Irreversibility in Heisenberg Spin Systems. II. Approximate Solution of the High-Temperature Kinetic Equations

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A systematic approximation scheme is proposed that permits solution of the kinetic equations, recently derived by the authors, describing the high-temperature behavior of the spin autocorrelation function $\Gamma_{ab}(t)$. A numerical solution and approximate analytical expressions are given in the first approximation and the importance of the neglected terms is discussed. It is shown that the direct autocorrelation function has an approximate Gaussian behavior for short times and decays then to zero through damped oscillations. A diffusion equation is derived for the short-wave-number Fourier components of $\Gamma_{ab}(t)$. We also compare this theory with previous work on the subject.

I. INTRODUCTION

IN the preceding paper[1] (hereafter referred to as RDL) we have derived kinetic equations governing the time evolution of the spin autocorrelation function (a.f.) $\Gamma_{ab}(t)$ in a Heisenberg spin system. These equations, which are exact in the double limit of high temperature and large number of neighbors, were obtained by a systematic reorganization of the perturbation expansion for $\Gamma_{ab}(t)$. The main feature of these equations is that they involve only quantities which remain meaningful in the limit of long times.

More precisely, it has been shown that the direct a.f. $\Gamma(t)=\Gamma_{aa}(t)$ (independent of the lattice point a) obeys the nonlinear equation

$$\partial_t\Gamma(t)=-\int_0^t \tilde{G}_0(t'|\Gamma)\Gamma(t-t')dt', \qquad \text{(I.1)}$$

while the Fourier transform $\Gamma_q(t)$ of the a.f. is given by the following:

$$\partial_t\Gamma_q(t)=\int_0^t [\tilde{G}_q(t'|\Gamma)-\tilde{G}_0(t'|\Gamma)]\Gamma_q(t-t')dt', \qquad \text{(I.2)}$$

which is linear once $\Gamma(t)$ has been determined by (I.1). In Eqs. (I.1) and (I.2), $\tilde{G}_q(t|\Gamma)$ denotes the Fourier transform of a kernel $G_{ij}(t|\Gamma)$, which can be calculated using rules given in RDL (Appendix C). Its most important property is its nonlinear functional dependence on $\Gamma(t)$ which insures that

$$\tilde{G}_q(t|\Gamma)\to 0 \quad (t\to\infty). \qquad \text{(I.3)}$$

This kernel is, however, defined as an infinite series of terms, and some approximation is needed in order to get an explicit expression for the temporal behavior of $\Gamma(t)$ and of $\Gamma_q(t)$. The present paper will be concerned with the development of such approximation methods.

In Sec. II, we point out the difficulties involved in the solution of the exact kinetic equations (I.1,2) and we formulate a self-consistent approximation scheme; we should stress, however, that we have not been able to establish the convergence of the procedure, which is largely based on physical intuition. A particularly simple result is obtained in the lowest order approximation, where $\tilde{G}_q$ is computed to second order in its *explicit* dependence upon the exchange integral J.

Although quite simple, the resulting equation for $\Gamma(t)$ is of course still nonlinear and cannot be solved in analytic form. Numerical solution is reported in Sec. III. We also discuss the exact short-time behavior of $\Gamma(t)$ and of the kernel $\tilde{G}_0^{(2)}$; the rapid decay of this kernel for moderately short times suggests a simple procedure for obtaining an approximate asymptotic solution in analytic form; the agreement with the exact numerical result is satisfactory. In particular, we show that $\Gamma(t)$ starts with a Gaussian behavior, followed by damped oscillations for longer times. A similar behavior is obtained for $\Gamma_q(t)$ for q large, while in the limit of long times and small wave number, $\Gamma_q(t)$ obeys a simple diffusion equation.

Finally, in Sec. IV, we evaluate the higher order terms coming from a better approximation for the kernel $\tilde{G}_q$; these terms are rather small. This gives some indication that the lowest order approximation might furnish a correct semiquantitative description of the phenomena. We also compare our results with previous work on the subject.

II. APPROXIMATION SCHEME AND THE FIRST APPROXIMATION

As mentioned above, and discussed in great detail in Sec. V and Appendix C of RDL, the kernel $G_{ij}(t|\Gamma)$, the Fourier transform of which appears in Eqs. (I.1) and (I.2), is given by an infinite series of terms: These terms

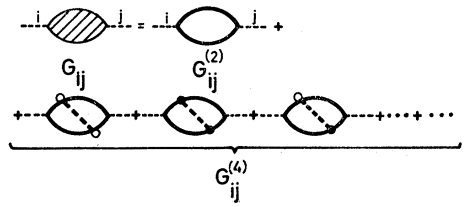

FIG. 1. First terms of $G_{ij}(t|\Gamma)$.

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[1] P. Resibois and M. De Leener, preceding paper, Phys. Rev. **151**, 305 (1966); we follow here the notation of this paper.

are associated with the so-called "renormalized basic irreducible skeleton graphs"; the first graphs of this series are given in Fig. 1.

As is readily seen by applying the rules of RDL (Appendix C), $G_{ij}(t|\Gamma)$ may be *formally* written as an expansion in the number of λ factors (measuring the strength of the exchange interaction) that appear *explicitly*:

$$G_{ij}(t|\Gamma)=\sum_{n=1}^{\infty}\lambda^{2n}G_{ij}^{(2n)}(t|\Gamma). \tag{II.1}$$

However, this classification is purely formal because the functional dependence on $\Gamma(t)$ hides a complicated implicit λ behavior

$$\Gamma(t)\equiv\Gamma(t;\lambda). \tag{II.2}$$

Worse than this, it is evident that the only three dimensional quantities which appear in the problem ($\hbar$, t, and J, the exchange interaction) can be eliminated by working with a suitable reduced unit system, whence any equation would contain only pure numbers! This feature of the problem comes from the absence of an unperturbed time scale; it is in contrast with the usual situation in transport theory: for instance, in the kinetic theory of gases, there is a smallness parameter, $a^3\rho$ (ρ is the particle density; a is the range of the forces) which allows a systematic expansion of the collision operator. No such parameter exists here: J is eliminated by the rescaling $(tJ/\hbar)$ and the only remaining parameter, which is the number of neighbors, has already been taken very large in order to derive the kinetic equations. There is thus no well-defined smallness parameter allowing us to expand (II.1); the eventual convergence of the series (II.1) for all times will be entirely due to the numerical factors weighting each term $G_{ij}^{(2n)}$ and to the highly nonlinear dependence on Γ. The analysis of such a convergence property seems outside the power of the present theory.

We shall then adopt a much more naïve attitude based on physical intuition and we shall only require two conditions:

(1) We want a theory that gives correctly the first terms in a short-time expansion:

$$\Gamma(t)=\sum_{n=0}^{\infty}a_n t^{2n}\quad (Jt/\hbar\ll 1). \tag{II.3}$$

(2) We also require that the same theory should lead to physically meaningful results in the limit of long times.

The first requirement forces us then to retain in Eq. (II.1) the n first terms of the sum; the second makes it necessary to retain the complete functional Γ dependence in each of the terms $G^{(2n')}(t|\Gamma)(n'\leqslant n)$; otherwise, as discussed in RDL, the theory would become meaningless in the limit of long times. By choosing successively $n=1, 2\cdots$, we are led to a sequence of approximations to the kinetic equations (I.1) and (I.2); we then write

$$\partial_t\Gamma^{(n)}(t)=-\int_0^t\Big[\sum_{n'=1}^{n}\tilde{G}_0^{(2n')}(t'|\Gamma^{(n)})\Big]\Gamma^{(n)}(t-t')dt', \tag{II.4}$$

$$\partial_t\Gamma_q^{(n)}(t)=\int_0^t\Big[\sum_{n'=1}^{n}(\tilde{G}_q^{(2n')}(t'|\Gamma^{(n)})-\tilde{G}_0^{(2n')}(t'|\Gamma^{(n)}))\Big]\times\Gamma_q^{(n)}(t')dt'. \tag{II.5}$$

Hopefully, this sequence will converge to the true equation when $n\to\infty$. Let us stress the self-consistent character of these equations (II.4) and (II.5); for each n, the kernel $\tilde{G}_q$ is calculated as a functional of the approximate $\Gamma^{(n)}$ itself.

In the first approximation, $n=1$, Eqs. (II.4) and (II.5) take a very compact form which we shall discuss in detail presently. Applying the rules of RDL (Appendix C), a simple calculation reproduced in Appendix A gives indeed for the kernel $G_{ij}^{(2)}(t|\Gamma)$ of Fig. 1 (setting now $\lambda=1$, $\hbar=1$):

$$G_{ij}^{(2)}(t|\Gamma)=2[J(i-j)]^2\Gamma^2(t). \tag{II.6}$$

Using the definition [RDL (V.13)] for the Fourier transform of G_{ij}, we get immediately:

$$\tilde{G}_q^{(2)}(t|\Gamma)=I_q\Gamma^2(t), \tag{II.7}$$

where we have set

$$I_q=2\sum_{i\neq j}J^2(i-j)\exp[iq(i-j)]. \tag{II.8}$$

If we now introduce the dimensionless time τ by the equation

$$\tau=t\sqrt{I_0} \tag{II.9}$$

we get for the first approximation:

$$\partial_\tau\Gamma^{(1)}(\tau)=-\int_0^\tau[\Gamma^{(1)}(\tau-\tau')]^2\Gamma^{(1)}(\tau')d\tau', \tag{II.10}$$

$$\partial_\tau\Gamma_q^{(1)}(\tau)=\frac{[I_q-I_0]}{I_0}\int_0^\tau[\Gamma^{(1)}(\tau-\tau')]^2\times\Gamma_q^{(1)}(\tau')d\tau'. \tag{II.11}$$

We shall now study the solution of these equations.

III. SOLUTION OF THE FIRST APPROXIMATION

The nonlinear character of the kernel in Eq. (II.10) makes it difficult to get any rigorous mathematical information on the direct a.f. $\Gamma(\tau)$.[2] In order to obtain

[2] In this paragraph, we drop the superscript (1).

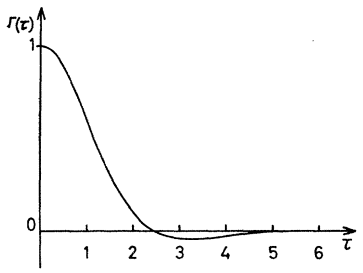

FIG. 2. The direct a.f. $\Gamma(\tau)$.

some hint about possible approximation methods, we have integrated this equation numerically using an IBM 7040 computer. The results are reported in Fig. 2. We shall discuss the physical consequences of this result a little later; for the moment, we just want to stress that indeed, as was anticipated in RDL, the autocorrelation function $\Gamma(\tau)$ tends to zero, through rapidly damped oscillations.

It is, moreover, quite easy to obtain an exact solution of Eq. (II.10) valid for short times:

$$\Gamma(\tau)=1-\tau^2/2+\tau^4/8-17\tau^6/720+\cdots. \quad \text{(III.1)}$$

The coefficients of this expansion are determined by expressing $\Gamma(\tau)$ as a power series in τ, inserting this series into (II.10), and equating equal powers of τ.

We see that for short times, the expansion (III.1) remains very close to the Taylor expansion of a Gaussian function:

$$\Gamma_{\text{Gauss}}(\tau)\equiv\exp(-\tau^2/2) =1-\tau^2/2+\tau^4/8-15\tau^6/720+\cdots. \quad \text{(III.2)}$$

It can be verified that, up to $\tau=1.2$, the difference between the exact solution and the Gaussian is less than 1%. But at this point the kernel $\tilde{G}_0(\tau|\Gamma)$, which is the square of $\Gamma(\tau)$, is already very much reduced from its value at $t=0$; indeed we have

$$\tilde{G}_0(1.2|\Gamma)/\tilde{G}_0(0|\Gamma)=\Gamma^2(1.2)/\Gamma^2(0)\simeq 0.24. \quad \text{(III.3)}$$

Because of the nonlinear character of the kernel $\tilde{G}_0(\tau|\Gamma)$ the dominant contributions to the right-hand side of the integro-differential equation (II.10) will thus come mainly from short time intervals $\tau-\tau'$; therefore we expect that a good approximation will be obtained by solving instead of (II.10) the following *linear* equation:

$$\partial_\tau\Gamma(\tau)=-\int_0^\tau \tilde{G}_0(\tau-\tau'|\Gamma_{\text{Gauss}})\Gamma(\tau')d\tau' \quad \text{(III.4)}$$

with

$$\tilde{G}_0(\tau|\Gamma_{\text{Gauss}})=\exp(-\tau^2). \quad \text{(III.5)}$$

In principle, Eq. (III.4) may be considered as the first step in an iterative sequence of linear approximations to the nonlinear equation (II.10); in the second step, we would take as the new kernel the square of the solution of Eq. (III.4) and so on. However, the convergence of this sequence is again difficult to establish, and we shall be content with solving Eq. (III.4) and comparing it with the exact numerical result.

Defining the Laplace transform of $\Gamma(\tau)$ by

$$\tilde{\Gamma}(S)=\int_0^\infty \exp(-S\tau)\Gamma(\tau)d\tau \quad \text{(III.6)}$$

we immediately obtain from (III.4)

$$\tilde{\Gamma}(S)=\{S+\tfrac{1}{2}\sqrt{\pi}\exp(\tfrac{1}{4}S^2)[1-\operatorname{erf}(\tfrac{1}{2}S)]\}^{-1}. \quad \text{(III.7)}$$

The inversion of Eq. (III.7) cannot be done analytically. It is, however, straightforward to deduce the solution for short times

$$\Gamma(\tau)=1-\tau^2/2+\tau^4/8-17\tau^6/720+\cdots, \quad \text{(III.8)}$$

which reproduces exactly the four first terms of the exact solution (III.1). Moreover, for long times, the inversion of Eq. (III.7) can be obtained by determining numerically the poles of (III.7) closest to the imaginary axis. We have shown that these poles $S_\pm$ occur in pairs, being complex conjugates of one another. Using tables for the complex error function,[3] we have found

$$S_\pm=-S'\pm iS'', \quad \text{(III.9)}$$

$$S'=1.08\pm 0.01, \quad \text{(III.10)}$$

$$S''=0.99\pm 0.01, \quad \text{(III.11)}$$

and the residue of $\tilde{\Gamma}(S)$ at these points is

$$\operatorname{Res}\tilde{\Gamma}(S)|_{S_\pm}=\left(\frac{\partial\tilde{\Gamma}^{-1}(S)}{\partial S}\right)^{-1}\Bigg|_{S_\pm}=2(1-S_\pm^2)^{-1}. \quad \text{(III.12)}$$

Trivial algebraic manipulations give then

$$\Gamma(\tau)=4\exp(-S'\tau) \times\left[\frac{(1-S'^2+S''^2)\cos S''\tau+2S'S''\sin S''\tau}{(1-S'^2+S''^2)^2+4(S'S'')^2}\right] \quad (\tau\to\infty). \quad \text{(III.13)}$$

Using Eqs. (III.10) and (III.11), we get the following formula for the asymptotic solution of Eq. (III.4):

$$\Gamma(\tau)=[0.62\cos 0.99\tau+1.64\sin 0.99\tau]\exp(-1.08\tau) \quad (\tau\to\infty). \quad \text{(III.14)}$$

We have also estimated the distance to the imaginary axis of the next important poles: It is larger than $2\sqrt{\pi}$. This indicates that the asymptotic expansion (III.14) is valid for fairly short times, when the series (III.7) is still converging: the two formulas (III.8) and (III.14) cover thus the entire range $0<\tau<\infty$. As may be seen from Table I, the agreement with the exact numerical solution is satisfactory. In particular, the approximation (III.14) reproduces the strongly damped oscillation of

[3] M. Abranowitz and J. A. Stegun, *Handbook of Mathematical Functions* (Dover Publications, Inc., New York, 1965).

TABLE I. Numerical value for $\Gamma(\tau)$.

	Exact solution	Asymptotic Eq. (III.14)	Gaussian approx.
0.0	1.000	...	1.000
0.4	0.923	...	0.923
0.8	0.725	...	0.726
1.2	0.482	0.475	0.487
1.6	0.263	0.288	0.278
2.0	0.104	0.144	0.135
2.4	0.010	0.052	0.056
2.8	−0.033	0.000	0.020
3.2	−0.044	−0.022	0.006
3.6	−0.039	−0.025	0.001
4.0	−0.028	−0.021	0.000
4.4	−0.016	−0.016	...
4.6	−0.008	−0.008	...
5.2	−0.002	−0.004	...
5.6	0.000	−0.001	...
6.0	0.001	0.000	...

the exact solution, except for an underestimate of the minimum in this oscillation.

Once $\Gamma(\tau)$ is determined, there is no difficulty in solving for $\Gamma_q(\tau)$. Let us discuss separately the cases of short times and of long times.

For small τ, one easily obtains from Eqs. (II.11) and (III.1) the following series expansion:

$$\Gamma_q(\tau)=1-\frac{(I_0-I_q)}{I_0}\frac{\tau^2}{2}+\left[\frac{2(I_0-I_q)}{I_0}+\frac{(I_0-I_q)^2}{I_0^2}\right]\frac{\tau^4}{24}+\cdots \quad \text{(III.15)}$$

which is not in general simply related to the Gaussian decay (III.7). However, it may easily be checked that the general expression (III.15) verifies (up to order Z^{-1}) the sum rule

$$\Gamma(\tau)=(1/N)\sum_q{}'\,\Gamma_q(\tau), \quad \text{(III.16)}$$

where $\sum_q{}'$ indicates a summation over the first Brillouin zone. Since, when q becomes large, taking the average of $\Gamma_q(\tau)$ over all orientations of the vector q is essentially equivalent to summing over the first Brillouin zone [see (A9)], it follows that the result $\langle\Gamma_q(\tau)\rangle_{\rm av}$ for large q obeys a Gaussian decay for short times:

$$\lim_{q\to\infty}\langle\Gamma_q(\tau)\rangle_{\rm av}=(1/N)\sum_q{}'\,\Gamma_q(\tau)=\Gamma(\tau).$$

For large τ, we may use the same method as for $\Gamma(\tau)$. With the approximate Gaussian kernel (III.5), we find for the Laplace transform of $\Gamma_q(\tau)$:

$$\tilde{\Gamma}_q(S)=\{S-\tfrac{1}{2}(\pi)^{1/2}((I_q-I_0)/I_0)\times\exp(\tfrac{1}{4}S^2)[1-\operatorname{erf}(\tfrac{1}{2}S)]\}^{-1}. \quad \text{(III.17)}$$

For large q, we obtain of course the same behavior as in (III.12). We have not, however, computed the poles of Eq. (III.17) for arbitrary q. Yet the small-wave-number limit is readily solved; indeed, we have

$$(I_q-I_0)/I_0=-\alpha q^2/I_0+O(q^4) \quad (q\to 0) \quad \text{(III.18)}$$

which defines the constant α.

Up to corrections of order q^4, Eq. (III.17) has then a single pole at

$$S=-Dq^2/\sqrt{I_0}, \quad \text{(III.19)}$$

where we have introduced a diffusion coefficient D,

$$D=\tfrac{1}{2}(\pi)^{1/2}\alpha/\sqrt{I_0}. \quad \text{(III.20)}$$

Laplace-transforming, and turning back to the ordinary time variable $t=\tau/\sqrt{I_0}$, we immediately obtain the familiar diffusion equation

$$\partial_t\Gamma_q(t)=-Dq^2\Gamma_q(t) \quad (q\to 0,\ t\to\infty). \quad \text{(III.21)}$$

Before closing this section, let us still point out that this diffusion equation is quite general, except for the explicit value of D, and can be deduced from the general kinetic equation (I.2) in the limit of small wave vector. It is indeed straightforward to verify that

$$\tilde{G}_q(t|\Gamma)-\tilde{G}_0(t|\Gamma)=\alpha' q^2+O(q^4) \quad (q\to 0), \quad \text{(III.22)}$$

whence $\Gamma_q(t)$ is a slowly varying function of t in this limit. Expanding $\Gamma_q(t')$ around t in (I.2), we then obtain

$$\partial_t\Gamma_q(t)=\int_0^t dt'[\tilde{G}_q(t'|\Gamma)-\tilde{G}_0(t'|\Gamma)]\times\left[\Gamma_q(t)-(t')\frac{\partial\Gamma_q(t)}{\partial t}+\cdots\right]. \quad \text{(III.23)}$$

If we assume that

$$\tilde{G}_q(t|\Gamma)\to 0 \quad (t\gg\tau_d), \quad \text{(III.24)}$$

where τ_d is some characteristic time independent of q, we see that for long times t, the last term in the second bracket of Eq. (III.23) gives a negligible contribution of order q^4. We then recover the diffusion equation (III.21) with a coefficient

$$D=-\frac{1}{2}\left[\frac{\partial^2}{\partial q^2}\int_0^\infty dt\,\tilde{G}_q(t|\Gamma)\right]_{q=0}. \quad \text{(III.25)}$$

This exact result generalizes Eq. (III.20).

IV. HIGHER ORDER APPROXIMATIONS

In the preceding section, explicit expressions have been obtained for $\Gamma(t)$ and $\Gamma_q(t)$ in the approximation that retains only the term $G_{ij}^{(2)}(t|\Gamma)$ in the expansion (II.1) for the kernel. A detailed analysis beyond this order is very difficult, but it is possible to get a rough estimate of the neglected terms by looking at the influence of the next term, $G_{ij}^{(4)}(t|\Gamma)$, on the behavior of $\Gamma(t)$. The graphs contributing to $G_{ij}^{(4)}(t|\Gamma)$ are drawn in Fig. 1; their evaluation is sketched in Appendix A.

For a typical simple cubic structure, with nearest-neighbor interactions, we obtain[4]

$$\tilde{G}_0^{(4)}(t|\Gamma)=-I_0^2\Phi(t|\Gamma), \tag{IV.1}$$

where the functional $\Phi(t|\Gamma)$ is defined by

$$\Phi(t|\Gamma)=\frac{1}{2}\int_0^t\int_0^{t'}dt'dt'' \times\Gamma(t-t')\Gamma(t-t'')\Gamma(t'-t'')\Gamma(t')\Gamma(t''). \tag{IV.2}$$

Other crystallographic structures would lead to similar results, but the advantage of the case treated in (IV.1) is that it leads to a kinetic equation involving no parameter; indeed, we get from (II.4) and (II.9)

$$\partial_\tau\Gamma^{(2)}(\tau)=-\int_0^\tau[(\Gamma^{(2)}(\tau-\tau'))^2 -\Phi(\tau-\tau'|\Gamma^{(2)})]\Gamma^{(2)}(\tau')d\tau'. \tag{IV.3}$$

In the limit of small τ, Eq. (IV.3) is readily solved; we obtain

$$\Gamma^{(2)}(\tau)=1-\tau^2/2+[7/6]\tau^4/8-\cdots. \tag{IV.4}$$

We have written Eq. (IV.4) in such a way that the departure from the Gaussian behavior is exhibited [compare with (III.2)]. For arbitrary τ, Eq. (IV.3) is quite difficult to solve, even numerically, and we have not yet undertaken this task. However, the small difference between (IV.4) and the Gaussian (III.2) (15% on the τ^4 term) suggests very much that, as in the preceding section, a fair estimate of $\tilde{G}_0^{(4)}(\tau|\Gamma)$ may be obtained by calculating it with the Gaussian approximation for Γ. In this case, it is possible to evaluate (IV.2) numerically; the results of this calculation are represented in Fig. 3 together with the kernel $\tilde{G}_0^{(2)}(\tau|\Gamma_{\text{Gauss}})$ and the sum $[\tilde{G}_0^{(2)}(\tau|\Gamma_{\text{Gauss}})+\tilde{G}_0^{(4)}(\tau|\Gamma_{\text{Gauss}})]$. It is seen that $\tilde{G}_0^{(4)}$ remains a small correction ($<20\%$) with respect to $\tilde{G}_0^{(2)}$ until $\tau=0.8$, where $\tilde{G}_0^{(2)}$ itself is already considerably reduced with respect to its value at $\tau=0$. Moreover, the integral of $\tilde{G}_0^{(4)}(\tau|\Gamma)$ from zero to infinity is less than 20% of the corresponding integral of $\tilde{G}_0^{(2)}(\tau|\Gamma)$. Consequently, we do not expect the solution of the corrected kinetic equation (IV.3) to be deeply modified by the term $\tilde{G}_0^{(4)}$; in particular, the approach toward equilibrium through strongly damped oscillations will remain valid. A similar argument may be developed for the behavior of $\Gamma_q(\tau)$.

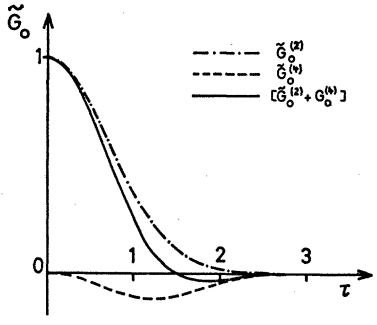

FIG. 3. The second approximation to the kernel with Gaussian $\Gamma(\tau)$.

Let us still make a few remarks about the higher order terms ($n>2$): First, we notice that they give contributions which behave at least like τ^6 for short times; they will thus not affect the terms indicated in Eq. (IV.4). Second, because of their increasing nonlinear dependence on $\Gamma(\tau)$, they will also decrease very rapidly for long times. We expect, thus, that these contributions will become smaller and smaller for bigger n, over the whole time range, ensuring thereby a rapid convergence of the expansion (II.1).

Finally, let us recall that the diffusion equation (III.21) is valid provided the very general condition (III.24) is satisfied.

V. DISCUSSION

In this paper, we have obtained approximate analytic solutions for the direct autocorrelation function $\Gamma(t)$ and for the Fourier transform of the indirect a.f. $\Gamma_q(t)$. The main results are summarized by Eqs. (III.1), (III.13) and (III.21).

It is interesting to compare these equations with previous calculations.[5–7] Let us discuss separately the cases of large wave number and of small wave number.

To study the large-wave-number limit, we average $\Gamma_q(t)$ over all orientations of the vector q. As remarked in Sec. III, the result behaves like the direct a.f. $\Gamma(t)$ when q becomes large. This large-momentum-transfer problem was first treated by de Gennes, who analyzed the so-called momenta of the autocorrelation function defined by

$$\langle\omega^{2n}\rangle=(-1)^n\frac{d^{2n}}{dt^{2n}}\Gamma(t)\bigg|_{t=0}. \tag{V.1}$$

This author noticed that for a Gaussian decay the quantity

$$\rho=3\langle\omega^2\rangle^2/\langle\omega^4\rangle \tag{V.2}$$

is equal to 1. Calculating $\langle\omega^2\rangle$ and $\langle\omega^4\rangle$ in the case of a simple cubic structure with nearest neighbor interactions and spin $S=\frac{1}{2}$, he finds $\rho=0.87$,[8] which is close to 1, and he suggests that the Gaussian will provide a good approximation for all times. However, we have seen here that if the Gaussian form is well satisfied for

[4] There is of course a slight inconsistency in taking nearest-neighbor interactions in a simple cubic structure ($Z=6$) within a theory valid in the Weiss limit $Z\to\infty$. This, however, does not affect the conclusions of this paragraph.

[5] P. G. de Gennes, (a) J. Phys. Chem. Solids 4, 223 (1958); (b) Centre d'Etudes Nucléaires de Saclay, France, Rapport No. CEA 925, 1959 (unpublished).

[6] H. Mori and K. Kawazaki, Progr. Theoret. Phys. (Kyoto) 27, 3 (1962).

[7] H. Bennett and P. Martin, Phys. Rev. 138, A608 (1965).

[8] In formulas (II.4) of Ref. 5(a) and (II.2.6) of Ref. 5(b), the factor $(224/3+2/S(S+1))$ is in error and should be replaced by $(224/3-2/S(S+1))$. The momentum calculation of de Gennes would agree then exactly with those of Ref. 6.

short times, the long-time behavior for $\Gamma(t)$ is described by damped oscillations [see Eq. (III.13)] which cannot be deduced from the analysis of a finite number of momenta. Although neither Mori and Kawazaki nor Bennett and Martin considered explicitly the large-momentum behavior of $\Gamma_q(t)$, it is very easy to obtain the value of ρ from their calculation. Mori and Kawazaki have calculated $\langle\omega^2\rangle_q$ and $\langle\omega^4\rangle_q$, by a perturbation calculus, and, except for a trivial mistake of sign,[9] this leads to the correct value of ρ. Bennett and Martin derived an integral equation for the Laplace transform of $\Gamma_q(t)$, which is obtained by a factorization assumption on the four-spin Green's function. Although they present their result as exact in the high-temperature region, it is easily verified that their integral equation leads to a value of ρ which is in error by about a factor of 2. In terms of our diagrams, the contributions retained by Bennett and Martin may be schematized as indicated in Fig. 4: Iteration of this equation gives the second moment correctly but ignores a large number of nonvanishing graphs already in the next order.

The case of short wave numbers is treated by de Gennes by using a Lorentzian behavior with a cutoff at a characteristic frequency τ_d^{-1}; this assumption rests largely upon the validity of a macroscopic diffusion

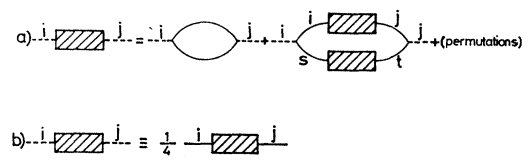

FIG. 4. Diagrammatic description of the Bennett-Martin equation.

equation; he writes

$$\tilde{\Gamma}_q(i\omega)=2Dq^2/(\omega^2+(Dq^2)^2), \quad |\omega|<\tau_d^{-1}$$
$$\tilde{\Gamma}_q(i\omega)=0, \quad |\omega|>\tau_d^{-1}. \tag{V.3}$$

The constants D and τ_d are then determined by identifying the exact small-wave-number momenta $\langle\omega_q^2\rangle$ and $\langle\omega_q^4\rangle$ with the corresponding momenta computed with (V.3). Together with a few other results, the values of D and τ calculated by this method are given in Table II. It should, however, be clear that this method is not satisfactory, because the major contribution to $\langle\omega^2\rangle_q$ and $\langle\omega^4\rangle_q$, when calculated with Eq. (V.3), comes from large values of ω for which Eq. (V.3) is uncertain.

A more satisfactory approach is given by Mori and Kawazaki, who first establish an exponential relation between the small-momentum Fourier component $\Gamma_q(t)$ and a higher autocorrelation function

$$\Gamma_q(t)\simeq\Gamma_q(0)\exp\left[t\langle\dot{S}_q^z(0)\dot{S}_{-q}^z(0)\rangle\int_0^\infty\Psi(t')dt'\right] \tag{V.4}$$

[9] There should be a + sign (instead of −) in the second term in the bracket of formula [(C.3), Ref. 6]; this does not, however, affect the limit of small q considered by these authors.

TABLE II. Comparison between various theories for cubic structure ($Z=6$; $S=\frac{1}{2}$).

	ρ (Exact: 0.92)	D/Jb^2	τ_dJ
de Gennes	0.87	0.40	0.12
Mori Kawazaki	(0.92)	0.59	0.29
Bennett Martin [a]	(1.80)	...	...
Bennett Martin [b]	...	0.46	...
This theory [c]	1	0.51	0.29
This theory [d]	0.86	...	...

[a] Integral equation.
[b] Momentum method.
[c] First approximation.
[d] Second approximation.

with

$$\Psi(t)=\langle\dot{S}_q^z(t)\dot{S}_{-q}^z(0)\rangle/\langle\dot{S}_q^z(0)\dot{S}_{-q}^z(0)\rangle. \tag{V.5}$$

They assume a rapid Gaussian decay for $\Psi(t)$, with a characteristic time computed by de Gennes's momentum method. They then readily derive a diffusion equation for $\Gamma(t)$ with[10]

$$D=\lim_{q\to0}(\pi/2)^{1/2}\frac{\langle\omega^2\rangle_q^{3/2}}{\langle\omega^4\rangle_q q^2} \tag{V.6}$$

while the characteristic time $\tau_d\simeq\langle\omega^2\rangle^{-1/2}$.

Up to terms of order Z^{-1},[11] this equation is easily shown to be identical to our first approximation, Eq. (III.20), as is not surprising in view of the similarity between Eqs. (V.5) with a Gaussian form for $\Psi(t)$ on the one hand, and the solution of the diffusion equation (III.21) with a Gaussian approximation to determine D from Eq. (III.25) on the other hand. Finally, Bennett and Martin proposed two different methods to analyze the short-wave-number limit: one is based on their integral equation, but has not been applied to the cubic structure discussed here; it gives, however, results which are rather close to those obtained in the second method, which is based on sum rules. As an intermediate step, they derive an equation identical to (V.6), but their explicit expression for the diffusion coefficient differs however from Mori and Kawazaki's value because the momenta $\langle\omega^2\rangle_q$ and $\langle\omega^4\rangle_q$ are again determined by a factorization of Green's functions.

As may be seen from Table II, even the first approximation to our exact kinetic equation seems to incorporate within a unified formalism the more satisfactory features of the previous theories. Moreover, it allows us to treat situations which were not discussed previously, as for example the damped oscillations in the long-time behavior of $\Gamma(t)$. Although this latter phenomenon is probably very difficult to observe experi-

[10] The form of D, as given in Eq. (V.6), was obtained first in Ref. 7.

[11] For consistency, we have not made any exclusion in calculating lattice sums in our theory; in the *highly unfavorable case* considered in Table II, this is the origin of the difference between $\rho=0.86$ and $\rho_{\text{exact}}=0.92$ as well as for the discrepancy between $D=0.51$ and the value obtained by Mori and Kawazaki.

mentally in a ferromagnet with strong exchange interactions, similar behavior has been reported in nuclear magnetic resonance with dipole-dipole interactions.[12] There seems to be no fundamental difficulty in extending the present theory to such cases, for spin $S=\frac{1}{2}$ at least. This problem, as well as other developments of the present work, will be considered in separate publications.

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APPENDIX: EVALUATION OF $G_{ij}^{(2)}(t|\Gamma)$ AND $G_{ij}^{(4)}(t|\Gamma)$

Applying the rules given in RDL (Appendix C), we get immediately from the first graph of Fig. 1:

$$G_{ij}^{(2)}(t|\Gamma)=-2\times4[\sum_{M_j} J^2(i-j)[\eta^{-1i}\eta^{1j}-\eta^{1i}\eta^{-1j}]\delta_{M_i,0}^{\mathrm{Kr}}\delta_{M_j,0}^{\mathrm{Kr}} \times\Gamma^2(t)[\eta^{1i}\eta^{-1j}-\eta^{-1i}\eta^{1j}]M_j\rho_0^{\mathrm{eq}}(M_j)\rho_0^{\mathrm{eq}}(M_i)|_{M_i=\frac{1}{2}}, \quad \text{(A1)}$$

where all symbols have been defined in RDL. Note that the factor 2 in front of Eq. (A1) comes from the two possible orientations of the arrows of the graph.

We perform the displacement operations and use the fact that $\rho_0^{\mathrm{eq}}(M_i)=\frac{1}{2}$ in the high-temperature limit; we then obtain

$$G_{ij}^{(2)}(t|\Gamma)=2J^2(i-j)\sum_{M_j}[\delta_{M_i,\frac{1}{2}}^{\mathrm{Kr}}\delta_{M_j,-\frac{1}{2}}^{\mathrm{Kr}}-\delta_{M_i,-\frac{1}{2}}^{\mathrm{Kr}}\delta_{M_j,\frac{1}{2}}^{\mathrm{Kr}}]|_{M_i=\frac{1}{2}}\Gamma^2(t) \quad \text{(A2)}$$

which immediately leads to Eq. (II.6).

The calculation of $G_{ij}^{(4)}(t|\Gamma)$ follows parallel lines; let us denote by $G_{ij}^{(4a)}(t|\Gamma)$ the contribution of the purely transverse graph of fourth order in Fig. 1, by $G_{ij}^{(4b)}(t|\Gamma)$ the contribution of the purely longitudinal graph, and by $G_{ij}^{(4c)}(t|\Gamma)$ the sum of all mixed fourth-order graphs (only one of which is represented on Fig. 1). We have

$$G_{ij}^{(4a)}(t|\Gamma)=2\times4\sum_s\sum_{M_s}\sum_{M_j}\int_0^t d\tau^2\{[J^2(i-s)J^2(i-j)\Gamma(t-\tau_1)\Gamma(t-\tau_2)\Gamma(\tau_1-\tau_2)\Gamma(\tau_1)\Gamma(\tau_2) \times\eta_{is}\delta_{M_i,0}^{\mathrm{Kr}}\delta_{M_s,0}^{\mathrm{Kr}}\eta_{ji}\delta_{M_j,0}^{\mathrm{Kr}}\eta_{si}\delta_{M_i,0}^{\mathrm{Kr}}\eta_{ij}]+[i\to s;s\to i;j\to j]+[i\to j;j\to s;s\to i]\}M_j \times\rho_0^{\mathrm{eq}}(M_j)\rho_0^{\mathrm{eq}}(M_i)\rho_0^{\mathrm{eq}}(M_s)|_{M_i=\frac{1}{2}}. \quad \text{(A3)}$$

In this formula, the symbol $[i\to s;s\to i;j\to j]$ indicates an obvious permutation of the indices in the first brackets. Similarly, one gets

$$G_{ij}^{(4b)}(t|\Gamma)=2\times4\times2\sum_s\sum_{M_s}\sum_{M_j}\int_0^t d\tau^2[J^2(i-j)J(i-s)J(s-j)\Gamma(t-\tau_1)\Gamma(t-\tau_2)\Gamma(\tau_1-\tau_2)\Gamma(\tau_1)\Gamma(\tau_2) \times\eta_{ij}\delta_{M_i,0}^{\mathrm{Kr}}\delta_{M_j,0}^{\mathrm{Kr}}(4M_s^2)\eta_{ji}]M_j\rho_0^{\mathrm{eq}}(M_j)\rho_0^{\mathrm{eq}}(M_s)\rho_0^{\mathrm{eq}}(M_i)|_{M_i=\frac{1}{2}}. \quad \text{(A4)}$$

For reasons which will shortly become clear, we shall not need the explicit form of $G_{ij}^{(4c)}(t|\Gamma)$.

When the operations are performed in (A3) and in (A4), the results are

$$G_{ij}^{(4a)}(t|\Gamma)=-4[J^2(i-j)\textstyle\sum_s J^2(i-s)-\sum_s J^2(i-s)J^2(s-j)+J^2(i-j)\sum_s J^2(j-s)]\Phi(t|\Gamma) \quad \text{(A5)}$$

and

$$G_{ij}^{(4b)}(t|\Gamma)=8J^2(i-j)[\textstyle\sum_s J(i-s)J(s-j)]\Phi(t|\Gamma). \quad \text{(A6)}$$

In these formulas, the notation of Eq. (IV.2) has been used. For the particular case of a simple cubic structure with nearest-neighbor interactions (and also for body-centered cubic structure), the sum over s vanishes identically in (A6), and, for the same reason, $G_{ij}^{(4c)}(t|\Gamma)$ is zero. We are thus left with a very simple result for the zero-wave number Fourier component:

$$\tilde{G}_0^{(4)}(t|\Gamma)=-\textstyle\sum_j G_{ij}^{(4a)}(t|\Gamma)=I_0^2\Phi(t|\Gamma), \quad \text{(A7)}$$

where

$$I_q=2\textstyle\sum_j J^2(i-j)\exp[iq(i-j)]. \quad \text{(A8)}$$

[12] See for instance: A. Abragam, *The Principles of Nuclear Magnetism* (The Clarendon Press, Oxford, England, 1961), Chap. IV, p. 123.

For explicit calculations, we have averaged (A8) over all directions of the vector q; this gives

$$\langle I_q\rangle_{\rm av}=2J^2Z(\sin qb/qb). \tag{A9}$$

Here, J is the exchange integral between two neighboring spins, and b is the lattice parameter. It may be worthwhile remarking that this usual averaging procedure, which is consistent with the experimental situation, has the nontrivial effect of destroying the periodicity of I_q in different Brillouin zones.

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Nuclear Hexadecapole Interactions

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The nuclear hexadecapole matrix elements for the static and the one-phonon nuclear interactions are developed and are evaluated for $\Delta m=\pm3$ and $\Delta m=\pm4$ nuclear transitions involving a spin-$\frac{9}{2}$ nucleus in a crystal with $\bar{4}3m$ symmetry. An expression for the saturation factor for a general interaction which gives rise to nuclear-spin transitions involving the change in the z component of the spin by any amount $\Delta m=\pm n$ is developed and is used to derive the angular variation of the one-phonon, $\Delta m=\pm3$ and $\Delta m=\pm4$ nuclear hexadecapole interactions. Finally a way to end the speculation about the observation of the hexadecapole interaction is presented.

1. INTRODUCTION

SINCE the first observation of the interaction of the nucleus with its environment through its electric moment, many experiments have been done to investigate both the static and the time-dependent effects of this phenomenon. In 1948, Pound[1] demonstrated that the time-dependent quadrupole interaction was responsible for the relaxation of the Br^{79} and Br^{81} nuclei in solution. He then observed the static effect through the splitting of the nuclear-resonance lines in a crystal with lower than cubic symmetry.[2] In 1956, Proctor and Tanttila[3] observed externally induced Cl^{35} quadrupole transitions between the degenerate quadrupole levels in $NaClO_3$.

In 1955, Wang[4] postulated that an unexplained shift in the pure quadrupole spectra in Sb^{121} and Sb^{123} was due to the static nuclear-electric hexadecapole interaction. In 1966, externally induced hexadecapole transitions between magnetically split In^{115} levels in InAs were believed to have been observed.[5]

The nuclear-electric moments are coupled to their electronic environment through the electric-field gradients of the electronic charge. To first approximation in an ionic crystal, the electronic charge is symmetric about the nucleus; thus there is no coupling between the nucleus and its surrounding electrons. In this approximation, the electric-field gradients arise solely from charges external to the ion. However, there is a distortion from this spherical symmetry due to the interaction with external charges and with the nuclear-quadrupole moment, which gives rise to an additive coupling characterized by an antishielding factor γ. Sternheimer and others have calculated these antishielding factors for both the quadrupole[6–10] and the hexadecapole interaction.[11,12] In addition to the antishielding factor, there is an additional contribution to the hexadecapole coupling due to the perturbation of the ion by the field of the nuclear-quadrupole moment.[13]

2. THEORY

The interaction energy of a nuclear-charge distribution $\rho_N(r_N)d\tau_N$ and an electron-charge distribution $\rho_E(r_E)d\tau_E$ can be written

$$U=\int_N\int_E \rho_N(r_N)\frac{\rho_E(r_E)}{|\mathbf{r}_E-\mathbf{r}_N|}d\tau_N d\tau_E. \tag{1}$$

Assuming the electron does not penetrate the nucleus,

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