of the role of the preexponential factor, the frequency dependences of three-spin cross-relaxation for three orientations of the magnetic field relative to the crystallographic axes, as calculated from the formula (23) with parameters (43) taken from Table II are displayed in Fig. 2. In contrast to Fig. 1, the exponentials for the curves in this figure have differing exponents. The ratio of the rates in the three orientations in Fig. 2 agree qualitatively with Pershan's experiment,[23] the strong bending of the [100] curve being explained by the high power of the frequency (ω^5) in the preexponential factor, which, in turn, was explained above by the change in the role played by the lithium nuclei in the spin dynamics.

In contrast to the last example, the frequency dependences of the cross-polarization rate of ^{43}Ca in the homonuclear system CaF$_2$ (Ref. 30) in the [110] and [111] orientations have the same form and differ only by the scale of the characteristic frequencies, which is determined by the change in M_2. The theory expounded above makes it possible to explain the large differences in the observed anisotropy in the two types of systems. In homonuclear systems, the exponents of the singularities of the ACFs and the relation $\tau_0^2 M_2$ for their coordinates remain the same when the crystal is rotated in a magnetic field, while in heteronuclear systems both the coordinate of the singularities $\tau_0^2 M_2$ of the AFC and the exponents of the singularities of the guided spins change when the ratio of the homo- and heteronuclear contributions to the dipole–dipole interaction changes. The exponents become fractional and can even change sign, as a result of which qualitative changes occur in the frequency dependences of the observed quantities.

As is evident in Fig. 1, there are quantitative discrepancies between theory and experiment. These discrepancies probably result not only from the fact that the real system is not big enough but also because the number of neighbors in it is limited. Estimates made in Ref. 33 for Bethe lattices showed that as the coordination number Z decreases, τ_0 will increase and the parameters β and C in Eq. (23) will also change. Increasing τ_0 from 45 μs to 55 μs indeed decreases the discrepancy observed in Fig. 1 in the case of three-spin cross-relaxation. The greatest difference in this case is determined, first, by the highest detunings and, second, by the fact that in an elementary event, the spin flip occurs in opposite directions. The form of the function $F_3(t)$ is therefore determined by the difference between the local fields, which decreases more rapidly with distance than the local field itself, which determines the form of the one-spin correlation functions in the other two cases.

Better agreement between the theoretical and experimental curves can be obtained by varying the parameters τ_0, β, and C. One can hope to obtain ultimately the true values of the parameters. In the present work we shall not do this, since, on the one hand, to extract reliable values of these parameters, experiments in which the spin-lattice relaxation times of the participating reservoirs are measured simultaneously must be performed. On the other hand, the integral equations (19)–(21) must be solved numerically to obtain not only the wings but also the central part of the shape function $f(\omega)$, since any deviations from the asymptotic behavior in the mathematical sense can be large, as, for example, in the cross-polarization experiments[24] (curve *1* in Fig. 1). We performed such a calculation for a homonuclear system[20], and the discrepancy between theory and experiment did indeed decrease. The correctness of the calculation of the central part of the shape function $f(\omega)$ from the formulas obtained above requires explanation. The point is that if the detunings are too small, the perturbation theory may no longer be applicable, and in deriving the equations for the correlation functions all parts of the Hamiltonian would have to be retained.[17,18] Such restrictions exist for the three-spin cross-relaxation in Fig. 1, whereas in the two other cases (curves *1* and *3*) the difference between the resonance frequencies of the main I and S spins remains constant and large, and the varying frequency refers to the ^{6}Li or ^{8}Li impurity spins, which act as probes of the $I-S$ system.

A theoretical interpretation has been given for each experimental curve presented in Fig. 1. Pershan[23] proposed that the shape function $f(\omega)$ is a Gaussian function and he described successfully the experimental field dependences in the [111] and [110] orientations but not the [100] orientation. To reproduce the latter field dependence, Grant[34] formed the convolution of a Gaussian curve with a broadening function of the interaction between the spins participating in an elementary cross-relaxation event. Both authors employed the second moment of the Gaussian function as an adjustable parameter. Stokes and Ailion[25] represented the function $f(\omega)$ as a sum of two exponential functions of the frequency from fluorine and lithium nuclei with theoretical second moments. Finally, Bulgakov *et al.*[27] successfully described the spectrum of the AFC of the ^{8}Li spin by means of the Anderson–Weiss formula[5] with the correlation function of the z component of the local field chosen on physical grounds.

Among other theoretical approaches to the calculation of cross-relaxation rates, we call attention to Refs. 17 and 18, where nonlinear integral equations of the type (17) are derived, but with a more complicated series for the memory function, since the authors retain the contributions with loops from the couplings and they also retain nonsecular terms in the Hamiltonian. Inclusion of the nonsecular parts is justified for small detunings, while for large detunings the result obtained is the same as with the perturbation theory (1)–(3). The authors do not use their complicated equations to calculate the correlation functions when finding the cross-relaxation rate, but rather they replace them with a Gaussian function.

The fundamental difference from our theory is that the results required to explain the experimental frequency dependences, both the frequency dependences considered above and any other, similar dependences, follow from the theory without any additional assumptions after restrictions on the motion of the interacting spins were imposed from the outset. The theory then makes it possible to understand better the dynamics of the spin system considered and to understand more clearly the meaning of some of the assumptions made in other works. First, it was shown that for a local Gaussian field in dense systems of interacting spins, the shape of the spectra of the correlation functions is not necessarily Gaussian, but rather the central part can be either narrow or broad, with the wings necessarily being exponential. Second, it is now understandable why Lorentzian correlation functions

$$F(t)=1/(1+t^2/\tau_c^2), \tag{47}$$

give a good description of experiments[11,25,30–32] in which exponential frequency dependences were observed, even though experimentally different dependences, most often exponential, are observed for long times.[35] The equations (17)–(21) lead to solutions with an exponential time dependence in the limit $t\to\infty$ on the real axis. On the imaginary axis this solution has singularities (22), which are symmetrically disposed with respect to the origin and whose sum can indeed give a Lorentzian function for the principal part in the special case $\beta=1$. To obtain exponential wings in the spectra, however, it is not at all necessary, as shown above, that this function have the same form over the entire complex-time plane. Third, the theory corrects the results of Ref. 25 for cross-polarization: it shows that instead of the sum of two exponentials with different exponents for lithium and fluorine nuclei, it is more accurate to use two terms in the preexponential factor (40).

In summary, a dynamical theory which makes it possible to calculate from a unified standpoint the detuning dependences of the rates of different cross-relaxation processes, as well as the spectra of other correlation functions in a heteronuclear spin system, has been constructed. For model infinite lattices the theory is strictly microscopic. For real systems it serves as an approximation of the self-consistent Gaussian fluctuating local field, and it has a number of advantages over existing theories for calculating the temporal correlation functions and primarily the far wings of their spectra, for which simple analytical expressions have been obtained. An important result of the theory is that the exponential cofactor in such expressions, which describe the frequency dependences of the rates of different cross-relaxation processes and the spectra of the correlation functions of different spins in a single system, is universal. This result agrees with experiment. The preexponential factor determines the observed diversity of the shapes. The form of the frequency dependence of this factor changes not only from process to process, but also when the crystal is rotated in a magnetic field.

APPENDIX A

In this appendix we estimate the lattice sum on a d-dimensional simple cubic lattice for a loop with m nodes

$$S_{dm}=\frac{1}{m}\sum_{i_1,i_2,\dots i_m} b_{i_1i_2}b_{i_2i_3}\dots b_{i_mi_1}, \tag{A1}$$

where N is the number of nodes and $b_{ii}=0$. Switching in Eq. (A1) to the reciprocal lattice vectors $\mathbf{k}$ we obtain

$$S_{dm}=\frac{1}{N}\sum_{\mathbf{k}}[b(\mathbf{k})]^m=(2\pi)^{-d}\int d\mathbf{k}[b(\mathbf{k})]^m, \tag{A2}$$

where

$$b(\mathbf{k})=\sum_j b_{ij}\exp[i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_j)],$$

$\mathbf{r}_i$ is the coordinate of the ith node, lengths are given as multiples of the lattice constant, and the integration extends over the volume of a d-dimensional hypercube with edge length 2π.

We consider two cases:

1) nearest-neighbor interaction

$$b(\mathbf{k})=2b\sum_{\alpha=1}^{d}\cos k_\alpha; \tag{A3}$$

2) same interaction inside a d-dimensional hypercube with edge $2r_0$ ($r_0 \gg 1$)

$$b(\mathbf{k})=2^d b\prod_{\alpha=1}^{d}\sin(k_\alpha r_0)/k_\alpha. \tag{A4}$$

In the first case we find for even m

$$S_{dm}=b^m\sum\frac{d(d-1)(d-2)\ldots\left(d-\sum p_q+1\right)m!}{p_1!p_2!\ldots p_l!(2!)^{2p_2}(3!)^{2p_3}\ldots(l!)^{2p_l}}, \tag{A5}$$

where the summation extends over all possible partitions of the integer $m=2\Sigma_{q=1}^{1}p_q q$ into p_1 pairs, p_2 quartets, and so on, under the constraint $\Sigma_q p_q \leqslant d$. The formula (A5) can be simplified in limiting cases:

$$S_{dm}\approx\begin{cases}b^m(Z/2)^{m/2}m!/(m/2)!, & d\gg m\\ b^m Z^m\{2d/[\pi(m+1)]\}^{d/2}, & d\ll m,\end{cases} \tag{A6}$$

where $Z=2d$.

In the second case we find

$$S_{dm}=Z^{m-1}b^m\left[\frac{2}{\pi}\int_0^{\pi r_0}(\sin x/x)^m dx\right], \tag{A7}$$

where now $Z=(2r_0)^d$. To high accuracy, the upper limit of the integral can be extended to infinity. Then

$$S_{d3}=Z^2b^3(3/4)^d,\quad S_{d4}=Z^3b^4(2/3)^d, \tag{A8}$$

and for $m \gg d$

$$S_{dm}\approx Z^{m-1}b^m[6/\pi(m+1)]^{d/2}. \tag{A9}$$

We note that in the real lattice sums appearing in the expression for the moment of order $2n$, the maximum value of m will be $m=n+1$, and some of the couplings b_{ij} in Eq. (A1) will be raised to the second power. For the types of distance dependences of b_{ij} which we have chosen, this leads only to b^m being replaced by $b^{2(m-1)}=b^{2n}$ in the coefficients of the formulas (A5)–(A9).

We now estimate the lattice sums without loops, i.e., sums for diagrams with a tree topology. For the $2n$th moment, trees with the maximum possible number of summations over the lattice indices have $n+1$ nodes connected by double bonds b_{ij}^2. In the leading order in the number of nearest neighbors such lattice sums can be expressed as

$$\left[\frac{1}{N}\sum_{i,j}b_{ij}^2\right]^n=Z^n b^{2n}.$$

Thus, in the limit $Z\to\infty$ the lattice sums for a loop equal $Z^{(n+1)/2}$ if the number of nearest neighbors increases as a result of the dimension of the space and Z^n if the number of nearest neighbors increases as a result of the interaction radius in a space of finite dimension, and in both cases sums without loops equal Z^n. Therefore, the lattice sums with loops are negligible in the case of the first method of increasing Z and they must be retained in the second method.

APPENDIX B

The kernel or the memory function of the integral equation (17) can be represented by a series[9]

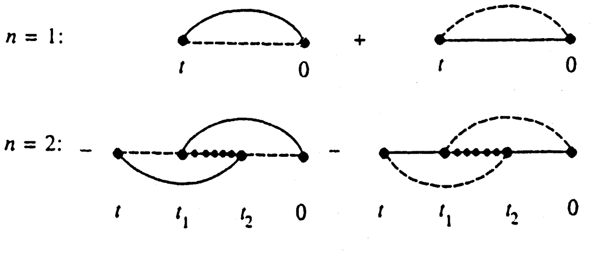
$$G_m(t)=\sum_{n=1}^{\infty}G_m^{(2n)}(t), \tag{B1}$$

where $G_m^{(2n)}(t)$ is a sum of integrals of the products of $(2n-1)$ autocorrelation functions $\Gamma_{m_l}(t)$ and n correlation functions $g_{m_k}(t)$ of the local Gaussian field (14) and (15) of the following form:

$$\int_0^t dt_1\int_0^{t_1}dt_2\ldots\int_0^{t_{2n-3}}dt_{2n-2}\prod_{l=0}^{2n-2}\Gamma_{m_l}$$

$$\times(t_l-t_{l+1})\prod_{k=1}^{n}g_{m_k}(t_{l_k}-t_{l'_k}). \tag{B2}$$

A separate term in the diagrammatic representation corresponds to an irreducible dressed skeleton diagram[16–18] with $2n$ vertices, and $G_m^{(2n)}(t)$ is the sum of all such diagrams. As an illustration, we present the diagrams for the first two terms of the series for $G_z(t)$:

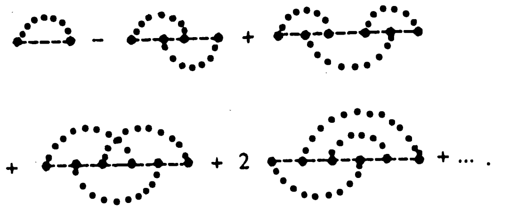


(B3)

The time variables appearing in the expression (B2) $t_0=t,t_1,t_2,\ldots,t_{2n-2},t_{2n-1}=0$ are arranged left to right along the $2n$ vertices of the corresponding diagram. Each segment between successive vertices t_l and t_{l+1} corresponds to a factor in the first product and each arc connecting the vertices t_{l_k} and $t_{l'_k}$ corresponds to a factor in the second product. The value of the indices m_l and m_k is determined by the form of the lines in the diagram: x for solid lines, y for dashed lines, and z for dot-dashed lines. The rules for constructing the diagrams and all diagrams with $n=3$ and $n=4$ were derived in Ref. 9. The diagrams for $G_x(t)$ and $G_y(t)$ are obtained from Eq. (B3) by cyclically permuting the indices x, y, and z of the lines.

We do not give the index for the type of nucleus (I, S, etc.). The result for nuclei of each type is obtained from the general formulas (B2) by substituting expressions for the correlation functions of the local field (14) and (15) corresponding to a given nucleus.

In a local Gaussian field, we retain only the z projection. In this case the first few diagrams of the diagrammatic series for the memory function $G_0(t)$ are as follows:



The solution of Eq. (17) with such a memory function will be the function $\Gamma_0(t)$. Laplace transforming Eqs. (17) for $\Gamma_x(t)$ and $\Gamma_0(t)$, we obtain the system of algebraic equations

$$s\Gamma_x(s)=1-G_x(s)\Gamma_x(s),$$

$$s\Gamma_0(s)=1-G_0(s)\Gamma_0(s),$$

where s is the Laplace transform variable. Dividing one equation by the other, we obtain

$$\Gamma_x(s)=\Gamma_0(s)-\Gamma_0(s)[G_x(s)-G_0(s)]\Gamma_x(s). \tag{B4}$$

Transforming Eq. (B4) back to the time domain, we obtain Eq. (18).

We note that the formal transformation, described above, remains valid for any other pair functions $\Gamma_0'(t)$ and $G_0'(t)$ satisfying Eq. (17). The desired form of Eq. (18) can be achieved by making appropriate choices of such functions.

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