

Spin Diffusion in the Heisenberg Paramagnet*

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In this paper, two methods are presented for calculating the spin diffusion coefficient, the long-wavelength low-frequency limit of the spin pair correlation function. These methods are used to evaluate this coefficient in the isotropic Heisenberg paramagnet. In the first method, successively higher correlations are neglected, and eventually an approximate nonlinear integral equation is obtained. In the second, a dispersion relation and sum-rule moment relations are utilized. Expressions are obtained for the diffusion coefficient both at high temperatures and near the Curie temperature. The two evaluations of the diffusion constant at high temperatures agree with each other extremely well, and are in qualitative agreement with two previous determinations.

I. INTRODUCTION

THAT part of the spin pair correlation function which gives the long-time large-distance behavior of the system contains a description of the spin diffusion process. However, in practice this part is the most difficult part to compute since it refers to a situation in which the behavior of the system is dominated by many collisions. Conventional perturbation theory is not suited to such a discussion. In the language of perturbation theory the treatment of the diffusive behavior in the isotropic Heisenberg ferromagnet requires integral equations or, equivalently, extensive resummation of diagrams.

We shall present two methods for calculating the spin diffusion coefficient. In the first, we use the equations of motion for the spin operators and certain boundary and subsidiary conditions to construct the equations of motion for the spin pair correlation functions. The resulting equations express the pair correlations in terms of the four spin correlations and lower order correlations. The first approximation consists of closing the system of equations by factoring the four spin correlations into products of pair correlations. From this factorization, exact in the high-temperature limit, we obtain nonlinear integrodifferential equations for the spin pair correlations. In principle, the nonlinear integrodifferential equations contain information about the behavior of the system for times both long and short compared to a characteristic time, $\tau_0 = (\hbar/J)$, where J is the exchange integral. We concern ourselves here with the former time domain. Because we cannot solve the resulting nonlinear equation, we complete our analysis by assuming that the correct form in the hydrodynamic limit (the limit in which all properties of the system vary sufficiently slowly in time and space to insure local thermodynamic equilibrium) can also be used in the kinetic region. We then obtain an expression for a temperature-dependent diffusion coefficient.

The second method employs an exact spectral representation for the spin correlation function which puts into evidence its frequency and wave-number dependence in the hydrodynamic limit. This spectral representation contains a smoothly varying function of frequency and wave number, whose moments are all determined by equal-time spin correlations. In the simplest approximation this smoothly varying function is assumed to be a single Gaussian. Its parameters are then determined by the first two moments which depend on the instantaneous correlations of two and four spins. The correlation functions are evaluated in an effective-field (random-phase) approximation which is exact at high temperatures. We thereby obtain a second expression for the temperature-dependent diffusion coefficient.

We represent the thermal average of the spin operator in the \hat{z} direction at the space-time point (\mathbf{r}, t) by $M(\mathbf{r}, t)$. An essential feature of the Heisenberg ferromagnet is that the total spin is a constant of the motion,

$$\frac{d}{dt} \left\{ \int d^3r M(\mathbf{r}, t) \right\} = 0. \quad (1)$$

The conservation law (1) has the differential form,

$$\partial M(\mathbf{r}, t) / \partial t + \nabla \cdot \mathbf{j}_s(\mathbf{r}, t) = 0, \quad (2)$$

where $\mathbf{j}_s(\mathbf{r}, t)$ is a spin current. When all properties of the system vary slowly in space and time we may relate the spin current to the quantity $M(\mathbf{r}, t)$,

$$\mathbf{j}_s(\mathbf{r}, t) = -D \nabla M(\mathbf{r}, t) = -D \chi \nabla B(\mathbf{r}, t) = -L \nabla B(\mathbf{r}, t). \quad (3)$$

The coefficient D is the spin diffusion coefficient; χ is the static susceptibility; B is the z component of the magnetic field; and L is the Onsager coefficient. Equations (2) and (3) combine to give us the diffusion equation for the spin magnetization,¹

$$\partial M(\mathbf{r}, t) / \partial t = D \nabla^2 M(\mathbf{r}, t). \quad (4)$$

From the hydrodynamic description given by Eq. (4), we shall determine the form of the slowly varying part of the spin pair correlation function. The hydro-

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¹L. Kadanoff and P. C. Martin, *Ann. Phys. (N. Y.)* **24**, 419 (1963).

dynamic description will involve the spin susceptibility (a thermodynamic derivative) and the spin diffusion coefficient (a transport coefficient). By comparing the hydrodynamic results with the equation-of-motion description of the pair correlation function, we shall show how a nonlinear integral equation obtained from these equations determines the diffusion coefficient. The only parameters which are available to characterize the high-temperature behavior of the system are J , d , and \hbar , where d is the distance between lattice sites. Dimensional analysis requires that at $\beta J=0$ the diffusion coefficient is a pure number times (Jd^2/\hbar) . Our two methods express this number in terms of the zero wave-vector and frequency limit of a dimensionless nonlinear integrodifferential equation, and in terms of the properties of a dimensionless spectral function. The values we obtain by these methods do not differ greatly from values obtained by de Gennes² and Mori and Kawasaki.³ Both yield the high-temperature diffusion coefficient and predict that the diffusion coefficient goes to zero at the critical point. They also provide interpolation approximations between these limits.

II. FORMULATION

A. Heisenberg Hamiltonian

For the physical description of the ferromagnetic crystal, we shall adopt the Heisenberg model of magnetism which attributes a localized spin to each site of the periodic crystal lattice. We assume that the correct crystal structure and lattice site spacings for a specified temperature have been given to us and that the mean-square deviation of the nuclei from their equilibrium positions is negligible. We will therefore devote our discussion to the statistical mechanics and to the spin correlations of the system described by the Heisenberg Hamiltonian,

$$H = - \sum_{\alpha} \{ [B + B^z(\alpha, t)] S_z(\alpha, t) + B^+(\alpha, t) S_+(\alpha, t) + B^-(\alpha, t) S_-(\alpha, t) - \frac{1}{2} \sum_{\alpha, \alpha'} J(\alpha - \alpha') \{ S_+(\alpha, t) S_-(\alpha', t) + S_z(\alpha, t) S_z(\alpha', t) \} \}. \quad (5)$$

The notation used in Hamiltonian (5) will be described in the following paragraph.

The spin operator in the Heisenberg representation for the localized spin at site α of the magnetic lattice and at time t is represented by $\mathbf{S}(\alpha, t)$. The exchange integral $J(\alpha - \alpha')$ describes the interaction between the spin at site α and the spin at site α' . We will use the convention that $J(0)=0$ so that we may extend the double summation over all lattice sites, including the term $\alpha = \alpha'$. The quantity μ is the ratio of the intrinsic

magnetic moment to the spin angular momentum, $\hbar \mathbf{S}(\alpha, t)$. The quantity $(B/\mu) \equiv B^0$ is a spatially uniform and time-independent external magnetic field in the \hat{z} direction. Finally, the Hamiltonian (5) contains an additional space and time varying magnetic field, $[B(\alpha, t)/\mu]$. This field will serve later as a mathematical device to generate higher order functions. Also, we define $B^{\pm} = \frac{1}{2}(B^x \mp iB^y)$.

Because we choose $\mathbf{B} = \hat{z}B$, the representation,

$$S_{\pm}(\alpha, t) = S_x(\alpha, t) \pm iS_y(\alpha, t), \quad (6)$$

is convenient. The equal-time commutation relations for these operators are

$$[S_+(\alpha, t), S_-(\alpha', t)] = 2\delta_{\alpha, \alpha'} S_z(\alpha, t), \quad (7)$$

$$[S_z(\alpha, t), S_{\pm}(\alpha', t)] = \pm \delta_{\alpha, \alpha'} S_{\pm}(\alpha, t), \quad (8)$$

and

$$[S_{\pm}(\alpha, t), S_{\pm}(\alpha', t)] = [S_z(\alpha, t), S_z(\alpha', t)] = 0. \quad (9)$$

We also have the subsidiary condition,

$$\mathbf{S}(\alpha, t) \cdot \mathbf{S}(\alpha, t) = S(S+1), \quad (10)$$

which specifies the magnitude of the spin.

When the ferromagnetic system is in thermodynamic equilibrium, we may compute the thermal expectation value of an operator by using the canonical ensemble

$$\langle X \rangle = \text{Tr}[e^{-\beta H} X] / \text{Tr}[e^{-\beta H}]. \quad (11)$$

The parameter β is the inverse temperature measured in energy units, i.e., $\beta = (1/kT)$, where k is Boltzmann's constant.

B. Dynamic Response Function

We shall discuss the properties of the ferromagnetic system in terms of the dynamic response function which expresses the linear response of the system to a weak field. We obtain this function by first-order perturbation theory,

$$\delta \langle S_i(\alpha, t) \rangle = \frac{i}{\hbar} \sum_{\alpha', i'} \int_{t_0}^t dt' \times \langle [S_i(\alpha, t), S_{i'}(\alpha', t')] \rangle_{B=0} B^{i'}(\alpha', t'). \quad (12)$$

The externally applied field, $B^{i'}(\alpha', t')$, is zero for $t' < t_0$. Its indices i range over the values $(+, -, z)$. If we introduce the response function, $\chi_{ii'}(\alpha t; \alpha' t')$,

$$\chi_{ii'}(\alpha t; \alpha' t') = (i/\hbar) \eta(t-t') \langle [S_i(\alpha, t), S_{i'}(\alpha', t')] \rangle_{B=0}, \quad (13)$$

where $\eta(t)$ is the step function, we may write,

$$\delta \langle S_i(\alpha, t) \rangle = \sum_{\alpha', i'} \int_{-\infty}^{+\infty} dt' \chi_{ii'}(\alpha t; \alpha' t') B^{i'}(\alpha', t'). \quad (14)$$

The invariance of the equilibrium system under time translation and the invariance of the crystal under translation through a lattice vector α allow us to express

² P. G. de Gennes, J. Phys. Chem. Solids 4, 223 (1958).

³ H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) 27, 529 (1962).

functions in terms of Fourier time-lattice transforms:

$$\langle [S_i(\alpha, t), S_{i'}(\alpha', t')] \rangle_{B=0} = \frac{1}{N} \sum'_{\mathbf{q}} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\mathbf{q} \cdot (\alpha - \alpha') - i\omega(t-t')} 2\hbar \chi_{ii'}''(\mathbf{q}, \omega), \quad (15)$$

and

$$\chi_{ii'}(\alpha t; \alpha' t') = \frac{1}{N} \sum'_{\mathbf{q}} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\mathbf{q} \cdot (\alpha - \alpha') - i\omega(t-t')} \chi_{ii'}(\mathbf{q}, \omega), \quad (16)$$

where the prime means that the summation is carried out over only those values of the wave vector q which lie in the first Brillouin zone.

From Eqs. (14), (15), and (16) we deduce the "Kramers-Kronig" relation,

$$\chi_{ii'}(\mathbf{q}, \omega) = 2 \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\chi_{ii'}''(\mathbf{q}, \omega')}{\omega' - \omega - i\epsilon}, \quad (17)$$

where ϵ is infinitesimal and positive. The spectral weight function $\chi_{ii'}''(\mathbf{q}, \omega)$, the imaginary part of $\chi_{ii'}(\mathbf{q}, \omega)$, gives the absorptive response.

C. Spectral Representation

We next present a useful spectral representation for the function $\chi_{zz}''(\mathbf{q}, \omega)$. To construct it, we first note that because $\omega \chi_{zz}''(\mathbf{q}, \omega)$ is even and positive, the quantity

$$[1 - \chi_{zz}(\mathbf{q}, 0)/\chi_{zz}(\mathbf{q}, z)]^{-1}$$

$$\chi_{zz}''(\mathbf{q}, \omega) = \chi_{zz}(\mathbf{q}, 0) D(\mathbf{q}, \omega) q^2 \omega / \left\{ \left[\omega - q^2 \omega P \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{D(\mathbf{q}, \omega')}{(\omega'^2 - \omega^2)} \right]^2 + [D(\mathbf{q}, \omega) q^2]^2 \right\}^{-1}. \quad (21)$$

The form of representation (21) incorporates the irregularity in $\chi_{zz}''(\mathbf{q}, \omega)$ for small \mathbf{q} and ω associated with the existence of the diffusion process. In addition, we see that the diffusion coefficient D is $D(0, 0)$;

$$D = D(0, 0) = \lim_{\omega \rightarrow 0} \left[\lim_{\mathbf{q} \rightarrow 0} \left\{ \frac{\omega \chi_{zz}''(\mathbf{q}, \omega)}{q^2 \chi_{zz}(\mathbf{q}, 0)} \right\} \right]. \quad (22)$$

D. Equations of Motion

The equations of motion for the Heisenberg spin operators,⁵

$$i\hbar \frac{\partial}{\partial t} S_i(\alpha, t) = [S_i(\alpha, t), H], \quad (23)$$

are obtained by using the commutation relations (7),

is an analytic function of complex z except on the real axis.⁴ Therefore, we may write for arbitrary frequency and wave vector,

$$-\frac{1}{q^2} \left[1 - \frac{\chi_{zz}(\mathbf{q}, 0)}{\chi_{zz}(\mathbf{q}, z)} \right]^{-1} = \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{D(\mathbf{q}, \omega')}{(\omega'^2 - z^2)}, \quad (18)$$

or

$$\left[1 - \frac{\chi_{zz}(\mathbf{q}, z)}{\chi_{zz}(\mathbf{q}, 0)} \right] = \left[1 + q^2 \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{D(\mathbf{q}, \omega')}{(\omega'^2 - z^2)} \right]^{-1}. \quad (19)$$

We evaluate the imaginary part of (19) for real ω by using,

$$\lim_{\epsilon \rightarrow 0} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{D(\mathbf{q}, \omega')}{\omega' - (\omega + i\epsilon)} = P \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{D(\mathbf{q}, \omega')}{\omega' - \omega} + \pi i D(\mathbf{q}, \omega),$$

where P represents the principal value integral. We obtain thereby the spectral representation for $\chi_{zz}''(\mathbf{q}, \omega)$ in terms of the static susceptibility,

$$\chi_{zz}(\mathbf{q}, 0) = 2 \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\chi_{zz}''(\mathbf{q}, \omega)}{\omega}, \quad (20)$$

and the function $D(\mathbf{q}, \omega)$;

(8), and (9),

$$i\hbar \frac{\partial}{\partial t} S_z(\alpha, t) = -B^+(\alpha, t) S_+(\alpha, t) + B^-(\alpha, t) S_-(\alpha, t) - \frac{1}{2} \sum_{\alpha'} J(\alpha - \alpha') \{ S_+(\alpha, t) S_-(\alpha', t) - S_+(\alpha', t) S_-(\alpha, t) \}, \quad (24)$$

and

$$i\hbar \frac{\partial}{\partial t} S_{\pm}(\alpha, t) = \pm [B + B^z(\alpha, t)] S_{\pm}(\alpha, t) \mp 2B^{\mp}(\alpha, t) S_z(\alpha, t) \mp \sum_{\alpha'} J(\alpha - \alpha') \{ S_z(\alpha, t) S_{\pm}(\alpha', t) - S_z(\alpha', t) S_{\pm}(\alpha, t) \}. \quad (25)$$

The total angular momentum of the N spin system is given by the expression,

$$\mathbf{S}_T(t) = \sum_{\alpha} \mathbf{S}(\alpha, t) = \mathbf{S}_T. \quad (26)$$

The rotational invariance of each term in the no-source

⁴ We refer the reader to Sec. II, Part E and to Appendix B of Ref. 1 for a more detailed discussion of spectral representations.

⁵ An extensive discussion of these equations and their consequences at low temperatures is contained in M. Wortis, thesis, Harvard University, 1963 (unpublished).

field Hamiltonian, $H_0 = H$ ($B=0$), leads to the conservation of total spin,

$$[\mathbf{S}_T, H_0] = 0. \quad (27)$$

Consequences of Eq. (27) include the conservation law (1) and the conservation law,

$$[i\hbar(\partial/\partial t) \mp B] S_{\pm T}(t) = 0. \quad (28)$$

In determining the diffusive behavior of the ferromagnetic crystal, it is more convenient to employ equations of motion for the spin pair correlations which explicitly contain second-order derivatives with respect to time. In deriving these equations we use the two additional identities:

$$\begin{aligned} \left[i\hbar \frac{\partial}{\partial t} S_z(\alpha, t), S_z(\alpha', t) \right] &= \frac{1}{2} \sum_{\alpha''} J(\alpha - \alpha'') \\ &\times \delta_{\alpha, \alpha'} \{ S_+(\alpha, t) S_-(\alpha'', t) + S_+(\alpha'', t) S_-(\alpha, t) \} \\ &- \frac{1}{2} J(\alpha - \alpha') \{ S_+(\alpha, t) S_-(\alpha', t) + S_+(\alpha', t) S_-(\alpha, t) \}, \end{aligned} \quad (29)$$

and

$$\begin{aligned} \left[i\hbar \frac{\partial}{\partial t} S_{\pm}(\alpha, t), S_{\mp}(\alpha', t) \right] \\ = 2\delta_{\alpha, \alpha'} [B + B^z(\alpha, t)] S_z(\alpha, t) + \sum_{\alpha''} J(\alpha - \alpha'') \\ \times \delta_{\alpha, \alpha'} \{ S_{\pm}(\alpha'', t) S_{\mp}(\alpha, t) + 2S_z(\alpha, t) S_z(\alpha'', t) \} \\ - J(\alpha - \alpha') \{ S_{\pm}(\alpha, t) S_{\mp}(\alpha', t) + 2S_z(\alpha, t) S_z(\alpha', t) \}. \end{aligned} \quad (30)$$

E. Green's Functions

For calculational purposes, it is convenient to study slightly different, less directly physical functions, the time-ordered spin correlation functions or Green's functions,

$$G_{ii'}(\alpha t; \alpha' t') \equiv \langle (S_i(\alpha, t) S_{i'}(\alpha', t'))_+ \rangle, \quad (31)$$

and their cumulants,

$$G_{ii'}'(\alpha t; \alpha' t') = G_{ii'}(\alpha t; \alpha' t') - \langle S_i(\alpha, t) \rangle \langle S_{i'}(\alpha', t') \rangle. \quad (32)$$

They are defined in terms of the unordered spin correlation functions,

$$G_{ii'}^>(\alpha t; \alpha' t') \equiv \langle S_i(\alpha, t) S_{i'}(\alpha', t') \rangle \equiv G_{ii'}^<(\alpha' t'; \alpha t),$$

as,

$$G_{ii'}(\alpha t; \alpha' t') = \eta(t - t') G_{ii'}^>(\alpha t; \alpha' t') + \eta(t' - t) G_{ii'}^<(\alpha t; \alpha' t'). \quad (33)$$

The fluctuation-dissipation theorem shows that the functions $G_{ii'}^> <(\alpha t; \alpha' t')$ and therefore G satisfy a periodic boundary condition in the time variable when it takes on imaginary values:

$$G_{ii'}^>(\alpha t; \alpha' t') = G_{ii'}^<(\alpha, t + i\hbar\beta; \alpha' t'). \quad (34)$$

One consequence of Eq. (34) is that we may introduce

the Fourier series transform of G with period β ,

$$G_{ii'}(\alpha t; \alpha' t') = \frac{1}{N\beta} \sum_{\mathbf{q}} \sum_{\nu} e^{i\mathbf{q} \cdot (\alpha - \alpha') - i\omega_{\nu}(t - t')} g_{ii'}(\mathbf{q}, \omega_{\nu}), \quad (35)$$

where $\omega_{\nu} = i(\pi\nu/\hbar\beta)$ and where ν assumes the values $0, \pm 2, \pm 4, \pm 6, \dots$, etc. To change from the coefficient g to the physical response χ , we replace ω_{ν} by $(\omega + i\epsilon)$, that is,

$$g_{ii'}(\mathbf{q}, \omega_{\nu}) = 2 \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\chi_{ii'}''(\mathbf{q}, \omega')}{(\omega' - \omega_{\nu})}. \quad (36)$$

The statements (34), (35), and (36) have been proven many times in the literature.⁶

Since three particular Green's functions will occur very frequently in our later studies, it is convenient to give them special names; the magnetization,

$$M(\alpha, t) \equiv \langle S_z(\alpha, t) \rangle; \quad (37)$$

the transverse spin pair correlation function,

$$G(\alpha t; \alpha' t') \equiv \langle (S_+(\alpha, t) S_-(\alpha', t'))_+ \rangle; \quad (38)$$

and the longitudinal spin pair correlation function,

$$\bar{M}_2(\alpha t; \alpha' t') \equiv \langle (S_z(\alpha, t) S_z(\alpha', t'))_+ \rangle. \quad (39)$$

The average spin per site M is,

$$M = \lim_{B \rightarrow 0} \langle S_z(\alpha, t) \rangle. \quad (40)$$

The commutation relation (7) and subsidiary condition (10) produce an expression for $\bar{M}_2(\alpha t, t)$,

$$M(\alpha, t) + S(S+1) = G^>(\alpha t; \alpha t) + \bar{M}_2(\alpha t; \alpha t). \quad (41)$$

In the following sections, we shall present two methods to determine the number D ; the first involves a nonlinear integral equation, the second a moment expansion. Both methods yield qualitative statements throughout the temperature domain of paramagnetism.

III. THE NONLINEAR INTEGRAL EQUATION

We will now employ the preceding formalism and mathematical tools to construct the equations of motion for G and \bar{M}_2 when the source field has only a z component; i.e., $\mathbf{B}(\alpha, t) = \hat{z}B^z(\alpha, t) = \hat{z}B(\alpha, t)$. There exist several ways by which the equations of motion may be constructed. However, we have found the one below fruitful:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t'} i\hbar \frac{\partial}{\partial t} G(\alpha t; \alpha' t') \\ = i\hbar \frac{\partial}{\partial t'} \{ i\hbar \delta(t - t') \} \langle [S_+(\alpha, t), S_-(\alpha', t)] \rangle \\ + i\hbar \delta(t - t') \left\langle \left[S_-(\alpha', t), i\hbar \frac{\partial}{\partial t} S_+(\alpha, t) \right] \right\rangle \\ + \left\langle \left(i\hbar \frac{\partial}{\partial t} S_+(\alpha, t) i\hbar \frac{\partial}{\partial t'} S_-(\alpha', t') \right)_+ \right\rangle, \end{aligned} \quad (42)$$

⁶ P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

and

$$\begin{aligned} & i\hbar \frac{\partial}{\partial t'} - i\hbar \frac{\partial}{\partial t} \bar{M}_2(\alpha t; \alpha' t') \\ &= i\hbar \delta(t-t') \left\langle \left[S_z(\alpha', t), i\hbar \frac{\partial}{\partial t} S_z(\alpha, t) \right] \right\rangle \\ &+ \left\langle \left(i\hbar \frac{\partial}{\partial t} S_z(\alpha, t) i\hbar \frac{\partial}{\partial t'} S_z(\alpha', t') \right)_+ \right\rangle. \quad (43) \end{aligned}$$

After we substitute Eqs. (24), (25), (29), and (30) into Eqs. (42) and (43), we find that the right-hand side of each equation contains very many terms. We schematically list the basic structures which occur:

$$M; BM; JG; J\bar{M}_2; BBG; BJ \left\{ -i\hbar \frac{\delta G}{\delta B} + MG \right\};$$

and

$$JJ \left\{ (-i\hbar)^2 \frac{\delta^2 G}{\delta B \delta B} + M(-i\hbar) \frac{\delta G}{\delta B} + M(-i\hbar) \frac{\delta G}{\delta B} + \bar{M}_2 G \right\}.$$

In the last two expressions we have introduced the

identity⁷

$$-i\hbar \frac{\delta \langle A \rangle}{\delta B^i(\alpha, t)} = \langle (S_i(\alpha, t) A)_+ \rangle - \langle S_i(\alpha, t) \rangle \langle A \rangle, \quad (44)$$

to write

$$\begin{aligned} & -i\hbar (\delta G(\alpha t; \alpha' t') / \delta B(\alpha_1, t_1)) \\ &= \langle (S_z(\alpha_1, t_1) S_+(\alpha, t) S_-(\alpha', t'))_+ \rangle \\ &- \langle S_z(\alpha_1, t_1) \rangle \langle (S_+(\alpha, t) S_-(\alpha', t'))_+ \rangle. \quad (45) \end{aligned}$$

We are interested in only the paramagnetic region with no external magnetic field present; thus $M=0$ and $B=0$. We also limit our considerations to the isotropic Heisenberg Hamiltonian with cubic symmetry. The latter provides us with the statement,

$$\lim_{M=0, B=0} G(\alpha t; \alpha' t') = 2 \lim_{M=0, B=0} \bar{M}_2(\alpha t; \alpha' t'). \quad (46)$$

The above two conditions greatly reduce the complexities of Eqs. (42) and (43).

Setting M and B equal to zero in Eq. (42) and applying the symmetry property (46) give us the nonlinear integrodifferential equation for $\bar{M}_2(\alpha t; \alpha' t')$:

$$\begin{aligned} & i\hbar \frac{\partial}{\partial t'} - i\hbar \frac{\partial}{\partial t} \bar{M}_2(\alpha t; \alpha' t') = -2i\hbar \delta(t-t') \left\{ \delta_{\alpha, \alpha'} \sum_{\bar{\alpha}} J(\alpha - \bar{\alpha}) \bar{M}_2(\alpha t; \bar{\alpha} t) - J(\alpha - \alpha') \bar{M}_2(\alpha t; \alpha' t) \right\} \\ &+ \sum_{\bar{\alpha}, \bar{\alpha}'} J(\alpha - \bar{\alpha}) J(\alpha' - \bar{\alpha}') \\ &\times \left\{ \left[\frac{(-i\hbar)^2}{2} \frac{\delta^2 G(\alpha t; \bar{\alpha}' t')}{\delta B(\bar{\alpha}, t) \delta B(\alpha', t')} \right]_{B=0} + \bar{M}_2(\bar{\alpha} t; \alpha' t') \bar{M}_2(\alpha t; \bar{\alpha}' t') \right. \\ &\left. - \left[\bar{\alpha} \rightarrow \alpha \right] - \left[\bar{\alpha}' \rightarrow \alpha' \right] + \left[\bar{\alpha} \rightarrow \alpha \right] \left[\bar{\alpha}' \rightarrow \alpha' \right] \right\}, \quad (47) \end{aligned}$$

where the notation

$$\begin{bmatrix} \alpha \rightarrow \bar{\alpha} \\ \bar{\alpha} \rightarrow \alpha \end{bmatrix}$$

means that α and $\bar{\alpha}$ of the first term enclosed in square brackets are interchanged.

In order to truncate this first equation of the hierarchy, we neglect the higher order fluctuations reflected by the second-order functional derivative; i.e., we assume,

$$(\delta^2 G / \delta B \delta B) \ll \bar{M}_2 \bar{M}_2. \quad (48)$$

The assumption (48) leads in fact to the following factorization of the four spin correlation function,

$$\begin{aligned} & \langle (S_z(\bar{\alpha}, t) S_+(\alpha, t) S_z(\alpha', t') S_-(\bar{\alpha}', t'))_+ \rangle \\ & \approx G(\alpha t; \alpha' t') \bar{M}_2(\bar{\alpha} t; \bar{\alpha}' t'). \quad (49) \end{aligned}$$

The analogous factorization,

$$\begin{aligned} & \langle (S_+(\alpha, t) S_-(\bar{\alpha}, t) S_+(\alpha', t') S_-(\bar{\alpha}', t'))_+ \rangle \\ & \approx G(\alpha t; \bar{\alpha}' t') G(\alpha' t'; \bar{\alpha} t), \quad (50) \end{aligned}$$

will arise for Eq. (43) and will reduce Eq. (43) to Eq. (42) when it is used in conjunction with condition (46).

The assumption (48) or equivalently the factorization (49) or (50) is exact in the $\beta J=0$ limit.

The functional derivative assumption (48) yields the approximate high-temperature (above the critical point β_c) equation of motion for the longitudinal correlation function \bar{M}_2 . This is Eq. (47) without the $(\delta^2 G / \delta B \delta B)$ terms. The space-time transform of the latter equation assumes the form:

$$\begin{aligned} & \omega_\nu^2 \bar{M}_2(\mathbf{q}, \omega_\nu) - \frac{i}{\hbar^3 \beta N} \sum'_{\mathbf{q}_1, \nu_1} [\mathfrak{I}(\mathbf{q}_1) - \mathfrak{I}(\mathbf{q}_1 - \mathbf{q})]^2 \\ & \times \bar{M}_2(\mathbf{q}_1, \omega_{\nu_1}) \bar{M}_2(\mathbf{q}_1 - \mathbf{q}, \omega_{\nu_1} - \omega_\nu) \\ & = -\frac{2}{\hbar^3 \beta N} \sum'_{\mathbf{q}_1, \nu_1} [\mathfrak{I}(\mathbf{q}_1) - \mathfrak{I}(\mathbf{q}_1 - \mathbf{q})] \bar{M}_2(\mathbf{q}_1, \omega_{\nu_1}). \quad (51) \end{aligned}$$

⁷ Equations (44) and (45) are based upon the use of the generating function,

$$\text{Tr} \left(\exp -\beta H_0 \left\{ \exp \left[- (i/\hbar) \int_0^{-i\hbar\beta} d\tilde{t} H_I(\tilde{t}) \right] \right\}_+ \right),$$

where $H_I(t) = -\sum_{\alpha} \mathbf{B}(\alpha, t) \cdot \mathfrak{S}(\alpha, t)$ and

$$\begin{aligned} & S_i(\alpha, t) = \left\{ \exp \left[(i/\hbar) \int_0^{-i\hbar\beta} d\tilde{t} H_I(\tilde{t}) \right] \right\} \\ & \times \mathfrak{S}_i(\alpha, t) \left\{ \exp \left[- (i/\hbar) \int_0^{-i\hbar\beta} d\tilde{t} H_I(\tilde{t}) \right] \right\}_+. \end{aligned}$$

The exchange interaction transform is given by,

$$\mathfrak{J}(\mathbf{q}) = \sum_{\alpha} J(\alpha) \cos \mathbf{q} \cdot \alpha, \quad (52)$$

where we have used the inversion symmetry of the lattice, $J(\alpha) = J(-\alpha)$. Since when ω is replaced by $(\omega + i\epsilon)$, the function χ is obtained and $\text{Im}\{\chi\} = \chi''$, we may express Eq. (51) as a nonlinear integral equation for the spectral weight function $\chi''(\mathbf{q}, \omega)$. Then as usual, using the fact that,

$$\frac{1}{\beta \hbar} \sum_{\nu_1} \frac{1}{(\omega - \omega_{\nu_1})} = [n(\omega) + \frac{1}{2}], \quad (53)$$

where $n(\omega) = [\exp(\beta \hbar \omega) - 1]^{-1}$, we obtain,

$$\begin{aligned} \omega^2 \chi''(\mathbf{q}, \omega) &= \frac{1}{\hbar N} \sum'_{\mathbf{q}_1} [\mathfrak{J}(\mathbf{q}_1) - \mathfrak{J}(\mathbf{q}_1 - \mathbf{q})]^2 \\ &\times \int_{-\infty}^{+\infty} \frac{d\omega_1}{\pi} \chi''(\mathbf{q}_1, \omega_1) \chi''(\mathbf{q}_1 - \mathbf{q}, \omega_1 - \omega) \\ &\times [n(\omega_1) - n(\omega_1 - \omega)]. \end{aligned} \quad (54)$$

We have also suppressed the subscripts z of χ'' . In the high-temperature limit $\beta \rightarrow 0$ we have

$$\begin{aligned} \omega \chi''(\mathbf{q}, \omega) &= \frac{1}{\beta \hbar^2 N} \sum'_{\mathbf{q}_1} [\mathfrak{J}(\mathbf{q}_1) - \mathfrak{J}(\mathbf{q}_1 - \mathbf{q})]^2 \\ &\times \int_{-\infty}^{+\infty} \frac{d\omega_1}{\pi} \frac{\chi''(\mathbf{q}_1, \omega_1)}{\omega_1} \frac{\chi''(\mathbf{q}_1 - \mathbf{q}, \omega_1 - \omega)}{(\omega_1 - \omega)}. \end{aligned} \quad (55)$$

Actually, for these diffusion processes, we may treat $\beta_c \hbar \omega \ll 1$, so that this equation holds for small ω throughout the paramagnetic region.

IV. THE DIFFUSION COEFFICIENT CALCULATION

A question now arises as to which approximate form for the spectral weight function is the most appropriate one to use in the nonlinear integral equation (55). This equation contains an integration over all values of ω_1 along the real ω_1 axis. But in addition, the choice for $\chi''(\mathbf{q}, \omega)$ ought to take into account the fact that due to the weighting factor $\{1/\omega_1(\omega_1 - \omega)\}$ appearing in Eq. (55), the low-frequency behavior of the spectral weight function will be most important in the evaluation of the integrals. According to the spectral representation (21) and assuming the phenomenological equation (4) to be correct, the spectral weight function must for sufficiently small q and ω behave like

$$\chi''(\mathbf{q}, \omega) \approx \chi(\mathbf{q}, 0) D q^2 \omega / (\omega^2 + (D q^2)^2). \quad (56)$$

This gives us a one-parameter spectral weight function if we use the effective field [random-phase approximation (RPA)] form for the \mathbf{q} and temperature dependence

of $\chi(\mathbf{q}, 0)$,

$$\chi(\mathbf{q}, 0; \text{RPA}) = \chi(0, 0) / (1 + \chi(0, 0) j(\mathbf{q})). \quad (57)$$

Here $j(\mathbf{q}) = \{\mathfrak{J}(0) - \mathfrak{J}(\mathbf{q})\}$. At high temperatures the form (57) for $\chi(\mathbf{q}, 0)$ is exact. Henceforth, we shall not distinguish between $\chi(0, 0; \text{exact})$ and $\chi(0, 0; \text{RPA})$, understanding that our results for finite βJ are certainly no more justifiable than those of the RPA.

When we insert the low-frequency spectral form (56) into the right-hand side of Eq. (55), we obtain

$$\begin{aligned} \omega \chi''(\mathbf{q}, \omega) &= \frac{\chi^2}{\beta \hbar^2 N} \sum'_{\mathbf{q}_1} \frac{[\mathfrak{J}(\mathbf{q}_1) - \mathfrak{J}(\mathbf{q}_1 - \mathbf{q})]^2}{[1 + \chi j(\mathbf{q}_1)][1 + \chi j(\mathbf{q}_1 - \mathbf{q})]} \\ &\times \left\{ \frac{D(\mathbf{q}_1 - \mathbf{q})^2 \{\omega^2 + D^2[(\mathbf{q}_1 - \mathbf{q})^4 - q_1^4]\}}{\{\omega^2 + D^2[(\mathbf{q}_1 - \mathbf{q})^4 - q_1^4]\}^2 + D^2 q_1^4 \omega^2} \right. \\ &\left. + \frac{D q_1^2 \{\omega^2 - D^2[(\mathbf{q}_1 - \mathbf{q})^4 - q_1^4]\}}{\{\omega^2 - D^2[(\mathbf{q}_1 - \mathbf{q})^4 - q_1^4]\}^2 + 4D^2(\mathbf{q}_1 - \mathbf{q})^4 \omega^2} \right\}, \end{aligned} \quad (58)$$

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

In accordance with the procedure indicated by Eq. (22), we obtain for the diffusion coefficient the expression

$$D_{\text{nl}} = \frac{j \lambda^2}{\hbar} \left[\frac{\chi}{\beta} \bar{B}(\chi j) \right]^{1/2}, \quad (59)$$

where

$$\bar{B}(\chi j) = \frac{v}{3\pi^2 \lambda^3} \int_0^{\gamma} \frac{x^2 dx}{[1 + x^2]^4 [1 + \chi j(x)]^2}, \quad (60)$$

and where the subscript nl means the value for D obtained from the nonlinear integral equation. In order to facilitate the computation of the limit of expression (22) we have invoked the spherical continuum model of Appendix A and carried out the angular integration. From our Eq. (59), we can determine an expression for D throughout the paramagnetic region. In the conclusion of this paper, we shall do this and also compare our results with those of the moment method and with those of other authors.

V. THE SUM-RULE MOMENT METHOD

In the previous section we pointed out that the low-frequency region gave considerable contribution in the integral equation that determines $\chi''(\mathbf{q}, \omega)$ and that in this region $\chi''(\mathbf{q}, \omega)$ had a Lorentzian form. We know, on the other hand, that for large frequencies $\chi''(\mathbf{q}, \omega)$ decreases much more rapidly than a Lorentzian since all its frequency moments exist. The present procedure treats more correctly this second facet of the behavior of $\chi''(\mathbf{q}, \omega)$. In this method we compute the diffusion coefficient in terms of parameters whose values are obtained in terms of these moments (which are equal-time spin correlation functions). This method has to some extent been employed previously by de Gennes.² He

uses a Lorentzian form for $\chi''(\mathbf{q}, \omega)$ and introduces a cutoff frequency in order to make the Lorentzian moments finite. He then employs two sum rules to determine the diffusion coefficient and the cut off frequency.

Our spectral representation (21) provides an apparently more satisfying form for incorporating the features which he noted and demonstrates the properties that for small ω and \mathbf{q} , $\chi''(\mathbf{q}, \omega)$ must be Lorentzian and $D(\mathbf{q}, \omega)$ must be a slowly varying regular function; but that on the other hand as $\omega \rightarrow \infty$ the tails of both functions must have finite moments of all orders. In our moment method the high-frequency form is dictated by the high-frequency dependence of $D(\mathbf{q}, \omega)$; while the low-frequency form is determined by the spectral representation (21) with the function $D(\mathbf{q}, \omega)$ taken to be the constant $D = D(0, 0)$.

The first two nonzero moments of the spectral weight function $\chi''(\mathbf{q}, \omega)$ give us,

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} -\hbar(\hbar\omega)\chi''(\mathbf{q}, \omega) \equiv \hbar^2 C_1^2(\mathbf{q})q^2 = \frac{1}{N} \sum_{(\alpha-\alpha')} e^{i\mathbf{q}\cdot(\alpha-\alpha')} \times \left\langle \left[\left(i\hbar \frac{\partial}{\partial t} S_z(\alpha, t), S_z(\alpha', t) \right) \right] \right\rangle_{B=0}, \quad (61)$$

and

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} -\hbar(\hbar\omega)^3 \chi''(\mathbf{q}, \omega) \equiv \hbar^4 C_3^2(\mathbf{q})q^2 = \frac{1}{N} \sum_{(\alpha-\alpha')} e^{i\mathbf{q}\cdot(\alpha-\alpha')} \times \left\langle \left[\left(i\hbar \frac{\partial}{\partial t} \right)^2 S_z(\alpha, t), \left(-i\hbar \frac{\partial}{\partial t} \right) S_z(\alpha', t) \right] \right\rangle_{B=0}. \quad (62)$$

Performing a high-frequency expansion in powers of ω^{-2} on the spectral representation (19) and equating the coefficients, we relate the moments of $D(\mathbf{q}, \omega)$ to the moments of $\chi''(\mathbf{q}, \omega)$. The first two identities expressing the moments of $D(\mathbf{q}, \omega)$ in terms of those of $\chi''(\mathbf{q}, \omega)$ are

$$\frac{C_1^2(\mathbf{q})}{\chi(\mathbf{q}, 0)} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} D(\mathbf{q}, \omega), \quad (63)$$

and

$$\frac{C_3^2(\mathbf{q})}{\chi(\mathbf{q}, 0)} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} -\omega^2 D(\mathbf{q}, \omega) + \frac{q^2 C_1^4(\mathbf{q})}{\chi^2(\mathbf{q}, 0)}. \quad (64)$$

We now introduce a two-parameter approximation to the function $D(\mathbf{q}, \omega)$ which incorporates all the properties mentioned previously. The two sum rules (63) and (64) then provide us with a sufficient number of conditions to compute these two parameters in terms of equal time commutators. The generalization of the example presented in this paper is to introduce a representation for $D(\mathbf{q}, \omega)$ containing n parameters and exhibiting all the correct properties, and then to use the first n nonzero moments to determine the n parameters.

We now suggest that a sufficient approximation to the function $D(\mathbf{q}, \omega)$ is the two-parameter Gaussian form:

$$D(\mathbf{q}, \omega) = \alpha(\mathbf{q})\tau(\mathbf{q}) \exp\{-[\omega\tau(\mathbf{q})]^2\}, \quad (65)$$

where we interpret the function $\tau(\mathbf{q})$ as the collision time for processes involving the wave-vector transfer \mathbf{q} . Inserting the Gaussian form (65) into Eqs. (63) and (64) yields the expressions for $\tau(\mathbf{q})$ and $\alpha(\mathbf{q})$ in terms of $C_1(\mathbf{q})$ and $C_3(\mathbf{q})$:

$$\alpha(\mathbf{q}) = \frac{\pi^{1/2} C_1^2(\mathbf{q})}{\chi(\mathbf{q}, 0)}, \quad (66)$$

and

$$\tau^2(\mathbf{q}) = \frac{C_1^2(\mathbf{q})\chi(\mathbf{q}, 0)}{2[\chi(\mathbf{q}, 0)C_3^2(\mathbf{q}) - q^2 C_1^4(\mathbf{q})]}. \quad (67)$$

In terms of the two parameters α and τ the diffusion coefficient $D = D(0, 0)$ becomes

$$D_{sm} = \alpha(0)\tau(0) = \frac{1}{\chi(0, 0)} \frac{\sqrt{\pi} C_1^3(0)}{\sqrt{2} C_3(0)}, \quad (68)$$

where the subscript sm means the value for D obtained from the sum-rule moment method. Using a different method, Mori and Kawasaki³ also obtain Eq. (68). We briefly discuss their method in Sec. VI.

It is interesting to compare our result (68) with the corresponding result of de Gennes. He approximates $\chi''(\mathbf{q}, \omega)$ by the Lorentzian form (56). However, because the moments of the Lorentzian form (56) are infinite, he neglects the tail of the Lorentzian. This truncation adds one more parameter to the problem, the cutoff frequency for the integration limits appearing in the equal-time commutation sum rules (61) and (62). In our notation, his method yields the diffusion coefficient,

$$D_{dG} = \frac{1}{\chi(0, 0)} \frac{\pi C_1^3(0)}{2\sqrt{3} C_3(0)}. \quad (69)$$

A close parallel exists between the shortcomings of the nonlinear integral equation method and those of the moment method. Just as we can not solve the nonlinear integral equation, we can not compute exactly the equal time commutators $\hbar^2 C_1^2(\mathbf{q})q^2$ and $\hbar^3 C_3^2(\mathbf{q})q^2$ at finite temperatures. Hence as before, we must seek approximations to the quantities $C_1^2(\mathbf{q})$ and $C_3^2(\mathbf{q})$. These equal-time commutators have been evaluated at $\beta J = 0$ for nearest-neighbor interactions by de Gennes and by Mori and Kawasaki. We shall evaluate them away from $\beta J = 0$ by invoking assumptions similar to those we employed with the integral-equation method.

Since the equal-time commutator $\langle \left[\left(i\hbar \frac{\partial}{\partial t} \right) S_z, S_z \right] \rangle_{B=0}$ contains only the correlation of two spins, we may readily express the function $C_1^2(\mathbf{q})$ in terms of the

spectral weight function:

$$C_1^2(\mathbf{q}) = (2/q^2 \hbar N) \sum'_{\mathbf{q}_1} [\mathfrak{F}(\mathbf{q}_1) - \mathfrak{F}(\mathbf{q}_1 - \mathbf{q})] g(\mathbf{q}_1), \quad (70)$$

where,

$$g(\mathbf{q}) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \chi''(\mathbf{q}, \omega) [n(\omega) + \frac{1}{2}].$$

Expression (70) is exact. The equal-time commutator $\langle [(i\hbar\partial/\partial t)^2 S_z, (-i\hbar\partial/\partial t) S_z] \rangle_{B=0}$ contains the correlation of four spins. We therefore introduce the factorization scheme

$$\langle S_+(1) S_-(2) S_+(3) S_-(4) \rangle \approx G(1,2)G(3,4) + G(1,4)G(3,2), \quad (71a)$$

and

$$\langle S_z(1) S_z(2) S_+(3) S_-(4) \rangle \approx \bar{M}_z(1,2)G(3,4), \quad (71b)$$

and thereby obtain an expression for the function $C_3^2(\mathbf{q})$ which is bilinear in the spectral-weight function:

$$C_3^2(\mathbf{q}) = \frac{10}{q^2 \hbar^2 N} \sum'_{\mathbf{q}_1, \mathbf{q}_2} \mathfrak{F}(\mathbf{q}_1) \mathfrak{F}(\mathbf{q}_1) \times [\mathfrak{F}(\mathbf{q}_2) - \mathfrak{F}(\mathbf{q}_2 - \mathbf{q})] g(\mathbf{q}_1) g(\mathbf{q}_2). \quad (72)$$

The random-phase approximation (RPA) to $\chi''(\mathbf{q}, \omega)$ for the paramagnetic region, which is exact at $\beta J = 0$, gives us the quantities $C_1^2(\mathbf{q})$ and $C_3^2(\mathbf{q})$ as functions of β :

$$C_1^2(\mathbf{q}) = \frac{2}{\beta \hbar^2 q^2 N} \sum'_{\mathbf{q}_1} [\mathfrak{F}(\mathbf{q}_1) - \mathfrak{F}(\mathbf{q}_1 - \mathbf{q})] \times \chi(\mathbf{q}_1, 0; \text{RPA}), \quad (73)$$

and

$$C_3^2(\mathbf{q}) = \frac{10}{\beta^2 \hbar^4 N^2} \sum'_{\mathbf{q}_1, \mathbf{q}_2} \mathfrak{F}(\mathbf{q}_1) \mathfrak{F}(\mathbf{q}_1) [\mathfrak{F}(\mathbf{q}_2) - \mathfrak{F}(\mathbf{q}_2 - \mathbf{q})] \times \chi(\mathbf{q}_1, 0; \text{RPA}) \chi(\mathbf{q}_2, 0; \text{RPA}). \quad (74)$$

Using the expressions (73) and (74) we obtain from Eq. (68) the expression for D as a function of temperature.

VI. CONCLUSION

We shall conclude our discussion by computing the high-temperature limit of the diffusion coefficient and its behavior near the critical point β_c . We shall also compare our results with those of other authors.

The function $\bar{B}(\chi j)$ obtained from the nonlinear integral-equation result (59) has the limits:

$$\lim_{\chi j \rightarrow 0} \bar{B}(\chi j) = \frac{v}{48\pi^2 \lambda^3} \tan^{-1} \gamma \quad (75)$$

for $\gamma \tan^{-1} \gamma \gg 1$ and

$$\lim_{\chi j \rightarrow \infty} \bar{B}(\chi j) = \frac{v}{12\pi \lambda^3} (\chi j)^{-3/2}. \quad (76)$$

The high-temperature limit for D_{n1} becomes,

$$D_{n1} \xrightarrow{\beta \rightarrow 0} \frac{j\lambda^2}{\hbar} \left[\frac{S(S+1)}{3} \frac{v \tan^{-1} \gamma}{48\pi^2 \lambda^3} \right]^{1/2}, \quad (77)$$

where we have used $(\chi/\beta)_{\beta \rightarrow 0} \rightarrow [S(S+1)/3] \approx \beta_c J$; the behavior of D_{n1} near the Curie point β_c assumes the form

$$D_{n1} \xrightarrow{\beta \rightarrow \beta_c} \frac{j\lambda^2}{\hbar} \left[\frac{v}{12\lambda^3 \pi \beta_c j (\chi j)^{1/2}} \right]^{1/2}. \quad (78)$$

The functions appearing in the expression (68) for D computed by the sum-rule moment method have the high-temperature limits:

$$C_1^2(\mathbf{q}) \xrightarrow{\beta \rightarrow 0} \frac{2\chi^2}{\beta \hbar^2 q^2 N} \sum'_{\mathbf{q}_1} \mathfrak{F}(\mathbf{q}_1) [\mathfrak{F}(\mathbf{q}_1) - \mathfrak{F}(\mathbf{q}_1 - \mathbf{q})], \quad (79)$$

and

$$C_3^2(\mathbf{q}) \xrightarrow{\beta \rightarrow 0} \frac{10\chi^3}{\beta^2 \hbar^4 q^2 N^2} \sum'_{\mathbf{q}_1, \mathbf{q}_2} \mathfrak{F}(\mathbf{q}_1) \mathfrak{F}(\mathbf{q}_1) \mathfrak{F}(\mathbf{q}_2) \times [\mathfrak{F}(\mathbf{q}_2) - \mathfrak{F}(\mathbf{q}_2 - \mathbf{q})], \quad (80)$$

where we have employed the statements

$$\chi(\mathbf{q}, 0; \text{RPA}) \xrightarrow{\beta \rightarrow 0} \chi \{1 - \chi j(\mathbf{q})\} \cdots \quad (81)$$

and

$$\sum'_{\mathbf{q}_1} \mathfrak{F}(\mathbf{q}_1) = 0. \quad (82)$$

Because expansion (81) reproduces the exact high-temperature expansion of $\chi(\mathbf{q}, 0)$ up to the second term, Eqs. (79) and (80) are exact. We must of course use the rigorous expansion

$$\chi = \frac{S(S+1)}{3} \left\{ 1 + \frac{\beta \mathfrak{F}(0) S(S+1)}{3} + \cdots \right\},$$

for the $\chi = \chi(0, 0)$ which appears in expansion (81).

The spherical continuum model of Appendix A then gives us for $\gamma \tan^{-1} \gamma \gg 1$:

$$C_1^2(0) \xrightarrow{\beta \rightarrow 0} \frac{v \chi^2 j^2}{8\pi^2 \lambda \beta \hbar^2} \tan^{-1} \gamma, \quad (83)$$

$$C_3^2(0) \xrightarrow{\beta \rightarrow 0} \frac{5v^2 \chi^3 j^4}{32\pi^4 \lambda^4 \beta^2 \hbar^4} (\tan^{-1} \gamma)^2, \quad (84)$$

$$C_1^2(0) \xrightarrow{\beta \rightarrow \beta_c} \frac{v \tan^{-1} \gamma}{\beta \hbar^2 \pi^2 \lambda}, \quad (85)$$

$$C_3^2(0) \xrightarrow{\beta \rightarrow \beta_c} \frac{5jv^2 (\tan^{-1} \gamma)^2}{2\beta^2 \hbar^4 \pi^4 \lambda^4}. \quad (86)$$

The corresponding limits for D_{sm} become

$$D_{sm} \xrightarrow{\beta \rightarrow 0} \frac{j\lambda^2}{\hbar} \left(\frac{S(S+1)}{3} \frac{v \tan^{-1}\gamma}{160\pi\lambda^3} \right)^{1/2} \quad (87)$$

and

$$D_{sm} \xrightarrow{\beta \rightarrow \beta_c} \frac{j\lambda^2}{\hbar} \frac{1}{\chi j} \left(\frac{v \tan^{-1}\gamma}{5\beta j\pi\lambda^3} \right)^{1/2}. \quad (88)$$

The high-temperature limits of D_{n1} and D_{sm} agree quantitatively very well, the ratio is $(D_{sm}/D_{n1})=0.97$. In addition, in a simple cubic lattice with a preponderance of nearest-neighbor interactions, we have

$$D_{n1}(\beta J=0)=0.20(Jd^2/\hbar)[S(S+1)]^{1/2}, \quad (89)$$

and

$$D_{sm}(\beta J=0)=0.19(Jd^2/\hbar)[S(S+1)]^{1/2}, \quad (90)$$

if we use $\lambda=1.13d$, $\gamma=4.40$, and $j=6J$ in relations (77) and (87).

Because analytic evaluation of $D_{n1}(\beta J=0)$ from Eq. (58) with the exact nearest-neighbor interaction

$$J(\alpha)=J, \quad \text{for } \alpha \text{ a nearest neighbor,} \quad (91) \\ =0, \quad \text{for } \alpha \text{ nor a nearest neighbor}$$

is not feasible, we have introduced the spherical continuum model. In order to be consistent, when we compare D_{sm} with D_{n1} for the $\beta J=0$ case, we have also used this model in the evaluation of D_{sm} [refer to Eqs. (83) and (84)].

The treatments of de Gennes² and of Mori and Kawasaki³ contain evaluations of $C_1^2(0)$ and $C_3^2(0)$ at $\beta J=0$ for the simple cubic lattice with the nearest-neighbor interaction (91). In order to compare the $\beta J=0$ predictions of our theory with those of the above authors, we use the interaction (91) in Eqs. (79) and (80) and evaluate the quantities C_1^2 and C_3^2 at $\beta J=0$ for the simple cubic lattice:

$$[C_1^2(0)/\chi]_{\beta J=0}=(2/3)S(S+1)(J/\hbar)^2d^2, \quad (92)$$

and

$$[C_3^2(0)/\chi]_{\beta J=0}=(20/3)S^2(S+1)^2(J/\hbar)^4d^2. \quad (93)$$

All evaluations of $[C_1^2(0)/\chi]$ agree. However, our evaluation of $[C_3^2(0)/\chi]$ differs from the evaluations of de Gennes and Mori and Kawasaki. de Gennes makes a spherical approximation for the Brillouin zone and finds,

$$[C_3^2(0); dG/\chi]_{\beta J=0} \approx (27/6)S^2(S+1)^2(J/\hbar)^4d^2. \quad (94)$$

Mori and Kawasaki make a small wave-number approximation and find

$$[C_3^2(0); MK/\chi]_{\beta J=0} \approx (16/3)S^2(S+1)^2(J/\hbar)^4d^2 \\ \times [1 - (13/60)\{1 + [3/26S(S+1)]\}]. \quad (95)$$

Our value, Eq. (93), is exact because we use expansion (81) which yields the rigorous high-temperature result up to the second term. Comparison is made more complicated because each of us has substituted into a

different form of the exact expression for C_3^2 . We have worked from

$$\langle [(i\hbar\partial/\partial t)^2 S_z(\alpha, t), (i\hbar\partial/\partial t) S_z(\alpha', t)] \rangle;$$

while de Gennes computes from

$$\langle (i\hbar\partial/\partial t)^4 S_z(\alpha, t) S_z(\alpha', t) \rangle;$$

and Mori and Kawasaki compute from

$$\langle (i\hbar\partial/\partial t)^2 S_z(\alpha, t) (i\hbar\partial/\partial t)^2 S_z(\alpha', t) \rangle$$

by assuming that

$$\langle [(i\hbar\partial/\partial t) S_z(\alpha, t), S_z(\alpha', t)] \rangle$$

decays in time according to a two-parameter Gaussian distribution.

The final $\beta J=0$ results for the simple cubic lattice with the interaction (91) are:

$$D_{sm}(\beta J=0) \approx 0.26(Jd^2/\hbar)[S(S+1)]^{1/2}, \quad (96)$$

$$D_{dG}(\beta J=0) \approx 0.23(Jd^2/\hbar)[S(S+1)]^{1/2}, \quad (97)$$

and

$$D_{MK}(\beta J=0) \approx 0.33(Jd^2/\hbar)[S(S+1)]^{1/2}. \quad (98)$$

The results (96) and (98) follow from Eq. (68), while the result (97) follows from Eq. (69). A more sensible comparison of approximation procedures involves using the exact evaluation of $C_3^2(0)$ in the compared expressions:

$$D_{dG}[\beta J=0; \text{Eq. (93)}] \\ \approx (0.72)(0.26)(Jd^2/\hbar)[S(S+1)]^{1/2}, \quad (99)$$

$$D_{MK}[\beta J=0; \text{Eq. (93)}] \\ \approx (0.26)(Jd^2/\hbar)[S(S+1)]^{1/2}. \quad (100)$$

In other words, with the same evaluation of C_3 the difference between D_{MK} and D_{dG} is smaller. On the other hand, the close agreement between D_{dG} and $D_{sm} \approx D_{n1}$ results from compensation between the different expressions (68) and (69) and different evaluations of $C_3(0)$. Equivalently, we may write,

$$D_{sm}[\beta J=0; \text{Eq. (94)}] \\ \approx (1.39)(0.23)(Jd^2/\hbar)[S(S+1)]^{1/2}, \quad (101)$$

$$D_{sm}[\beta J=0; \text{Eq. (95)}] \\ \approx (0.33)(Jd^2/\hbar)[S(S+1)]^{1/2}. \quad (102)$$

Our Eq. (78) predicts that D_{n1} behaves as $(\chi j)^{-1/4}$ for β near β_c ; while our Eq. (88) predicts that D_{sm} behaves as $(\chi j)^{-1}$ for β near β_c . Thus, both methods agree qualitatively with the conclusions of other authors^{3,8} predicting that D vanishes at the transition point. These conclusions are essentially assertions that in the Einstein relationship $D=(L/\chi)$, Eq. (3), L is not as badly divergent at β_c as χ . If, for example, $[C_1^3(0)/C_3(0)]$, and therefore L , is not singular at $\beta=\beta_c$ the coefficient D behaves as $(\chi j)^{-1}$ for β near β_c . Since different inter-

⁸ L. Van Hove, Phys. Rev. **95**, 1374 (1954).

polation procedures give different singularities for L , quantitative agreement is not obtained in the transition region. Indeed we feel that all estimations of the behavior near β_c are so unreliable that even a non-vanishing value of D has not been truly ruled out.

To summarize, we have presented two methods for treating the time-dependent finite-temperature behavior of the paramagnetic state of the isotropic Heisenberg ferromagnet. We obtained two diffusion coefficients, D_n and D_{sm} , which characterized long-wavelength decay in the paramagnetic state of the system. The two estimates agreed closely in the high-temperature limit and were in qualitative agreement with other treatments. Both methods predicted that the diffusion coefficient vanished near β_c , but the predictions in this region are much less reliable.

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APPENDIX A: THE SPHERICAL CONTINUUM MODEL

The physical content of Eqs. (58), (73), and (74) will be much more accessible after we introduce into the theory simplifications concerning the lattice structure and the exchange interaction.

The first simplification assumes that the first Brillouin zone of the wave-vector space contains many points. This is equivalent to stating that N is extremely large. Replacing the discrete summation by an integral is justified in the limit as N approaches infinity, that is,

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{\mathbf{q}}' (\dots) = \frac{v}{(2\pi)^3} \int' d^3q (\dots). \quad (\text{A1})$$

To effect a further simplification we approximate the polyhedron for the first Brillouin zone by a sphere in wave-vector space. The identity

$$(1/N) \sum_{\mathbf{q}}' = 1 \quad (\text{A2})$$

determines the radius q_0 of this sphere and in the continuum limit, identity (A2) assumes the form

$$\frac{v}{(2\pi)^2} \int_0^{q_0} q^2 dq \int_0^{2\pi} d\phi \int_{-\pi}^{\pi} \sin\theta d\theta = 1, \quad (\text{A3})$$

or,

$$q_0 = (6\pi^2/v)^{1/3}.$$

We must know the behavior of the exchange interaction $J(\alpha - \alpha')$ before we can make any additional statements about $j(\mathbf{q})$ beyond those implied by

$$j(\mathbf{q}) = 2 \sum_{\alpha} J(\alpha) \sin^2(\mathbf{q} \cdot \alpha/2). \quad (\text{A4})$$

A rigorous investigation of the function $j(\mathbf{q})$ would be out of place due to the complex nature of the equations. Therefore, we will motivate a crude approximation for $j(\mathbf{q})$ which simulates the behavior of the exact expression (A4) in a qualitative manner.

When there is one electron per site, the Heisenberg model gives the result

$$J(\alpha - \alpha') = e^2 \int d^3r_{\alpha} \int d^3r_{\alpha'} \frac{U_{n_i}^*(\mathbf{r}_{\alpha}) U_{n_i'}(\mathbf{r}_{\alpha'})}{|\mathbf{r}_{\alpha} - \mathbf{r}_{\alpha'}|}, \quad (\text{A5})$$

where $U_{n_i}(\mathbf{r}_{\alpha})$ is a bound-state eigenfunction localized about the site at α . Because a bound state is characterized by an exponential decay at large distances, it is not unreasonable to replace the exchange interaction by

$$J(\alpha) = J\lambda(e^{-|\alpha|\lambda}/|\alpha|), \quad (\text{A6})$$

where $J > 0$ for a ferromagnetic crystal, $\lambda > 0$, and $\alpha \neq 0$. The quantity λ plays the role of an effective interaction range.

When we replace the discrete summation by an integral, we obtain

$$j(\mathbf{q}) = \frac{1}{v} \int d^3\alpha [1 - e^{i\mathbf{q} \cdot \alpha}] J(\alpha) = [jx^2/(1+x^2)], \quad (\text{A7})$$

where $x = \lambda|\mathbf{q}|$, $j = [4\pi J\lambda^2/v]$, and where the crystal is of infinite extent in the evaluation of the integral in Eq. (A7). The function $j(\mathbf{q})$ as given by Eq. (A7) behaves as $(\dots)q^2$ when \mathbf{q} approaches zero, in accord with the exact expression (A4). Also, the form (A7) for values of \mathbf{q} near the Brillouin zone simulates more closely the behavior of the exact Eq. (A4) than the form

$$j(\mathbf{q}) \approx jx^2 \quad (\text{A8})$$

used by other authors.⁹

The parameter λ (the effective interaction range) determines an effective number of neighbors which interact with a given site. These neighbors contribute most significantly to the function $j(\mathbf{q})$ and are contained inside a sphere of radius λ which is centered at the site in question; i.e., $Z_{\text{eff}} = (4\pi\lambda^3/3v)$ is the number of lattice sites within a sphere of radius λ . There are six nearest neighbors in a simple cubic lattice and hence the condition $Z_{\text{eff}} \geq 6$ must be satisfied if the continuum limit is to be representative of the physical system. We then have a lower bound on λ ,

$$\lambda \geq [6(3v/4\pi)]^{1/3} = 1.13d.$$

We denote by γ the dimensionless quantity λq_0 .

⁹ D. N. Zubarev, Usp. Fiz. Nauk, **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].