

Dynamics of nuclear spins at high polarizations

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The equilibrium temporal spin autocorrelation and cross-correlation functions, which determine, for example, the rate of thermal mixing in a system of abundant and rare nuclear spins at high polarizations of the abundant spins, are calculated using the spin-wave approximation. The properties of the correlation functions obtained are studied. It is shown that the cross-correlation functions decay exponentially as the distance between the nuclei increases. The autocorrelation functions have an oscillatory character at low dipole temperatures. © 1995 American Institute of Physics.

1. INTRODUCTION

The study of the dynamics of nuclear spins in a solid diamagnetic insulator at high polarizations is of considerable interest owing to the development of dynamic nuclear polarization methods,^{1,2} which have made it possible to obtain values for the polarization of nuclear spins close to unity, as well as the very unusual behavior of spin systems at low temperatures observed in numerous experiments.¹ Among the most interesting phenomena observed in the system of nuclear spins in a solid insulator is the transition to a magnetically ordered state occurring when the nuclear subsystem is cooled to spin temperatures comparable to the strength of the internuclear dipole–dipole interactions.¹ Absolute temperatures matching the present record low, i.e., temperatures below 1 nK, have been successfully achieved in the nuclear spin systems of metals.³ Such experiments raise the question of devising an adequate theoretical description of spin dynamics at low temperatures.

Quantities measured at magnetic resonance are usually simply related to temporal spin correlation functions,⁴ but some correlation functions are measured directly with a high accuracy in experiments. For example, correlation functions can be measured down to amplitudes amounting to 10^{-5} of the initial amplitude using the NMR of β -active nuclei.⁵ The calculation of various correlators is thus a central problem in spin dynamics.

Practically all the work in this area has hitherto been restricted to the development of methods for calculating temporal correlation functions in the limiting case of infinitely high spin temperatures. The behavior of a spin system becomes significantly more complicated when the temperature is lowered. The dynamic correlations in the motion of the spins become stronger. Static correlations, which are responsible for transitions to various magnetically ordered states, also appear.¹ At the same time, if we restrict ourselves to the case of high nuclear polarizations alone, there is an approach which gives even a simpler description of the dynamics of systems than in the high-temperature case over the entire range of dipolar spin temperatures and makes it possible to directly calculate the temporal correlation functions. It is based on going over to the spin-wave formalism.^{6,7} The simplification attained here is associated with the diagonaliza-

tion of a large part of the Hamiltonian of the system achieved in the transition to spin waves or, after quantization, to magnons. This transition is analogous to the transition to phonons in the description of small vibrations of atoms in a solid. It reduces the study of the dynamics of a spin system to the study of the dynamics of a low-density magnon gas.

We shall consider a system of nuclear spins ($S=1/2$) which are located at the sites of a simple cubic lattice and are coupled by a dipole–dipole interaction. Thus, in a strong applied field H_0 directed along the z axis the Hamiltonian has the form

$$\mathcal{H} = -\omega_S \sum_I S_I^z + \mathcal{H}_{dz} = -\omega_S \sum_I S_I^z + \frac{1}{2} \sum_{I,I'} b_{II'} (3S_I^z S_{I'}^z - \mathbf{S}_I \mathbf{S}_{I'}), \quad (1)$$

where $\omega_S = \gamma_S H_0$, γ_S is the gyromagnetic ratio of the nuclei with a spin S , S_I^α is the α component of the nuclear spin at lattice site I ($\alpha = x, y, z$), \mathcal{H}_{dz} is the secular (with respect to the z axis) part of the dipole–dipole interactions, and $b_{II'}$ is the constant of that interaction for the spins located at lattice sites I and I' . The transition to the spin-wave formalism can be accomplished by replacing the spin operators S_I^z and $S_I^\pm = S_I^x \pm iS_I^y$ by the Bose creation and annihilation operators a_I^+ and a_I using the Dyson–Maleev transformation⁸

$$S_I^+ = a_I, \quad S_I^- = a_I^+ - a_I^+ a_I^+ a_I, \quad S_I^z = \frac{1}{2} - a_I^+ a_I \quad (2)$$

followed by the Fourier transform

$$a_k^+ = \frac{1}{\sqrt{N}} \sum_I a_I^+ \exp(-i\mathbf{kI}), \quad b_k = \sum_\delta b_\delta \exp(i\mathbf{k}\delta), \quad (3)$$

where $\delta = \mathbf{I} - \mathbf{I}'$ and N is the number of S spins. As a result, the Hamiltonian takes on the form^{6,7}

$$\mathcal{H} = \sum_k \epsilon_k a_k^+ a_k + \frac{1}{4N} \sum_{k,p,q} \Gamma_{k,p,q}^q a_{k-p}^+ a_{p+q}^+ a_k a_p, \quad (4)$$

the energy ϵ_k of a magnon with a momentum \mathbf{k} being given by the formula

$$\epsilon_k = \omega_S - b_0 - \frac{1}{2} b_k. \quad (5)$$

Henceforth the sample is assumed to be spherical, so that $b_0 = 0$. Each magnon carries a quantum of magnetization corresponding to the flipping of one spin in the sample. Thus, the polarization p is simply related to the overall magnon density:

$$1 - p = 2n/N, \quad (6)$$

where $n = \sum_k n_k = \sum_k \langle a_k^+ a_k \rangle$ is the total number of magnons.

The dynamics of nuclear spins at high polarizations is considered here in the example of the problem of the thermal mixing of rare nuclei of spin I interacting with a system of nuclei of spin S . On the one hand, this makes it possible to show how the correlation functions are related to the observable physical quantities and to discuss some general properties of the correlation functions. On the other hand, the problem of the thermal mixing of the abundant spins at high polarizations is of considerable interest. In fact, important information on the dynamics of nuclear spins in a solid can often be obtained by studying the NMR spectra of impurity nuclei, which are always present, as a rule, in crystals. These impurity nuclei essentially serve as natural probes, which monitor the processes occurring in the spin system of the host. The simplest example is provided by the ^{43}Ca nuclei (their natural abundance is 0.13%, and their spin $I = 7/2$) in a CaF_2 crystal. The observation of ^{43}Ca NMR makes it possible to obtain diverse information on the transition of the spins of the ^{19}F nuclei to an ordered state at a spin temperature of order $1 \mu\text{K}$ (Ref. 9) and on the nature of such ordering.^{1,9} The sensitivity problem is solved here by achieving a high polarization of the ^{43}Ca nuclei (up to 80%) through thermal contact between their effective Zeeman subsystem and the dipole-dipole reservoir of the fluorine nuclei.¹ The literature does not offer a theoretical investigation of the process of thermal mixing when the temperature of the reservoir of dipole-dipole interactions is low.

In the next section we obtain the kinetic equations for thermal mixing at low temperatures, which describe, in particular, the temporal evolution of the polarization of the rare spins using a quasithermodynamic approach.^{10,11} In the following sections of this paper we calculate (in the spin-wave approximation) the correlation functions appearing in these equations. The general properties of the correlation functions are also studied, and the relationship between the results obtained and the fluctuation-dissipation theorem is pointed out.

The approaches developed in this paper can also be applied to the study of the cross-relaxation,² cross-polarization,^{12,13} and spin-lattice relaxation of nuclear spins¹⁴ at low temperatures.

2. KINETIC EQUATIONS

Let us consider a system of nuclear spins in a solid consisting of abundant nuclei with a spin $S = 1/2$ and rare nuclei with an arbitrary spin I in a constant magnetic field $H_0 \parallel z$. Since the concentration of rare nuclei is assumed to be small, we can consider the interaction of one rare I nucleus with a system of abundant S nuclei. The Hamiltonian of such a problem has the form

$$\mathcal{H} = -\omega_S \sum_I S_I^z + \mathcal{H}_{dz} - \omega_I I^z + V_{IS}, \quad (7)$$

where $\omega_I = \gamma_I H_0$, γ_I is the gyromagnetic ratio of the I spins, \mathcal{H}_{dz} is the secular part of the dipole-dipole interaction of the S spins, which is defined by Eq. (1). The interaction V_{IS} between the S and I spins is assumed to be small. To consider the problem of the thermal mixing of the nuclear spins it is sufficient to restrict ourselves to the following expression for the Hamiltonian V_{IS}

$$V_{IS} = \sum_I (F_I S_I^z I^+ + F_I^* S_I^z I^-), \quad (8)$$

where F_I is the constant of the interaction of an I spin with an S spin at site I , and $I^\pm = I^x \pm iI^y$. The structure of the interaction (8) shows that fluctuations of the z component of the S spin due to its interaction with the environment cause flipping of the I spin. In other words, the relaxation rate of the z component of the I spin makes it possible to evaluate the intensity of the fluctuations of the z component of the S spins at the transition frequency ω_I .

After a time $\tau \approx [(1-p)\omega_{\text{loc}}]^{-1}$ ($\omega_{\text{loc}}^2 = \text{Tr } \mathcal{H}_{dz}^2 / \text{Tr } S_z^2$, and p is the polarization of the S spins) a quasiequilibrium state is established in the system, in which the density matrix ρ_0 has the form

$$\rho_0 = \frac{1}{Z} \exp \left\{ \beta_I \omega_I I^z + \beta_S \omega_S \sum_I S_I^z - \beta_d \mathcal{H}_{dz} \right\}, \quad (9)$$

where β_I^{-1} , β_S^{-1} , and β_d^{-1} are the values of the temperatures of the I and S spins and of the reservoir of dipole-dipole interactions of the S spins, and the statistical sum Z equals

$$Z = \text{Tr} \exp \left\{ \beta_I \omega_I I^z + \beta_S \omega_S \sum_I S_I^z - \beta_d \mathcal{H}_{dz} \right\}. \quad (10)$$

The kinetic equations for the temporal evolution of the mean values of the observable quantities at $t \gg \tau$ can be obtained by the standard method.¹¹ After performing two iterations of the equation for the density matrix in the representation of the interaction, we obtain, in particular, an equation for the evolution of the polarization of the rare spins:

$$\begin{aligned} \frac{d\langle I^z \rangle}{dt} = & -2\langle I^z \rangle \sum_{I,I'} F_I F_{I'}^* \int_{-\infty}^{\infty} e^{i\omega_I t} G_{II'}^+(t) dt \\ & - 2A \sum_{I,I'} F_I F_{I'}^* \int_{-\infty}^{\infty} e^{i\omega_I t} G_{II'}^-(t) dt, \end{aligned} \quad (11)$$

where

$$A = I(I+1) - \langle (I^z)^2 \rangle, \quad (12)$$

and the angle brackets denote the average at equilibrium: $\langle B \rangle \equiv \text{Tr}(\rho_0 B)$. The correlation functions $G_{II'}^\pm(t)$ are defined by the expression

$$G_{II'}^\pm(t) = \frac{1}{2} \langle S_I^z(0) S_{I'}^z(t) \pm S_{I'}^z(t) S_I^z(0) \rangle, \quad (13)$$

where

$$S_I^z(t) = e^{i\mathcal{H}_{dz} t} S_I^z e^{-i\mathcal{H}_{dz} t}. \quad (14)$$

It follows directly from the definition (13) that

$$G_{ll'}^+(t) = G_{ll'}^+(-t), \quad G_{ll'}^-(t) = -G_{ll'}^-(t). \quad (15)$$

Therefore, the cross-correlation functions $G_{ll'}^+(t)$ are real, and the $G_{ll'}^-(t)$ are imaginary functions of time. Equation (11) contains both an autocorrelation function and cross-correlation functions of the S spins. In the next section we shall see that the autocorrelation function plays a major role in the calculation of the rate of thermal mixing. In the limit $\beta_d \rightarrow 0$ the correlation functions $G_{ll'}^-(t)$ are equal to zero, and the second term in (11) vanishes. However, at finite dipolar temperatures just this term ensures a nonzero value for the equilibrium polarization of the I spins, which is obtained from (11) when $d\langle I^z \rangle / dt = 0$:

$$\langle I^z \rangle_{st} = -A \frac{\sum_{l,l'} F_l F_{l'}^* g_{ll'}^-(\omega_l)}{\sum_{l,l'} F_l F_{l'}^* g_{ll'}^+(\omega_l)}. \quad (16)$$

In (16) the spectral densities $g_{ll'}^\pm(\omega_l)$ of the correlation functions $G_{ll'}^\pm(t)$ are given by the formula

$$g_{ll'}^\pm(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} G_{ll'}^\pm(t) dt. \quad (17)$$

The relation (16) can be simplified significantly by introducing the eigenfunctions of the operator \mathcal{H}_{dz} and expressing the correlation functions appearing in (16) in terms of the sums of the matrix elements of the corresponding operators. Then going from summation to integration, after several transformations we can obtain

$$\langle I^z \rangle_{st} = A \tanh\left(\frac{1}{2} \beta_d \omega_l\right). \quad (18)$$

Comparing (16) and (18), we find

$$\frac{\sum_{l,l'} F_l F_{l'}^* g_{ll'}^-(\omega_l)}{\sum_{l,l'} F_l F_{l'}^* g_{ll'}^+(\omega_l)} = -\tanh\left(\frac{1}{2} \beta_d \omega_l\right). \quad (19)$$

Thus, there is a definite relationship between the correlation functions $g_{ll'}^-(\omega)$ and $g_{ll'}^+(\omega)$. It is a direct consequence of the fluctuation-dissipation theorem,^{15,16} which relates the imaginary part of the susceptibility (for the S spins) and the spectral density of the fluctuations.

Of course, the expression (18) for the equilibrium polarization must coincide with the ordinary thermodynamic mean

$$\langle I^z \rangle_{st} = \frac{\text{Tr}(I^z e^{\beta_d \omega_l I^z})}{(e^{\beta_d \omega_l I^z})}. \quad (20)$$

For a spin $I=1/2$ the identical nature of (18) and (20) is obvious, and this property is proved for an arbitrary spin in the appendix.

Equation (11) must be supplemented by an equation for the rate of variation of the dipolar energy of the abundant spins. It can be found from the conservation law of the total energy of the spins, which, with consideration of the maintenance of the polarization of the S spins with time in the problem under consideration, gives

$$\frac{d\langle \mathcal{H}_{dz} \rangle}{dt} = \omega_l N_l \frac{d\langle I^z \rangle}{dt}, \quad (21)$$

where N_l is the number of rare spins in the sample. The system of equations (11) and (21) completely describes the process of the thermal mixing of the rare spins with the dipolar subsystem of the abundant spins at low temperatures and generalizes Provotorov's approach^{10,11} to the case of arbitrary temperatures.

3. CALCULATION OF CORRELATION FUNCTIONS IN THE SPIN-WAVE APPROXIMATION

With the aid of (2) and (3) the spin operator S_l^z at the site l can be expressed in terms of the magnon creation and annihilation operators:

$$S_l^z = \frac{1}{2} - \alpha_l^+ \alpha_l = \frac{1}{2} - \frac{1}{N} \sum_{k,m} \alpha_k^+ \alpha_m \exp[-i(\mathbf{k}-\mathbf{m})l]. \quad (22)$$

Hence, after some elementary calculations we find that

$$G_{ll'}(t) = \langle S_l^z(t) S_{l'}^z(0) \rangle = \frac{p^2}{4} + \frac{1}{N^2} \sum_{k \neq m} \exp[i(\epsilon_k - \epsilon_m)t - i(\mathbf{k}-\mathbf{m})(l-l')] n_k (n_m + 1), \quad (23)$$

where the energy ϵ_k of a magnon is given by Eq. (5), and the equilibrium Planck distribution^{6,7} should be used for the occupation numbers of the magnon energy levels:

$$n_k = \frac{1}{e^{\beta_d(\epsilon_k - \mu)} - 1}. \quad (24)$$

Here the chemical potential μ plays the role of a second independent thermodynamic parameter. The presence of two independent parameters in the equilibrium distribution is due to the existence of two integrals of motion: the dipolar energy and the polarization or, in terms of magnons, the energy and the number of particles. At a given temperature the polarization (the total number of magnons) can be varied by varying the chemical potential μ . The correlation functions $G_{ll'}^\pm(t)$ are defined using (23) in the following manner:

$$G_{ll'}^+(t) = \frac{p^2}{4} + \frac{1}{N^2} \sum_{k \neq m} \cos[(\mathbf{k}-\mathbf{m})(l-l')] + (\epsilon_k - \epsilon_m)t] n_k (n_m + 1), \quad (25)$$

$$G_{ll'}^-(t) = -\frac{i}{N^2} \sum_{k \neq m} \sin[(\mathbf{k}-\mathbf{m})(l-l')] + (\epsilon_k - \epsilon_m)t] n_k (n_m + 1). \quad (26)$$

Below we shall assume that the deviation of the polarization from unity, which is equal to twice the magnon density [see (6)], is a small parameter, and we shall neglect the terms which are quadratic with respect to the number of magnons. In this approximation we can neglect the interactions between the magnons. The interactions result in scattering of the magnons by one another and a finite lifetime in one state $\tau^{-1} \approx (1-p)\omega_{loc}$. Therefore, the approach developed here makes it possible to calculate the correlation func-

tions only at times $t \ll \tau$. Nevertheless, it is obvious that diffusion-controlled transfer of the z component of the magnetization will occur at times $t \gg \tau$.

In experiments performed at a high polarization of the nuclear spins the temperature of the reservoir of dipole-dipole interactions can vary over a very broad range. The cases of high and low dipole temperatures will be considered below.

3.1. High dipole temperatures ($\beta_d \omega_{loc} \ll 1$)

Since ω_{loc} coincides in order of magnitude with the width of the magnon spectrum, at high dipolar temperatures ($\beta_d \omega_{loc} \ll 1$), as is seen from (24), all the occupation numbers of the magnon energy levels can be assumed to be identical: $n_k = n/N$. Neglecting the terms which are quadratic with respect to the number of magnons in Eqs. (25) and (26), we obtain

$$G_{ll'}^+(t) = G_{ll'}(t) = \frac{p^2}{4} + \frac{n}{N} |C_{ll'}(t)|^2, \quad (27)$$

$$G_{ll'}^-(t) = 0, \quad (28)$$

where

$$C_{ll'} = \frac{1}{N} \sum_{\mathbf{k}} \exp\{i[\epsilon_k t - \mathbf{k}(\mathbf{l} - \mathbf{l}')]\}. \quad (29)$$

In the high-temperature limit the correlation functions sought can be obtained using Eqs. (27)–(29).

The magnon spectrum ϵ_k has a complicated anisotropic character. Qualitatively, it can be treated as the sum of two contributions: a contribution from the nearest neighbors, which can be represented in the $\mathbf{H}_0 \parallel [001]$ orientation in the form⁶

$$\epsilon_k^0 = \frac{\gamma^2 \hbar}{2a^3} (2 \cos k_z a - \cos k_x a - \cos k_y a) \quad (30)$$

(a is the lattice constant), and a contribution from large distances, which produces a singularity in the spectrum when $\mathbf{k} \rightarrow 0$. This spectrum can be obtained with a high accuracy only by a numerical calculation using the algorithm proposed in Ref. 17. Nevertheless, the nearest-neighbor approximation (30) is a good approximation for the magnon spectrum for the $\mathbf{H}_0 \parallel [001]$ orientation.¹⁸ Since, as will be shown below, the correlation functions can be calculated analytically in this case, it would be expedient to use the simplified expression (30) for the spectrum in order to be able to study some general properties of the correlation functions.

Passing from summation to integration in (29), we obtain

$$C_{ll'}(t) = \frac{V}{N} \int \int \int_{-\pi/a}^{\pi/d} \frac{d^3 \mathbf{k}}{(2\pi)^3} \exp\{i[\epsilon_k t - \mathbf{k}(\mathbf{l} - \mathbf{l}')]\}. \quad (31)$$

Here V is the volume of the sample, and the integration is performed over the Brillouin zone. Next, it is convenient to move over to dimensionless variables which are such that $a = 1$. Now the vector $\mathbf{l} - \mathbf{l}'$ is a vector with integer compo-

nents. After replacing ϵ_k in (31) by ϵ_k^0 from (30) and using the known integral representation of Bessel functions,¹⁹ we obtain

$$C_{ll'}(t) = \exp\left[-i \frac{\pi}{2} \{(l-l')_x + (l-l')_y + (l-l')_z\}\right] \times J_{(l-l')_z}(2\alpha t) J_{(l-l')_x}(\alpha t) J_{(l-l')_y}(\alpha t), \quad (32)$$

where $\alpha = \gamma^2 \hbar / 2a^3$, the $(l-l')_{x,y,z}$ are the projections (which are also integers) of the internuclear vector $\mathbf{l} - \mathbf{l}'$, and $J_n(x)$ are Bessel functions of order n . Taking into account that $J_{-n}(x) = (-1)^n J_n(x)$ (Ref. 19), from (27) and (32) we obtain

$$G_{ll'}^+(t) = G_{ll'}(t) = \frac{p^2}{4} + \frac{n}{N} J_{(l-l')_z}^2(2\alpha t) J_{(l-l')_x}^2(\alpha t) J_{(l-l')_y}^2(\alpha t). \quad (33)$$

Since the asymptotes of the Bessel functions $J_\lambda(x)$ at large values of λ and fixed values of x have the form¹⁹

$$J_\lambda(x) \approx \frac{1}{2} \sqrt{\frac{2}{\pi}} \lambda^{-1/2} \exp\left(-\lambda \ln \frac{2\lambda}{x}\right), \quad (34)$$

the correlator $G_{ll'}^+(t)$ decays exponentially as the distance between the nuclei increases. A special role is played by the autocorrelation function $G_{ll}^+(t)$:

$$G_{ll}^+ = \frac{p^2}{4} + \frac{n}{N} J_0^2(2\alpha t) J_0^4(\alpha t). \quad (35)$$

We also point out that at large times the correlators oscillate with a small amplitude and decay according to a $(\alpha t)^{-3}$ law.

The total z component of the magnetization is an integral of motion. Therefore, it follows from (13) that in the limit of high dipole temperatures considered here the correlation functions must satisfy the condition $\sum_{l'} G_{ll'}^+(t) = \text{const}$. Taking into account the known property of Bessel functions $\sum_{n=-\infty}^{\infty} J_n^2(x) = 1$, we see that our calculated correlation functions (33) do, in fact, satisfy the condition of the conservation of the total z component of the magnetization.

It would also be of interest to compare the second moment of the correlation function of the z component of the electron spin calculated in Ref. 20 and the second moment of the correlation function (35). Expanding the Bessel function (35) into a series, we can easily see that these moments coincide, if the calculation of the lattice sum in Ref. 20 is restricted to nearest neighbors.

Figure 1 presents the correlators calculated from Eq. (33) for nuclear spins at neighboring lattice sites, as well as the autocorrelation function (35). It is seen from Fig. 1 that the correlations of the z components of spins positioned along the direction of the applied field \mathbf{H}_0 significantly surpass the analogous correlations of spins in a plane perpendicular to \mathbf{H}_0 . Figure 2 shows the spectral densities of these correlators.

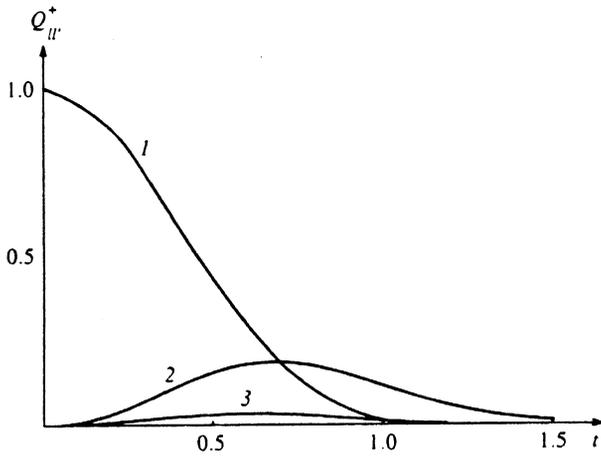


FIG. 1. Time dependence of the correlation functions $Q_{ll'}^+(t) = [2/(1-p)][G_{ll'}^+ - (p^2/4)]$ at high dipole temperatures. Curve 1 corresponds to $l=l'$, and the autocorrelation function $G_{ll'}^+(t)$ was calculated from Eq. (35). Curves 2 and 3 correspond to $l-l' = ae_z$ and $l-l' = ae_x$ (e_z and e_x are unit vectors along the z and x axes, and $x \perp z$). The correlation functions $G_{ll'}^+(t)$ were calculated from Eq. (33). The time t was made dimensionless by multiplication by the frequency α .

We stress that the nearest-neighbor approximation used in this section for the energy spectrum of magnons is not fundamental and can be discarded in numerical calculations of the correlation functions.

3.2. Low dipole temperatures ($\beta_d \omega_{loc} \gg 1$)

In the case of low dipole temperatures ($\beta_d \omega_{loc} \gg 1$), only energy levels near the bottom of the band are populated. Neglecting the terms which are quadratic in the magnon number in (23), we obtain the following expression for the correlator

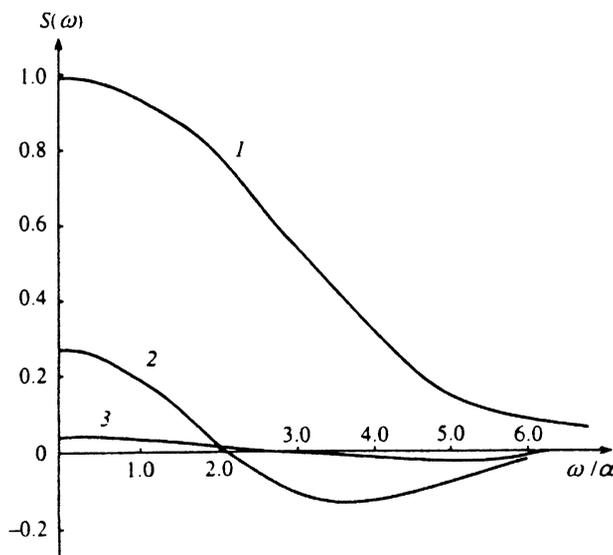


FIG. 2. Spectral densities of the correlators $S(\omega) = \int_{-\infty}^{\infty} e^{i\omega t/\alpha} Q_{ll'}^+(t) dt$ presented in Fig. 1. The numbers just above the curves correspond to the numbers in Fig. 1.

$$G_{ll'}(t) \equiv \langle S_l^z(t) S_{l'}^z(0) \rangle = \frac{p^2}{4} + C_{ll'}^*(t) B_{ll'}(t), \quad (36)$$

where $C_{ll'}(t)$ is defined in Eq. (29), and

$$B_{ll'}(t) = \frac{1}{N} \sum_{\mathbf{k}} \exp\{i[\epsilon_{\mathbf{k}} t - \mathbf{k} \cdot (\mathbf{l} - \mathbf{l}')]\} n_{\mathbf{k}}. \quad (37)$$

Near the minimum of the magnon spectrum, which is achieved in the $H_{011} \parallel [001]$ orientation at $\mathbf{k} = \mathbf{k}^* = (0, 0, \pi/a)$, the spectrum can be represented as¹⁸

$$\epsilon_{\mathbf{k}} = -2C_1 + C_1 A_1 (\delta \mathbf{k})^2 \alpha^2, \quad (38)$$

where $\delta \mathbf{k} = \mathbf{k} - \mathbf{k}^*$, $A_1 \approx 0.31$, and $C_1 = 1.211 \gamma^2 \hbar / a^3$. Now passing from summation to integration in (37), we obtain

$$B_{ll'}(t) = \frac{V}{4\pi^2 N} \exp[i\pi(l-l')_z] \times \int_0^\pi d\theta \sin\theta \int_0^\infty dk k^2 \times \frac{\exp\{i[(-2C_1 + C_1 A_1 k^2 a^2)t - k|\mathbf{l} - \mathbf{l}'| \cos\theta]\}}{\exp\{\beta_d[-2C_1 + C_1 A_1 k^2 a^2 - \mu]\} - 1} \quad (39)$$

for $\beta_d C_1 \gg 1$ we can utilize a known technique^{6,15,18} and rewrite (39) in the following manner

$$B_{ll'}(t) = \frac{V e^{i\pi(l-l')_z}}{4\pi^2 N} \sum_{m=1}^{\infty} \int_0^\pi d\theta \sin\theta \int_0^\infty dk k^2 \times \exp\{i[(-2C_1 + C_1 A_1 k^2 a^2)t - k|\mathbf{l} - \mathbf{l}'| \cos\theta] - m\beta_d C_1 A_1 k^2 a^2 + m\beta_d \bar{\mu}\}, \quad (40)$$

where $\bar{\mu} = \mu - 2C_1$ is the chemical potential calculated relative to the bottom of the band. After some simple transformations, from (40) we obtain

$$B_{ll'}(t) = \frac{\exp\{i\pi[(l-l')_z - 2C_1 t]\}}{8(\pi C_1 A_1)^{3/2}} \times \sum_{m=1}^{\infty} \frac{e^{m\beta_d \bar{\mu}}}{(m\beta_d - it)^{3/2}} \exp\left\{-\frac{|\mathbf{l} - \mathbf{l}'|^2}{4(m\beta_d - it)C_1 A_1}\right\}. \quad (41)$$

Equations (32), (36), and (41) make it possible to calculate the correlator $G_{ll'}(t)$, i.e., the correlation functions $G_{ll'}^\pm(t)$. The Gaussian decay $B_{ll'}(t)$ with the distance between the nuclei is, in fact, not so rapid, since we have $\beta_d C_1 \gg 1$ in (41).

Let us go into greater detail on the derivation of simpler formulas for the autocorrelation functions $G_{ll'}^\pm(t)$. Setting $l=l'$ in (41), we can easily find that

$$B_{ll}(t) = \frac{1}{8(\pi C_1 A_1)^{3/2}} \sum_{m=1}^{\infty} \frac{e^{m\beta_d \bar{\mu}}}{(m^2 \beta_d^2 + t^2)^{3/4}} \times \exp\left[i\left(\frac{3}{2}\phi_m - 2\pi C_1 t\right)\right], \quad (42)$$

where $\phi_m = \arctan(t/m\beta_d)$. Using Eqs. (13), (32), (36), and (42), we obtain

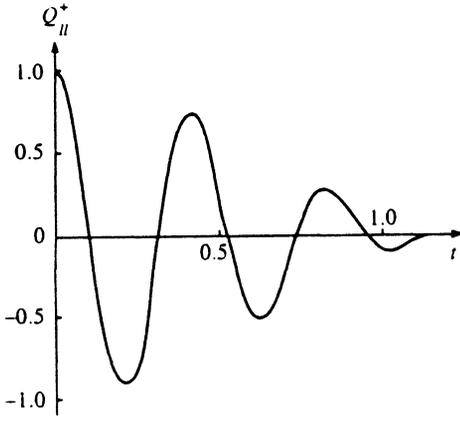


FIG. 3. Time dependence of the autocorrelation functions $Q_{II}^+(t) = [G_{II}^+(t) - p^2/4] / [G_{II}^+(0) - p^2/4]$ at low dipole temperatures. The autocorrelator $G_{II}^+(t)$ was calculated from Eq. (43); $\mu/\alpha = -0.05$, $\beta_d \alpha = 10$.

$$G_{II}^+(t) = \frac{p^2}{4} + \frac{J_0(2\alpha t)J_0^2(\alpha t)}{8(\pi C_1 A_1)^{3/2}} \sum_{m=1}^{\infty} \frac{e^{m\beta_d \bar{\mu}}}{(m^2 \beta_d^2 + t^2)^{3/4}} \times \cos\left(\frac{3\phi_m}{2} - 2\pi C_1 t\right), \quad (43)$$

$$G_{II}^-(t) = i \frac{J_0(2\alpha t)J_0^2(\alpha t)}{8(\pi C_1 A_1)^{3/2}} \sum_{m=1}^{\infty} \frac{e^{m\beta_d \bar{\mu}}}{(m^2 \beta_d^2 + t^2)^{3/4}} \times \sin\left(\frac{3\phi_m}{2} - 2\pi C_1 t\right). \quad (44)$$

The most effective method for obtaining low dipole temperatures is adiabatic demagnetization in the rotating frame (ADRF).¹ Here the initial state with high polarization is the high-temperature equilibrium state in the laboratory frame ($\bar{\mu} \approx -\omega_0$). After the rf field is turned on, the system tends to achieve equilibrium in the rotating frame, and the chemical potential $\bar{\mu}$ begins to increase, tending to the value $\bar{\mu} = 0$, which corresponds to the new equilibrium.¹⁸ When the value $\bar{\mu} = 0$ is achieved, the magnons in the system undergo Bose condensation,^{7,18,21,22} which results in a transition to a magnetically ordered state with a tilted magnetization and ordering of the transverse spin components. During further demagnetization, the spin temperature ceases to decrease, but the percentage of particles in the condensate increases. Thus, under the conditions of this experiment a spin system cooled to low dipole temperatures ($\beta_d \omega_{loc} \gg 1$) above the phase-transition point is characterized by a negative value of the chemical potential and $|\bar{\mu}| \ll \omega_{loc}$.

Figure 3 presents the autocorrelation function $G_{II}^+(t)$ calculated from Eq. (43). Note the oscillatory character of $G_{II}^+(t)$, which arises because the bulk of the magnons are located near the bottom of the energy spectrum at low dipole temperatures. This produces strong correlations in the motions of neighboring spins. Destructive interference, which results in the disappearance of beats at high temperatures, is practically absent here.

4. CONCLUSIONS

The theory developed in this paper, which is based on the use of the spin-wave approach, makes it possible to calculate spin auto- and cross-correlation functions and provides a detailed description of the spin dynamics at high values of the nuclear polarization. The problem of thermal mixing considered here can serve as a model example of the application of the quasithermodynamic approach at low temperatures. Cross relaxation, cross polarization, spin-lattice relaxation, and other problems concerning the thermal mixing of several subsystems can be treated in a similar manner.

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APPENDIX A:

Proving the identical nature of Eqs. (18) and (20) reduces to proving the identity

$$q(x) = \tanh\left(\frac{x}{2}\right) \frac{d^2 f(x)}{dx^2} + \frac{df(x)}{dx} - \tanh\left(\frac{x}{2}\right) I(I+1)f(x) = 0. \quad (A1)$$

Here we have written $x = \beta_d \omega_l$, $f(x) = \text{Tr}\{\exp(xI^z)\}$, and the definition (12) was taken into account in the derivation of (A1). The use of the familiar equation²³

$$I^2 = (I^z)^2 + I^z + I^- I^+ \quad (A2)$$

reduces (A1) for $q(x)$ to

$$q(x) = \left(1 - \tanh\frac{x}{2}\right) \text{Tr}\{I^z e^{xI^z}\} - \tanh\frac{x}{2} \text{Tr}\{I^- I^+ e^{xI^z}\}. \quad (A3)$$

Now, using the formulas²³ for the matrix elements of the operators I^\pm

$$\langle M | I^+ | M-1 \rangle = \langle M-1 | I^- | M \rangle = \sqrt{(I+M)(I-M+1)}, \quad (A4)$$

we obtain

$$q(x) = \frac{2e^{-x/2}}{e^{x/2} + e^{-x/2}} \text{Tr}\{I^z e^{xI^z}\} - \frac{1}{e^{x/2} + e^{-x/2}} \times \left\{ \sum_{M=-I}^I e^{x(M+1/2)} \langle M | I^- | M+1 \rangle \langle M+1 | I^+ | M \rangle - \sum_{M=-I}^I e^{x(M-1/2)} \langle M | I^- | M+1 \rangle \times \langle M+1 | I^+ | M \rangle \right\}. \quad (A5)$$

In the first sum on the right-hand side of (A5) we replace M by $M-1$. Using (A4) we now have

$$q(x) = \frac{2e^{-x/2}}{e^{x/2} + e^{-x/2}} \text{Tr}\{I^z e^{xI^z}\} - \frac{1}{e^{x/2} + e^{-x/2}} \left\{ \sum_{M=-I+1}^{I+1} e^{x(M-1/2)} (I+M)(I-M+1) \right\}$$

$$\begin{aligned}
& - \sum_{M=-I}^I e^{x(M-1/2)}(I+M+1)(I-M) \Big\} \\
& = \frac{2e^{-x/2}}{e^{x/2} + e^{-x/2}} \text{Tr}\{I^z e^{xI^z}\} - \frac{2e^{-x/2}}{e^{x/2} + e^{-x/2}} \sum_{M=-I}^I M e^{xM} = 0.
\end{aligned}
\tag{A6}$$

Thus, Eqs. (18) and (20) lead to identical values for the polarization of the rare nuclei.

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