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Stochastic theory of spin-phonon relaxation*

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Spin-phonon relaxation is interpreted as a quantum stochastic process. Time-dependent magnetization correlation functions are written in general exponential form, and the phase-modulation terms occurring in them are evaluated approximately to second order with respect to the coupling parameter. The spin-phonon interaction is described by the isotropic model of Huber and Van Vleck. A physical parameter corresponding to an effective Larmor precession frequency is introduced and determined from the zero-frequency longitudinal susceptibility, which is made consistent with the thermodynamic derivative of the magnetization. Longitudinal and transverse dynamic susceptibilities are calculated for all frequencies. At low frequencies they agree with the usual Lorentzian model as expected from the asymptotic exponential decay of the correlation functions. The high-frequency spectra differ from the Lorentzian form and contain information on the short-time history of spin-phonon collisions.

I. INTRODUCTION

The theory of spin-lattice relaxation dates back to the work of Waller.[1] In subsequent refinements of the theory and their applications, considerable interest has been focused on the calculation of spin-lattice relaxation rates for specific cases of crystal symmetry and coupling mechanism,[2,3] assuming a simple exponential decay of the magnetization with the time to follow any change of the external magnetic field. The dynamic frequency response of the system would thus be characterized by a simple Lorentzian shape, and has in fact been observed in this form in many experiments.[4] However, it has also become clear that deviations from this simple relaxation behavior could exist in certain ranges of frequency and temperature.[5] Namely, the assumption of an exponentially decaying magnetization is meaningful only on a time scale embracing several elementary processes responsible for the relaxation; furthermore, a thermodynamic quasiequilibrium should be maintained during each process. Hence, at high enough frequencies or at low temperatures the dynamic response may exhibit a more complicated behavior, which one would like to predict from a microscopic model for the spin-lattice interaction.

Historically, two contrasting philosophies for systematically developing approximations to the dynamics have been formulated: In the first of these, the emphasis is on the equations of motion for the response functions in the frequency domain; in the second—of which the "stochastic" method is an example—the relaxation is naturally associated with the time evolution of the spin correlation functions. In the present work we use the simple example of linear spin-phonon interaction to compare these ideas. We have several objectives: (a) to develop a stochastic approach and find a physical interpretation for the various steps in the approximation; (b) to present results for the relaxation spectra and understand their dependence on frequency and coupling parameter; (c) to review the general methodological background for perspective.

In the system considered, the relaxation consists of a sequence of processes in which the magnetic energy of the spin is exchanged for a single quantum of normal vibrations of the lattice. The basic physical idea of the stochastic theory is that this relaxation mechanism can be interpreted as a series of random collisions between the spin and a gas of phonons. Unlike classical particles, both phonons and spins behave as quantum excitations with characteristic dynamic and statistical features, which is reflected in the analytic properties of the time-dependent spin correlation functions. For example, in a collision a phonon can either be annihilated or created; the second event is simply viewed as the time-inverted version of the first. Not surprisingly we find that only for asymptotically large times does the dynamic response decay approximately with a constant rate; at intermediate and short times its behavior is determined by the detailed time dependence of the spin-phonon scattering operator.

Our approach is formally related to the stochastic theory of line shape and relaxation by Kubo,[6–8] but in a formulation which makes it possible to solve the interacting spin-phonon model in considerable detail, including a discussion of the state properties.

The response-function (frequency-domain) methods have been discussed previously[5,9,10]; here we will only mention some aspects of the memory-function approach to provide a contrasting example to the stochastic theory. This will be done in Sec. II where we first present the model, and later a preview of the stochastic method. In Sec. III we derive a formal perturbation expansion for the correlation functions. Section IV contains the details of this expansion for the correlation functions appropriate to the longitudinal and transverse susceptibilities. The derivation of the results for the dynamic and static susceptibilities is given in Sec. V. A discussion of these results follows in Sec. VI.

II. GENERAL BACKGROUND

A. Model of Huber and Van Vleck

The physical system which we consider consists of a pair of Zeeman levels of a paramagnetic ion in an insulator. The Hamiltonian is written

$$H=H_0+V, \tag{1}$$

where H_0 contains the lattice Hamiltonian and the Zeeman energy of the spin $\vec{S}$:

$$H_0=\sum_{\vec{k}p}\omega(\vec{k}p)\,(a^\dagger_{\vec{k}p}a_{\vec{k}p}+\tfrac{1}{2})+\omega_0 S_z. \tag{2}$$

We use $\hbar=1$ throughout this paper. In (2), $\omega(\vec{k}p)$ is the frequency of the lattice wave with wave vector $\vec{k}$ and polarization p, and $a^\dagger_{\vec{k}p}$, $a_{\vec{k}p}$ represent the phonon creation and annihilation operators, respectively, for this mode. ω_0 is the Larmor frequency due to a static external field $\mathcal{H}_z$. For a doublet with spin $S=\frac{1}{2}$ this means $\omega_0=g\mu_B\mathcal{H}_z$. We will consider the case of a spin $S=1$ for which the two levels $M_S=\pm 1$ can be described by a fictitious spin $S=\frac{1}{2}$ and hence $\omega_0=2g\mu_B\mathcal{H}_z$. We ignore all other magnetic levels of the system. For the spin-phonon coupling we choose the model of Huber and Van Vleck[5]:

$$V=\sum_{\vec{k}p}[A_x(\vec{k}p)S_x+A_y(\vec{k}p)S_y+A_z(\vec{k}p)S_z]\times(a^\dagger_{\vec{k}p}+a_{-\vec{k}p}), \tag{3}$$

Where $A_\mu(\vec{k}p)$ ($\mu=x,y,z$) is the coupling constant between S_μ and a phonon of the mode $\vec{k}p$. This expression is still perfectly general and can be applied to any practical situation with a suitable choice for the $\vec{k}p$ dependence of each of the components $A_\mu(\vec{k}p)$. However, as shown in Ref. 5, it is advantageous to study an idealized isotropic coupling case where all components $A_\mu(\vec{k}p)$ are independent of μ and p and equal to a single constant $A_{\vec{k}}$. Thus we will write

$$V=\sum_{\vec{k}p}A_{\vec{k}}[S_xe_x(\vec{k}p)+S_ye_y(\vec{k}p)+S_ze_z(\vec{k}p)]\times(a^\dagger_{\vec{k}p}+a_{-\vec{k}p}), \tag{4}$$

where $e_\mu(\vec{k}p)$ are the components of the phonon polarization vector. Since V must be Hermitian we shall assume that $A_{-\vec{k}}=A^*_{\vec{k}}$ and $\vec{e}(-\vec{k}p)=\vec{e}(\vec{k}p)^*$. The polarization vectors satisfy the orthogonality relation[5]

$$\sum_p e_\mu(\vec{k}p)e_\nu(\vec{k}p)^*=\delta_{\mu\nu}. \tag{5}$$

For the frequency dependence of $A_{\vec{k}}$ we will use the form corresponding to the so-called non-Kramers case[2]

$$A_{\vec{k}}=\frac{1}{4}\left(\pi\frac{\eta\omega_{\vec{k}}}{N\omega_m}\right)^{1/2}e^{-i\vec{k}\cdot\vec{r}}, \tag{6}$$

where η is a dimensionless coupling parameter, N is the number of unit cells, ω_m is the maximum phonon frequency, and $\vec{r}$ is the position of the spin. We also assume that the phonon spectrum is isotropic and independent of p.[5] For the density of phonon states in a single branch we will use the expression[9,10]

$$D(\omega_{\vec{k}})=(16N/\pi\omega_m)(\omega_{\vec{k}}/\omega_m)^2[1-(\omega_{\vec{k}}/\omega_m)^2]^{1/2}, \tag{7}$$

where $\omega_{\vec{k}}$ from now on replaces $\omega(\vec{k}p)$. For $\omega_{\vec{k}}\ll\omega_m$ the spectrum (7) corresponds to the Debye approximation but contains a Van Hove-type singularity at $\omega_{\vec{k}}=\omega_m$.

We will learn later through specific examples how the isotropic model simplifies the discussion of the stochastic method and, in fact, of any other method.[5,10] This happens, however, at the expense of a considerable loss of generality. The extension of the stochastic method to anisotropically coupled systems falls beyond our present scope and will not be pursued here.

B. Response functions

Formally, all relevant information on the dynamics of the system is contained in a set of correlation functions defined in terms of the Hamiltonian of the system H. For a pair of dynamical variables A, B the correlation function is written as

$$C_{AB}(t)=\mathrm{Tr}(B\rho e^{iLt}A)=\langle A(t)B(0)\rangle, \tag{8}$$

where ρ is the canonical density matrix operator,

$$\rho=e^{-\beta H}/\mathrm{Tr}(e^{-\beta H}),\quad \beta\equiv 1/k_BT, \tag{9}$$

and L is the quantum Liouville operator acting on all operators standing to its right according to

$$LA=[H,A];\quad e^{iLt}A=e^{iHt}A\,e^{-iHt}\equiv A(t). \tag{10}$$

The last expression in (8) is the more familiar form for the correlation function.

The dynamical variables A, B are chosen such that their thermodynamic averages are zero: $\langle A\rangle=\langle B\rangle=0$. For a given operator A_1 with $\langle A_1\rangle\neq 0$, the corresponding dynamical variable A becomes $A=A_1-\langle A_1\rangle$. Thus, in our case, we will be dealing with variables related to the spin operators in the following way:

$$A = S_\mu - \langle S_\mu \rangle, \;\; B = S_\nu^\dagger - \langle S_\nu^\dagger \rangle \;\; (\mu, \nu = x, y, z), \tag{11}$$

where the components S_μ obey the commutation relations $[S_x, S_y] = iS_z$, etc.

The Fourier spectrum of $C_{AB}(t)$ is related to the generalized frequency response of the variable A to a periodic disturbance of frequency ω which couples to B,[11]

$$\chi_{AB}(\omega) = \lim_{\epsilon \to 0} i \int_0^\infty dt\, e^{i\omega t - \epsilon t}[\, C_{AB}(t) - C_{BA}(-t)] \;. \tag{12}$$

The zero-frequency response is equal to the isothermal static susceptibility χ_{AB} (we consider ergodic systems):

$$\chi_{AB}(0) = \chi_{AB} \equiv \int_0^\beta d\lambda\, C_{BA}(-i\lambda) \;, \tag{13}$$

where $C_{BA}(-i\lambda) = \mathrm{Tr}(A\rho e^{\lambda L} B$. In order for (13) to be valid, the function $C_{AB}(t)$ must be analytic for complex times t in the region $0 \le |\mathrm{Im} t| \le \beta$, and must vanish at $|t| \to \infty$. The function $C_{BA}(-t)$ in (12) can then be obtained from the relationship

$$C_{BA}(-t) = C_{AB}(t - i\beta), \tag{14}$$

which follows from the definitions (8) and (9).

Another quantity which can be used in the description of the dynamics of the system is the relaxation function

$$\Phi_{AB}(t) = \int_0^\beta d\lambda \, \langle B(-i\lambda) A(t) \rangle$$
$$= \int_0^\beta d\lambda\, C_{BA}(-t - i\lambda), \tag{15}$$

which is related to the correlation function $C_{AB}(t)$ through Eq. (14) and the last integral of (15). Note that $\Phi_{AB}(0) = \chi_{AB}$. Also,

$$\dot{\Phi}_{AB}(t) = i[\, C_{AB}(t) - C_{BA}(-t)] \;.$$

Thus the dynamic susceptibility can be obtained from $\Phi_{AB}(t)$ by the relation[11]

$$\chi_{AB}(\omega) = \chi_{AB} + i\omega \int_0^\infty dt\, e^{i\omega t}\, \Phi_{AB}(t) \;. \tag{16}$$

C. Stochastic method

The correlation and relaxation functions have their exact definitions in Eqs. (8) and (15), respectively, which relate the microscopic variables of the system to the observed dynamic response. These formal relations are of little help, however, when we attempt to calculate the functions. With very few exceptions, the calculation can only be carried out by using an approximate method. In general, the understanding of the physical processes responsible for the dynamic behavior provides a valid starting point for the selection of a suitable approximation scheme.

In the stochastic method we draw the parallel between the spin-phonon relaxation and the collision broadening of atomic lines in a gas.[12,13] This analogy can be illustrated by considering the characteristic form of the differential equation satisfied by the correlation functions. In the isotropic coupling case, and for a special choice of the variables A, B whose unperturbed motion is simply harmonic, the time derivative of the correlation function $C_{AB}(t)$ is proportional to the value of the function at that particular time, that is,

$$\dot{C}_{AB}(t) \equiv \frac{d}{dt} C_{AB}(t) = -[\, i\Omega_{AB} - \dot{f}_{AB}(t)] C_{AB}(t), \tag{17}$$

where Ω_{AB} is an effective Larmor frequency for the precession of the variables A or B in the coupled system, and $f_{AB}(t)$ represents a complex phase-modulation function. The analytic properties of $C_{AB}(t)$ discussed above and Eq. (14) provide the criteria that the function $f_{AB}(t)$ has to satisfy.

Note that the values of $C_{AB}(t)$ at times earlier than t do not enter Eq. (17) explicitly. This general form of the equation of motion is characteristic of a stochastic theory; it should be emphasized, however, that in a stochastic theory the function $\dot{f}_{AB}(t)$ usually represents a random process which is independent of any events that took place at times $t' < t$. In our model, on the contrary, the exact $\dot{f}_{AB}(t)$ as defined later may formally contain some information on the past history of the system. However, the approximation scheme used in evaluating $f_{AB}(t)$ suggests an interpretation in terms of random collisions between an isolated spin and phonons, thus providing the essential element of a stochastic method. We expect this interpretation to be justified at higher temperatures where many of the eigenstates of the system are occupied and for weak spin-lattice coupling. If the coupling is strong, or if the temperature is low, memory effects may play a major role in determining the behavior of $f_{AB}(t)$, and hence $C_{AB}(t)$.

D. Alternative approaches

It is instructive to compare the stochastic method with an alternative approach which uses the memory-function formalism. The latter method is based on the relaxation function (15).[11,14] For a pair of variables A and $B = A^+$, and for an isotropic coupling the relaxation function can be shown to satisfy an integro-differential equation of the form

$$\dot{\Phi}_{AB}(t) + i w_{AB} \Phi_{AB}(t) - i \int_0^t dt'\, M_{AB}(t - t') \Phi_{AB}(t') = 0. \tag{18}$$

Here, w_{AB} is a Larmor frequency (not necessarily equal to Ω_{AB}). The memory kernel $M_{AB}(t-t')$ connects the time derivative of the relaxation function with its values at earlier times t'. A formal expression for $M_{AB}(t-t')$ can be obtained by the technique of Mori.[14,15] If $B \neq A^+$, or when the system is described by many variables $A_1, \ldots A_n$, Eq. (18) must be written in a more general form of a matrix equation.[15]

The contrast between Eq. (18) and the equivalent equation for $C_{AB}(t)$, Eq. (17), is obvious. The basic assumption in theories based on the relaxation function is that the memory function $M_{AB}(t)$ has a simpler behavior as a function of time (or frequency) and coupling parameter than the dynamic susceptibility, and is therefore more easily accessible by various approximations.[16-18] An analogous assumption will be made in the stochastic approach for the phase function $f_{AB}(t)$. Practically every problem can be formulated both ways, and $f_{AB}(t)$ can be obtained from $M_{AB}(t)$ and vice versa. Thus the distinction between the two approaches may seem artificial, which would indeed be true if one could carry out both exactly. However, if we start from two independent approximation schemes, one for $f_{AB}(t)$ and another for $M_{AB}(t)$, we will obtain two different results for $\chi_{AB}(\omega)$. The selection must be made on physical basis, that is, we keep the result which gives a better description of the properties of the system as needed.

When Fourier transformed, Eq. (18) is factorized and thus leads to a particularly simple relation between $\chi_{AB}(\omega)$ and $M_{AB}(\omega)$, namely,

$$\chi_{AB}(\omega) = \chi_{AB} \frac{M_{AB}(\omega) - \omega_{AB}}{\omega + M_{AB}(\omega) - w_{AB}} , \tag{19}$$

as follows from (16). In the stochastic approach, the factorization occurs in the time domain, and the Fourier transform needed in Eq. (12) has to be found numerically.

Several other methods can be used to calculate $\chi_{AB}(\omega)$. The Green's-function decoupling method gives results which are formally similar to Eq. (19).[5,10] Recently, some problems associated with that method and with the memory-function approach have been discussed for a much simpler spin-phonon coupling with only one nonzero component $A_\mu(\vec{k}p)$ in (3) and no static field, in which case the exact $\chi_{AB}(\omega)$ is also known.[9] There, approximate methods were found to be applicable in the weak coupling case only, and in a limited range of frequencies. It should be mentioned, however, that the stochastic method is identical with the exact solution in that particular case. These facts together with preliminary results for the present model[10] have prompted a more detailed study of spin-phonon relaxation, which is presented here.

III. FORMAL TREATMENT

In the following we will discuss a comulant expansion for the correlation function (8). Our approach is similar to that of Kubo.[6-8]

We need an interaction representation for the time evolution of the operator A in Eq. (8). For this purpose we will treat the first term of the Hamiltonian (1) as the unperturbed Hamiltonian H_0, and the rest as a perturbation V. In the absence of collisions the motion of A is determined by the unperturbed Liouville operator L_0,

$$e^{iL_0 t} A = e^{iH_0 t} A e^{-iH_0 t} \equiv A(t)_0 . \tag{20}$$

The complete time dependence of A can then be expressed as

$$A(t) = U(t) A(t)_0, \quad U(t) = e^{iLt} e^{-iL_0 t} \tag{21}$$

introducing a "scattering" operator $U(t)$ which satisfies the equation of motion[12]

$$\dot{U}(t) = iU(t)\tilde{W}(t), \quad U(0) = 1 \tag{22}$$

where

$$\tilde{W}(t) = e^{iL_0 t} W e^{-iL_0 t}; \quad W \equiv L - L_0 . \tag{23}$$

The Liouville perturbation W is simply related to V according to $WA = [(H - H_0), A] = [V, A]$.

Integrating Eq. (22) and substituting the result into (21) finally leads to the following expression for the correlation function (8)[6,12]:

$$C_{AB}(t) = \mathrm{Tr}\left[B\rho T^+ \exp\left(i \int_0^t \tilde{W}(t')\, dt' \right) e^{iL_0 t} A \right] . \tag{24}$$

The symbol T^+ stands for a time-ordering operator which arranges a product of operators $\tilde{W}(t')$ in such a way that their arguments increase from left to right.

Equation (24) can be further rewritten by introducing a generalized time-dependent average of an operator R as follows:

$$\langle\langle R \rangle\rangle_{AB} = \frac{\mathrm{Tr}(B\rho R e^{iL_0 t} A)}{\mathrm{Tr}(B\rho e^{iL_0 t} A)} . \tag{25}$$

This average is linear and properly normalized since $\langle\langle 1 \rangle\rangle_{AB} = 1$. The denominator of (25) is the correlation function (24) with an unperturbed time dependence for which we introduce a new symbol

$$K_{AB}(t) \equiv \mathrm{Tr}(B\rho\, e^{iL_0 t} A) = \langle A(t)_0 B \rangle . \tag{26}$$

It should be noted that the thermal average in (26) is still defined with respect to the total Hamiltonian (1).

Using (25) and (26) we can write (24) as

$$C_{AB}(t) = K_{AB}(t) \left\langle \left\langle T^+ \exp\left(i \int_0^t \tilde{W}(t')\, dt' \right) \right\rangle \right\rangle_{AB} , \tag{27}$$

and then transform the average into a cumulant average in the exponent.[6] The function (24) thus appears in the general form

$$C_{AB}(t)=K_{AB}(t)\,e^{g_{AB}(t)}, \tag{28}$$

where

$$g_{AB}(t)\equiv\left\langle\left\langle\left[T^{+}\exp\left(i\int_0^t \tilde{W}(t')\,dt'\right)-1\right]\right\rangle\right\rangle^{c}_{AB}, \tag{29}$$

and the superscript c refers to the fact that the average must be interpreted as a cumulant expansion. The first few terms of this expansion are

$$g_{AB}(t)=i\int_0^t dt_1\langle\langle\tilde{W}(t_1)\rangle\rangle_{AB}-\int_0^t dt_2\int_0^t dt_1\,\langle\langle\tilde{W}(t_1)\,\tilde{W}(t_2)\rangle\rangle_{AB}+\frac{1}{2}\left(\left\langle\left\langle\int_0^t dt_1\,\tilde{W}(t_1)\right\rangle\right\rangle_{AB}\right)^2+\cdots. \tag{30}$$

The averages in (30) can in principle be evaluated for any given system, however, they can be very complicated due to the fact that they contain the full statistical operator ρ of Eq. (9).

The usefulness of the above procedure depends on the properties of the function $g_{AB}(t)$. In particular, it has to be a well-behaved function of time and of the interaction Hamiltonian V in order to be calculable by some approximation from (30). Furthermore, the formulation outlined above will be meaningful only when the function $K_{AB}(t)$ is diagonal in the space of variables A and B needed to fully describe the dynamics of the system. In our case, this requirement is satisfied thanks to the isotropic model for the spin-phonon coupling. Namely, we can choose the variables in such a way that their unperturbed motion is purely harmonic,

$$A(t)_0=A\,e^{-i\omega_A t}, \tag{31}$$

where ω_A is the unperturbed Larmor frequency. The variables associated with the spin operators S_-, S_+, S_z introduced later will indeed have this property. If this were not the case, the functions $K_{AB}(t)$, $C_{AB}(t)$, and $g_{AB}(t)$ would become matrices in the space of variables A, B and would be interrelated by a complicated matrix equation analogous to Eq. (28).

Because of (31) and the conditions just mentioned, our discussion is limited to the case where each correlation function contains only one resonance, even though the whole system may still contain several resonances.

The correlation function (28) now has the form

$$C_{AB}(t)=\langle AB\rangle\,e^{-i\omega_A t+g_{AB}(t)}. \tag{32}$$

In general, the time dependence of $g_{AB}(t)$ must be such as to ensure the decay of $C_{AB}(t)$ at large times as required by Eq. (12). However, as $t\to\infty$, $g_{AB}(t)$ may also contain an imaginary term that goes linearly with time. Its rate of change,

$$\gamma_{AB}=\operatorname{Im}\lim_{\epsilon\to 0}\epsilon\int_0^\infty dt\,e^{-\epsilon t}\,\mathring{g}_{AB}(t), \tag{33}$$

represents a shift of the Larmor frequency due to the interaction. Introducing further

$$\Omega_{AB}\equiv\omega_A-\gamma_{AB}, \tag{34}$$

as an effective Larmor frequency, and

$$f_{AB}(t)\equiv g_{AB}(t)-i\gamma_{AB}t, \tag{35}$$

we can thus write

$$C_{AB}(t)=\langle AB\rangle\,e^{-i\Omega_{AB}t+f_{AB}(t)}. \tag{36}$$

Differentiating (36) with respect to the time yields Eq (17). Thus the cumulant-expansion method provides the machinery to calculate the terms appearing in the stochastic equation of motion.

The complex phase-modulation function $f_{AB}(t)$ in (36) is responsible for the analytic behavior of $C_{AB}(t)$. In particular, we see from (36) that $f_{AB}(0)=0$, while the real part of $f_{AB}(t)$ for $|t|\to\pm\infty$ should be large and negative, for example, $\operatorname{Re}f_{AB}(t)\sim-|t|^{\alpha}$, $\alpha>0$.

For $B=A^{+}$ the imaginary part of the susceptibility (12) must have the property $\chi''_{AB}(\omega)/\omega>0$.[15] It can be shown that $g_{AB}(\omega)>0$ guarantees this inequality, where $g_{AB}(\omega)$ is the Fourier transform of $g_{AB}(t)$ from Eq. (32).

We now examine the perturbation expansion of $f_{AB}(t)$ in powers of V. The question is under what conditions can be cumulant expansion in (29) be terminated at the first few terms displayed in (30), and whether these terms can be evaluated in a low-order perturbation exapnsion in V. Let us associate any pair of operators $W(t_i)$, $W(t_j)$ with a scattering event that occurs in a time interval $t_1=t_i-t_j$. We may then neglect all averages containing more than one such event if, first, there is no correlation between two events occurring in two different time intervals separated by more than a certain correlation time t_c, and second, if the coupling is weak enough so that the contributions of multiple scattering events taking place within an interval t_c is much smaller than that of a single scattering. The first condition implies the assumption of randomness of collisions and has to be fulfilled even in case of weak coupling (second condition) because the function $g_{AB}(t)$ in (30) might otherwise increase as a high positive power of t.

An alternative interpretation suggests itself when we look at the actual form of the averages in (30). As shown in Sec. IV, the lowest term in $f_{AB}(t)$ is proportional to a sum over all phonon vectors $\vec{k}$

of the square of the coupling constant, $|A_{\vec{k}}^{z}|^2$. Higher-order terms would thus involve multiple sums over $\vec{k}$, $\vec{k}'$, $\vec{k}''$, etc. However, since $|A_{\vec{k}}^{z}|^2 \propto 1/N$ by Eq. (6), we must have $\vec{k} \neq \vec{k}' \neq \vec{k}''$, etc. in an infinite system. Thus, if we omit these higher terms, we essentially neglect all correlations between the collisions involving two or more phonons belonging to different modes. Our approximation is therefore analogous to the independent-collision approximation used in the theory of pressure broadening of spectral lines in gases.[12]

The frequency shift γ_{AB} cannot be calculated by a similar low-order expansion in V. The reason is that the renormalized Larmor frequency Ω_{AB} in addition to being responsible for the long-time oscillatory behavior of $C_{AB}(t)$ enters the expression for the thermodynamic average $\langle AB\rangle$ in (36). The derivative of this average with respect to the static field must be consistent with the definition of the static susceptibility in Eq. (13). Thus we obtain a condition which must be satisfied by Ω_{AB}, or equivalently γ_{AB}, as a function of the coupling parameter.

The approximation method based on the perturbation expansion of $f_{AB}(t)$, although the most plausible one, is by no means unique. For example, rather than expanding the averages in (30) in powers of V one can apply a decoupling scheme in order to express $f_{AB}(t)$ as a functional of the product between $C_{AB}(t')$ and a corresponding phonon correlation function.[19] In this way, one generates a set of self-consistent equations for the correlation functions which are generally difficult to solve and do not offer a simple physical interpretation.

IV. SPIN CORRELATION FUNCTIONS

A. Definitions and general properties

The first quantity which is of interest is the longitudinal dynamic susceptibility. From (1), (8), (11), and (12) we see that the correlation function involved will be

$$C_{zz}(t) = \langle S_z(t) S_z(0)\rangle - \langle S_z\rangle^2. \tag{37}$$

The unperturbed time dependence of S_z is $S_z(t)_0 = S_z$, and the corresponding Larmor frequency introduced in Eq. (31) is $\omega_z = 0$. We may also anticipate that $C_{zz}(t)$ will not oscillate as $t\to\infty$, that is, $\Omega_{zz} = 0$. Using the fact that $S_z^2 = \frac{1}{4}$ we can thus write $C_{zz}(t)$ in the form of Eq. (36),

$$C_{zz}(t) = [\tfrac{1}{4} - \langle S_z\rangle^2] e^{f_{zz}(t)}, \tag{38}$$

introducing the phase-modulation function $f_{zz}(t) = g_{zz}(t)$. The longitudinal susceptibility $\chi_{zz}(\omega)$ is obtained by inserting (38) into Eq. (12). The factor $(g\beta_0)^2$ has been incorporated into the definition of $\chi_{AB}(\omega)$.

To determine the transverse susceptibility we first introduce the usual spin-flip operators S_+ and S_-,

$$S_\pm = S_x \pm i S_y. \tag{39}$$

If a transverse probe field is applied along the x axis, we find for the corresponding susceptibility

$$\chi_{xx}(\omega) = \tfrac{1}{2}[\chi_{-+}(\omega) + \chi_{+-}(\omega)], \tag{40}$$

where $\chi_{-+}(\omega)$ is obtained from (12) with $A = S_- - \langle S_-\rangle$ and $B = S_+ - \langle S_+\rangle$. Thus we will need the correlation function

$$C_{-+}(t) = \langle S_-(t) S_+(0)\rangle - \langle S_-\rangle\langle S_+\rangle. \tag{41}$$

The function $C_{+-}(t)$ can be found from (41) with the help of (14). The averages $\langle S_\pm\rangle$ are different from zero if the general spin-phonon coupling (3) is used. However, it can be shown that in the isotropic coupling case introduced in Eqs. (4)–(7) they vanish rigorously. To prove this, one can use the usual perturbation expansion for the density matrix (9) in powers of V and find that all terms are zero because of the orthogonality relation (5) and the fact that the unperturbed averages $\langle S_\pm\rangle$ are zero.

From the unperturbed time dependence $S_\pm(t) = S_\pm = S_\pm e^{\pm i\omega_0 t}$ and (31) we find the zero-order Lamor frequencies $\omega_+ = \omega_0$ and $\omega_- = -\omega_0$. Following the steps leading from (32) to (36) we then introduce an effective Larmor frequency $\Omega_{-+} \equiv \Omega_0$ and a phase-modulation function $f_{-+}(t)$ in terms of which the correlation function (41) finally becomes

$$C_{-+}(t) = \langle S_- S_+\rangle e^{-i\Omega_0 t + f_{-+}(t)}, \tag{42a}$$

$$C_{+-}(t) = \langle S_+ S_-\rangle e^{+i\Omega_0 t + f_{+-}(t)}. \tag{42b}$$

The averages $\langle S_z\rangle$ and $\langle S_\mp S_\pm\rangle$ in (37) and (42), respectively, are connected by the relations

$$\langle S_+ S_-\rangle - \langle S_- S_+\rangle = 2\langle S_z\rangle, \tag{43a}$$

$$\langle S_+ S_-\rangle + \langle S_- S_+\rangle = 1, \tag{43b}$$

which follow from the commutation relations for the spin-$\frac{1}{2}$ operators.

We must now calculate the functions $f_{zz}(t)$ and $f_{-+}(t)$ figuring in (37) and (42), the Larmor frequency Ω_0, and one of the averages, say $\langle S_z\rangle$. In Sec. IV B we will discuss a perturbation expansion for the phase functions. To determine Ω_0 and $\langle S_z\rangle$ however, we need two more equations. The first of these is provided by the relation (14) the functions $C_{-+}(t)$ and $C_{+-}(t)$ must satisfy. Applying (14) to (42) and comparing the exponents in $C_{-+}(-t)$ and $C_{+-}(t - i\beta)$ we find the following relations:

$$f_{-+}(-t) = f_{+-}(t - i\beta); \tag{44}$$

$$\langle S_- S_+\rangle = \langle S_+ S_-\rangle e^{\beta\Omega_0}. \tag{45}$$

Together with (43) the last equation leads to

$$\langle S_- S_+\rangle = (e^{-\beta\Omega_0} + 1)^{-1},\ \langle S_+ S_-\rangle = (e^{+\beta\Omega_0} + 1)^{-1}; \tag{46a}$$

$$\langle S_z\rangle = -\tfrac{1}{2}\tanh(\tfrac{1}{2}\beta\Omega_0). \tag{46b}$$

The remaining unknown parameter Ω_0 can be determined from the requirement that the static longitudinal susceptibility χ_{zz} must be equal to the derivative of the spin polarization $\langle S_z\rangle$ with respect to the static external field $\mathcal{H}_z=\omega_0/g\mu_B$, or in our system of units,

$$\chi_{zz}=[\tfrac{1}{4}-\langle S_z\rangle^2]\int_0^\beta d\lambda\, e^{f_{zz}(-i\lambda)}=-\frac{\partial\langle S_z\rangle}{\partial\omega_0}, \qquad (47)$$

where the first equation follows from (13) and (38). A consistency condition of the type (47) has been proposed by Götze and Schlottman[18] for the case of a spin-$\frac{1}{2}$ impurity in metals.

In the memory-function method or in various Green's-function approaches additional conditions may arise. They usually have the form of a frequency sum rule for the dynamic susceptibility $\chi_{AB}(\omega)$ which is equivalent to the requirement that the correlation function $C_{AB}(t)$ must have a prescribed value at $t=0$. For example, $[C_{-+}(0)+C_{+-}(0)]=1$ in view of Eq. (46b). In the stochastic approach, the analyticity of the correlation functions guarantees the correct behavior of the frequency dependence of $\chi_{AB}(\omega)$ and hence the frequency sum rules are automatically satisfied. There is furthermore no distinction at all between the results derived from the commutator or anticommutator correlation (or Green's) functions. This is not the case with other approaches where approximations are based on the frequency rather than the time dependence of the correlation functions, a point we discussed in Ref. 9.

B. Perturbation expansion for f_{AB} (t)

When we try to calculate the first few terms in the expansion (30) for $g_{-+}(t)$, we realize that it contains a number of unknown averages like $\langle S_-a_{\vec{k}p}\rangle$, $\langle S_+S_-a^\dagger_{\vec{k}p}a_{-\vec{k}'p'}\rangle$, etc. To determine these we would need a number of additional parameters and conditions of the type (47). In order to keep the number of parameters minimal, we will limit ourselves here to one unknown parameter only, that is, the effective Larmor frequency Ω_0 introduced earlier. In this approximation we shall, therefore, calculate the averages in (30) and hence the functions $f_{-+}(t)$ by a finite-order perturbation expansion in powers of V, however, with Ω_0 figuring everywhere in lieu of the unperturbed Larmor frequency ω_0. Introducing

$$\bar{K}_{-+}(t)=\langle S_-S_+\rangle e^{-i\Omega_0 t}, \qquad (48)$$

and using Eq. (42), we can thus write

$$\bar{C}_{-+}(t)=\bar{K}_{-+}(t)e^{\bar{f}_{-+}(t)}, \qquad (49)$$

where a bar over a symbol indicates an approximate quantity which is a function of Ω_0, and Ω_0 itself has to be determined from the self-consistency condition (47).

As a convenient way to calculate $\bar{f}_{-+}(t)$, we now imagine that both $\bar{C}_{-+}(t)$ and $\bar{f}_{-+}(t)$ have been expanded into a power series with respect to V, and let $\bar{C}^n_{-+}(t)$ and $\bar{f}^n_{-+}(t)$ denote the nth terms in this expansion. Only even powers of V appear. From (49) we find

$$e^{\bar{f}^2(t)+\bar{f}^4(t)+\cdots}=[\bar{K}(t)]^{-1}[\bar{C}^0(t)+\bar{C}^2(t)+\bar{C}^4(t)+\cdots]$$
$$=1+[\bar{K}(t)]^{-1}[\bar{C}^2(t)+\bar{C}^4(t)+\cdots], \qquad (50)$$

where we have dropped all the subscripts, and in the last line we used the fact that $\bar{C}^0=\bar{K}(t)$. At $t=0$ we have $\bar{f}^n(0)=0$, hence

$$[\bar{K}(0)]^{-1}[\bar{C}^2(0)+\bar{C}^4(0)+\cdots]=0. \qquad (51)$$

Subtracting (51) from (50) and comparing the terms of the same order on both sides of the equation, we derive

$$\bar{f}^2_{-+}(t)=\langle S_-S_+\rangle^{-1}[e^{i\Omega_0 t}\,\bar{C}^2_{-+}(t)-\bar{C}^2_{-+}(0)]; \qquad (52a)$$

$$\bar{f}^4_{-+}(t)=\langle S_-S_+\rangle^{-1}[e^{i\Omega_0 t}\,\bar{C}^4_{-+}(t)-\bar{C}^4_{-+}(0)]-\tfrac{1}{2}[\bar{f}^2_{-+}(t)]^2; \qquad (52b)$$

etc. This is, of course, just another form of a cumulant expansion.

Finally, an analogous procedure can be set up for the function $\bar{C}_{zz}(t)$. Starting from Eq. (38) we find that in this case

$$\bar{f}^2_{zz}(t)=[\tfrac{1}{4}-\langle S_z\rangle^2]^{-1}\,\bar{C}^2_{zz}(t),\ \text{etc.}, \qquad (53)$$

where we have also used $\bar{C}^2_{zz}(0)=0$.

V. CALCULATION OF SUSCEPTIBILITIES

A. Longitudinal relaxation

We will first investigate the simpler and physically more interesting longitudinal case. To calculate the function $\bar{f}_{zz}(t)$ in the lowest- (second-) order approximation we need $C^2_{zz}(t)$ according to Eq. (53). It turns out to be easiest to do the calculation for imaginary times $t=-i\tau$ using the Matsubara perturbation technique.[20] The second-order term of $C_{zz}(-i\tau)$ is

$$C^2_{zz}(-i\tau)=\int_0^\beta d\tau_2\int_0^{\tau_2}d\tau_1\,[\langle T_\tau V(-i\tau_2)_0V(-i\tau_1)_0S_z(-i\tau)_0S_z\rangle_0-\langle S^2_z\rangle_0\langle V(-i\tau_2)_0V(-i\tau)_0\rangle_0], \qquad (54)$$

where T_τ is the time-ordering operator which orders all operators with time arguments τ_i on the interval $0\le\tau_i\le\beta$ in ascending order from the right to the left. The second term in (54) follows from the expansion of the trace of the statistical operator in (9).

To evaluate the averages in (54) we use the explicit form of the perturbation V, Eq. (4), and note that the unperturbed spin and phonon averages can be separated. The orthogonality relation (5) is used to eliminate all crossterms of the type $S_\mu(-i\tau_2)_0 S_\nu(-i\tau_1)_0$, $\mu \neq \nu$. Owing to the cancellation of spin averages between the first and the second term of (54), we get a nonzero contribution only for $\tau_1 \leq \tau \leq \tau_2$. The calculation of the integrals is trivial, and the result is

$$C_{zz}^2(-i\tau) = -\frac{1}{4}\Bigg[\sum_{\vec{k}}\left(\frac{|A_{\vec{k}}|^2}{(\omega_0-\omega_{\vec{k}})^2}\;\frac{(e^{(\omega_0-\omega_{\vec{k}})\tau}-e^{(\omega_0-\omega_{\vec{k}})\beta})\,(e^{-(\omega_0-\omega_{\vec{k}})\tau}-1)}{(e^{\beta\omega_{\vec{k}}}-1)\,(e^{\beta\omega_0}+1)}\right)$$
$$+\sum_{\vec{k}}(\omega_{\vec{k}}\rightarrow-\omega_{\vec{k}})+\sum_{\vec{k}}(\omega_0\rightarrow-\omega_0)+\sum_{\vec{k}}(\omega_{\vec{k}},\omega_0\rightarrow-\omega_{\vec{k}},-\omega_0)\Bigg]\,. \tag{55}$$

This expression is first converted into $\overline{C}_{zz}^2(-i\tau)$ by replacing ω_0 everywhere by Ω_0. Next, we substitute (it) for τ in order to obtain $\overline{C}_{zz}^2(t)$. Using Eq. (53) with

$$[\tfrac{1}{4}-\langle \overline{S}_z\rangle^2]^{-1} = 4\cosh^2(\tfrac{1}{2}\beta\Omega_0),$$

we finally have

$$\overline{f}_{zz}^{\,2}(t) = \cosh(\tfrac{1}{2}\beta\Omega_0)\Bigg[\sum_{\vec{k}}\left(\frac{|A_{\vec{k}}|^2}{(\Omega_0-\omega_{\vec{k}})^2}\;\frac{\cosh[\frac{1}{2}\beta(\Omega_0-\omega_{\vec{k}})]}{\sinh(\frac{1}{2}\beta\,\omega_{\vec{k}})}\,(e^{-i(\Omega_0-\omega_{\vec{k}})t}-1)\right)+\sum_{\vec{k}}(\Omega_0\rightarrow-\Omega_0)\Bigg]\,. \tag{56}$$

The terms with $\omega_{\vec{k}}\rightarrow\omega_{\vec{k}}$ have already been taken into account.

To evaluate the above expression we make use of Eqs. (6) and (7), and introduce dimensionless quantities $x\equiv\omega_k/\omega_m$, $x_0\equiv\Omega_0/\omega_m$, and $b\equiv\frac{1}{2}\beta\omega_m$. The result is written

$$\overline{f}_{zz}^2(t) \equiv X_{zz}(t) - i\,Y_{zz}(t)\,, \tag{57}$$

with both $X_{zz}(t)$ and $Y_{zz}(t)$ real, and equal to

$$X_{zz}(t) = \eta\cosh(bx_0)\int_{-1}^{+1}dx\,\frac{x^3(1-x^2)^{1/2}\cosh[b(x-x_0)]}{(x-x_0)^2\sinh(bx)}\,\{\cos[(x-x_0)\omega_m t]-1\}; \tag{58}$$

$$Y_{zz}(t) = \eta\cosh(bx_0)\int_{-1}^{+1}dx\,\frac{x^3(1-x^2)^{1/2}\sinh[b(x-x_0)]}{(x-x_0)^2\sinh(bx)}\,\sin[(x-x_0)\omega_m t]. \tag{59}$$

The final expression for the longitudinal susceptibility $\chi_{zz}(\omega)$ is derived by using the approximate result (57) and (58) for $f_{zz}(t)$ in Eq. (38), and then inserting the function $C_{zz}(t)$ thus obtained into Eq. (12):

$$\chi_{zz}(\omega) = \tfrac{1}{2}\,\mathrm{sech}^2(bx_0)\int_0^\infty dt\,e^{i\omega t}\sin[Y_{zz}(t)]\,e^{X_{zz}(t)}\,. \tag{60}$$

The integrations in (58)–(60) must be done numerically. We must, however, first find the value of the parameter $x_0=\Omega_0/\omega_m$ from Eq. (47), and investigate the analytic behavior of the integrand in (60), in particular at large times.

The asymptotic behavior of the integrals in (58), (59) is governed by the singularity which occurs at $x=x_0$, assuming $x_0<1$. Introducing a new variable $z=x-x_0$ we find that the leading terms of $X_{zz}(t)$ at $\omega_m t \gg 1$ are

$$X_{zz}(t)\sim\eta x_0^3(1-x_0^2)^{1/2}\coth(bx_0)\int_{-1-x_0}^{1-x_0}\frac{dz}{z^2}\,[\cos(z\omega_m t)-1]+\cdots$$
$$\sim-\eta x_0^3(1-x_0^2)^{1/2}\coth(bx_0)\Bigg((\omega_m t)\,\{\mathrm{Si}[(1+x_0)\omega_m t]+\mathrm{Si}[(1+x_0)\omega_m t]\}$$
$$+\frac{\cos[(1+x_0)\omega_m t]-1}{1+x_0}+\frac{\cos[(1-x_0)\,\omega_m t]-1}{1-x_0}\Bigg)+O(1/|t|). \tag{61}$$

In the same approximation $Y_{zz}(t)$ behaves like

$$Y_{zz}(t)\sim\eta x_0^3(1-x_0^2)^{1/2}\,b\coth(bx_0)\{\mathrm{Si}[(1+x_0)\omega_m t]+\mathrm{Si}[(1-x_0)\omega_m t]\}+O(1/t)\,. \tag{62}$$

In these expressions $\mathrm{Si}(x)$ is the sine-integral function which for large arguments behaves like[21] $\mathrm{Si}(x) \sim \frac{1}{2}\pi - (\cos x)/x + O(x^{-2})$. Hence, the leading asymptotic term in (61) is simply

$$X_{zz}(t) \sim - |t|/T_1 \ (x_0 < 1), \tag{63}$$

where

$$T_1 = \tanh(bx_0)\,[\eta\pi\omega_m x_0^3(1-x_0^2)^{1/2}]^{-1}. \tag{64}$$

Thus for $t \gg 1/(\omega_m - \Omega_0)$ the correlation function $C_{zz}(t)$ decays exponentially with a relaxation time T_1. The process involved is the direct (one-phonon) transition[2] in which a phonon supplies the energy corresponding to the effective Larmor frequency Ω_0. The temperature dependence of T_1 is determined by the parameters b and x_0 in (64) and is in general quite complicated. However, if the variation with T of Ω_0 happens at high temperatures to be weak, we may expect the usual $T_1 \propto 1/T$ dependence of the relaxation time.

The imaginary part of $\bar{f}_{zz}^2(t)$ approaches a constant value as $t \to \infty$,

$$Y_{zz}(t) \sim \eta\pi x_0^3(1-x_0^2)^{1/2} b \coth(bx_0) = \beta/T_1, \tag{65}$$

which would be roughly temperature independent at high T, but may increase sharply on lowering the temperature if $T < \Omega_0/k_B$.

The asymptotic behavior of $C_{zz}(t)$ is relevant to the low-frequency behavior of $\chi_{zz}(\omega)$. For small values of η the integrand in (60) behaves roughly as $\sim(\beta/T_1)\, e^{i\omega t - |t|/T_1}$ and we can expect a Lorentzian shape for the low-frequency susceptibility. Such estimates are not too reliable, however: If one would use the anticommutator form, $C_{zz}(t) + C_{zz}(-t)$, and the fluctuation-dissipation theorem to find the susceptibility, the same asymptotic $C_{zz}(t)$ as above would lead to a non-Lorentzian line shape.[5,9] The problem lies in the detailed time dependence of the functions $X_{zz}(t)$ and $Y_{zz}(t)$, in particular at small times, which should not be disregarded. Thus it is hard to see how the correct frequency dependence of $\chi_{zz}(\omega)$ could be predicted from simple phenomenological approaches, since these usually involve an exponentially decaying correlation function at all times.[22]

For large η (strong coupling) or low temperature ($\beta \gg T_1$), the function $Y_{zz}(t)$ can reach asymptotic values near $\sim\frac{1}{2}\pi$ or larger. This means that the oscillating character of $\sin[Y_{zz}(t)]$ becomes important, and the behavior of $\chi_{zz}(\omega)$ may become very different from a simple Lorentzian at all frequencies. From (65) we realize that the critical value of T_1 is roughly given by $1/T_1 \approx \frac{1}{2}\pi k_B T$, that is, the relaxation rate is equal to π times the average thermal energy. The relaxation rate would thus play a role in statistical factors, something we have neglected by introducing a real Larmor frequency in the averages (46). This suggests that the validity of our approximations is limited to such values of η and temperature for which $Y_{zz}(\infty)$ never exceeds the value $\frac{1}{2}\pi$.

If $x_0 > 1$, that is, $\Omega_0 > \omega_m$, the renormalized Larmor frequency lies outside the range of available phonon frequencies, the direct relaxation processes become forbidden. The asymptotic behavior of the function $X_{zz}(t)$ is then such that it vanishes as $\sim 1/|t|$ for $t \to \infty$. Similarly, $Y_{zz}(t) \sim 1/t$. The correlation function $\bar{C}_{zz}(t)$ no more vanishes at infinity and thus violates the requirements imposed upon $C_{zz}(t)$ in connection with Eq. (12). The trouble lies in the approximations made in calculating $\bar{f}_{zz}(t)$, specifically in limiting the perturbation expansion to the second-order term $\bar{f}_{zz}^2(t)$. If one would carry on the calculation to higher orders in V, collisions involving two or more phonons would be properly taken into account. The calculation of $\bar{f}_{zz}^4(t)$ is, however, not trivial as it involves fourfold time-ordered integrals. Furthermore, such a result would be of little practical value because the quasi-two-phonon processes involved have to compete in reality with real processes arising from that part of the spin-lattice coupling which is quadratic in lattice displacements.[2] We have neglected any such terms in our interaction Hamiltonian, and will not consider the case $x_0 > 1$ in any detail.

B. Spin magnetization and static susceptibility

We must calculate the spin magnetization $\langle S_z\rangle$ and the static susceptibility χ_{zz} to determine the value of the parameter Ω_0 from the relations (46b) and (47). We will use a procedure similar to that of Ref. 18. First we note that Ω_0 is a function of ω_0, that is, $\Omega_0 = \Omega_0(\omega_0)$. Conversely, $\omega_0 = \omega_0(\Omega_0)$. Thus we may rewrite the derivative in (47) as

$$\frac{\partial\langle S_z\rangle}{\partial\omega_0} = \frac{\partial\langle S_z\rangle}{\partial\Omega_0}\frac{\partial\Omega_0}{\partial\omega_0} = -\tfrac{1}{4}\beta\,\mathrm{sech}^2(\tfrac{1}{2}\beta\Omega_0)\left(\frac{\partial\omega_0}{\partial\Omega_0}\right)^{-1}, \tag{66}$$

where we have used Eq. (46b). For a prescribed value of the effective Larmor frequency, say Ω_0', we can always calculate χ_{zz} from the first of Eqs. (47) into which we substitute $\bar{f}_{zz}^2(-i\lambda)$ from (57)–(59) for $f_{zz}(-i\lambda)$. The value of χ_{zz} thus obtained will be denoted as $\chi_{zz}(\Omega_0')$. Inserting (66) into Eq. (47), and integrating both sides with respect to Ω_0' between zero and Ω_0 yields

$$\omega_0(\Omega_0) = \frac{\beta}{4}\int_0^{\Omega_0} d\Omega_0'\,[\cosh^2(\tfrac{1}{2}\beta\Omega_0')\,\chi_{zz}(\Omega_0')]^{-1}, \tag{67}$$

where we have used the boundary condition $\omega_0(0) = 0$. Since we know $\chi_{zz}(\Omega_0')$ for any value of Ω_0', we can calculate the integral in (67) numerically with a variable upper limit and stop as soon as we reach the known value of ω_0. Intermediate steps give us the function $\Omega_0(\omega_0)$ from which we can find $\langle S_z\rangle$ as a function of the static external field $H_z = \omega_0/2g\mu_B$, coupling parameter η, and the temperature. The parameter Ω_0 has thus been determined self-consistently for any value of the unperturbed Larmor frequency ω_0, and can now be used to calculate the dynamic susceptibility from Eq. (60).

C. Transverse susceptibility

The calculation of $\bar{f}^{\,2}_{-+}(t)$ in (52a) proceeds in a manner very similar to the derivation of Eq. (56). First we consider the second-order terms of the imaginary-time correlation function $C_{-+}(-i\lambda)$:

$$C^2_{-+}(-i\lambda)=\int_0^\beta d\tau_2\int_0^{\tau_2}d\tau_1\,[\langle T_\tau V(-i\tau_2)_0V(-i\tau_1)_0S_-(-i\tau)_0S_+\rangle_0-\langle S_-S_+\rangle_0\,e^{-\omega_0\tau}\langle V(-i\tau_2)_0V(-i\tau_1)_0\rangle_0]\,. \tag{68}$$

There are now three different integration regions which give nonzero contributions to the integral in (68), depending on the position of $S_-(-i\tau)_0$ relative to $V(-i\tau_2)_0$ and $V(-i\tau_1)_0$. After finding $C^2_{-+}(-i\tau)$ we substitute (it) for τ and Ω_0 for ω_0, and then use Eq. (52a) in order to derive $\bar{f}^{\,2}_{-+}(t)$. The result is

$$\bar{f}^{\,2}_{-+}(t)=\sum_{\vec{k}}\frac{|A_{\vec{k}}|^2}{\omega_{\vec{k}}^2}\,\frac{2}{1-e^{-\beta\omega_{\vec{k}}}}\,(e^{-i\omega_{\vec{k}}t}-1)+\left[\sum_{\vec{k}}\left(\frac{|A_{\vec{k}}|^2}{(\omega_{\vec{k}}-\Omega_0)^2}\,\frac{1+e^{-\beta\Omega_0}}{1-e^{-\beta\omega_{\vec{k}}}}\,(e^{-i(\omega_{\vec{k}}-\Omega_0)t}-1\right)+\sum_{\vec{k}}(\omega_{\vec{k}}-\omega_{\vec{k}})\right]. \tag{69}$$

All imaginary terms that go linearly with time as $t\to\infty$ have been dropped from $C^2_{-+}(t)$ because they are part of the oscillating factor $e^{-i\Omega_0 t}$ in (48) according to the definition of $\bar{f}_{-+}(t)$ in Eqs. (35) and (49).

The calculation of $\bar{f}^{\,2}_{-+}(t)$ is completed by making use of the models for the coupling constant $A_{\vec{k}}$, Eq. (4) and the phonon spectrum (7), and leads to the result

$$\bar{f}^{\,2}_{-+}(t)=\frac{\eta}{2}\int_{-1}^{+1}dx\,x(1-x^2)^{1/2}\,\frac{2}{1-e^{-2bx}}\,(e^{-ix\omega_m t}-1)+\frac{\eta}{2}\int_{-1}^{+1}dx\,\frac{x^3(1-x^2)^{1/2}}{(x-x_0)^2}\,\frac{1+e^{-2bx_0}}{1-e^{-2bx}}\,(e^{-i(x-x_0)\omega_m t}-1), \tag{70}$$

where the notation is the same as in Eqs. (58) and (59). The second integral is a principal-value integral because the singularity at $x=x_0$, which would give an imaginary term proportional to t, has been removed by the term $-i\Omega_0 t$ in (42) according to (32)–(36). The corresponding function $\bar{f}^{\,2}_{+-}(t)$ needed in $C_{+-}(t)$ can be derived from (70) by using the general relationship (44). We can then verify that

$$\bar{f}^{\,2}_{+-}(t)=\bar{f}^{\,2}_{-+}(t)\,\big|_{\Omega_0\to-\Omega_0}. \tag{71}$$

Separating the real and imaginary parts of $\bar{f}^{2}_{-+}(t)$ as in (57) we write

$$\bar{f}^{\,2}_{-+}(t)\equiv X_{-+}(t)-iY_{-+}(t)\,, \tag{72}$$

and similarly for $\bar{f}^{\,2}_{+-}(t)$. The final result for the transverse susceptibility $\chi_{xx}(\omega)$ as introduced by Eq. (40) can be written

$$\chi_{xx}(\omega)=2\int_0^\infty dt\,e^{i\omega t}\left(e^{X_{-+}(t)}\,\frac{\sin[\Omega_0 t+Y_{-+}(t)]}{e^{-\beta\Omega_0}+1}-e^{X_{+-}(t)}\,\frac{\sin[\Omega_0 t-Y_{+-}(t)]}{e^{\beta\Omega_0}+1}\right). \tag{73}$$

As before, we must investigate the asymptotic behavior of the function $\bar{f}^{\,2}_{-+}(t)$. The integrand of the first term in (70) has no singularities (it has a square-root branch point at $x=\pm1$) and is expected to vanish as $t\to\infty$. It becomes particularly simple at high temperatures ($b\omega_m\ll1$), where we have

$$\begin{aligned}\bar{f}^{\,I}_{-+}(t)&\equiv\frac{\eta}{2}\int_{-1}^{+1}dx\,x(1-x^2)^{1/2}\,\frac{2}{1-e^{-2bx}}\,(e^{-ix\omega_m t}-1)\cong\frac{\eta}{2}\int_{-1}^{+1}dx\,(1-x^2)^{1/2}\left(\frac{1}{b}\,[\cos(x\omega_m t)-1]-ix\sin(x\omega_m t)\right)\\&=\frac{\eta\pi}{2b}\left(\frac{J_1(\omega_m t)}{\omega_m t}-\frac{1}{2}\right)-i\,\frac{\eta\pi}{2}\,\frac{\partial}{\partial(\omega_m t)}\left(\frac{J_1(\omega_m t)}{\omega_m t}\right).\end{aligned} \tag{74}$$

Here $J_1(x)$ is the ordinary Bessel function whose asymptotic behavior is[21]

$$J_1(x)\sim[2/(\pi x)]^{1/2}[\cos(x-\tfrac{3}{4}\pi-3\sin(x-\tfrac{3}{4}\pi)/(8x)]+\cdots.$$

Thus we realize that $\bar{f}^{\,I}_{-+}(t)$ falls off at infinity as $\sim|t|^{-1/2}$ and does not contribute to the relaxation behavior of the correlation function $C_{-+}(t)$. Note that $\bar{f}^{\,I}_{-+}(t)$ does not depend in any way on the Larmor frequency Ω_0. The processes involved in this part of $\bar{f}_{-+}(t)$ are adiabatic (in quantum-mechanical sense) phase interrupting collisions[5] in which no real transitions between the two magnetic states occur. Mathematically speaking, one could produce a function $\bar{f}^{\,I}_{-+}(t)$ that goes as $\approx-|t|$ at large t by choosing $A_{\vec{k}}\propto\omega_{\vec{k}}^{-1/2}$ rather than $A_{\vec{k}}\propto\omega_{\vec{k}}^{1/2}$ as in Eq. (6). Such a coupling constant would correspond to the piezoelectric coupling of donor impurities in insulators,[23,24] but does not seem to be relevant to the present problem.

The second integral in (70) has an asymptotic behavior very similar to that of $\bar{f}^{\,2}_{zz}(t)$. Indeed, if we apply the same method as in deriving (61), (62), we observe that

$$\bar{f}^{\,II}_{-+}(t) \equiv \bar{f}^{\,2}_{-+}(t) - \bar{f}^{\,I}_{-+}(t) \sim \tfrac{1}{2}[X_{zz}(t) - iY_{zz}(t)]_{\text{asympt}}\,, \tag{75}$$

where the asymptotic forms of $X_{zz}(t)$ and $Y_{zz}(t)$ are given by Eqs. (61) and (62). Thus the leading term in $X_{-+}(t)$ at large t will behave as

$$X_{-+}(t) \sim -\,|t\,|/T_2, \tag{76}$$

where $T_2 = 2T_1$. This relationship between the transverse and longitudinal relationship is characteristic of spin-phonon relaxation. In the limit $\omega_0 \to 0$, we would expect $T_2 = T_1$ owing to the isotropy of the coupling in (6); however, both T_2 and T_1 become infinite in this case as can be seen from Eq. (64). On the other hand, if we choose the hypothetical coupling $A_{\vec{k}} \propto \omega_{\vec{k}}^{-1/2}$ mentioned above, T_1 and T_2 are both finite as $\omega_0 \to 0$ and become exactly equal in this limit, because the two terms in (71) contribute equal amounts to the function $\bar{f}^{\,2}_{-+}(t)$, which is further equal to $\bar{f}^{\,2}_{zz}(t)$.

V. DISCUSSION

In order to study the character of the results derived in Sec. IV, we have carried out numerical calculations of the static and dynamic susceptibilities. First we had to determine the parameter Ω_0 for a given temperature, static field $\mathcal{H}_z$ (or $\omega_0 = 2g\mu_B\mathcal{H}_z$), and the coupling parameter η from Eq. (67). In Fig. 1 the spin magnetization is plotted for four values of η as a function of ω_0 and compared with the curve for a free spin ($\eta = 0$).

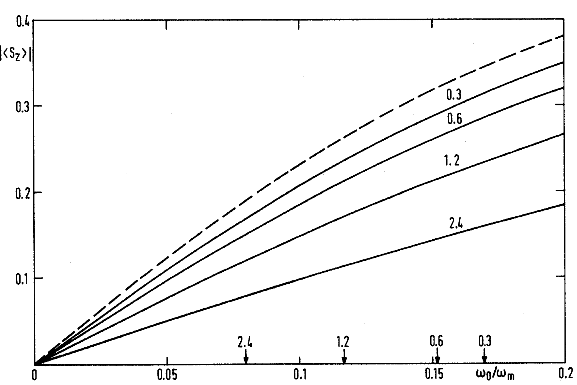

FIG. 1. Static spin magnetization at constant temperature ($\beta\omega_m = 10$) as function of the external field (in units of ω_0/ω_m). Arrows indicate the positions of the effective Larmor frequencies corresponding to four values of the coupling parameter η (0.3, 0.6, 1.2, and 2.4). Dashed line: free-spin magnetization ($\eta = 0$).

The static susceptibility is given by the derivative of $\langle S_z \rangle$ with respect to ω_0 according to (47), and is not displayed. In general, the value of $|\langle S_z \rangle|$ decreases with increasing η for the range of parameters chosen. The frequency Ω_0 can be obtained from $\langle S_z \rangle$ by the relation

$$\Omega_0 = (2/\beta)\tanh^{-1}(2|\langle S_z \rangle|)\,,$$

and is itself a decreasing function of η. The behavior of $\langle S_z \rangle$ at low temperatures and for strong coupling ($\eta \gg 1$) cannot be studied in the approximation used for reasons discussed in Sec. IV. There are, however, no obvious limitations on the high-temperature side. The relaxation rate $1/T_1$ from Eq. (64) can become very large without causing any problems while $Y_{zz}(t \to \infty)$ remains finite, as we saw. In general, we may even expect the validity of the stochastic theory to improve as we go towards higher temperatures for physical reasons mentioned at the end of Sec. II C. The temperature dependence of Ω_0 has not been investigated because of the length of the computations involved. Physically, we can expect that the properties of the complicated low-lying excited states of the coupled spin-lattice system dominates the scene as $T \to 0$. Different methods should, therefore, be sought to describe the behavior of $\langle S_z \rangle$ in this limit.

Having found Ω_0 for a given η, ω_0, and temperature, we can now calculate the complex longitudinal susceptibility $\chi_{zz}(\omega)$ from Eqs. (57)–(60). The function $\bar{f}^{\,2}_{zz}(t)$ at small values of the time t is obtained by numerical integration from (58), (59), while for t large we can use an asymptotic expansion of the type (61), (62). The imaginary (absorptive) part of the relaxation spectrum, $\chi''_{zz}(\omega)$, appears in Fig. 2 for the same range of parameters as used in connection with $\langle S_z \rangle$ above. The frequency scale is logarithmic. The maximum at low frequencies occurs at $\omega \approx 1/T_1$ in agreement with the usual qualitative picture of the longitudinal relaxation. Its shape at low frequencies is reasonably close to a simple Lorentzian, indicated by the dashed line for $\eta = 2.4$, as expected on the basis of the asymptotic exponential form of $C_{zz}(t)$.

The high-frequency part of $\chi''_{zz}(\omega)$ exhibits some structure which is unrelated to the long-time exponential decay of the correlation function. The details of the phonon spectrum near $\omega_k \approx \omega_m$ now play a role; the maximum occurs near ω_m and then the spectrum falls off sharply near $\omega \approx \omega_m + \Omega_0$, the highest possible frequency transfer in a spin-phonon collision. However, the spectrum does not drop to zero and remains finite at even higher frequencies. This behavior suggests the existence of short-time correlations between the motions of the spin and the phonons, which are not negligible because of the finite duration of each scattering

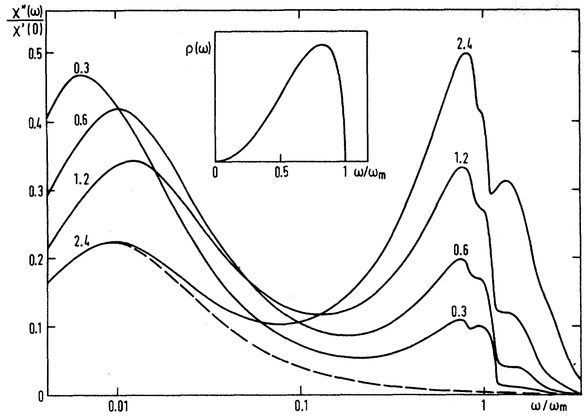

FIG. 2. Longitudinal relaxation spectrum in units of static isothermal susceptibility. The value of the static field corresponds to $\omega_0/\omega_m = 0.2$. The temperature and the values of η are the same as in Fig. 1. The Lorentzian curve (dashed line) is shown for the case $\eta = 2.4$ and is normalized so that it overlaps with the corresponding spectrum at low frequencies. Inset: phonon density of states (vertical scale arbitrary).

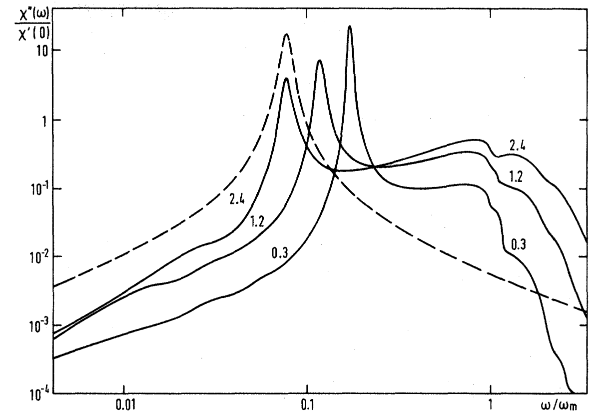

FIG. 3. Transverse spectrum, exhibiting a resonance near $\omega = \omega_0$, for three values of η. All other parameters same as before. Dashed line: Lorentzian model for $\eta = 2.4$ (unnormalized). Both scales are logarithmic.

event. Note that these effects could not be described by a Green's-function decoupling treatment in the same (second) order. From a physical point of view, the details of the calculated high-frequency longitudinal spectrum may not be very important for the problem studied. The problem is that ω_m, and hence the second maximum of $\chi''_{zz}(\omega)$, will typically lie in the range of optical frequencies, that is, far above the frequencies at which the longitudinal relaxation is usually observed. In addition, there are processes not considered here which may influence the shape of $\chi''_{zz}(\omega)$ at high frequencies, namely, the relaxation via higher magnetic levels and the two-phonon transitions due to the quadratic spin-lattice coupling.[2]

The calculation of the transverse susceptibility $\chi_{xx}(\omega)$ proceeds in a manner similar to the longitudinal relaxation. The imaginary part $\chi''_{xx}(\omega)$ is shown in Fig. 3 for three values of η and the same ω_0 and T as before. The resonance lines are located at $\omega \approx \Omega_0$ and their positions vary with η, as expected. The lines are very nearly Lorentzian except at high frequencies where the influence of the second maximum prevails. Again, the processes mentioned above and the effects of spin-spin interactions will alter the picture in practice.

Knowing the correlation functions $C_{zz}(t)$ and $C_{-+}(t)$, we could easily calculate the moments of the corresponding spectra. Unlike in the simple Lorentzian model, all moments exist because they are related to the derivatives of the correlation functions at $t=0$, which are finite since the correlation functions are well behaved at all times.

To summarize, we conclude that the stochastic theory is applicable to the calculation of both the longitudinal relaxation and the transverse resonance absorption at all frequencies. Our study was simplified through the use of an isotropic model for spin-phonon coupling; however, the method could probably be extended to more general cases of spin-lattice interaction. The Lorentzian model is only recovered in the limit of very low frequencies, that is, when the collisions take place on a time scale short compared to the changes of the external field. The high-frequency relaxation and resonance spectra, however, reveal some structure which is due to the real physical details of the collisions, and is furthermore related to the high-frequency part of the phonon density of states.

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