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Kinetic-Theory Calculation of the Nuclear-Magnetic-Resonance Line Shape in Dipolar and Exchange-Coupled Systems

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A set of kinetic equations for the anisotropic Heisenberg paramagnet is presented. These are an extension of equations derived previously for the isotropic system and used to predict the spectral densities in $\mathrm{RbMnF_3}$. The equations conserve the total spin and energy and have for their stationary solution the anisotropic-spherical-model correlation functions. An approximate solution of these equations using a constant-relaxation-time approximation yields results for the free-induction decay of the transverse magnetization in a dipolar lattice in a strong magnetic field that is in good agreement with the experiments on $\mathrm{CaF_2}$.

In this paper we present a kinetic theory for the anisotropic Heisenberg paramagnet with application to a microscopic calculation of the free-induction decay and diffusion coefficient in a dipole lattice subject to a large external field. This problem has been the source of considerable theoretical work.[1-5] Previous treatments, however, have either introduced *ad hoc* assumptions about the shape of one or another of the spectral functions involved in the calculation, and hence must be considered phenomenological, or were based upon arbitrary operator expansions, which do not give the correct long-time behavior, and in any case yield little insight into the physics of the problem. The first attempt at a microscopic theory was due to Borckmans and Walgraef,[6] who used a set of kinetic equations analogous to those derived in the early work of Resibois and DeLeneer,[7] and obtained rather good agreement with experiment by iterating their equations using as zeroth-order solution the phenomenological form suggested by Abragam[8] as a fit to the data, with the parameters of this form calculated from the exact second and fourth moment. This procedure is inconsistent, however, since the fourth moment predicted by their equation is seriously in error, which would lead, if the equation were solved exactly, to a solution that seriously underestimates the damping of the oscillations appearing in the data. This inadequacy is a reflection of the fact that their equations do not include any scattering processes for the intermediate fluctuation modes in the "mass operator" [$\Phi^\alpha(q, z)$ in this paper]. This is a deficiency also of more refined theories based upon the independent mode approximation for the mass operator that could be applied to this problem, such as the equation derived by Kawasaki, Resibois and DeLeneer, Wegner, and Blume and Hubbard.[9]

The calculation we shall present is based upon a kinetic theory for the anisotropic Heisenberg Hamiltonian,

$$H = -\tfrac{1}{2}\sum_{j,k} a_{jk}\vec{S}_j\cdot\vec{S}_k + b_{jk}S_j^z S_k^z , \tag{1}$$

and is an extension of a theory for the isotropic system developed by one of us.[10] As for the isotropic case, the theory gives the correct second and fourth moments of the spectral density to lowest order in $1/z$, where z is the number of spins in the range of the interaction and the kinetic equations conserve the total spin and energy. They include the effect of the scattering of intermediate fluctuation modes. The equations are valid at any temperature for which there is no long-range order, and describe as special cases the Ising, X-Y, Heisenberg, and truncated-dipolar models. The latter is appropriate for the calculation of the NMR line shape at infinite temperature (or equivalently the free-induction decay) in a dipole lattice subject to a magnetic field much stronger than the dipolar coupling between the spins. An arbitrary combination of Heisenberg and dipole interaction, in this limit, can be treated by making the choice

$$a_{jk} = V_{jk} + [(\gamma\hbar)^2/2R_{jk}^3](1-3\cos^2\theta_{jk}),$$

$$b_{jk} = -3[(\gamma\hbar)^2/2R_{jk}^3](1-3\cos^2\theta_{jk}) .$$

V_{jk} is the exchange interaction, γ is the gyromagnetic ratio of the spins, and θ_{jk} is the angle between the quantization axis, taken as the direction of the external field, and the vector $\vec{R}_j - \vec{R}_k = \vec{R}_{jk}$. The operator $\vec{S}(\vec{q})$ is defined as $N^{-1/2}\sum_i e^{-i\vec{q}\cdot\vec{R}_i}\vec{S}_i$,

$$a(\vec{q}) = \textstyle\sum_i e^{-i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}a_{ij}, \quad b(\vec{q}) = \sum_i e^{-i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}b_{ij} .$$

The response of the system to an external perturbation is given by

$$\Sigma^{\alpha}(\vec{q}, z) = \int_0^{\infty} e^{izt} \langle S^{\alpha}(q) | S^{\alpha}(q, t)\rangle dt , \qquad (2)$$

where

$$\langle A | B\rangle = \langle\langle \textstyle\int_0^{\beta} e^{\tau H} A^{\dagger} e^{-\tau H} B \, d\tau \rangle\rangle, \quad \langle\langle O\rangle\rangle = \mathrm{Tr}\rho_{\mathrm{eq}} O,$$

$$\rho_{\mathrm{eq}} = e^{-\beta H}/\mathrm{Tr}\, e^{\beta H} .$$

It can be shown that

$$\Sigma^{\alpha}(\vec{q}, z) = i\chi^{\alpha}(\vec{q}, 0)\,[z - \Phi^{\alpha}(q, z)]^{-1}, \qquad (3)$$

where

$$\Phi^{\alpha}(q, z) = \langle (I - P^{\alpha})\mathfrak{L} S^{\alpha}(\vec{q}) \,|\, [z - (I - P^{\alpha})\mathfrak{L}(I - P^{\alpha})]^{-1} \,| \times (I - P^{\alpha})\mathfrak{L} S^{\alpha}(\vec{q})\rangle / \chi^{\alpha}(\vec{q}, 0),$$

$$\chi^{\alpha}(q, 0) = \langle S^{\alpha}(q) | S^{\alpha}(q)\rangle,$$

$\mathfrak{L}$ is the Liouville operator for the system, P^{α} is the projection operator

$$\textstyle\sum_q |S^{\alpha}(q)\rangle\langle S^{\alpha}(q)| / \chi^{\alpha}(q, 0),$$

and I is the identity operator. We define the vertex function

$$\Gamma^0(\bar{q}_1, \bar{q}_2, z) \equiv \langle S^-(q_1) S^+(q_2) \times | [z - (I - P^0)\mathfrak{L}(I - P^0)]^{-1} | \mathfrak{L} S^0(\bar{q})\rangle / \chi^0(q, 0) , \qquad (4)$$

$$\Gamma^-(\bar{q}_1, \bar{q}_2, z) \equiv \langle S^0(\vec{q}_1) S^-(\vec{q}_2) \times | [z - (I - P^-)\mathfrak{L}(I - P^-)]^{-1} | \mathfrak{L} S^-(\vec{q})\rangle / \chi^-(q, 0) , \qquad (5)$$

with $\vec{q} = \vec{q}_1 + \vec{q}_2$; we have then

$$\Phi^0(\vec{q}, z) = \tfrac{1}{2} N^{-1/2} \textstyle\sum_{q'} [a(\vec{q} - \vec{q}\,') - a(\vec{q}\,')] \times \Gamma^0(\vec{q}\,', \vec{q} - \vec{q}\,', z) , \qquad (6)$$

$$\Phi^-(\vec{q}, z) = -N^{-1/2} \textstyle\sum_{q'} [a(\vec{q}\,') - a(\vec{q} - \vec{q}\,') + b(\vec{q}\,')] \times \Gamma^-(\vec{q}\,', \vec{q} - \vec{q}; z) . \qquad (7)$$

The spectral function is given by

$$\mathrm{Re}\,\Sigma^{\alpha}(q, \omega + i\epsilon) = \chi^{\alpha\,\prime\prime}(\vec{q}, \omega)/\omega \equiv f(\omega) . \qquad (8)$$

In order to calculate the response function $\Sigma^{\alpha}(\vec{q}, \omega)$ we must determine the functions $\Gamma^{\alpha}(\vec{q}_1, \vec{q}_2, z)$ which describe the time behavior of the longitudinal and transverse two-spin correlation function for particular initial conditions. This is obtained by constructing a set of kinetic equations for the two-spin correlation functions. The derivation of those equations will be done elsewhere. The equations we propose for $\Gamma^0(\vec{q}_1, \vec{q}_2; z)$ and $\Gamma^-(\vec{q}_1, \vec{q}_2; z)$ are

$$\begin{aligned} z\Gamma^0(\vec{q}_1, \vec{q}_2; z) = {} & N^{-1/2}[n(\vec{q}_2) - n(\vec{q}_1)]/\chi^z(q_1 + q_2, 0) + [\Phi^-(\vec{q}_1; z) + \Phi^-(\vec{q}_2, z)]\,\Gamma^0(\vec{q}_1, \vec{q}_2; z) \\ & + N^{-1/2} \textstyle\sum_{q'} [a(\vec{q}_1 - \vec{q}\,') - a(\vec{q}\,') + b(\vec{q}_1 - \vec{q}\,')]\,\Gamma^-(\vec{q}_1 - \vec{q}\,', \vec{q}_2; z)\,\Gamma^0(\vec{q}\,', q_1 + q_2 - \vec{q}\,'; z) \\ & + N^{-1/2} \textstyle\sum_{q'} [a(\vec{q}_2 - \vec{q}\,') - a(\vec{q}\,') + b(\vec{q}_2 - \vec{q}\,')]\,\Gamma^-(\vec{q}_2 - \vec{q}\,', \vec{q}_1; z)\,\Gamma^0(\vec{q} - \vec{q}\,', \vec{q}\,'; z) , \end{aligned} \qquad (9)$$

$$\begin{aligned} z\Gamma^-(\vec{q}_1, \vec{q}_2; z) = {} & N^{-1/2}[n(\vec{q}_2) - 2m(\vec{q}_1)]/\chi^-(\vec{q}_1 + \vec{q}_2, 0) + [\Phi^0(\vec{q}_1, z) + \Phi^-(\vec{q}_2, z)]\,\Gamma^-(\vec{q}_1, \vec{q}_2; z) \\ & + \tfrac{1}{2} N^{-1/2} \textstyle\sum_{q'} [a(q_1 - q') - a(q')]\,\Gamma^0(q_2, q_1 - q'; z)\,\Gamma^-(q - q', q'; z) \\ & - N^{-1/2} \textstyle\sum_{q'} [a(q') - a(q_2 - q') + b(q')]\,\Gamma^-(q_1, q_2 - q'; z)\,\Gamma^-(q', q - q'; z) , \end{aligned} \qquad (10)$$

where

$$q = q_1 + q_2 ,$$

$$n(q) = \langle\langle S^-(q) S^+(-q)\rangle\rangle,$$

$$m(q) = \langle\langle S^z(q) S^z(-q)\rangle\rangle .$$

$n(q)$ and $m(q)$ are obtained from a rate-balance equation for the decay rates of the fluctuation modes that arises as the condition for a stationary solution of the kinetic equations to exist, and are the anisotropic-spherical-model values. These can be obtained, of course, directly by making the usual spherical-model approximations on the Hamiltonian given in (1). The equivalence of the stationary solution and the spherical model is a consequence of evaluating the decay rates correctly to lowest order in $1/z$.

The problem of the isotropic Heisenberg paramagnet has been treated by the kinetic equation formalism[10] and has been shown to give very good agreement with the neutron-scattering measurements of the spectral density in the isotropic Heisenberg antiferromagnet RbMnF$_3$ by Tucciarone, Hastings, and Corliss.[11] The set of equations (9) and (10) enables one to treat all cases ranging from the pure exchange case to the pure dipole case. [They reduce to the equation of Ref. 10 when $b(q) = 0$.] Furthermore, the same approximation that was used to obtain the approximate solution used to fit the data in RbMnF$_3$, the constant-relaxation-time approximation, can be used to obtain a good fit to the data in CaF$_2$.

The constant-relaxation-time approximation for

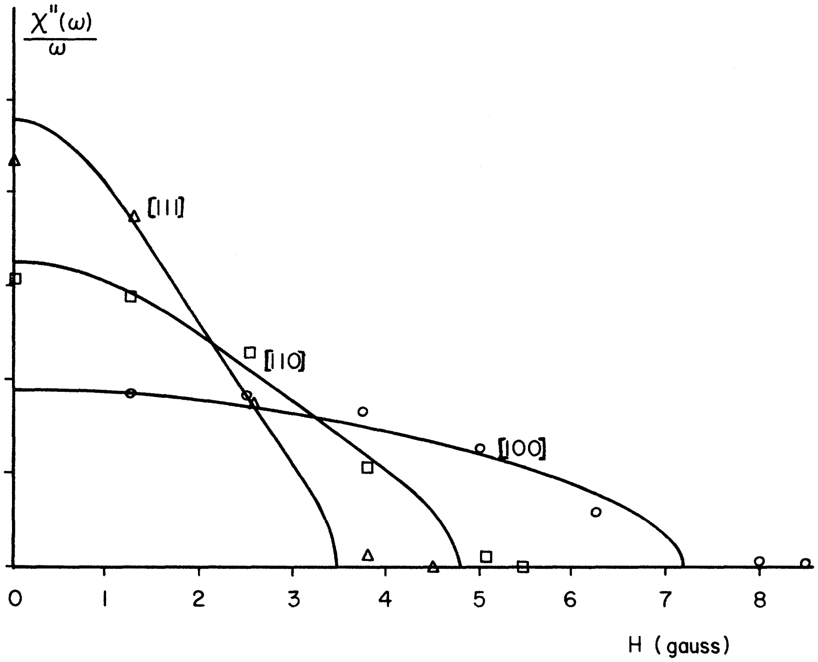


FIG. 1. Comparison of theoretical spectral densities calculated from Eq. (16) with the line-shape measurements of Bruce on CaF_2, for several orientations of the magnetic field with respect to the crystal axes. The theoretical curves have been normalized to agree with the data at $\omega = 0$ for the [100] direction.

the vertex functions $\Gamma^\alpha(q_1, q_2, z)$ is defined, at $T = \infty$, by the assumption that the vertex functions can be written in the form

$$\Gamma^0(\vec{q}_1, \vec{q}_2; z) \simeq N^{-1/2} \tfrac{2}{3} S(S+1)[a(\vec{q}_2) - a(\vec{q}_1)]/\nu(z) , \tag{11}$$

$$\Gamma^-(\vec{q}_1, \vec{q}_2; z) \simeq -N^{-1/2} \tfrac{1}{3} S(S+1) \times [a(\vec{q}_1) - a(\vec{q}_2) + b(\vec{q}_1)]/\mu(z) . \tag{12}$$

The approximation states that the relaxation of the functions $\Gamma^\alpha(\vec{q}_1, \vec{q}_2; z)$ is independent of $\vec{q}_1$ and $\vec{q}_2$. The approximation is successful because at temperatures away from the transition point fluctuations of any wave vector will decay primarily into short-wavelength fluctuations, since the phase space available for such decays is large, and the relaxation times of the short-wavelength fluctuations are roughly constant. The functions $\nu(z)$ and $\mu(z)$ are determined in such a way that the second and fourth moments are given by the [correct to $O(1/z)$] values that one would have obtained from (9) and (10) if they had been solved exactly.

We take the case $V_{ij} = 0$ and the limit $\vec{q} = 0$ corresponding to the free-induction decay of the magnetization in a dipole lattice. The $q \neq 0$ spectral densities can be used to describe experiments such as the double-resonance experiments on Ca in CaF_2.[12]

In order to solve for the transverse relaxation let us insert expression (11) and (12) in the right-hand side of (10), divide by z, and substitute the resultant expression for $\Gamma^-(\vec{q}_1, \vec{q}_2; z)$ in (7) to evaluate $\Phi^-(\vec{q}, z)$. We obtain

$$\Phi^-(\vec{q}, z) = z^{-1} \langle \omega^2 \rangle^-_{q=0} + z^{-1} \nu(z)^{-1} \mu(z)^{-1}\, {}^A\langle \Omega^4 \rangle_{q=0} + z^{-1} \mu(z)^{-2} \langle \Omega^4 \rangle_{q=0} , \tag{13}$$

where $\langle \omega^2 \rangle^-_{q=0}$ is the second moment and ${}^{A,B}\langle \Omega^4 \rangle_{q=0}$ are related to the fourth moment by

$${}^A\langle \Omega^4 \rangle^-_{q=0} + {}^B\langle \Omega^4 \rangle^-_{q=0} = \langle \Omega^4 \rangle^-_{q=0} = \langle \omega^4 \rangle^-_{q=0} - \langle \omega^2 \rangle^2_{q=0} .$$

The value for $\Phi^-(\vec{q}, z)$ when (12) is inserted directly in (7) is given by

$$\Phi^-(\vec{q}, z) = \mu(z)^{-1} \langle \omega^2 \rangle_{q=0} . \tag{14}$$

Because for the pure dipole case the value for ${}^A\langle \Omega^4 \rangle^-_{q=0}$ is $\frac{1}{5}$ of ${}^B\langle \Omega^4 \rangle^-_{q=0}$ there is little accuracy lost by assuming $\nu(z) = \mu(z)$ in Eq. (13). Requiring that (13) and (14) be consistent, we find for $\mu(z)$

$$\mu(\omega + i\epsilon) = \tfrac{1}{2}\omega + i \left[\langle \Omega^4 \rangle^-_{q=0} / \langle \omega^2 \rangle^-_{q=0} - \tfrac{1}{4}\omega^2 \right]^{1/2} ,$$

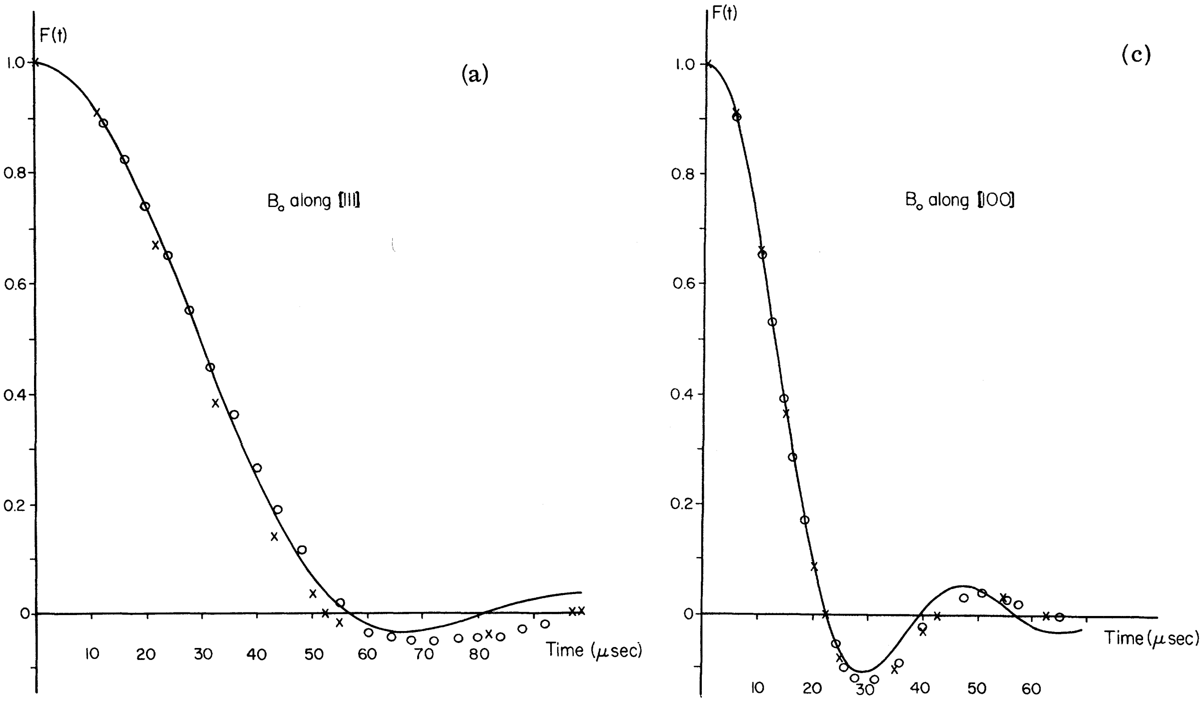
when

$$\omega < 2 \left(\langle \Omega^4 \rangle^-_{q=0} / \langle \omega^2 \rangle^-_{q=0} \right)^{1/2} . \tag{15}$$

The spectral function is obtained from (15), (14) and (8):

$$f(\omega) = \frac{1}{\langle \omega^2 \rangle^-} \left(\frac{\langle \Omega^4 \rangle^-}{\langle \omega^2 \rangle^-} \right)^{1/2} \left(1 - \frac{\omega^2}{4} \frac{\langle \omega^2 \rangle^-}{\langle \Omega^4 \rangle^-} \right)^{1/2} \times \left[1 + \frac{\omega^2}{\langle \omega^2 \rangle^-} \left(\frac{\langle \Omega^4 \rangle^-}{\langle \omega^2 \rangle^-} - 1 \right) \right]^{-1} . \tag{16}$$

The line shape for general q with the approximation (11) and (12) is obtained by using the form (16) with the appropriate q-dependent moments. To compare with CaF_2, we will use the exact values of the



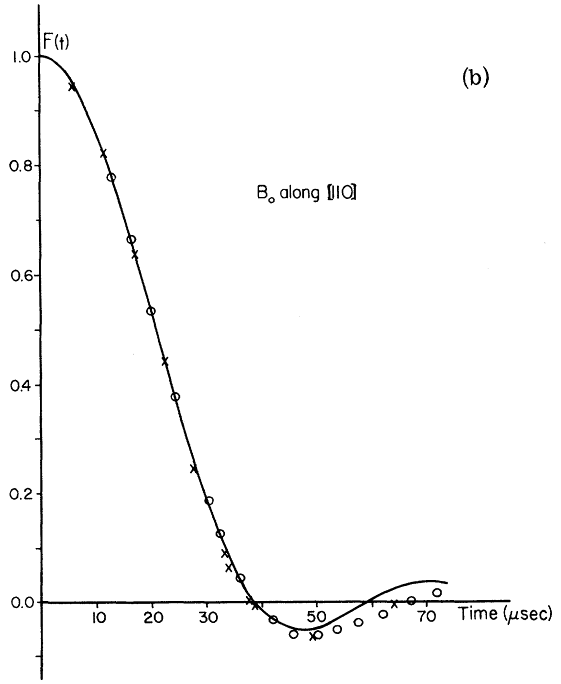


FIG. 2. (a)–(c): Comparison of the theoretical free-induction decay $F(t)$ obtained by Fourier transforming the spectral densities predicted by Eq. (16), with experimental results on CaF_2. The crosses are the data of Lowe and Norberg; the circles are the Fourier transforms of Bruce's data.

moments.[8] The second moment predicted by (9) and (10) is exact. The fourth moment differs by a few percent from the exact value. We show in Fig. 1 the line shape for three different directions of the external field, normalized to the same area. The points represent Bruce's data.[13] An absolute normalization of Bruce's data for the scale of $\chi''(\omega)/\omega$ is not available and so we chose to normalize the experimental data by fitting $\chi''(\omega)/\omega$ at zero frequency for the [100] direction. This difficulty is not encountered when one compares the results in the time domain. The Fourier transform of the line shape, the free-induction decay, is shown in Fig. 2 for the three different directions of the external field. The points represent Lowe and Barnaal's data.[14]

$\nu(z)$ can be calculated in a similar fashion to $\mu(z)$ and from it the approximation for $\Phi^z(q, z)$ analogous to (14). Since $\langle\omega^2\rangle_q^0 \,\alpha q^2$ for small q, whereas $\nu(0)$ is a purely imaginary constant, $\Phi^0(q, \omega) = -iDq^2$ for $q \to 0$, $\omega \to 0$. The longitudinal fluctuations at long wavelengths are therefore diffusive. We find for the diffusion coefficient in the dipole lattice the result

$$D = \tfrac{1}{3}S(S+1)\,0.3\,(\lambda^2\hbar/d)$$

and for $S=\frac{1}{2}$ (CaF_2), $D = 0.15(\gamma^2\hbar/d)$, where d is the lattice spacing. This result is in agreement with other theories.[15]

It is clear that the approximation accounts satisfactorily for the systematic variation of the free-induction decay with the direction of the magnetic field and gives a good qualitative line shape. The quantitative differences between the theoretical and experimental curves for $\chi''(\omega)/\omega$ are comparable to the corrections that we expect to the approximate solution (16) from solving (9) and (10) exactly. Iterative solutions based upon Eq. (16) as a zeroth approximation for the isotropic case indicate that the corrections to (16) will be on the order of 20% at most (for the zero-frequency spectral densities). We expect that the constant relaxation time is a better approximation for the dipole system, since there is no combination of wave vector for which the relaxation time goes to infinity as it does in the isotropic case when both wave vectors q_1 and q_2 in the vertex function go to zero. In the isotropic case, the deviations of the iterated solutions from the experimental data are on the order of 10% at most for short wavelengths.

In conclusion, we think that the present results, together with the neutron-scattering results on $RbMnF_3$, demonstrate clearly the utility and lower limits on the accuracy of the kinetic equation in describing paramagnetic systems with arbitrary ratios of dipole to exchange energy, at least at infinite temperature. The constant-relaxation-time approximation which leads to the rather simple expression for the spectral densities, Eq. (16), when used in conjunction with the kinetic equations, seems to capture the essential features of the dynamics. It can be used as it stands for rough calculations, or as the basis for an iterative solution of the kinetic equations to obtain more accurate results. It is reasonable to expect that the equation will provide solutions for the *X*-*Y* and Ising limits that have comparable accuracy to those obtained here and, since they are valid at all temperatures in the paramagnetic regime and for arbitrary dimensionality, should provide the context for correlating a wide range of experimental results.

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[1] J. H. VanVleck, Phys. Rev. 74, 1168 (1948).

[2] R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).

[3] I. J. Lowe and R. E. Norberg, Phys. Rev. 107, 46 (1957).

[4] S. Clough and I. R. McDonald, Proc. Phys. Soc. (London) 86, 833 (1965).

[5] P. Mansfield, Phys. Rev. 151, 199 (1966).

[6] P. Borckmans and D. Walgraef, Phys. Rev. 167, 282 (1968); Physica 35, 80 (1967).

[7] P. Resibois and M. DeLeneer, Phys. Rev. 152, 305 (1966); 152, 318 (1966).

[8] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[9] K. Kawasaki, J. Phys. Chem. Solids 28, 1277 (1967); P. Resibois and R. DeLeneer, Phys. Rev. 178, 806 (1969); 178, 819 (1969); F. Wegner, Z. Physik 216, 433 (1968); 218, 260 (1969); M. Blume and J. Hubbard, Phys. Rev. B 1, 3815 (1970).

[10] G. F. Reiter, Solid State Commun. 7, 1327 (1969); Phys. Rev. B 5, 222 (1972); (unpublished).

[11] A. Tucciarone, J. M. Hastings, and L. M. Corliss, Phys. Rev. Letters 26, 257 (1971).

[12] D. A. McArthur, E. L. Hahn, and R. E. Walstedt, Phys. Rev. 188, 609 (1969).

[13] C. R. Bruce, Phys. Rev. 107, 43 (1957).

[14] I. J. Lowe and D. E. Barnaal, Phys. Rev. 148, 328 (1966).

[15] S. Gade and I. J. Lowe, Phys. Rev. 156, 817 (1967).