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Spin Fluctuations in Heisenberg Paramagnets. II. Kinetic Theory and Approximate High-Temperature Solutions*†

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A set of kinetic equations describing the time evolution of the two-spin correlation functions $\langle S^-(q_1,\ t)S^+(q_2,\ t)\rangle$ and $\langle S^z(q_1,\ t)S^z(q_2,\ t)\rangle$ is derived. The derivation is based upon a cluster expansion of the equations of motion and an intuitively plausible renormalization. The resultant equations may be interpreted graphically, and the derivation of the kinetic equations taken to be a partial justification of the summation of a particular set of graphs in the moment expansion for the spectral density. The kinetic equations have the property that they conserve the total spin $\sum\langle\vec{S}(\vec{q},\ t)\cdot\vec{S}(-\vec{q},\ t)\rangle$ and the total energy $\sum_q V(q)\,\langle\vec{S}(\vec{q},\ t)\cdot\vec{S}(-\vec{q},\ t)\rangle$. The second and fourth moments of the spectral density for fluctuations in the magnetization predicted by these equations are correct to lowest order in $1/c$, where c is the number of spins in the range of the interaction. Numerical calculations of the spectral density, based upon an approximate solution of the kinetic equations that is valid outside of the critical region, are compared with the neutron-scattering data for a wide range of temperatures and wave vectors and found to be in good agreement. The temperature dependence of the diffusion coefficient in the high-temperature region is calculated and compared with experiment.

INTRODUCTION

The problem of calculating the dynamical response of the Heisenberg paramagnet to external fields is not susceptible to standard methods of calculation. The fluctuations in the system do not take place in well-defined modes, but exist instead as heavily damped excitations which interact strongly with each other, thus precluding any standard perturbation analysis. There is, furthermore, no small parameter in the problem which might allow an asymptotic solution, although some important simplifications are achieved by assuming the parameter $1/c$, where c is the effective number of spins in the range of the exchange interaction, is small. Progress has been made in recent years[1–4] by using a treatment which regards the fluctuation modes as being independent of each other, and corresponds to the first term in a renormalized perturbation theory[5] which is ordered in terms of the number of interactions the modes are assumed to undergo. Such a treatment is unable, in the first approximation, to account for the details of the spectral density in the paramagnet. Although it gives results that have qualitative validity, it gives incorrect values for the fourth moment of the spectral density, and does not include some important physical constraints on the dynamics, such as the conservation of energy and total spin. This work presents an alternative treatment of the dynamics, based upon a set of kinetic equations that incorporate these constraints, and which lead to values of the second and fourth moments that are correct to lowest order in $1/c$. The equations will be derived from a decoupling of the equations of motion by means of a cluster expansion and a subsequent renormalization, but may be shown *a posteriori* to correspond to a particular prescription for the resummation of diagrams for the spectral function $\Sigma(q, z)$ introduced in a previous paper[5] (hereafter referred to as I). The basic object of the theory is not $\Sigma(q, z)$, however, but $\Gamma(q_1, q_2, z)$, which describes the decay of a fluctuation of wave vector $q = q_1 + q_2$ into two fluctuations of wave vectors q_1 and q_2. As a result, it is possible to treat multiple interactions between the modes, and it is the inclusion of these interactions that leads to the conservation of total spin and energy. These processes are most important for the short wavelength modes, which cancannot be adequately described by the independent-mode approximation. It will be shown that the spectral densities that are predicted by these equations agree very well with the experimental results on $RbMnF_3$ [6] at short wavelengths outside of the critical region.

The result of the analysis, in addition to equations for Γ and Σ, is a set of kinetic equations for the two-spin correlation functions $\langle S^-(q_1)S^+(q_2);\ t\rangle$ and $\langle S^z(q_1)S^z(q_2);\ t\rangle$. These may be used to interpret experiments that depend upon multiple-spin correlations, such as ultrasonic absorbtion,[7] light scattering,[8] and EPR-linewidth measurements,[9] and can be used to determine the thermal conductivity.[10] These equations are in some respects analogous to the Boltzmann equation for a gas. They differ most significantly in that there is no separation of time scales for the "internal" relaxation processes and the time scale for the modes of interest. They may, in fact, be used to describe the details of the internal relaxation processes.

In Sec. I we give the derivation of the kinetic equations; for Sec. II we demonstrate that the equations conserve the energy and total spin. In Sec. III an approximate solution of the equations is found using a constant-relaxation-time approximation for the vertex function as a first approximation, and then iterating the equations of motion to obtain improved values for the spectral density. These are compared with the neutron scattering data on $RbMnF_3$. The diffusion coefficient at infinite temperatures and its behavior at high temperatures is also calculated and compared with experiments. In Sec. IV we compare our results with other theoretical calculations.

I. DERIVATION OF THE KINETIC EQUATIONS

A kinetic theory provides closed equations of motion for some set of correlation functions. The equations are supposed to hold for arbitrary initial values of these correlation functions, and then determine the behavior of these functions for all times thereafter.

In I we developed a diagrammatic expansion for $\Sigma(\vec{q}, z)$, which gives the response of the magnetization to an initial disturbance introduced isothermally by a unit magnetic field of wave vector $\vec{q}$. $\Sigma(q,z)$ is defined as

$$\Sigma(q, z) = \int_0^\infty e^{izt} \langle S^z(q, 0) \,|\, S^z(q, t)\rangle \, dt \; , \tag{1.1}$$

where

$$\langle A \,|\, B\rangle = \langle\langle \int_0^\beta e^{\tau H} A^+ e^{-\tau H} B d\tau \rangle\rangle$$

and $\langle\langle \;\; \rangle\rangle$ denotes a thermal average. $\Sigma(q, z)$ may be written from (1.1) as

$$\Sigma(q, z) = i \langle S^z(q) \,|\, [z - \mathfrak{L}\,]^{-1} \,| S^z(q)\rangle \; ,$$

where $\mathfrak{L}$ is the Liouville operator for the system. $\Sigma(q, z)$ is related to the dynamical susceptibility of the system, defined as

$$\chi(q, z) = i \int_0^\infty \langle\langle [S^z(q, t), \; S^z(-q, 0)]\rangle\rangle \, e^{izt} \, dt, \qquad \mathrm{Im} z > 0 \tag{1.2}$$

by the relation

$$\Sigma(q, z) = [\chi(q, z) - \chi(q, 0)]/iz \; , \tag{1.3}$$

so that

$$\mathrm{Re}\Sigma(q, \; \omega + i) = \chi''(q, \omega)/\omega \; , \tag{1.4}$$

where $\chi''(q, \omega)$ is the imaginary part of the susceptibility. By introducing a projection operator P onto the subspace of the Hilbert space of all linear operators on the spin-state space consisting of all linear combinations of the operator $\{S_0^z\}$, it can be shown that

$$\Sigma(q, z) = i\chi(q, 0)[z - \varphi(q, z)]^{-1} \; , \tag{1.5}$$

where $\varphi(q, z)$ is defined as

$$\varphi(q, z) = \langle (I - P)\mathfrak{L}S^z(q) \,|\, [z - (I - P)\mathfrak{L}(I - P)\;]^{-1} \times \,|\, (I - P)\mathfrak{L}S^z(q)\rangle / \chi(q, 0) \; . \tag{1.6}$$

To calculate $\varphi(q, z)$, one must be able to calculate the time of evolution of $\langle S^-(\vec{q}^1)S^+(\vec{q} - \vec{q}^1)\rangle$. We are using the single bracket $\langle \;\; \rangle$ to denote an average over an arbitrary nonequilibrium density matrix. It is understood that the averages are time dependent, but for simplicity of notation we shall not, in most cases, indicate this explicitly. If it is necessary, we will use the notation $\langle \;\; ; t\rangle$, since all operators appearing in the product will be evaluated at the same time. The Laplace transform of an average will be denoted by $\langle \;\; ; z\rangle$.

Since $\Sigma(\vec{q}, z)$ can be regarded in the linear response of the magnetization to a particular initial condition, one might hope to relate $\langle S^-(\vec{q}')S^+(\vec{q} - \vec{q}')\rangle$ and $\langle S^z(\vec{q})\rangle$ through a system of kinetic equations.

Although a meaningful set of kinetic equations does not exist if one limits consideration only to these quantities, the attempt to derive such an equation will indicate clearly the relationship between the decoupling scheme that we will use and the expansion of the moments in powers of $1/c$ described in I, as well as the limitations of the decoupling scheme.

The equations of motion for $\langle S^z(q)\rangle$ and $\langle S^-(\vec{q}_1) \times S^+(\vec{q}_2)\rangle$ are

$$i \frac{\partial}{\partial t} \langle S^z(\vec{q})\rangle = \tfrac{1}{2} N^{-1/2} \sum_{q'} [V(\vec{q} - \vec{q}') - V(\vec{q}')\,] \langle S^-(\vec{q}')S^+(\vec{q} - \vec{q}')\rangle \; , \tag{1.7}$$

$$\begin{aligned} i \frac{\partial}{\partial t} \langle S^-(\vec{q}_1)S^+(\vec{q}_2)\rangle = {} & N^{-1/2} \sum_{q_3} [V(\vec{q}_1 - \vec{q}_3) - V(\vec{q}_3)] \langle S^-(\vec{q}_1 - \vec{q}_3)S^z(\vec{q}_3)S^+(\vec{q}_2)\rangle \\ & - N^{-1/2} \sum_{q_3} [V(\vec{q}_2 - \vec{q}_3) - V(\vec{q}_3)\,] \langle S^-(\vec{q}_1)S^z(\vec{q}_3)S^+(\vec{q}_2 - \vec{q}_3)\rangle \; . \end{aligned} \tag{1.8}$$

We observe that the initial density matrix, if it is to describe a physically realizable situation, will have the cluster property. That is, if two groups of spins are separated by a large distance, they will behave independently. Hence we expect that for any physical density matrix

$$\langle S_i^- S_j^z S_k^+ \rangle \to \langle S_i^- S_k^+ \rangle \langle S_j^z \rangle$$

when the site j is sufficiently far from the sites i and k. Furthermore, we expect that the cluster property will hold for all times, so that it forms the basis for a rational means of decoupling the equations of motion for the magnetization and the various correlation functions. The general procedure for the decoupling at a particular level of approximation is to replace a correlation function involving n spins on different sites by the sum of all the cumulant averages involving less than n spins. In the present case, the equations of motion for the nonequilibrium averages corresponding to (1.7) and (1.8) can be closed by means of the approximation

$$\begin{aligned}\langle S_i^- S_j^z S_{k'}^+ \rangle \simeq \langle S_i^- \rangle \langle S_j^z S_k^+ \rangle + \langle S_k^+ \rangle \langle S_j^z S_i^- \rangle \\ + \langle S_j^z \rangle \langle S_i^- S_{k'}^+ \rangle - 2 \langle S_i^- \rangle \langle S_{k'}^+ \rangle \langle S_k^z \rangle, \\ i \neq j \neq k \ . \end{aligned} \quad (1.9)$$

Such an approximation neglects only those correlations which are nonvanishing when all of the spins involved in the average are "close" to one another. The range of these "short-range" correlations will depend in general upon the number and components of the spins involved in the averages, and the initial conditions. It may, in fact, not be possible to define a range for these correlations in any meaningful way. For instance, in the ordered phase of the ferromagnet, the quantity $\sum_{i=1}^{N} \langle \langle S_0^- S_i^+ \rangle \rangle$ diverges as N approaches infinity, and it is not possible to regard these correlations as being negligible when the distance between the two lattice sites exceeds some characteristic length. In general, we can define a range for a cumulant correlation function involving n spins if the quantity one obtains by fixing a particular site and summing over all the possible sites for the remaining $n-1$ spins is finite in the limit of an infinite crystal. If this is not the case, then the cumulant correlation function will be said to show long-range order.

In the absence of long-range order for the cumulant average $\langle S_i^- S_k^z S_j^+ \rangle_c$, which we define as the difference between the left- and right-hand sides of Eq. (1.9), the approximation (1.9) can be viewed as leading to asymptotically correct expressions for the time derivatives of the correlation functions in the limit of long-range exchange forces.

To see this, consider a particular term contributing to $-\partial^2 \langle S_i^z \rangle / \partial t^2$:

$$\sum_k \sum_{k'} V_{ik} V_{kk'} \langle S_i^- S_k^z S_{k'}^+ \rangle \ . \quad (1.10)$$

We will assume that $V_{ik} = V$ for $|\vec{r}_i - \vec{r}_k| < R$, and vanishes otherwise. If the range of the exchange interaction is much larger than the range of the three-spin cumulant correlation functions, then $\langle S_i^- S_k^z S_{k'}^+ \rangle_c$ will contribute to only a fixed number of terms in the sum, whereas the terms kept in the approximation (1.9) can contribute to all of them. If the number of spins in the interaction range is c, then the contribution to the sum (1.4) from the cumulant term will be smaller by a factor of at least c^{-1} than the contribution from the terms in (1.9). In a three-dimensional crystal where c has a value on the order of 10, results valid in the Weiss limit can have quantitative validity for realistic systems.

As far as the interpretation in terms of an expansion in $1/c$ is concerned, terms in a three-spin correlation function involving spins on the same site are not important, and can be handled cavalierly. Thus for the case of $S = \frac{1}{2}$, it does not matter whether we factor a term such as $\langle S_i^- S_i^z S_k^+ \rangle$, or treat it exactly as $\frac{1}{2} \langle S_i^- S_k^+ \rangle$.

The equations of motion one obtains with the approximation (1.9) are nonlinear and couple $\langle S^{\pm} \rangle$ and $\langle S^z \rangle$. When equations similar to (1.7) and (1.8) are written for the time behavior of $S_i^{\pm}$, and the approximation analogous to (1.9) is made, one obtains a closed set of coupled nonlinear equations. These have a stationary solution if the magnetization and correlation functions satisfy the relations

$$\begin{aligned} &\langle S_i^z \rangle = \lambda, & &\langle S_i^{\pm} \rangle = 0 \ , \\ &\langle S_i^- S_j^+ \rangle = \langle S_i^+ S_j^- \rangle = \bar{n}(i-j) \ , & &\langle S_i^z S_j^z \rangle = \bar{m}(i-j). \end{aligned}$$

The parameter λ and the functions $\bar{m}, \bar{n}$ can be arbitrary, in the sense that any choice will lead to to a stationary solution of the equations. We will choose them to be the values appropriate to thermal equlibrium, and will linearize the nonlinear equations obtained from the cluster approximation about this stationary solution. We then obtain a set of linear equations that describe the behavior in time of small disturbances from equilibrium. We find, in the paramagnetic regime, where $\lambda = 0$ and $\bar{n}(i-j) = 2\bar{m}(i-j)$, that the two-spin correlation function satisfies

$$i \frac{\partial}{\partial t} \delta \langle S^-(\vec{q}_1) S^+(\vec{q}_2) \rangle = N^{-1/2} \gamma^0(\vec{q}_1, \vec{q}_2) \delta \langle S^z(\vec{q}_1 + \vec{q}_2) \rangle \ , \quad (1.11)$$

where $\delta\langle \ \rangle$ indicates the deviation from equilibrium, and

$$\begin{aligned}\gamma(\vec{q}_1, \vec{q}_2) = V(\vec{q}_1 + \vec{q}_2) [n(\vec{q}_1) - n(\vec{q}_2)] \\ + V(\vec{q}_2) n(\vec{q}_2) - V(\vec{q}_1) n(\vec{q}_1) \ , \end{aligned} \quad (1.12)$$

$$n(\vec{q}_1) = \langle \langle S^-(\vec{q}_1) S^+(-\vec{q}_1) \rangle \rangle \ .$$

The bracket $\langle\langle \ \rangle\rangle$ indicates an average over the equilibrium density matrix. These equations are supposed to hold for arbitrary initial conditions. In particular, if we choose the initial density matrix to be

$$\rho=\rho_{\mathrm{eq}}+\left[\int_0^\beta e^{\tau\mathcal{H}}S^z(-\vec{\mathrm{q}})e^{-\tau\mathcal{H}}\,d\tau\right]\rho_{\mathrm{eq}}\,\delta h(\vec{\mathrm{q}})\ , \tag{1.13}$$

then $\delta\langle S^z(\vec{\mathrm{q}})\,;\,t\rangle=\delta h(\vec{\mathrm{q}})\Sigma(\vec{\mathrm{q}},t)$. The parameter $\delta h(\vec{\mathrm{q}})$ is irrelevant, since the equations have been linearized, and can be taken to be 1. The kinetic equations (1.7) and (1.11) with particular initial conditions thus provide a concrete approximation for $\Sigma(\vec{\mathrm{q}},t)$. If we Laplace transform these equations, we find

$$z\Sigma(\vec{\mathrm{q}},z)=i\chi(\vec{\mathrm{q}},0)+\tfrac{1}{2}N^{-1/2}\sum_{q'}\left[V(\vec{\mathrm{q}}-\vec{\mathrm{q}}\,')-V(\vec{\mathrm{q}}\,')\right]\delta$$
$$\times\langle S^-(\vec{\mathrm{q}}\,')S^+(\vec{\mathrm{q}}-\vec{\mathrm{q}}\,')\,;\,z\rangle\ , \tag{1.14a}$$

$$z\delta\langle S^-(\vec{\mathrm{q}}\,')S^+(\vec{\mathrm{q}}-\vec{\mathrm{q}}\,')\,;\,z\rangle$$
$$=i[S^-(\vec{\mathrm{q}}\,')S^+(\vec{\mathrm{q}}-\vec{\mathrm{q}}\,'),\ S^z(-\vec{\mathrm{q}})]$$
$$+N^{-1/2}\gamma^0(\vec{\mathrm{q}}\,',\vec{\mathrm{q}}-\vec{\mathrm{q}}\,')\Sigma(\vec{\mathrm{q}},z)\ , \tag{1.14b}$$

where the bracket (A,B) is defined as $\langle\langle\int_0^\beta e^{\tau\mathcal{H}}Ae^{-\tau\mathcal{H}}\times B\,d\tau\rangle\rangle$. Solving for $\Sigma(\vec{\mathrm{q}},z)$, we obtain

$$\varphi(\vec{\mathrm{q}},z)=\omega^2(\vec{\mathrm{q}})/z \tag{1.15a}$$

and

$$\Sigma(\vec{\mathrm{q}},z)=i\chi(\vec{\mathrm{q}},0)\,\frac{1}{z-\dfrac{\omega^2(\vec{\mathrm{q}})}{z}}\ . \tag{1.15b}$$

We have used the fact that $(S^z(q),\mathcal{L}S^z(-q))=0$ to obtain (1.15) from (1.12) and (1.14). The quantity $\omega^2(q)$ is explicitly

$$\omega^2(\vec{\mathrm{q}})=\tfrac{1}{2}N^{-1}\sum_{q'}\left[V(\vec{\mathrm{q}}-\vec{\mathrm{q}}\,')-V(\vec{\mathrm{q}}\,')\right]\gamma^0(\vec{\mathrm{q}}\,',\vec{\mathrm{q}}-\vec{\mathrm{q}}\,')\ . \tag{1.15c}$$

If (1.15) were taken literally, one would conclude that there were poles on the real axis at the frequency $\omega=\pm[\omega^2(q)]^{1/2}$, corresponding to well-defined normal modes for each wave vector q.

In fact, we expect, although we cannot prove, that $\varphi(\vec{\mathrm{q}},z)$ is analytic in z near $z=0$, and has the form (see Appendix)

$$\varphi(\vec{\mathrm{q}},\omega+i\epsilon)=-iDq^2+\alpha\omega q^2+O(q^4)+O(\omega^2q^2)\ ,$$

which would lead to diffusive behavior for small q. We conclude, therefore, that (1.11) can only hold for small times.

We have observed that the cumulants that we have neglected contribute terms in the expression for $\partial^2\langle S_0^z\rangle/\partial t^2$ that are smaller by a factor of $1/c$ than those that we have kept. However, after a time $t\sim c^{1/2}$, the effect of these terms on $\langle S_i^z\,;\,t\rangle$ can be as large as the effect of the terms we have kept. Since the frequencies $[\omega^2(q)]^{1/2}$ are at most proportional to $c^{-1/2}$, our equations of motion are reliable for at most one period of oscillation, even in the limit that $c\to\infty$.

A further difficulty with the equations can be seen by considering the case for which $q=0$. Equation (1.11) then predicts that $\partial\langle S^-(q')S^+(-q')\rangle\!\rangle/\partial t=0$. This is clearly false, since a disturbance of the two-spin correlation function, produced by a temperature gradient perhaps, would not persist in time, but would decay until the correlation functions reached their equilibrium values. The processes that produce the decay are completely neglected in (1.11). If we add a term $-\nu\langle S^-(q')S^+\times(q-q')\rangle$ to the right-hand side of (1.5), to simulate these decay processes, which we shall call internal relaxation processes, in a phenomenological way, then we find for $\Sigma(q,z)$ the expression (1.16),

$$\Sigma(\vec{\mathrm{q}},z)=i\chi(\vec{\mathrm{q}},0)\,\frac{1}{z-\dfrac{\omega^2(\vec{\mathrm{q}})}{z+i\nu}}\ . \tag{1.16}$$

This expression does have the proper behavior for small z. Furthermore, the details of the internal relaxation processes can be important. A more sophisticated phenomenological treatment of the internal relaxation processes, which would account for the fact that there will be some characteristic time that the system requires in order to respond to a disturbance of the internal structure, can be had by including a term such as

$$-\Omega^2\int_0^t e^{-(t-t')/\tau c}\langle S^-(q_1)S^+(q_2)\,;\,t'\rangle\,dt'$$

on the right-hand side of (1.11). This leads to a spectral density of the form

$$\Sigma(q,z)=i\chi(q,0)\,\frac{1}{z-\dfrac{\omega^2(q)}{z-\dfrac{\Omega^2\tau_c}{i+z\tau_c}}}\ . \tag{1.17}$$

If $\omega(q)\ll\Omega$, this is equivalent to 1.10 with $\nu=\Omega^2\tau_c$. If $\omega(q)\tau_c\gg1$, i.e., the external disturbance has a characteristic frequency much greater than the internal relaxation frequency, the spectral density will reflect the details of the internal relaxation. In fact if the conditions $\Omega\tau_c\gg1$ and $\omega^2(q)\gg\Omega^2$ are also met, the spectral density will show a peak at $\omega=0$, of width $1/\tau_c$, that corresponds precisely to the relaxation of $\langle S^-(q_1)S^+\times(q_2)\rangle$. In the paramagnet, at high temperatures, we expect that the short-wavelength fluctuations will have frequencies comparable to those of the internal relaxation processes, while as the system approaches the critical point, the internal processes will slow down, and the situation can be similar to that just described. In either case, a detailed treatment of the decay of the correlation function $\langle S^-(q_1)S^+(q_2)\rangle$ due to the internal relaxation processes is essential for understanding the dynamics of the spin fluctuations.

In order to develop such a treatment, we introduce the function $\Gamma(\vec{q}_1, \vec{q}_2, t)$, defined by

$$\Gamma(q_1, q_2, t) = -i \langle S^-(q_1) S^+(q_2) | \times e^{-i\mathcal{L}' t} | \mathcal{L} S^z(q_1+q_2) \rangle / \chi(q_1+q_2) ,$$

where $\mathcal{L}'$ is defined as $(I-P)\mathcal{L}(I-P)$, with $\mathcal{L}$ the Liouville operator defined in I, and P the projection operator onto the set of states containing a single spin fluctuation. $\mathcal{L}'$ describes the propagation of spin fluctuations in the absence of any external fluctuation. Γ gives the rate of decay of a fluctuation of wave vector $\vec{q}_1 + \vec{q}_2$ at time $t = 0$ into two fluctuations of wave vector $\vec{q}_1$ and $\vec{q}_2$ at time t. In terms of its Laplace transform $\Gamma(\vec{q}_1, \vec{q}_2, z)$, $\varphi(q, z)$ is given by

$$\varphi(q, z) = \tfrac{1}{2} N^{-1/2} \sum_{q'} [V(q-q') - V(q')] \Gamma(q', q-q', z) , \tag{1.18}$$

so that knowledge of Γ suffices to determine φ. If one compares (1.18) with (1.15a) and (1.15c), one sees that the approximation that leads to (1.9) can be succinctly summarized as

$$\Gamma(q_1, q_2, z) = N^{-1/2} \Gamma^0(q_1, q_2)/z \equiv \Gamma^0(q_1, q_2, z) . \tag{1.19}$$

(1.19) asserts that $\Gamma(q_1, q_2 t)$ is a constant, independent of the time since the fluctuation was introduced into the lattice, and that this constant is given by the value obtained from the cluster expansion, $-i\gamma^0(q_1, q_2)$. The assertion that the decay rate is a constant corresponds to the neglect of the internal relaxation processes, i.e., the decay of $\langle S^-(q_1) S^+ \times (q_2) \rangle$.

To describe the decay processes neglected in making the approximation (1.19), we must be able to predict the behavior of the correlation functions in the absence of any perturbation in the magnetization. We will therefore consider the equations of motion for the case that the initial density matrix is chosen so that $\langle S^z(\vec{q}) ; t = 0 \rangle = 0$. In calculating the subsequent behavior, we shall assume that the time dependence is determined by the modified Liouville operator $\mathcal{L}'$, and hence the magnetization will be zero for all subsequent times. Clearly, the approximation (1.9) is useless in this case, as the time dependence of the two-spin correlation function is determined entirely by the three-spin correlation function. The kinetic equations must therefore relate $\langle S^-(\vec{q}_1) S^+(\vec{q}_2) \rangle$ and $\langle S^-(\vec{q}_1) S^z(\vec{q}_2) S^+(\vec{q}_3) \rangle$. The equation of motion for the three-spin correlation function is

$$\begin{aligned} i \frac{\partial}{\partial t} \langle S^-(\vec{q}_1) S^z(\vec{q}_2) S^+(\vec{q}_3) \rangle = &- N^{-1/2} \sum_{q_4} [V(\vec{q}_4) - V(\vec{q}_1 - \vec{q}_4)] \langle S^-(\vec{q}_1 - \vec{q}_4) S^z(\vec{q}_4) S^z_z(\vec{q}_2) S^+(\vec{q}_3) \rangle \\ &- \tfrac{1}{2} N^{-1/2} \sum_{q_4} [V(\vec{q}_4) - V(\vec{q}_2 - \vec{q}_4)] \langle S^-(\vec{q}_1) S^-(\vec{q}_4) S^+(\vec{q}_2 - \vec{q}_4) S^+(\vec{q}_3) \rangle \\ &+ N^{1/2} \sum_{q_4} [V(\vec{q}_4) - V(\vec{q}_3 - \vec{q}_4)] \langle S^-(\vec{q}_1) S^z(\vec{q}_2) S\,(\vec{q}_4) S^+(\vec{q}_3 - \vec{q}_4) \rangle . \end{aligned} \tag{1.20}$$

We shall assume that the initial density matrix is rotationally invariant about the z axis, so that $\langle S^z_i S^\pm_j \rangle = \langle S^\pm_i \rangle = 0$. If we make a cluster approximation for the four-spin correlation functions, we will will have

$$\langle S^-(\vec{q}_1) S^z(\vec{q}_2) S^Z(\vec{q}_2) S^+(\vec{q}_4) \rangle \cong \langle S^z(\vec{q}_2) S^z(\vec{q}_3) \rangle \langle S^-(\vec{q}_1) S^+(\vec{q}_4) \rangle , \tag{1.21a}$$

$$\begin{aligned} \langle S^-(\vec{q}_1) S^-(\vec{q}_2) S^+(\vec{q}_3) S^+(\vec{q}_4) \rangle &\cong \langle S^-(\vec{q}_1) S^+(\vec{q}_3) \rangle \langle S^-(\vec{q}_2) S^+(\vec{q}_4) \rangle \\ &+ \langle S^-(\vec{q}_1) S^+(\vec{q}_4) \rangle \langle S^-(\vec{q}_2) S^+(\vec{q}_3) \rangle . \end{aligned} \tag{1.21b}$$

The equations of motion couple terms such as $\langle S^-_i S^+_j \rangle$ with terms such as $\langle S^z_i S^z_j \rangle$. Hence, in addition to Eqs. (1.8) and (1.20), and the approximation (1.21), we will require an equation of motion for $\langle S^z(\vec{q}_1) S^z(\vec{q}_2) \rangle$:

$$\begin{aligned} i \frac{\partial}{\partial t} \langle S^z(\vec{q}_1) S^z(\vec{q}_2) \rangle = &\tfrac{1}{2} N^{-1/2} \sum_{q_3} [V(\vec{q}_1 - \vec{q}_3) - V(\vec{q}_3)] \langle S^-(\vec{q}_3) S^z(\vec{q}_2) S^+(\vec{q}_1 - \vec{q}_3) \rangle \\ &+ \tfrac{1}{2} N^{-1/2} \sum_{q_3} [V(\vec{q}_2 - \vec{q}_3) - V(\vec{q}_3)] \langle S^-(\vec{q}_3) S^z(\vec{q}_1) S^+(\vec{q}_2 - \vec{q}_3) \rangle . \end{aligned} \tag{1.22}$$

From (1.20) and (1.21) we obtain a nonlinear equation for the rate of change of the three-spin correlation function, (1.23) [in obtaining (1.23) we have used the fact that $\langle S^z(\vec{q}) \rangle = 0$]:

$$i \frac{\partial}{\partial t} \langle S^-(\vec{q}_1) S^Z(\vec{q}_2) S^+(\vec{q}_3) \rangle = - N^{-1/2} \sum_{q_4} [V(\vec{q}_4) - V(\vec{q}_1 - \vec{q}_4)] \langle S^-(\vec{q}_1 - \vec{q}_4) S^+(\vec{q}_3) \rangle \langle S^z(\vec{q}_4) S^z(\vec{q}_2) \rangle$$

$$-\tfrac{1}{2}N^{-1/2}\sum_{q_4}[V(\vec{q}_4)-V(\vec{q}_2-\vec{q}_4)]\langle S^-(\vec{q}_1)S^+(\vec{q}_2-\vec{q}_4)\rangle\langle S^-(\vec{q}_4)S^+(\vec{q}_3)\rangle$$

$$+N^{1/2}\sum_{q_4}[V(\vec{q}_4)-V(\vec{q}_3-\vec{q}_4)]\langle S^-(\vec{q}_1)S^+(\vec{q}_3-\vec{q}_4)\rangle\langle S^z(\vec{q}_2)S^z(\vec{q}_4)\rangle\ . \quad (1.23)$$

Since we are interested only in the linear response, we will linearize this equation about equilibrium. For this procedure to be successful, the equilibrium values of $\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\rangle$ and $\langle S^z(\vec{q}_1)S^z(\vec{q}_2)\rangle$ must be such as to make the time derivative of the three-spin correlation function vanish. Observing that as a result of translational invariance and isotropy,

$$\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\rangle=\delta(\vec{q}_1+\vec{q}_2)n(\vec{q}_1)=2\langle S^z(\vec{q}_1)S^z(\vec{q}_2)\rangle\ ,$$

we find, setting the right-hand side of (1.23) to zero,

$$[V(\vec{q}_2)-V(\vec{q}_3)]n(\vec{q}_2)n(\vec{q}_3)$$
$$+[V(\vec{q}_3)-V(\vec{q}_1)]n(\vec{q}_1)n(\vec{q}_3)$$
$$+[V(\vec{q}_1)-V(\vec{q}_2)]n(\vec{q}_1)n(\vec{q}_2)=0\ , \quad (1.24)$$

where $\vec{q}_1+\vec{q}_2+\vec{q}_3=0$.

Equation (1.24) is precisely the condition that was derived diagrammatically in I. It is a necessary restriction on the equilibrium correlation functions if they are to be stationary when the Liouville operator is evaluated to lowest order in $1/c$, and has a straightforward physical interpretation in terms of the picture of the dynamics that was introduced in I. If (1.24) is divided by $[n(q_1)n(q_2)\times n(q_3)]^{1/2}$, each term in (1.24) corresponds to the analytic expression for the matrix element giving the rate of decay of one mode into two others (see Fig. 12 of I). (1.18) is therefore a rate balance equation, and the restriction on the equilibrium correlation functions implied by (1.24) is a consequence of the requirement of detailed balance. It may be expressed graphically as in Fig. 1. The analogy here with the Boltzmann equation is particularly strong.

A sufficient condition that (1.24) is satisfied is that $n(q)$ be given by the spherical model. This may be shown to be a necessary condition by comparing the exact value of $\Gamma(q_1,q_2,z)$ with the approximate expression (1.19). If one expands $\Gamma(q_1,q_2,z)$ for large z, one finds that

$$\Gamma(\vec{q}_1,\vec{q}_2,z)=\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\,|\,\mathfrak{L}S^z(\vec{q})\rangle/\chi(\vec{q},0)z+O(1/z^3).\quad (1.25)$$

Comparing (1.25) with (1.19) we see that the cluster approximation which gives the initial rate of change of $\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\rangle$ correct to lowest order in $1/c$ leads to an explicit approximation for the matrix element of $\mathfrak{L}$,

$$\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\,|\,\mathfrak{L}S^z(\vec{q})\rangle=N^{-1/2}\gamma(\vec{q}_1,\vec{q}_2)\chi(\vec{q}_1+\vec{q}_2,0)\ .$$

Making use of the identity $\langle A|\mathfrak{L}\,|\,B\rangle=\langle\langle[B,A^+]\rangle\rangle$, we have

$$\langle\langle[S^z(\vec{q}_1+\vec{q}_2),S^+(\vec{q}_1)S^-(\vec{q}_2)]\rangle\rangle$$
$$=N^{-1/2}\gamma(\vec{q}_1,\vec{q}_2)\chi(\vec{q}_1+\vec{q}_2,0)$$

or

$$n(\vec{q}_2)-n(\vec{q}_1)=\gamma(\vec{q}_1,\vec{q}_2)\chi(\vec{q}_1+\vec{q}_2,0)$$
$$=\{V(\vec{q}_1+\vec{q}_2)[n(\vec{q}_1)-n(\vec{q}_2)]+V(\vec{q}_2)n(\vec{q}_2)$$
$$-V(\vec{q}_1)n(\vec{q}_1)\}\chi(\vec{q}_1+\vec{q}_2,0)\ . \quad (1.26)$$

One can now show that $n(q)$ is of necessity the spherical-model value. The approximate equation (1.26) is a difference equation for $n(\vec{q})$. If we let $\vec{q}_1=\vec{q}\,'$, $\vec{q}_2=\vec{q}-\vec{q}\,'$, and take the limit of (1.26) as $\vec{q}\to 0$, we obtain (1.27):

$$\vec{q}\cdot\nabla_{q'}(\{1+\chi(0,0)[V(0)-V(\vec{q}\,')]\}n(\vec{q}\,'))=0.$$

Hence (1.27)

$$n(\vec{q})=n(0)/\{1+\chi[V(0)-V(\vec{q})]\}\ ,$$

where $\chi=\chi(0,0)$.

Since $n(0)=2\chi/\mathfrak{B}$, we find that $n(\vec{q})$ must be given by the spherical-model expression

$$n(\vec{q})=\frac{2}{\mathfrak{B}[1/\chi+V(0)-V(\vec{q})]}\ . \quad (1.28)$$

This is to be expected, since the quantity $n(\vec{q}\,')-n(\vec{q}-\vec{q}\,')$ is $O(1/c)$, and the right-hand side of (1.26) is correct to terms that are $O(1/c)$, the errors being of order $(1/c)^2$. $n(\vec{q})$ can therefore be determined correctly to order $1/c$.

Although the behavior of the spherical-model susceptibility, if it is determined from the sum rule $\sum_q n(\vec{q})=\frac{2}{3}S(S+1)$, is known to be incorrect in the region of the critical point, it is a good approximation for temperatures outside of the range $[(T-T_c)^{1/2}/Tc]<1/c$. The model gives the Ornstein–Zernike behavior for the correlation functions at long wavelength, in the region of the critical point. We shall use it for all explicit calcula-

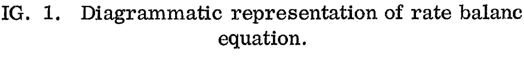

FIG. 1. Diagrammatic representation of rate balance equation.

tions.

If we linearize (1.23) about a correlation function satisfying (1.18), we obtain the equation of motion (1.23),

$$i\,\frac{\partial}{\partial t}\,\delta\langle S^-(\vec{q}_1)S^z(\vec{q}_2)S^+(\vec{q}_3)\rangle = -\tfrac{1}{2}N^{-1/2}\,\gamma(\vec{q}_1,\vec{q}_2)n(\vec{q}_1+\vec{q}_3)$$
$$-\tfrac{1}{2}N^{-1/2}\,\gamma(\vec{q}_2,\vec{q}_3)n(\vec{q}_1,\vec{q}_2+\vec{q}_3)+N^{-1/2}\,\gamma(\vec{q}_1,\vec{q}_3)m(\vec{q}_1+\vec{q}_3,\vec{q}_2)\ . \qquad (1.29)$$

$\gamma^0(\vec{q}_3,\vec{q}_2)$ is the quantity defined by (1.6), $n(\vec{q}_1,\vec{q}_2) = \delta\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\rangle$, and $m(\vec{q}_1,\vec{q}_2)=\delta\langle S^z(\vec{q}_1)S^z(\vec{q}_2)\rangle$; i.e., they are the deviations from equilibrium.

Equation (1.29) has a straightforward interpretation. If one has two-spin fluctuations in the lattice, as indicated by a nonzero value of $n(\vec{q}_1,\vec{q}_2)$ or $m(\vec{q}_1,\vec{q}_2)$, the rate at which one generates three-spin fluctuations is equal to the sum of the rates at which one of those fluctuations decays into two. This rate for fluctuations of wave vector $(\vec{q}_1+\vec{q}_2)$, in the present approximation, is simply $\gamma^0(\vec{q}_1,\vec{q}_2)$.

Equation (1.29) has the same limitation that Eq. (1.11) had. It does not include the internal relaxation processes in the vertex function $\Gamma(\vec{q}_1,\vec{q}_2,t)$. We shall therefore modify (1.29) to include these processes. If we Laplace transform (1.29), and assume that the initial value of $\delta\langle S^-(\vec{q}_1)S^z(\vec{q}_2) \times S^+(\vec{q}_3)\rangle=0$ we will obtain

$$\delta\langle S^-(\vec{q}_1)S^z(\vec{q}_2)S^+(\vec{q}_3);\,z\rangle = -\tfrac{1}{2}\Gamma^0(\vec{q}_1,\vec{q}_2;\,z)$$
$$=(\vec{q}_1+\vec{q}_2,\vec{q}_3;\,z)-\tfrac{1}{2}\Gamma^0(\vec{q}_2,\vec{q}_3;\,z)n(\vec{q}_1,\vec{q}_2+\vec{q}_3;\,z)+\Gamma^0(\vec{q}_1,\vec{q}_3;\,z)m(\vec{q}_1+\vec{q}_3,\vec{q}_2;\,z)\ . \qquad (1.30)$$

The neglect of the initial three-spin correlations is equivalent to neglecting the possibility of a fluctuation decaying simultaneously into three fluctuations, since the initial value, if kept, would enter the equations of motion that will be derived subsequently for $\Gamma(\vec{q}_1,\vec{q}_2,z)$ in the form $\langle S^-(\vec{q}_1)S^z(\vec{q}_2) \times S^+(\vec{q}_3)\,|\,\mathcal{L}\,|\,S^z(\vec{q})\rangle$. This matrix element is smaller, by a factor of $1/c$, than the terms that we have kept.[5] To include the internal relaxation processes, we will replace $\Gamma^0(\vec{q}_1,\vec{q}_2;\,z)$ in (1.30) by the exact vertex function $\Gamma(\vec{q}_1,\vec{q}_2,z)$. This approximation neglects many features of the decay of $\langle S^-(q_1) \times S^z(q_2)S^+(q_3)\rangle$, but it is the simplest approximation one can make that incorporates the relaxation of the two-spin correlation function in a self-consistent manner.

The approximation may be interpreted graphically. We will represent the response of the three-spin correlation function to a perturbation in the two-spin function by the vertex shown in Fig. 2(a). If we define an irreducible vertex by the condition that it contains no intermediate two-spin fluctuation states, then the vertex of Fig. 2(a) can be written as in Fig. 2(b), where the crosshatching indicates the irreducibility. The approximation is shown in Fig. 3(c). We see that it neglects virtual decays of the fluctuations not involved in the vertex as well as multiple scattering of this fluctuation with others. Essentially, the approximation states that once a fluctuation has decayed into two others, the resultant two-spin correlation function decays much faster than does a single-spin correlation function. Clearly this will not be a good approximation when the isolated fluctuation is of short wavelength and both of the modes in the vertex are of long wavelength, but the phase space where this occurs is small compared to the remainder, at least in three dimensions. Upon substituting (1.30) with this modification into the Laplace transformed version of (1.8) and (1.22) we obtain the kinetic equations (1.31a) and (1.31b):

$$z\,n(\vec{q}_1,\vec{q}_2,z)=in(\vec{q}_1,\vec{q}_2;\,t=0)+[\varphi(\vec{q}_1,z)+\varphi(\vec{q}_2,z)]n(\vec{q}_1,\vec{q}_2,z)$$
$$-\tfrac{1}{2}N^{-1/2}\sum_{q'}[V(\vec{q}_2-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_1,\vec{q}_2-\vec{q}\,',z)n(\vec{q}-\vec{q}\,',z)$$
$$-\tfrac{1}{2}N^{-1/2}\sum_{q'}[V(\vec{q}_1-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_2,\vec{q}_1-\vec{q}\,',z)n(\vec{q}\,',\vec{q}-\vec{q}\,',z)$$
$$-N^{-1/2}\sum_{q'}[V(\vec{q}_2-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_1,\vec{q}_2-\vec{q}\,',z)m(\vec{q}-\vec{q}\,',\vec{q}\,',z)$$
$$-N^{-1/2}\sum_{q'}[V(\vec{q}_1-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_2,\vec{q}_1-\vec{q}\,',z)m(\vec{q}-\vec{q}\,',\vec{q}\,',z)\ , \qquad (1.31a)$$

$$
\begin{aligned}
zm(\vec{q}_1,\vec{q}_2,z) = {} & im(\vec{q}_1,\vec{q}_2,t=0)+[\varphi(\vec{q}_1,z)+\varphi(\vec{q}_2,z)]m(\vec{q}_1,\vec{q}_2,z)\\
& -\tfrac{1}{4}\sum_{q'}[V(\vec{q}_1-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_2,\vec{q}-\vec{q}\,',z)[n(\vec{q}\,',\vec{q}-\vec{q}\,',z)+n(\vec{q}-\vec{q}\,',\vec{q}\,',z)]\\
& -\tfrac{1}{4}\sum_{q'}[V(\vec{q}_2-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_1,\vec{q}_2-\vec{q}\,',z)[n(\vec{q}\,',\vec{q}-\vec{q}\,',z)+n(\vec{q}-\vec{q}\,',\vec{q}\,',z)]. \qquad (1.31\text{b})
\end{aligned}
$$

Equations (1.31a) and (1.31b) are a set of linear equations that determine the two-spin correlation function in terms of its initial values. They are not a closed set, since the quantity $\Gamma(\vec{q}_1,\vec{q}_2,z)$ remains to be determined. But it is clear from the definition of Γ that $\Gamma(\vec{q}_1,\vec{q}_2,t)$ is simply $\langle S^-(\vec{q}_1)\times S^+(\vec{q}_2);t\rangle$ for a particular initial condition, i.e.,

$$
\begin{aligned}
\langle S^-(\vec{q}_1)S^+(\vec{q}_2);t=0\rangle &= i\Gamma(\vec{q}_1,\vec{q}_2,0)\\
&=\langle S^-(\vec{q}_1)S^+(\vec{q}_2)\,|\,\mathcal{L}S^z(\vec{q})\rangle/\chi(\vec{q},0)\\
&=N^{-1/2}[n(\vec{q}_2)-n(\vec{q}_1)]/\chi(\vec{q},0)\,. \qquad (1.32)
\end{aligned}
$$

The equation for Γ can be simplified by using the fact, which follows from the rotational symmetry, that

$$\Gamma(\vec{q}_1,\vec{q}_2,z)=-\Gamma(\vec{q}_2,\vec{q}_1,z)\,. \qquad (1.33)$$

Thus, from (1.31b), $m(\vec{q}_1,\vec{q}_2)$ and $n(\vec{q}_1,\vec{q}_2)$ are uncoupled, and since $m(\vec{q}_1,\vec{q}_2;t=0)=\langle S^z(\vec{q}_1)S^z(\vec{q}_2)\,|\mathcal{L}S^z(\vec{q})\rangle=0$, $m(\vec{q}_1,\vec{q}_2,z)=0$. Hence, Γ satisfies the nonlinear equation (1.34):

$$
\begin{aligned}
z\Gamma(\vec{q}_1,\vec{q}_2,z) = {} & N^{-1/2}\,\frac{n(\vec{q}_2)-n(\vec{q}_1)}{\chi(\vec{q}_1+\vec{q}_2,\,0)}+[\varphi(\vec{q}_1,z)+\varphi(\vec{q}_2,z)]\Gamma(\vec{q}_1,\vec{q}_2,z)\\
& -\tfrac{1}{2}N^{-1/2}\sum_{q'}\{[V(\vec{q}_2-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_1,\vec{q}_2-\vec{q}\,',z)-[V(\vec{q}_1-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_2,\vec{q}_1-\vec{q}\,',z)\}\\
& \times\Gamma(\vec{q}_1+\vec{q}_2-\vec{q}\,',\vec{q}\,',z)\,. \qquad (1.34)
\end{aligned}
$$

Equations (1.31a), (1.31b), and (1.34) form a closed set of equations from which most of the dynamical properties of the Heisenberg paramagnet can be calculated. Equations of motion for two-spin correlation functions of the form $\langle S^-(q_1)\times S^-(q_2);t\rangle$ may be needed to describe some experiments, such as EPR, but equations of motion for these correlation functions may be obtained, in terms of Γ, in a manner analogous to that which we have described. We shall not present these here, however, as we shall not use them in this paper.

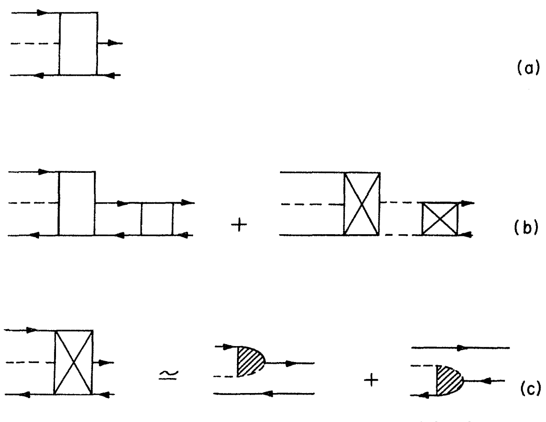

FIG. 2. Diagrammatic representation of fundamental approximation for the time dependence of the three-spin correlation function.

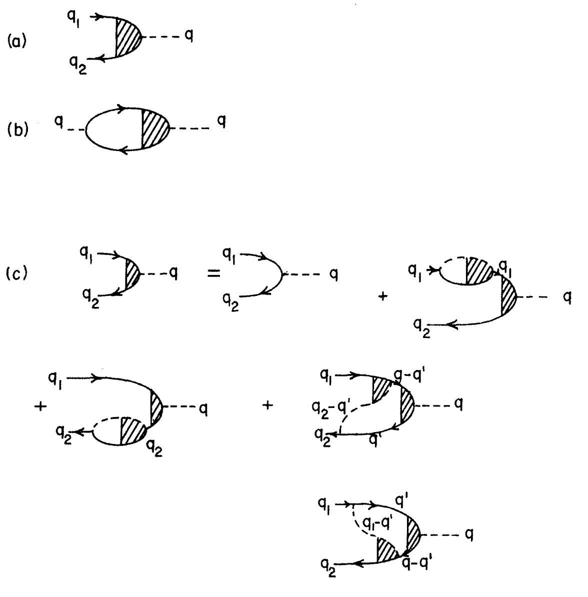

FIG. 3. Diagrammatic representation of vertex function (a), $\varphi(q,z)/z$ (b), and equation of motion for the vertex function (c).

II. PROPERTIES OF THE KINETIC EQUATIONS

A kinetic equation should satisfy whatever physical constraints exist in the form of conservation laws. In the present case, in addition to the trivially satisfied constraint that $\langle S^z(0)\rangle$ be a constant, we have the conservation of the total spin and energy

$$\frac{\partial}{\partial t} N^{-1} \sum_q \langle \vec{S}(\vec{q}) \cdot \vec{S}(-\vec{q});\, t\rangle = 0\,, \tag{2.1a}$$

$$\frac{\partial}{\partial t} N^{-1} \sum_q V(\vec{q}) \langle \vec{S}(\vec{q}) \cdot \vec{S}(-\vec{q});\, t\rangle = 0\,. \tag{2.1b}$$

Actually, we have, in the Heisenberg model, N constraints of the form $\vec{S}_i(t)\cdot\vec{S}_i(t) = S(S+1)$. However, since the stationary correlation functions are calculated from the spherical model, where there is only the single constraint $N^{-1}\sum_i \vec{S}_i(t)\cdot\vec{S}_i(t) = S(S+1)$, we can only expect the dynamics to conserve this latter weaker property of the stationary solutions of the equations of motion. Equations (2.1a) and (2.1b) can be derived from (1.25a), (1.25b), and the antisymmetry of Γ.

Let us note first of all that

$$\begin{aligned}\langle S^+(\vec{q}_1) S^-(\vec{q}_2);\, t\rangle &= \langle S^-(\vec{q}_2) S^+(\vec{q}_1);\, t\rangle + N^{1/2}\langle S^z(\vec{q}_1+\vec{q}_2);\, t\rangle \\ &= n(\vec{q}_2, \vec{q}_1;\, t) + 2N^{1/2}\langle S^z(\vec{q}_1+\vec{q}_2);\, t\rangle\,.\end{aligned}$$

Hence, since we can take $\langle S^z(0);\, t\rangle = 0$,

$$\begin{aligned}\langle \vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, t\rangle &= \langle \tfrac{1}{2}S^-(\vec{q})S^+(-\vec{q}) + \tfrac{1}{2}S^+(\vec{q})S^-(-\vec{q}) + S^z(\vec{q})S^z(-\vec{q})\rangle \\ &= n(\vec{q}, -\vec{q};\, t) + n(-\vec{q}, \vec{q};\, t) + m(\vec{q}, -\vec{q};\, t)\,.\end{aligned} \tag{2.2}$$

The kinetic equations were derived for the case that the time development operator was $\mathcal{L}'$, while the time development operator in (2.1a) and (2.1b) should be taken to be $\mathcal{L}$. However, the distinction is not material if $\vec{q}_1+\vec{q}_2 = 0$, since we require in deriving (1.25), only that $\langle S^z(\vec{q}_1+\vec{q}_2)\rangle$ vanish for all time if it vanishes initially. This is true for both $\mathcal{L}'$ and $\mathcal{L}$.

From (1.25) and (2.2) we have (2.3):

$$\begin{aligned}z\langle \vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, z\rangle = {}& i\langle \vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, t=0\rangle + [\varphi(\vec{q}, z) + \varphi(-\vec{q}, z)\langle \vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, z\rangle \\ & - N^{-1/2}\sum_q [V(\vec{q}-\vec{q}\,') - V(\vec{q}\,')]\Gamma(-\vec{q}, \vec{q}-\vec{q}\,';\, z)\langle \vec{S}(\vec{q}\,')\cdot\vec{S}(-\vec{q}\,');\, z\rangle \\ & - N^{-1/2}\sum_q [V(-\vec{q}-\vec{q}\,') - V(\vec{q}\,')]\Gamma(\vec{q}, -\vec{q}-\vec{q}\,';\, z)\langle \vec{S}(\vec{q}\,')\cdot\vec{S}(-\vec{q}\,');\, z\rangle\,\cdot\end{aligned} \tag{2.3}$$

If (2.3) is summed over q, the last term on the right-hand side of (2.3) becomes

$$-N^{-1/2}\sum_q\sum_{q'} [V(-\vec{q}-\vec{q}\,') - V(\vec{q}\,')] \times \Gamma(\vec{q}, -\vec{q}-\vec{q}\,';\, z)\langle \vec{S}(\vec{q}\,')\cdot\vec{S}(-\vec{q}\,');\, z\rangle\,. \tag{2.4}$$

Since Γ is antisymmetric,

$$\sum_q \Gamma(\vec{q}, -\vec{q}-\vec{q}\,') = 0$$

and the summation over q in (2.4) reduces to

$$\begin{aligned}-N^{-1/2}\sum_q V(-\vec{q}-\vec{q}\,')\Gamma(\vec{q}, -\vec{q}-\vec{q}\,', z) &= -\tfrac{1}{2}N^{-1/2}\sum_q V(-\vec{q}-\vec{q}\,')[\Gamma(\vec{q}, -\vec{q}-\vec{q}\,', z) \\ &\qquad - \Gamma(-\vec{q}-\vec{q}\,', \vec{q};\, z)] \\ &= -\tfrac{1}{2}N^{-1/2}\sum_q [V(-\vec{q}-\vec{q}\,') - V(\vec{q})]\Gamma(\vec{q}, -\vec{q}-\vec{q}\,';\, z) \\ &= -\varphi(-\vec{q}\,', z)\,.\end{aligned}$$

Hence (2.4) is equal to

$$-\sum_{q'} \varphi(-\vec{q}\,', z)\langle \vec{S}(\vec{q}\,')\cdot\vec{S}(-\vec{q}\,');\, z\rangle\,,$$

which cancels the result one obtains from the third term on the right-hand side of (2.3), when it is summed over q.

A similar cancellation occurs between the second and fourth terms, with the result that

$$zN^{-1}\sum_q \langle \vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, z\rangle = iN^{-1}\sum_q \langle \vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, t=0\rangle = iS(S+1)\,,$$

which is the Laplace transform of the conservation law (2.1a).

To derive (2.1b), multiply (2.3) by $V(\vec{q})$ and sum on $\vec{q}$. The last term on the right-hand side of (2.3) becomes

$$-N^{-1/2}\sum_q\sum_{q'} [V(\vec{q})V(-\vec{q}-\vec{q}\,') - V(\vec{q})V(\vec{q}\,')] \times \Gamma(\vec{q}, -\vec{q}-\vec{q}\,';\, z)\langle \vec{S}(\vec{q}\,')\cdot\vec{S}(-\vec{q}\,');\, z\rangle\,.$$

The first term in the square brackets vanishes upon interchanging the order of summations and performing the sum over $\vec{q}$. The second term becomes

$$\sum_{q'} V(\vec{q}\,')N^{-1/2}\sum_q V(\vec{q})\Gamma(\vec{q}, -\vec{q}-\vec{q}\,', z)\langle \vec{S}(\vec{q}\,')\vec{S}(-\vec{q}\,');\, z\rangle = -\sum_{q'} V(\vec{q}\,')\varphi(-\vec{q}\,', z)\langle \vec{S}(\vec{q}\,');\, z\rangle\,.$$

Again this term cancels the result one obtains from the third term on the right of (2. 3). Similar cancellation of the remaining term leads to the conservation law (2. 1b):

$$z\sum_{q} V(\vec{q})\langle\vec{S}(\vec{q})\cdot\vec{S}(-\vec{q});\, z\rangle = i\langle\mathcal{H};\, t=0\rangle \;.$$

The kinetic equations allow one to calculate, in principle, any dynamical property that depends upon the time development of the two-spin correlation function. Since the equations conserve energy, it is also reasonable to use them to calculate the thermal conductivity, which depends upon the time development of a three-spin correlation function if calculated using a Kubo formula. This can be accomplished in much the same way that the Boltzmann equation is used to calculate the thermal conductivity of a gas, and will be presented elsewhere.

The conservation laws place constraints on the long-time behavior of the system. The method we have used to derive the equations of motion ensures that the short-time behavior will not be too seriously in error, since the terms neglected in making a cluster expansion of correlation functions appearing in the expression for the time derivative of $\langle S^-(\vec{q}_1)S^z(\vec{q}_2)S^+(\vec{q}_3)\rangle$ will be smaller by a factor of $1/c$ than the terms that are kept. In particular, the second and fourth moments of the spectral density will be correct to order $1/c$. This should be clear from the discussion in Sec. I, but can easily be checked explicitly. If we divide (1. 28) by z and iterate it once, we obtain the first two terms in the expansion of $\Gamma(\vec{q}_1, \vec{q}_2, z)$ as a power series in $1/z$:

$$\begin{aligned}\Gamma(\vec{q}_1, \vec{q}_z, z) = {} & \Gamma^0(\vec{q}_1, \vec{q}_2) + [\omega^2(\vec{q}_1) + \omega^2(\vec{q}_2)]\Gamma^0(\vec{q}_1, \vec{q}_2)/z^2 \\ & - \tfrac{1}{2}N^{-1/2}\sum_{q'}\{[V(\vec{q}_2-\vec{q}\,') - V(\vec{q}\,')]\Gamma^0(\vec{q}_1, \vec{q}_2-\vec{q}\,') - [V(\vec{q}_1-\vec{q}\,') - V(\vec{q}\,')]\Gamma^0(\vec{q}_2, \vec{q}_1-\vec{q}\,')\} \\ & \times\Gamma^0(\vec{q}_1+\vec{q}_2-\vec{q}\,'\,\vec{q}\,')/z + O(1/z^5) \;. \qquad (2.5)\end{aligned}$$

If we substitute (2. 5) into (1. 12), and compare with Eq. (1. 18) of I, we find (2. 6):

$$\omega^2(\vec{q}) = \tfrac{1}{2}N^{-1}\sum_{q'}[V(\vec{q}-\vec{q}\,') - V(\vec{q}\,')]\,[n(\vec{q}-\vec{q}\,') - n(\vec{q}\,')]/\chi(\vec{q}, 0) \;, \qquad (2.6a)$$

$$\begin{aligned}\Omega^4(\vec{q}) = {} & N^{-1}\sum_{q'}[V(\vec{q}-\vec{q}\,') - V(\vec{q}\,')]\omega^2(\vec{q}\,')[n(\vec{q}-\vec{q}\,') - n(\vec{q}\,')]/\chi(\vec{q}, 0) \\ & - \tfrac{1}{2}N^{-2}\sum_{q'q''}[V(\vec{q}-\vec{q}\,') - V(\vec{q}\,')][V(\vec{q}-\vec{q}\,'-\vec{q}\,'') - V(\vec{q}\,'')][n(\vec{q}-\vec{q}\,'-\vec{q}\,'') - n(\vec{q}\,')] \\ & \times[n(\vec{q}\,'') - n(\vec{q}-\vec{q}\,'')]/\chi(\vec{q}-\vec{q}\,'', 0)/\chi(\vec{q}, 0). \qquad (2.6b)\end{aligned}$$

Since

$$\begin{aligned}&[n(\vec{q}_2) - n(\vec{q}_1)]/\chi(\vec{q}_1+\vec{q}_2, 0) \\ &\quad = \tfrac{2}{3}S(S+1)[V(\vec{q}_2) - V(\vec{q}_1)]\rho(\vec{q}_2)\rho(\vec{q}_1)/\rho(\vec{q}_1+\vec{q}_2) \;,\end{aligned}$$

with $\rho(q)$ defined as $n(q)/\sum_q n(q)$, the expressions for the moment given by (2. 6a) and (2. 6b) agree with Eqs. (3. 24) and (3. 25) of I, respectively, and hence are correct to order $1/c$.

The approximate equation (1. 28) may be written graphically using the notation of I, and it may be interpreted as providing a particular prescription for the summation of an infinite subset of the diagrams for the spectral density. If we renormalize at finite temperatures only the right-hand vertex in the diagrams of I, and associate a factor of $1/z$ with each vertex, as discussed in Sec. IV of I, we can represent the quantity $\frac{1}{2}[\frac{1}{3}S(S+1)]^{-1/2}\Gamma(q_1, q_2, z)$ by the symbol shown in Fig. 3(a). The crosshatching indicates that all possible diagrams are included. The quantity $\varphi(q, z)/z$ is represented, according to (1. 12) and the rules for calculating the moments given in I, by the diagram shown in Fig. 3(b). The approximate equation (1. 28) is then given by the graphical equation shown in Fig. 3(c). Comparison of the results one obtains by iterating (1. 28), obtained by eliminating the crosshatching in Fig. 3(c) with the diagrammatic expressions for the second and fourth moments shown in Fig. 3 of I, should make clear the result just shown analytically concerning the second and fourth moments. Similar equations could be written for (1. 25). Figure 3(c) should make clear the interpretation of the various terms appearing in (1. 28). The rate of change of the vertex function is determined by two effects, the decay of the individual excitations involved, described by the second and third term on the right of (1. 28), and the scattering of these excitations from one another by means of their interaction with a third mode, described by the last two terms in the equation. The cancellation of the rate of change of the energy and total spin produced by these two mechanisms results in the conservation laws.

A final property of the kinetic equations is that they lead to the dynamical scaling laws at the critical point. This will be discussed in a subsequent paper.

III. APPROXIMATE HIGH-TEMPERATURE SOLUTION

Although the kinetic equations are capable of interpreting a wide range of experiments, the most direct test of the validity of the theory is provided by the neutron scattering results on $RbMnF_3$.[6] This material is a simple cubic antiferromagnet with spin $\frac{5}{2}$, and is well described by the Heisenberg Hamiltonian with nearest-neighbor interactions. We have, therefore, applied the results of the preceding analysis to a calculation of the spectral density in this material.

An accurate numerical solution of (1.28) has not yet been carried out. However, a good analytic approximation to the spectral density predicted by (1.28) can be obtained on the basis of a simple physically motivated approximation for the vertex function $\Gamma(q_1, q_2, z)$ at high temperatures.

The approximation that we shall make is given by (3.1):

$$\Gamma(\vec{q}_1, \vec{q}_2;\, z) \cong \{N^{-1/2}\tfrac{2}{3}S(S+1) \times[\rho(\vec{q}_2)-\rho(\vec{q}_1)]/\rho(\vec{q}_1+\vec{q}_2)\}/\nu(z). \tag{3.1}$$

The function $\nu(z)$ is to be determined. Observe that the quantity in curly brackets is simply $i\Gamma(\vec{q}_1, \vec{q}_2;\, t=0)$, so that the content of the approximation (3.1) is the statement that the relaxation of the vertex function is independent of q_1 and q_2. At first sight this may seem a drastic approximation, since if q_1 and q_2 are both small, the relaxation time of the vertex function will be much longer than if either q_1 or q_2 is near a zone boundary. The success of the approximation depends upon the observation that at high temperatures, fluctuations of any wave vector will decay primarily into short-wavelength fluctuations, since the phase space available for such decays is large. Since the relaxation time for short-wavelength fluctuations is roughly constant, the relaxation of the vertex function is nearly independent of wave vector over much of the zone. Furthermore, the contribution of the short-wavelength region to $\varphi(q, z)$ dominates that of the long-wavelength region and hence the resulting values for φ can be reasonably accurate. The exception to this statement occurs at the critical point, where the relative probability of decay into the critical modes increases to the point that the contribution to φ from the decay into wave vectors in the critical region of phase space dominates. The approximation (3.1) is one that breaks down near the critical temperature and, indeed, its breakdown can be used to define the boundaries of the critical region.

The function $\nu(z)$ is determined by the condition that it be such as to maintain the correct values of the second and fourth moments as predicted by (1.28). This can be accomplished by inserting (3.1) in (1.28), dividing by z, and using the resultant expression to evaluate $\varphi(\vec{q}, z)$. We have then that

$$\varphi(\vec{q}, z)=\omega^2(\vec{q})/z+\Omega^4(\vec{q})/z\nu(z)^2\,. \tag{3.2}$$

Since for large values of z, $\nu(z)\simeq z$ [compare (3.1) with (1.18) of I], (3.2) does guarantee that the approximate expression for $\varphi(\vec{q}, z)$ will have the correct second and fourth moments. Comparing (3.2) with the value of $\varphi(\vec{q}, z)$ obtained directly from (3.1),

$$\varphi(\vec{q}, z)=\omega^2(\vec{q})/\nu(z)\,, \tag{3.3}$$

we find that $\nu(z)$ must satisfy

$$z\nu(z)\omega^2(\vec{q})=\nu(z)^2\omega^2(\vec{q})+\Omega^4(\vec{q}) \tag{3.4}$$

or

$$\nu(z)=\tfrac{1}{2}\{z+[z^2-4\Omega^4(q)/\omega^2(\vec{q})]^{1/2}]^{1/2}\}\,. \tag{3.5}$$

The positive sign in (3.5) is dictated by the requirement that $\nu(z)\rightarrow z$ for large z. We note that $\nu(z)$ is real for z on the real axis as long as $\omega>2\,[\Omega^4(\vec{q})/\omega^2(\vec{q})]^{1/2}$, and is equal to

$$\nu(\omega+i\epsilon)=\tfrac{1}{2}\omega+i[\Omega^4(\vec{q})/\omega^2(\vec{q})-\tfrac{1}{4}\omega^2]^{1/2} \tag{3.6}$$

when $\omega<2[\Omega^4(\vec{q})/\omega^2(\vec{q})]^{1/2}$.

There is, of course, an inconsistency in (3.6) in that we have assumed that $\nu(z)$ was independent of wave vector, which is not true unless $\Omega^4(\vec{q})/\omega^2(\vec{q})$ is. From (2.6) of I we have, at infinite temperatures in the Weiss limit,

$$\Omega^4(\vec{q})/\omega^2(\vec{q})=\tfrac{2}{3}S(S+1)\{2V^2(0)+\tfrac{1}{2}[V^2(0)-V^2(\vec{q})]\}\,. \tag{3.7}$$

Thus $|\nu(0)|$ only varies by about 20% throughout the zone, which gives some *a posteriori* justification to the approximation. At higher frequencies, the variation is less, and our approximation will be more accurate. From the physical argument we used to justify the approximation (3.1), one can infer that (3.1) should be most accurate at short wavelengths. This is suggested also by the observation that at $T=\infty$, and for wave vector q_1, q_2 such that $\vec{q}_1+\vec{q}_2=\vec{K}_0$, where K_0 corresponds to the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ point in the reciprocal lattice, (3.1) provides a self-consistent solution of (1.28). For this wave vector, we have

$$V(\vec{q}+K_0)=-V(\vec{q})\,. \tag{3.8}$$

Substituting (3.1), evaluated at infinite temperature, into (1.28) and using (3.8), we have

$$z[V(\vec{q}_2)-V(\vec{q}_1)]/\nu(z)=[V(\vec{q}_2)-V(\vec{q}_1)]+\tfrac{2}{3}S(S+1)2V^2(0)[V(\vec{q}_2)-V(\vec{q}_1)]/\nu(z)^2$$
$$-\tfrac{1}{3}S(S+1)N^{-1/2}\sum_{q'}[V(\vec{q}_2-\vec{q}\,')-V(\vec{q}\,')][V(\vec{q}_2-\vec{q}\,')-V(\vec{q}_1)]2V(\vec{q}\,')/\nu(z)^2$$
$$-\tfrac{1}{3}S(S+1)N^{-1/2}\sum_{q'}[V(\vec{q}_1-\vec{q}\,')-V(\vec{q}\,')][V(\vec{q}_1-\vec{q}\,')-V(\vec{q}_2)]2V(\vec{q}\,')/\nu(z)^2 . \quad (3.9)$$

Since $\sum_{q'} V(\vec{q}\,')^2 V(\vec{q}_2-\vec{q}\,')=\sum_{q'} V(\vec{q}_2-\vec{q}\,')^2 V(\vec{q}\,')=0$ for the simple cubic lattice, (3.9) reduces to

$$\begin{aligned} z[V(\vec{q}_2)-V(\vec{q}_1)]/\nu(z) &= [V(\vec{q}_2)-V(\vec{q}_1)] \\ &\quad +2S(S+1)V^2(0) \\ &\qquad \times[V(\vec{q}_2)-V(\vec{q}_1)]/\nu(z)^2 . \end{aligned} \quad (3.10)$$

For this wave vector, $\nu(z)$ is given by

$$\nu(z)=\tfrac{1}{2}\{z+i[2S(S+1)V^2(0)-z^2]^{1/2}\},$$

and since

$$z\nu(z)=\nu(z)^2+2S(S+1)V^2(0),$$

(3.10) is an identity for all values of q_1, q_2 such that $\vec{q}_1+\vec{q}_2=\vec{K}_0$.

Even though (3.1) provides a self-consistent solution for $q=K_0$, it is not, of course, exact even for this wave vector, since the value of the vertex for $q=K_0$ depends on that for $q\neq K_0$. Nevertheless, by continuity, one expects (3.1) to be a good approximation for a range of wave vectors about $\vec{q}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and a range of temperatures below $T=\infty$.

The spectral density may be calculated directly from (3.3) and (3.5). If we define a shape factor,

$$x=\omega^2(\vec{q})^2/\Omega^4(\vec{q})$$

and a dimensionless frequency,

$$\xi=\omega/\omega^2(\vec{q})^{1/2},$$

we will have

$$\chi''(\vec{q},\zeta)/\xi=\chi(\vec{q},0)\frac{1}{x^{1/2}}\,\frac{(1-\frac{1}{4}\xi^2x)^{1/2}}{1+\xi^2(1/x-1)},$$
$$\xi^2\leq 2/x . \quad (3.11)$$

The normalized spectral density, for various values of the parameter x is shown in Fig. 4. The value of $x=\frac{2}{3}$ corresponds to the simple cubic lattice, at $T=\infty$ and $\vec{q}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. As the wave vector decreases, x decreases, and is proportional to q^2 for small values of q. Reference to (3.11) indicates that the shape of the spectral density becomes that of a Lorentzian, with deviations from

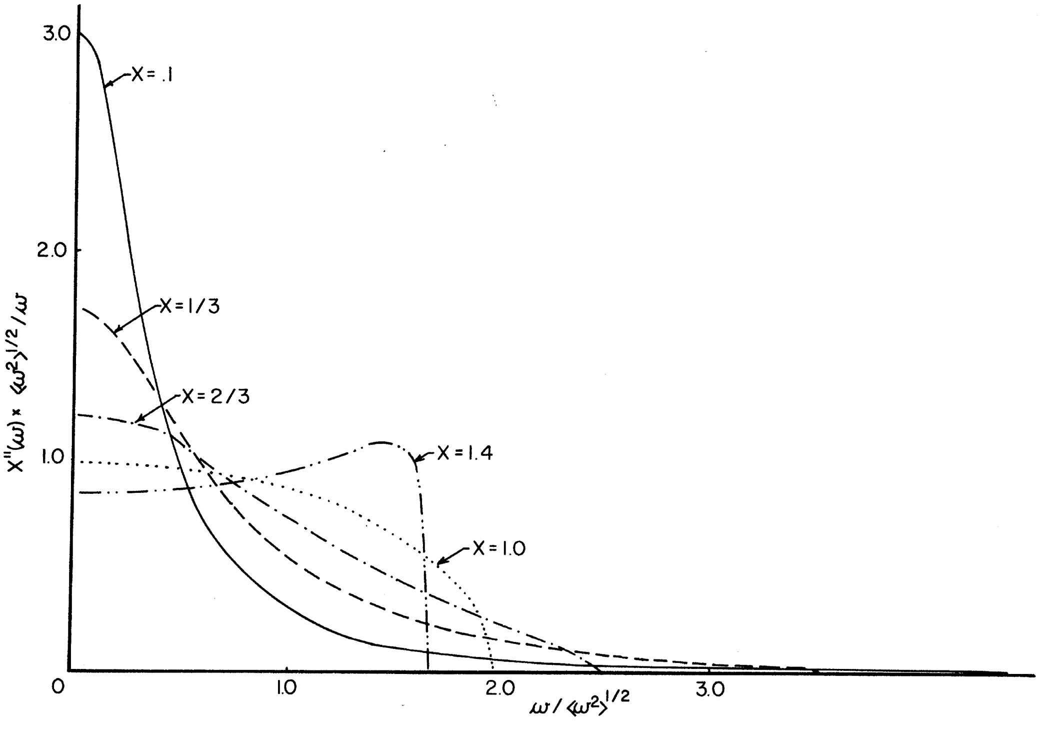

FIG. 4. Shapes of spectral densities resulting from constant-relaxation-time approximation.

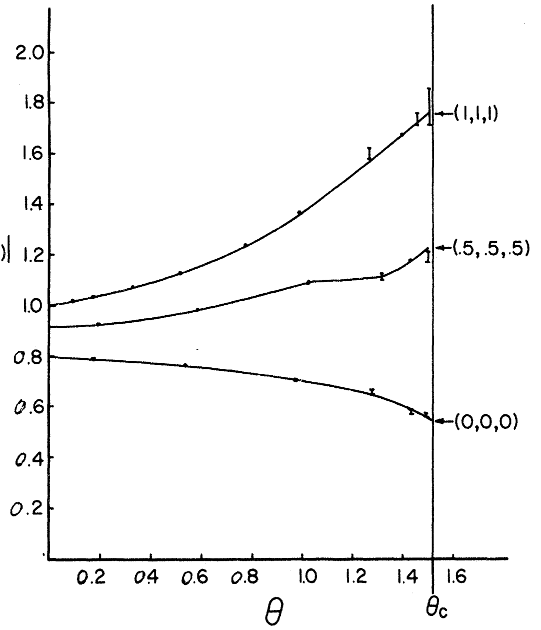

FIG. 5. Variation of relaxation frequency with temperature and wave vector in the simple cubic ferromagnet with nearest-neighbor interactions.

that shape appearing only far out in the wings. Thus the theory predicts a diffusion process at long wavelengths, in agreement with the discussion in the Appendix. The value of the diffusion coefficient is given by

$$D=\lim_{q\to 0} q^{-2}\,\omega^2(q)\,[\Omega^4(q)/\omega^2(q)]^{-1/2}$$

$$=0.408\,[1/3S(S+1)]^{1/2}\,Va^2\,, \qquad (3.12)$$

where V is the interaction constant between nearest neighbors and a the lattice spacing.

The spectral density predicted by (3.11) has been compared with the neutron scattering data of Windsor[11] on $\mathrm{RbMnF_3}$ in an earlier work.[12] The agreement is generally good, but the inaccuracies of the data, in particular, the asymmetry between positive and negative frequencies after the detailed balance factor has been corrected for, are comparable to the discrepancy between theory and experiment, so that no firm conclusion about the accuracy of the theory can be drawn from that comparison.

To apply (3.11), one must know $\omega^2(\vec{q})$ and $\Omega^4(\vec{q})$. The second moments can be evaluated analytically, using (3.26) of I. The fourth moments were evaluated by a Monte Carlo method, since they involve six-dimensional integrals. This proved to be quite satisfactory at high temperatures, but the convergence was poor near the critical point, since the integrands take values over a very large range. We have therefore indicated with error bars the numerical uncertainty in the result. The results are expressed in terms of the spin-independent quantity $|\nu(0)|^* = [\Omega^4(\vec{q})/\omega^2(\vec{q})\frac{1}{3}S(S+1)]^{1/2}$. The temperature is given in terms of the dimensionless variable $\theta=\beta V(0)\frac{1}{3}S(S+1)$. The results are displayed in Figs. 5 and 6.

As long as (3.1) is a good approximation, $|\nu^*(0)|$ can be interpreted as the effective relaxation frequency of the two-spin correlation function. It must be nearly constant over the zone if the approximation (3.1) is to be successful. From Fig. 5, we see that this condition fails badly in the ferromagnet as the temperature is lowered from $T=\infty$. In the antiferromagnet (Fig. 6) $|\nu^*(0)|$ is nearly constant at $\theta=0.8$. [This does not imply that the approximation is exact at $\theta=0.8$, since the vertex function need not satisfy (3.1) even if $|\nu^*(0)|$ is a constant.]

In order to obtain better values for the spectral density, and to obtain an estimate of the discrepancy between the spectral density calculated using the approximation (3.1) and the value that would result from an exact numerical solution of (1.38), we have used the result of the approximation (3.1) as the first step in an iterative solution of (1.38), which we write in the form (3.13):

$$\begin{aligned}\Gamma(\vec{q}_1,\vec{q}_2,z)={}&N^{-1/2}\,\frac{n(\vec{q}_2)-n(\vec{q}_1)}{\chi(\vec{q}_1+\vec{q}_2,0)}\,[z-\varphi(\vec{q}_1,z)-\varphi(\vec{q}_2,z)]^{-1}\\&-[z-\varphi(\vec{q}_1,z)-\varphi(\vec{q}_2,z)]^{-1}N^{-1/2}\sum_{q'}\{[V(\vec{q}_2-q')-V(\vec{q}\,')]\Gamma(\vec{q}_1,\vec{q}_2-\vec{q}\,',z)\\&-[V(q_1-\vec{q}\,')-V(\vec{q}\,')]\Gamma(\vec{q}_2,\vec{q}_1-\vec{q}\,',z)\}\Gamma(\vec{q}_1+\vec{q}_2-\vec{q}\,',\vec{q}\,',z)\,. \qquad (3.13)\end{aligned}$$

If we substitute the approximation (3.1) and the value of $\varphi(\vec{q},z)$ obtained from it, (3.3), into the right-hand side of (3.13), we will obtain a second approximation for Γ and, indeed, we could presumably use (3.13) to obtain the exact solution by iteration.

If we consider only the first term on the right of (3.12), we see immediately that the approximation (3.1) must fail completely whenever z, $\vec{q}_1$, and $\vec{q}_2$ all approach zero. However, even when $\vec{q}_1+\vec{q}_2=\vec{q}=0$, and $z=0$, the contributions to $\varphi(\vec{q},z)$ arising from the region of phase space in which $\vec{q}_1$ and $\vec{q}_2$

are large dominate, for temperatures outside the critical region, and the corrections to $\varphi(\vec{q}, z)$ arising from the second approximation are small. We denote by $\varphi^1(\vec{q}, z)$ the expression $\omega^2(\vec{q})/\nu(\vec{q}, z)$, where $\nu(q, z)$ is given by the right-hand side of (3.5). Then the first iteration of (3.13) yields (3.14):

$$
\begin{aligned}
\varphi^2(\vec{q}, z) = {} & \tfrac{1}{3}S(S+1)N^{-1}\sum_{q'}[V(\vec{q}-\vec{q}\,') - V(\vec{q}\,')]^2[z-\varphi^1(\vec{q}\,', z)-\varphi^1(\vec{q}-\vec{q}\,', z)]^{-1}\,\rho(\vec{q}\,')\rho(\vec{q}-\vec{q}\,')\rho(\vec{q})^{-1} \\
& + 2[\tfrac{1}{3}S(S+1)]^2N^{-2}\sum_{q'}\sum_{q''}[V(\vec{q}-\vec{q}\,') - V(\vec{q}\,')][z-\varphi^1(\vec{q}\,', z)-\varphi^1(\vec{q}-\vec{q}\,', z)]^{-1} \\
& \times[V(q'') - V(\vec{q}-\vec{q}\,'-\vec{q}\,'')][V(\vec{q}\,'+\vec{q}\,'') - V(\vec{q}-\vec{q}\,'-\vec{q}\,'')] \\
& \times[V(\vec{q}\,'') - V(\vec{q}\,')]\nu(\vec{q}\,'+\vec{q}\,'', z)^{-1}\nu(\vec{q}, z)^{-1}\rho(\vec{q}\,'')\rho(\vec{q}-\vec{q}\,'-\vec{q}\,'')\rho(\vec{q})^{-1}\,. \qquad (3.14)
\end{aligned}
$$

We shall refer to the solution for φ given by 3.14 as the *first-iteration solution* of the kinetic equations. It should be noted that this solution partially includes the effect of the long relaxation time for the long-wavelength vertices but, because this is not done in a self-consistent fashion, the result is still not applicable in the critical region.

In order to compare the predictions of our theory with experiment, we have made calculations of the spectral density based upon (3.14) for a range of wave vectors and temperatures. To evaluate the multiple integrals appearing in (3.14) we have used a Monte Carlo procedure, as in the evaluation of the moments, with the same sample of points in phase space being used for all values of the frequency. The rms error introduced by the method was made less than 3% of the value of the spectral density at zero frequency by choosing a sufficiently large sample size. The uncertainty at finite frequencies was considerably less, being on the order of 1% for frequencies corresponding to half intensity. The calculations at finite temperatures could not be made directly from (3.14) as expressions for $\Omega^4(q)$ at temperatures for which the linear expansion (3.16) becomes dubious are not available. We chose, therefore, to replace the q-dependent quantity $\nu(q,z)$ appearing in the integrals by its value at a particular value of q, for each temperature. Of course, at $\theta = 0.8$, this would not be an additional approximation. We note that if we had not made this additional approximation, the sharp cutoff feature of the first approximate solution would disappear upon iteration, but that this feature is retained in the present approximation. We did not attempt to fit the parameter $\nu(q, 0)$, but chose its value so that for each wave vector, the cutoff remained invariant in going from the first to the second approximation. Thus, if we are evaluating the spectral density for $\vec{q} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, the value of $\nu(q, 0)$ used in calculating the integrals was taken to be the constant appropriate to that value of q. We shall refer to the solution (3.14) with this additional approximation as the *improved first approximation*. From the prior discussion, the improved first approximation agrees with the first approximation at $\vec{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $T = \infty$.

A comparison of the calculations based upon the improved first approximation with the experimental data obtained by neutron scattering from $\mathrm{RbMnF_3}$[6] is shown in Figs. 7(a)–7(i). The experimentally measured cross section is actually proportional to

$$S(q, \omega) \equiv (1/2\pi)\int_{-\infty}^{\infty}\langle\langle S^z(q, t)S^z(-q, 0)\rangle\rangle e^{i\omega t}dt,$$

which is related to $\chi''(q, \omega)$ by

$$\omega^{-1}\chi''(q, \omega) = (1-e^{-\hbar\omega\beta})\,(\hbar\omega\beta)^{-1}S(q, \omega).$$

The detailed balance factor has been incorporated into the data, so that the readings in counts per

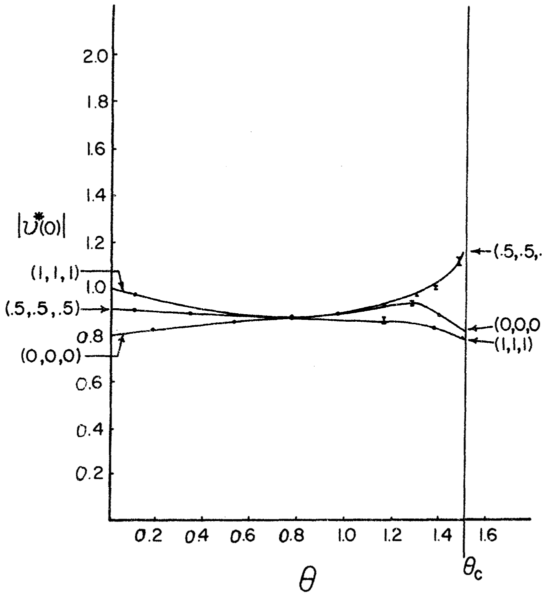

FIG. 6. Variation of effective relaxation frequency with temperature and wave vector in the simple cubic antiferromagnet with nearest-neighbor interaction.

minute are proportional to $\chi''(q, \omega)/\omega$. The absolute intensities are normalized to the experimental value of the static susceptibility rather than the spherical-model values, so that the comparison is a test only of the line shape. Since there is significant instrumental resolution in the frequency variable, the theoretical curves shown are the result of convoluting the improved-first-approximation line shapes with the experimentally known instrumental resolution function. The value of θ

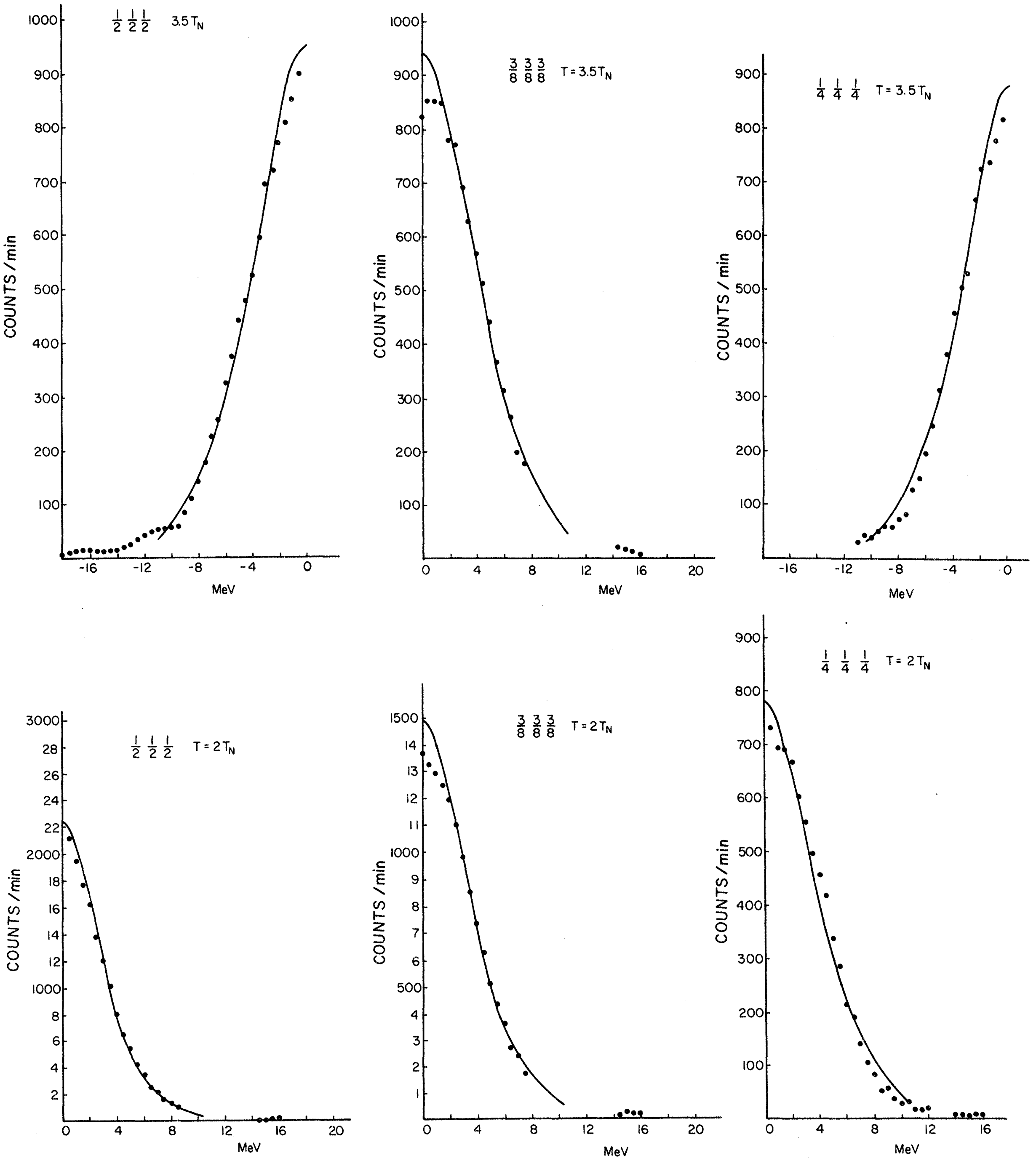

FIG. 7. Comparison of theoretical predictions based upon improved first-approximation spectral densities with neutron scattering results. The theoretical curves are obtained by folding the spectral density with the instrumental resolution function.

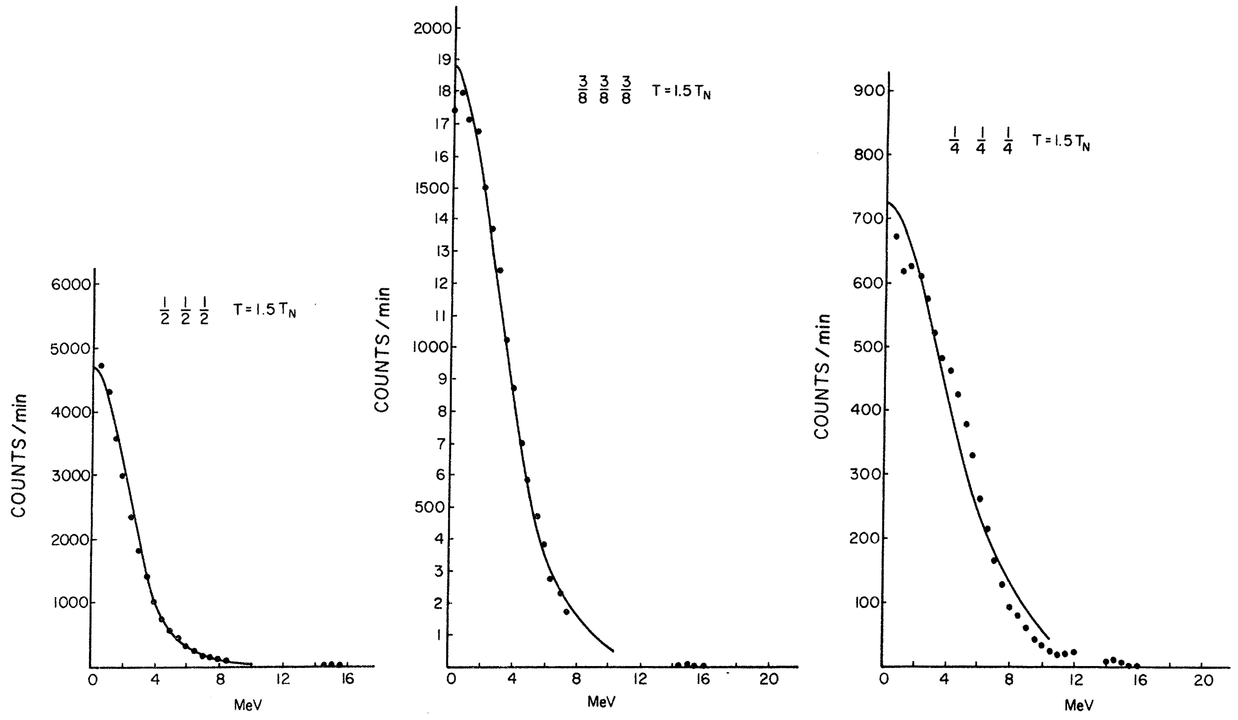

FIG. 7. *(Continued)*.

that was used in the theoretical calculations, where it determines the equilibrium correlation functions, was obtained by using the experimental values of T and the exchange constants in the formula $\theta = \frac{1}{3}S(S+1)\,V(0)/kT$. Since T_N is not given experimentally by the spherical-model value, as calculated from the measured exchange constant, but is slightly higher (i.e., $T_N = 83.3$ °K, whereas $T_{\text{spherical}} = 78$ °K), there is some arbitrariness in the comparison of the theoretical and experimental temperature scales. However, this correction will have a negligible effect on the comparison of theory with experiment in the temperature range considered, since the changes produced by the uncertainty in the temperature scale in the theoretical calculations are small compared to the other theoretical uncertainties. The agreement between theory and experiment is generally good, the significant discrepancies occurring near zero frequency for all wave vectors and temperatures, and in the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ data as the temperature is lowered. The latter disagreement we interpret as a result of remnants of the structure in the critical region, which leads to a three-peaked form for the spectral density,[13] and which cannot be accounted for by our approximation. We believe that it is precisely the variation in the relaxation times that is responsible for this three-peaked form. [See the discussion in Sec. I of Eq. (1.11).] The discrepancy at zero frequency may be the result of the approximations, since it is the zero-frequency values that are most sensitive to the behavior of the vertex function in the long-wavelength region.

An estimate of the difference between the results of an exact solution of (1.28) and the values of the spectral density predicted by the improved first approximation can be had by comparing the results for the first approximation and the first-iteration solution (3.14) at infinite temperatures, where the values for the fourth moment are known analytically. The results for the wave vectors $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ are shown in Figs. (8) and (9). The discrepancies at zero frequency between the first approximation and the iterative solutions is only about 10%, which suggests that the iterative procedure is a valid means of solving the equations. The spectral density at the $\frac{1}{4}\,\frac{1}{4}\frac{1}{4}$ point is the least sensitive to temperature of any point in the zone, so that the experimental values at room temperature should be very nearly those at infinite temperature.[6] In Fig. 10 we have compared the first-iteration solution at $T = \infty$, folded with the instrumental resolution function, with the data for the $\frac{1}{4}\frac{1}{4}\,\frac{1}{4}$ point, and the results of the calculation of Blume and Hubbard,[7] also folded with the resolution function. Further comparisons are made and discussed in Sec. IV. The differences between the first-iteration solution and the improved first approximation appear to reduce the discrepancy between theory and experiment at zero frequency.

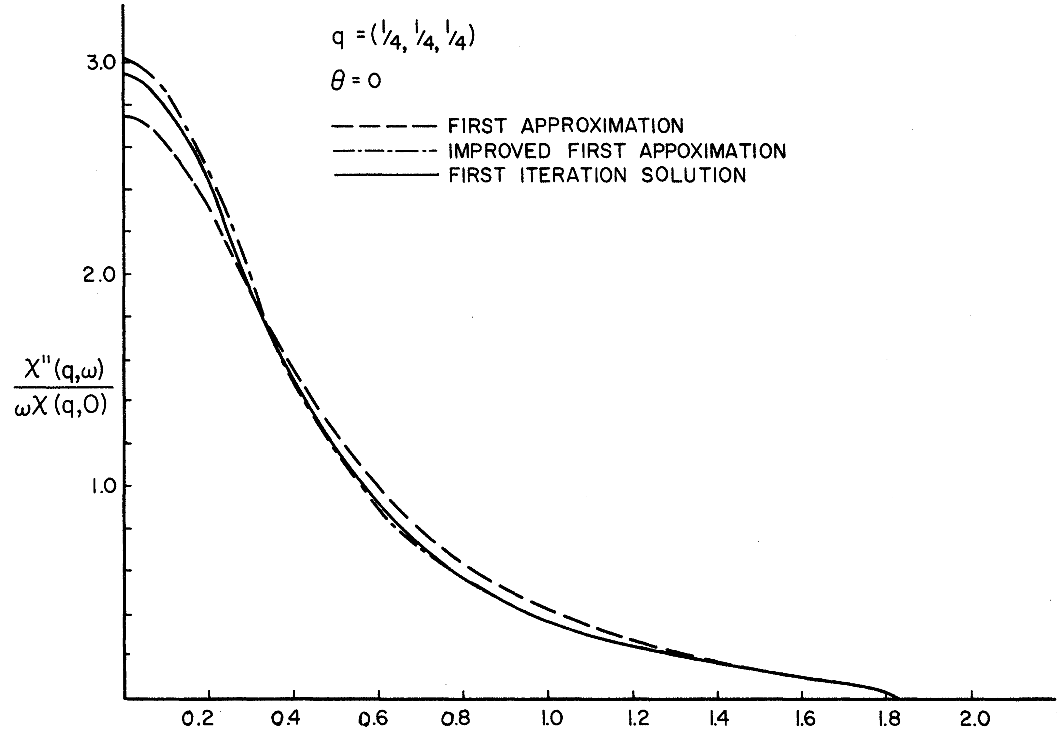

FIG. 8. Comparison of theoretical spectral densities based upon constant-relaxation-time approximation and its improvements for infinite temperatures.

No conclusion can be drawn about whether this would be true of the other points in the zone, where the temperature corrections in the data are more significant than the differences between the two approximations.

The shape of the spectral function at long wavelengths will be a Lorentzian, for either the first approximation or the improved first approximation, with only slight differences between the two appearing in the wings of the line, where they would be unobservable by neutron scattering. Furthermore the linewidth will be proportional to q^2 in either case, and hence may be characterized by a diffusion constant. Hence it suffices to compare the theoretical and experimental values for the diffusion coefficient in order to obtain a comparison of the spectral densities. The diffusion coefficient calculated from (3.14) is given by (3.15), where $D^* = D/[\frac{1}{3}S(S+1)]^{1/2}$:

$$D^* = N^{-1}\sum_{q'} [\vec{\nabla} V(\vec{q}\,')]^2 \frac{\rho(\vec{q}\,')^2 \Omega^4(\vec{q}\,')^{1/2}}{\rho(0)\, 2\omega^2(\vec{q}\,')^{3/2}}$$

$$+N^{-2}\sum_{q'}\sum_{q''} \nabla V(\vec{q}\,')\cdot\nabla V(\vec{q}\,'')\,[V(\vec{q}\,'-\vec{q}\,'') - V(\vec{q}\,'')][V(\vec{q}\,'-\vec{q}\,'') - V(\vec{q}\,')]$$

$$\times \frac{\Omega^4(\vec{q}\,')^{1/2}}{\omega^2(\vec{q}\,')^{3/2}} \left(\frac{\omega^2(0)\omega^2(\vec{q}\,'')}{\Omega^4(0)\Omega^4(\vec{q}\,'')}\right)^{1/2} \rho(\vec{q}\,')\rho(\vec{q}\,'-\vec{q}\,'')\rho(\vec{q}\,'')/\rho(0)\,. \qquad (3.15)$$

In calculating D^*, we would again need to know the fourth moments at finite temperatures. We have, therefore, made the same approximation as in calculating the spectral densities of Fig. 7, and replaced $[\Omega^4(q)/\omega^2(q)]^{1/2}$ by its value at $q=0$ in the integrals, which can be taken from Fig. 6. In addition, the expressions for the second and fourth moments have been evaluated to first order in θ, making possible the calculation of the linear term in the diffusion coefficient as a function of θ, either from (3.15) for from (3.12). The moments in terms of the reduced quantities $\omega^2(q)^*$ and $\Omega^4(q)^*$ are given by (3.16) (the positive sign corresponds to the antiferromagnet):

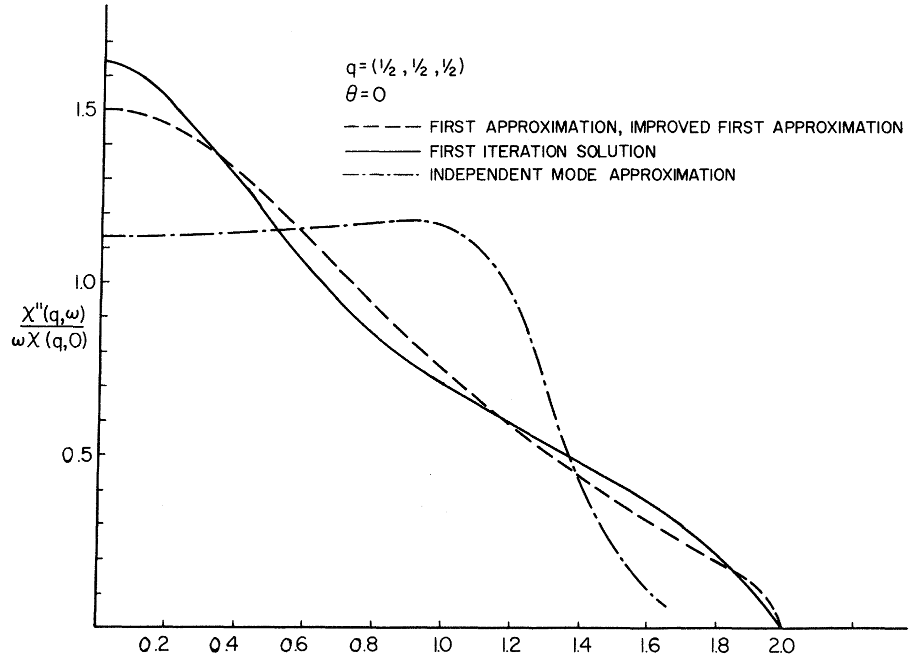

FIG. 9. Comparison of theoretical spectral densities based upon constant-relaxation-time approximation and its improvements with the results of the independent mode approximation.

$$\omega^2(\vec{q})^*_\theta = 2[V^2(0) - V^2(\vec{q})][1 - \theta V(\vec{q})/|V(0)| + O(\theta^2)] , \tag{3.16a}$$

$$\begin{aligned}\Omega^4(\vec{q})^*_\theta = \Omega^4(\vec{q})^*_{\theta=0}[1 - \theta V(\vec{q})/|V(0)| + O(\theta^2)] \pm \theta \{ \tfrac{5}{18} V(0)^2[V^2(0) - V^2(\vec{q})] \\ - V(0)^4 \tfrac{2}{81} [\sin(\tfrac{1}{2}\vec{q}_x a)^4 + \sin(\tfrac{1}{2}\vec{q}_y a)^4 + \sin(\tfrac{1}{2}\vec{q}_z a)^4) \\ - V(0)^4 \tfrac{8}{81} [\sin(\tfrac{1}{2}\vec{q}_x a)^2 \sin(\tfrac{1}{2}\vec{q}_y a)^2 + \sin(\tfrac{1}{2}\vec{q}_x a)^2 \sin(\tfrac{1}{2}\vec{q}_y a)^2 + \sin(\tfrac{1}{2}\vec{q}_z a)^2 \sin(\tfrac{1}{2}\vec{q}_y a)^2]\} .\end{aligned} \tag{3.16b}$$

In Fig. 11 we have compared the experimental values of the diffusion coefficient, obtained by Tucciarone, Hastings, and Corliss,[14] with the theoretical results obtained from the improved first approximation [Eq. (3.15) with the substitution just mentioned] and the full first-iteration solution [Eq. (3.15) using (3.16)]. In both cases, we find that the theoretical results are consistently smaller, and that the discrepancies are larger (20–30%) than the corresponding discrepancies in the zero-frequency spectral density at short wavelengths. This is understandable, in that the constant-relaxation-time approximation is expected to be worse for long wavelengths. The improvement in the agreement with experiment in going from the first approximation to the full first-iteration solution suggests that further iterations would improve the agreement.

Collins[15] recently has calculated the linear term in the fourth moment exactly by a series expansion method. His results are, of course, spin dependent. For $S = \frac{5}{2}$, we obtain the result from (3.16), for the ratio $\Omega^4(0)^*_\theta/\Omega^4(0)^*_{\theta=0}$ of $1 + 4.12\,\beta V(0)$, in the antiferromagnet. We obtain for the ratio $\Omega(k_0)^*_\theta/\Omega^4(k_0)^*_{\theta=0}$ the value of $1 - 2.92\beta V(0)$, while Windsor obtains $1 - 3.49\beta V(0)$.

IV. COMPARISON WITH OTHER THEORETICAL WORK

Previous theoretical calculations of the spectral density fall into three categories. They have been either numerical computer calculations[16–18] or phenomenological calculations, or have been based upon a particular decoupling approximation for the two-spin time-dependent correlation function, i.e.,

$$\begin{aligned}&(S^-(q_1, t)S^+(q_2, t), S^-(q_3, 0)S^+(q_4, 0)) \\ &\quad = \delta(q_1 + q_4)\delta(q_2 + q_3)\beta^{-1}(S^-(q_1, t), S^+(-q, 0)) \\ &\qquad \times (S^-(q_2, t), S^+(-q_2, 0)) .\end{aligned} \tag{4.1}$$

The semiempirical work attempts to characterize the spectral density in terms of the second and fourth moments, which requires some sort of *ad hoc* assumption about the line shape itself or the function $\varphi(q, \omega)$. De Gennes,[19] who did the earliest calculation of this kind assumed that the line shape could be approximated by a cutoff Lorentzian, in order to calculate the diffusion coefficient. Mori

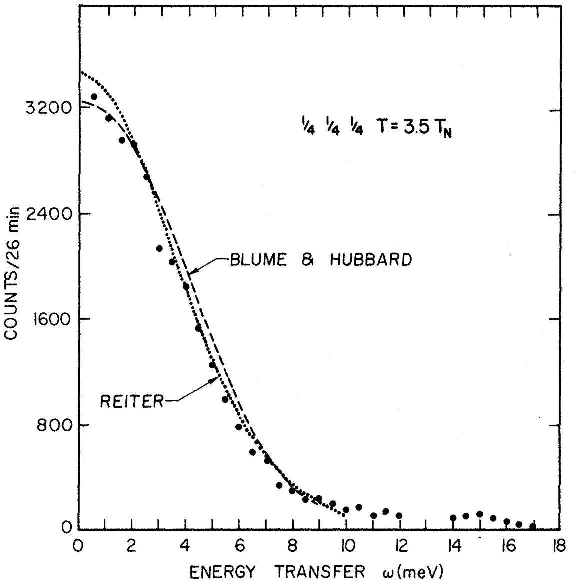

FIG. 10. Comparison of theoretical spectral densities calculated from full first-iteration solution with neutron scattering results (dotted line) and results of calculations of Blume and Hubbard using the independent-mode approximation (dashed line). Both theoretical curves have been folded with the instrumental resolution function. The calculations are based upon the infinite-temperatures results.

and Kawasaki,[20] in calculating the diffusion coefficient, assumed that the function $\varphi(q, z)$ was proportional to $e^{-\gamma(q)^2 t^2}$. Martin and Bennett[21] defined a "diffusivity function" $D(q, \omega)$ which is related to $\varphi(q, z)$ by means of (8.2),

$$\varphi(q, z) = \frac{z}{\pi} \int_{-\infty}^{\infty} \frac{D(q, \omega)}{z^2 - \omega^2}, \quad \mathrm{Im} z > 0 \tag{4.2}$$

and assumed that it was proportional to $e^{-\gamma(q)^2 \omega^2}$, again in order to calculate the diffusion coefficient.

The diffusion coefficient calculated in this way, either from Mori and Kawasaki or Bennett and Martin is

$$D = \lim_{q \to 0} \frac{1}{q^2} \left(\frac{\pi}{2}\right)^{1/2} \frac{\omega^2(q)^{3/2}}{\Omega^4(q)^{1/2}}, \tag{4.3}$$

which differs by a numerical factor from the result of our first approximation (3.12). The value of D calculated from (4.3) using Windsor's values for the moments is shown in Fig. 11, and gives the best fit to the data in the high-temperature region of the alternatives we have considered. This method has been shown by Tahir-Kheli and McFadden[22] to yield results that are in fair agreement with numerical calculations in one, two, and three dimensions. This approach does not yield much insight into the dynamics, however, and is incapable of treating the critical region, where the moments have no direct connection with the characteristic relaxation time (in three dimensions).

The approximation (4.1), or a closely related approximation, appears in the work of Bennett and Martin, Kawasaki, Resibois and DeLeneer, Wegner, and Blume and Hubbard, although the motivation and the extent to which the calculations have been carried differ. Since $\varphi(q, z)$ is given in terms of $\Sigma(q, z)$ by means of this approximation, one can calculate $\Sigma(q, z)$ self-consistently (see I). Blume and Hubbard have calculated Σ in this

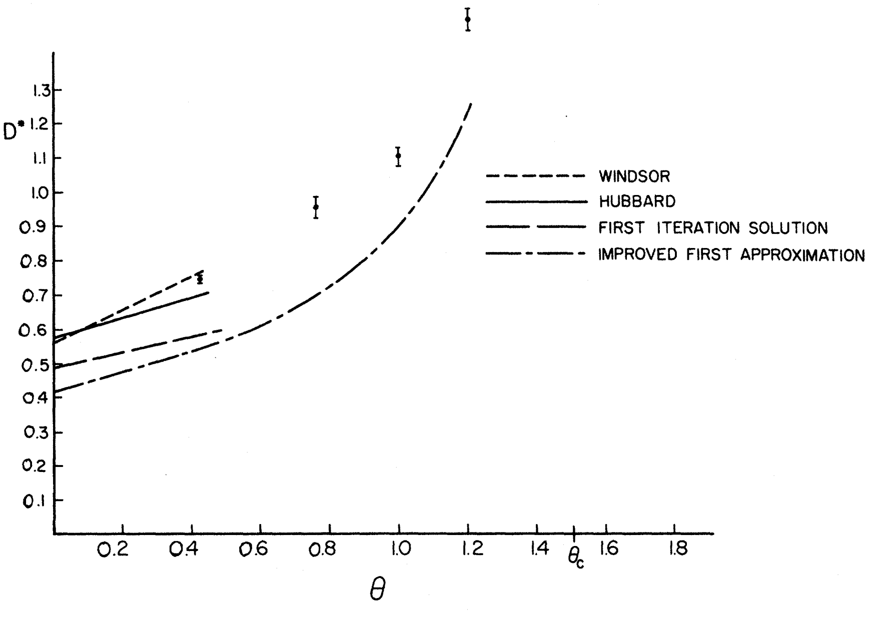

FIG. 11. Diffusion constant as a function of temperature. Windsor's results are obtained using the expression for the diffusion coefficient in terms of moments given by Eq. (4.2), Hubbard's results by reversing the sign of the coefficient of θ in his calculation for the ferromagnet. The temperature dependence of the moments in the first-iteration solution is obtained from Eq. (3.16). The experimental results are due to Tucciarone, Hastings, and Corliss.

approximation at infinite temperature, and Hubbard[23] has calculated Σ for the ferromagnet at all temperatures. We have shown in Fig. 11 the value for the diffusion coefficient in the antiferromagnet obtained from Hubbard's calculation by reversing the sign of the coefficient of θ.

The most significant difference between spectral densities based upon (4.1) and the present theory, at infinite temperatures, shows up at short wavelengths. In Fig. 9 we have compared our results with Blume and Hubbard's calculation for $\vec{q} = K_0(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The Blume and Hubbard results show a sharp shoulder, indicating that the mode is just overdamped, whereas our calculations show considerably more damping, with no evidence of a shoulder. We believe the discrepancy is due to the omission of the scattering processes between the modes appearing in the self-energy φ, which is implicit in the approximation (4.1), and which leads to additional damping of the K_0 mode. An immediate consequence of this omission is that the fourth moment calculated from the self-consistent equation based upon (4.1) will be smaller than the correct value, yielding a value for the ratio $\langle \omega^2 \rangle^2 / (\langle \omega^4 \rangle - \langle \omega^2 \rangle^2)$ of 1 rather than $\frac{2}{3}$. If the incorrect fourth moment is used in the approximate expression (3.11), we see from Fig. 4 that the spectral density shows an increased lifetime for the excitation, similar to the results of Blume and Hubbard.

A further difficulty of the approximation is that it does not predict the correct shape of the scaling function at the critical point in the antiferromagnet, where the experimental results[13] show a distinct three-peaked structure. Our equations have not yet been solved at the critical point, but the argument of Sec. I would indicate that the scattering processes, which were lumped into a phenomenological relaxation time in Eq. (1.11), will be responsible for that structure, and are an essential part of the dynamics.

There is also no possibility of incorporating the conservation laws into the dynamics within an approximation such as (4.1) or the extension that can be obtained by keeping higher-order terms in the renormalized expansion for $\varphi(q, z)$, so that a treatment of energy transport is, in principle, inaccessible to such approximations.

CONCLUSION

It is evident that the kinetic equations provide a basis for detailed, semiquantitative calculations of a wide range of dynamical properties of the Heisenberg paramagnet. The discrepancies that exist between the theoretical calculations and the numerical and experimental results for the spectral density are comparable to the uncertainties introduced by using analytic approximations to the exact solution of the equations, and hence a detailed analysis of the limits of accuracy of the equations can be made only after obtaining accurate numerical solutions.

In any case, it is clear that the constant-relaxation-time approximation provides a useful description of the dynamics, insofar as it is reflected in the spectral density, at high temperatures. The kinetic equations have fundamental limitations near the critical point, as the decay processes made possible by including the effect of higher-order cumulant terms cannot be readily taken into account. It does give a description of the dynamical spherical model near the critical point, however, and as such remains interesting even if the deviations from the behavior of the Heisenberg model proves to be large. The implications of the equations near the critical point will be discussed in a subsequent paper.

ACKNOWLEDGMENTS

I would like to thank Aldo Tucciarone, Julius Hastings, and Lester Corliss for making their results for the diffusion coefficient available to me prior to publication.

APPENDIX: HYDRODYNAMIC LIMIT

We expect that the function $\varphi(\vec{q}, z)$ can be expanded, for small ω and $\vec{q}$, as

$$\varphi(q, \omega + i\epsilon) = -iDq^2 + \alpha\omega q^2 + O(q^4) + O(\omega^2 q^2) \qquad \text{(A1)}$$

and we should like in this appendix to reduce the assumptions needed to give (A1) to a minimum. (A1) implies that the behavior of the long-wavelength modes is diffusive. To be precise, given any real quantity ρ, for all $\omega < \rho Dq^2$, if (A1) holds, then we find a value of $\vec{q}$ sufficiently small so that

$$\sum(q, \omega + i\epsilon) = i\chi(q, 0) \frac{1}{\omega + iDq^2} [1 + O(q^2)]. \qquad \text{(A2)}$$

Thus, for a range of frequencies up to any arbitrary multiple of the decay frequency Dq^2, the decay of fluctuations of wave vector $\vec{q}$ can be described by a diffusion equation, plus a correction that can be made arbitrarily small by allowing $\vec{q}$ to become small.

A formal expression for D, and a justification of the form (A1) can be obtained by a consideration of the spectrum of the operator $\mathfrak{L}' = (I - P)\mathfrak{L}(I - P)$. We observe, first of all, that $\mathfrak{L}'$ is a Hermitian operator on V, since both $\mathfrak{L}$ and P are. Thus the spectrum of $\mathfrak{L}'$ is real. If λ is in the spectrum of $\mathfrak{L}'$, then so is $-\lambda$. If L_λ is the operator corresponding to the eigenvalue λ, then $L_\lambda^\dagger$ corresponds to the eigenvalue $-\lambda$. To see this, observe that

$$\mathfrak{L}' | L_\lambda \rangle = (1/\hbar)(I - P) \times [(I - P) \times L_\lambda, \mathcal{H}] = \lambda | L_\lambda \rangle$$

implies that

$$(I - P) \times L_\lambda = L_\gamma \qquad \text{(A3a)}$$

and

$$(1/\hbar)[L_\lambda, \mathcal{H}] = \lambda L_\lambda - \sum_q \alpha_q S^z(\vec{q}), \tag{A3b}$$

where α_q is a complex number, equal to $\langle S^z(\vec{q})|\mathcal{L}| \times L_\lambda\rangle/\chi(\vec{q},0)$. Equation (A3a) implies that $\langle S^z(q)\,|\,L_\lambda\rangle = 0$. From the definition of the inner product, it is easy to see that $\langle A\,|\,B\rangle^* = \langle A^\dagger|\,B^\dagger\rangle$, so that $\langle S^z(q)|L_\lambda^\dagger\rangle = 0$ for every $\vec{q}$. Therefore

$$(I-P)\times L_\lambda^\dagger = L_\lambda^\dagger . \tag{A4}$$

Taking the adjoint of (A3b) we obtain

$$(1/\hbar)[L_\lambda^\dagger, \mathcal{H}] = -\lambda L_\lambda^\dagger - \sum_q \overline{\alpha}_q S^z(-\vec{q}). \tag{A5}$$

Upon multiplying from the left with $I-P$, and using (A4), we obtain the result

$$\mathcal{L}'\,|L_\lambda^\dagger\rangle = -\lambda\,|L_\lambda^\dagger\rangle. \tag{A6}$$

This symmetry of the spectrum has important consequences. The resolvent operator $[z-\mathcal{L}']^{-1}$ can be written, using the spectral decomposition of the operator $\mathcal{L}'$,

$$[z-\mathcal{L}']^{-1} = \int_{\sigma(\mathcal{L}')} d\lambda\,|L_\lambda\rangle\langle L_\lambda|\,[z-\lambda]^{-1}, \tag{A7}$$

where $\sigma(\mathcal{L}')$ denotes the spectrum of $\mathcal{L}'$. The integration is actually a sum as long as the number of sites N is finite. Thus on the real axis,

$$\varphi(q, \omega + i\epsilon) = \Big\{\mathcal{P}\!\!\int_{\sigma_{\mathcal{L}'}} d\lambda\,|\langle \mathcal{L}S^z(q)|L_\lambda\rangle|^2[\omega-\lambda]^{-1} - i\pi\int_{\sigma(\mathcal{L}')}\delta(\omega-\lambda)\,|\langle\mathcal{L}S^z(\vec{q})|L_\lambda\rangle|^2\Big\}\Big/\chi(\vec{q},0), \tag{A8}$$

since $|\langle\mathcal{L}S^z(\vec{q})|L_\lambda\rangle|^2$ is a symmetric function of λ. This follows from (A6) and the invariance of $\mathcal{L}'$ to translations and inversions. The diffusion coefficient is then defined by the relation (A9),

$$D = \lim_{q\to 0} q^{-2}\pi\int_{\sigma(\mathcal{L}')} d\lambda\,\delta(\lambda)\,|\langle\mathcal{L}S^z(\vec{q})|L_\lambda\rangle|^2/\chi(\vec{q},0), \tag{A9}$$

and is clearly a positive quantity. We have left the integral in (A9) in order to emphasize that $|L_0\rangle$ is in general degenerate, and one must sum over these degenerate states.

Equation (A9) indicates that the expression (A1) holds when $\omega = 0$. To obtain (A1) in the general case, we observe that $\varphi(\vec{q}, z)$ satisfies the conditions (a)–(c) for all z such that $\mathrm{Im}z > 0$:

(a) $\varphi(\vec{q}, z)$ analytic,

(b) $\varphi(\vec{q}, \omega + i\sigma) = -\varphi(q, -\omega + i\sigma)^*$,

(c) $\mathrm{Im}\varphi(\vec{q}, z) \le 0$.

$i\varphi(\vec{q}, z)$ is therefore a positive real function, and hence, according to Youla's theorem as extended by Beltrami and Wohleri,[12] the boundary value of $\varphi(\vec{q}, z)$ on the real axis satisfies

$$i\varphi(\vec{q}, \omega + i\epsilon) = i\omega\int_{-\infty}^{\infty} dM(\vec{q},\tau)\,d\tau - i(1+\omega^2)\,\mathcal{P}\!\!\int_{-\infty}^{\infty}\frac{DM(\vec{q},\tau)}{\omega-\tau}\,d\tau + \pi(1+\omega^2)DM(\vec{q},\omega) \tag{A10}$$

$M(\vec{q}, \omega)$ is a bounded, odd, nondecreasing function of ω and hence $DM(\vec{q}, \omega)$ is a non-negative measure, symmetric in ω. The principal-value integral must be understood in terms of the convolution of distributions and, indeed, the right-hand side of (A10) is in general a distribution. For all ω, the rotational invariance of the Hamiltonian assures that $DM(\vec{q}, \omega)$ vanishes as $q \to 0$. We will assume that $\lim_{q\to 0} DM(\vec{q}, \omega)/q^2$ exists, and is a continuous function of ω near $\omega = 0$. Equation (A1) then follows from (A11) if we observe that the principal-value integral is proportional to ω for small ω. This assumption is almost certainly satisfied for temperatures away from the transition temperature.

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[1] K. Kawasaki, Prog. Theor. Phys. 37, 285 (1968).

[2] P. Resibois and M. DeLeneer, Phys. Rev. 152, 305 (1966); Phys. Rev. 152, 318 (1966); Phys. Rev. 178, 806 (1969); Phys. Rev. 178, 819 (1969).

[3] F. Wegner, Z. Physik 216, 433 (1968); Z. Physik 218, 260 (1969).

[4] M. Blume and J. Hubbard, Phys. Rev. B 1, 3815 (1970).

[5] G. F. Reiter, Phys. Rev. B 5, 222 (1971).

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

[7] P. A. Fedders, Phys. Rev. B 5, 181 (1972).

[8] P. A. Fleury, Phys. Rev. 180, 591 (1969).

[9] J. E. Gulley, D. Hone, D. J. Scalopino, and B. Silbernagel, Phys. Rev. B 1, 1020 (1970).

[10] K. Kawasaki, Prog. Theor. Phys. 29, 801 (1963).

[11] C. G. Windsor, G. A. Briggs, and M. Kestigian, J. Phys. C 1, 940 (1968).

[12] G. F. Reiter, J. Appl. Phys. 41, 1368 (1970).

[13] A. Tucciarone, H. Y. Lau, L. M. Corliss, A. Delapalme, and J. M. Hastings (to be published).

[14] A. Tucciarone, J. Hastings, and L. Corliss (private communication).

[15] M. F. Collins (to be published).

[16] R. E. Watson, M. Blume, and G. H. Vineyard, Phys. Rev. 181, 811 (1969).

[17] C. G. Windsor, Proc. Phys. Soc. (Lond.) 91, 353 (1967).

[18] F. Carboni and P. Richards, Phys. Rev. 177, 889 (1969).

[19] P. De Gennes, J. Chem. Phys. Solids 4, 223 (1958).

[20] H. Mori and K. Kawasaki, Prog. Theoret. Phys. 27, 529 (1962).

[21] H. Bennett and P. C. Martin, Phys. Rev. 138, 607 (1965).
[22] R. A. Tahir-Kheli and D. G. McFadden, Phys. Rev. 182, 604 (1969).
[23] J. Hubbard, J. Phys. C 4, 53 (1971).

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Methods of Series Analysis. I. Comparison of Current Methods Used in the Theory of Critical Phenomena*

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We survey the principal types of methods of series analysis which have been used in the study of critical phenomena with a view to determining their accuracy and applicability to the treatment of the critical-point singularities. These methods include the ratio method and its variants, such as the Neville-table method; the Padé-approximant procedures; and the procedures based on the generalized-Polya theorems of Thompson *et al.* We show that the actual procedures of Thompson *et al.* are mathematically equivalent to certain of the Padé-approximant procedures. We give a general error analysis for the series-analysis procedures and derive a relation between the expected magnitude of the errors in the parameters of $A(1-yx)^{-\gamma}$, namely, $\Delta y:\Delta\gamma:\Delta A$ as $1:J:J\ln J$, where J is the order of the last term of the series analyzed. This relation is briefly illustrated by numerical data. We further give procedures for establishing estimates of the magnitude of errors in the parameters that have the same type of validity as those commonly used to determine the accuracy of a truncated Taylor series. We discuss the commonly occurring but anomalous case of "defects" (errant close pole and zero) in Padé-approximant procedures. We show them to be related to Padé's block structure of the approximant table and emphasize the artificial nature of the apparently rapid convergence that they cause. By numerical investigation of many test functions, similar in structure to those believed to appear in problems of critical phenomena, we have illustrated the following conclusions. First, for series where there is only a simple algebraic singularity; closer to the origin and well separated from any other singularity, the ratio method, perhaps with Neville-table improvement, is the most effective procedure. Second, for series where there are interfering singularities close to the one considered, or where there are singularities either closer than or nearly at the same distance from the origin as the one considered, the Padé procedures are best. Finally, for not exactly representable singularity structures of the type just decscribed, the convergence of even the Padé-approximant procedures are significantly slowed. None of the general methods described does a very impressive job in computing the γ value if the function is in fact of the form $A(1-yx)^{-\gamma}\ln|1-yx|$.

I. INTRODUCTION AND SUMMARY

Many important results in the theory of critical phenomena have been obtained by deducing the asymptotic behavior of functions from their series expansions. Relatively few rigorous results are available for the many models that have been introduced to describe systems in the region of a phase transition. In the absence of many exact results, considerable effort has been directed toward calculating series expansions, often of considerable length, for the model partition functions, and thence the thermal and magnetic (or a counterpart) functions. Various methods have been used to extract estimates of the critical points and critical exponents from the series. Many of the results that have been obtained in this way are summarized in two review articles[1] and in a recent book.[2] Other developments that have heightened interest in the field have been the derivation of the rigorous exponent inequalities,[3] the predictions of scaling theory,[4] and, more recently, the attempts to deduce equations of state that reflect all the critical properties.[5]

However, while many expansions have proved amenable to accurate estimation of the critical parameters using the current analysis techniques, others subjected to the same analysis have yielded results which are too uncertain to reach definite conclusions regarding, for example, the validity of scaling theory for a particular model. In many cases, the series expansions are not long enough to make accurate predictions; in other cases, the series would appear to be long enough, but the structure of the function seems to be too complicated for current methods to treat accurately. This is especially true of the low-temperature series for the three-dimensional Ising model, where there are known to be other singularities in the functions closer to the origin than the one corresponding to the physical transition. On the other hand, there has not been any rigorous way to assess