$E_1^0$, $E_2^0 \rightarrow C$, and $Z_1 \rightarrow Y$. The allowed electric-dipole transitions which conserve energy are to $C_3+Y_5$, $C_3+Y_6$, $C_4+Y_5$, and $C_4+Y_6$. Using the results of Varsanyi and Dieke for $Z_1 \rightarrow Y_5$, $Y_6$ corrected for index of refraction and local field effects (a cubic field approximation and visible value of $n$ were used) and an overlap integral for each pair of levels of $1/(3\ \mathrm{cm}^{-1})$, Eq. (10) yields a rate of $1\times10^3\ \mathrm{sec}^{-1}$ at 7.5 Å if the oscillator strengths to $C_3$ and $C_4$ are each $3\times10^{-8}$. Such oscillator strengths are reasonable.

It is not possible, then, to ascertain the nature of the ion-pair interaction. Although electric dipole-electric quadrupole or electric quadrupole-electric quadrupole interactions are expected, reasonable values of the $E \rightarrow C$ electric-dipole oscillator strength give the transition rate. For this reason, better estimates of the oscillator strengths involved must be obtained before the type of interaction can be decided.

## V. CONCLUSION

Energy transfer between $Ho^{3+}$ ions in a $LaCl_3$ lattice has been studied by means of careful fluorescence intensity measurements. Unequivocal direct evidence has been found that $E$ to $C$ is a pair transition. The upper limit of radiative and multiphonon rates from $E$ to $C$ were found to be much less than the ion-pair rate. In a 3.5% concentration sample of $LaCl_3:Ho^{3+}$, 41% of the ions in $E$ decayed to $C$ via a pair transition. Assuming a simple model this corresponded to an interaction range of at least 7.5 Å. The concentration dependence was linear, agreeing with the model. Adjusting the transition rate for concentration dependence and using the lifetime of the $E$ state obtained by Barasch and Dieke[10] for a 2% sample a pair transition rate of $\sim1\times10^3\ \mathrm{sec}^{-1}$ was obtained. It was not possible to ascertain the detailed nature of the interaction.

PHYSICAL REVIEW VOLUME 152, NUMBER 1 2 DECEMBER 1966

# Irreversibility in Heisenberg Spin Systems. I. General Formalism and Kinetic Equations in the High-Temperature Limit

P. RÉSIBOIS AND M. DE LEENER*
*Université Libre, Brussels, Belgium*
(Received 13 June 1966)

Starting from the von Neumann equation for the spin density matrix of a Heisenberg system, we analyze the perturbation expansion of the spin autocorrelation function by the diagrammatic technique previously applied to quantum gases. We demonstrate a number of theorems which allow us to express this perturbation series in terms of renormalized graphs only; we then derive a kinetic equation for the autocorrelation function. The main feature of this equation is that the kernel, which is highly nonlinear in the autocorrelation function itself, tends to zero in the limit of long times. The results, which are exact in the high-temperature region and in the Weiss limit (number of neighbors $Z \rightarrow \infty$), allow us to consider the behavior of the autocorrelation function for times both short and long. This model is a typical example of a system with a discrete unperturbed spectrum showing an irreversible behavior.

## I. INTRODUCTION

MODERN development in the $N$-body problem has led to considerable progress in the understanding of the equilibrium properties of the Heisenberg spin system.[1,2] A qualitative description is now available that covers the whole range from the low-temperature spin-wave region to the high-temperature paramagnetic region. Moreover, the Heisenberg model also offers the possibility of testing various approximation methods for analyzing the phase transition at the Curie point $T_c$.

On the other hand, except in the well-known spin-wave region,[3] very little is known about the nonequilibrium behavior of the Heisenberg model. However, this problem has much interest: First, it furnishes a typical example of a dynamical system the dissipative properties of which may not be described by a Boltzmann-like equation; indeed, except again for spin waves, the meaning of the concept of a "collision" between spins cannot be guessed from what is known in other situations. Second, the knowledge of the time behavior of a spin system is essential to analyze the numerous experiments on ferromagnets, among which neutron-scattering measurements take an important place.

In these latter experiments, a central role is played by the so-called spin autocorrelation functions[4]

$$\Gamma_{ab}{}^{\alpha\beta}(t)=\langle S_a{}^{\alpha}(t)S_b{}^{\beta}(0)\rangle, \qquad (I.1)$$

where $S_a{}^{\alpha}(t)$ denotes the Heisenberg representation of spin component $\alpha(\alpha=z,+,-)$ at lattice point $a$, and the

* Chargé de Recherches au Fonds National de la Recherche Scientifique de Belgique.

[1] See, for instance, R. Brout, *Phase Transitions* (W. A. Benjamin and Company, Inc., New York, 1965), Chaps. I, II, V and references quoted therein.

[2] See also D. Mattis, *The Theory of Magnetism* (Harper & Row, New York, 1964).

[3] F. J. Dyson, Phys. Rev. **102**, 1217 (1956); **102**, 1230 (1956).

[4] L. Van Hove, Phys. Rev. **95**, 1374 (1954).

bracket $\langle\cdots\rangle$ indicates the average over the equilibrium canonical distribution.

Pioneer work towards the evaluation of the quantity (I.1) has been done by de Gennes[5] and by Mori and Kawazaki.[6] However, while the calculation of (I.1) at high temperature is straightforward for short times $t$, the long-time behavior is much more difficult to obtain and is usually deduced from some heuristic argument on the short-time behavior; a clear justification of this procedure is not known.

In recent work, Bennett and Martin[7] derived an approximate kinetic equation for $\Gamma_{ab}{}^{\alpha\beta}(t)$, valid for all times; however, this equation is very complicated and they have to resort finally to the same type of approximations as were made by de Gennes, and by Mori and Kawazaki in order to get explicit results.

In the present paper, we want to develop a systematic resummation scheme which allows us to derive kinetic equations for the autocorrelation functions $\Gamma_{ab}{}^{\alpha\beta}(t)$; approximate solutions of these equations will be obtained in the second paper of this series. Although the method is quite general, we shall for simplicity limit ourselves to the high-temperature region ($\beta ZJ=0$, where $J$ is the exchange integral, $Z$ is the number of neighbors, and $\beta=1/kT$). We hope to discuss the finite-temperature region, mainly around the critical temperature, in future publications.

Using the method based on the Liouville–von Neumann equation as developed by Prigogine and co-workers in their study of nonequilibrium processes in quantum gases,[8] we make a systematic analysis of the perturbative solution of Eq. (I.1) (to all orders in $J$); this formalism is outlined in Sec. II.

In Sec. III, we introduce a diagram technique which is very useful for representing the various terms of this formal expansion; special emphasis is laid on the rules that allow us to determine the $Z$ dependence of a given graph.

It is then shown that if we take the Weiss limit,[1] where the number of neighbors is large, the dominant graphs are of order $J^2(J^2Z)^n$, in contrast with the ferromagnetic region ($T<T_c$) where the spin waves arise from contributions of order $J(JZ)^n$.

Even with this simplifying condition, a straightforward perturbation calculus is not possible, except for short times. If one considers for instance the transition probability between two given spins, it grows like $t^2$ instead of the $t$ dependence in usual scattering problems. Mathematically, this difference arises because the spectrum of the unperturbed states of the system is completely degenerate; physically, it corresponds to the fact that two interacting spins are fixed on the lattice and therefore never separate.

It is suggested then that one is not allowed to consider a given finite number of spins as isolated; one has instead to take into account that the other spins of the system play the role of a "bath" which dissipates the magnetization put initially on the given spins; we then develop a renormalization scheme that expresses this idea (Sec. IV).

In Sec. V, we derive exact kinetic equations, valid in the Weiss limit and in the high-temperature region, for the direct autocorrelation function $[\Gamma(t)\equiv 4\Gamma_{aa}{}^{zz}(t)]$ and for the Fourier transform $\Gamma_q(t)$ of the indirect correlation function. We show that $\Gamma(t)$ obeys a nonlinear non-Markoffian kinetic equation of the form:

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

where the kernel $\tilde{G}_0$ is itself a nonlinear functional of the unknown $\Gamma(t)$, while we get for $\Gamma_q(t)$:

$$\partial_t\Gamma_q(t)=\int_0^t [\tilde{G}_q(t-t'\,|\,\Gamma)-\tilde{G}_0(t-t'\,|\,\Gamma)]\Gamma_q(t')dt' \qquad \text{(I.3)}$$

which may be considered as linear once the kernel $\tilde{G}_q$ has been determined from the solution of Eq. (I.2). Let us point out the non-Boltzmann character of this equation: in particular the $\Gamma$ dependence of the non-Markoffian kernel is typical of a system with a discrete unperturbed spectrum. Approximate solution of Eqs. (I.2) and (I.3), as well as a comparison with previous work, will be considered in the following paper of this series.

Finally, a few formal proofs have been relegated to appendices.

## II. THE GENERAL FORMALISM

We consider a system of $N$ spins $|S|=\frac{1}{2}$ $(1,2,\cdots j,\cdots N)$ fixed on the sites of a three-dimensional lattice. In the absence of an external field, it is described by the Heisenberg Hamiltonian ($\hbar=1$):

$$H=-\sum_{i\neq j} J(i-j)[S_i{}^zS_j{}^z+S_i{}^+S_j{}^-], \qquad \text{(II.1)}$$

where $J(i-j)$ is the exchange integral between the lattice points $i$ and $j$ and where the spin operators obey the well-known commutation relations (see for instance Refs. 1 and 2):

$$\begin{aligned}[S_i{}^z,S_j{}^\pm]&=\pm S_i{}^\pm\delta^{\mathrm{Kr}}{}_{i,j},\\ [S_i{}^+,S_j{}^-]&=2S_i{}^z\delta^{\mathrm{Kr}}{}_{i,j}.\end{aligned} \qquad \text{(II.2)}$$

If we work in the localized spin representation

$$|m\rangle\equiv\prod_i |m_i\rangle, \qquad \text{(II.3)}$$

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

[6] H. Mori and K. Kawazaki, Progr. Theoret. Phys. (Kyoto) **27**, 529 (1962).

[7] H. Bennett and P. C. Martin, Phys. Rev. **138**, 607 (1965).

[8] See for instance: I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962); P. Résibois, Physica **27**, 541 (1961).

where

$$S_i{}^z|m_i\rangle=m_i|m_i\rangle \quad (m_i=\pm\tfrac{1}{2}) \tag{II.4}$$

describes a state where spin $i$ has the $z$ component $m_i$, we may rewrite the autocorrelation functions (I.1) as

$$\Gamma_{ab}{}^{\alpha\beta}(t)=\sum_{m,m'}\langle m|S_a{}^\alpha|m'\rangle\langle m'|\rho^\beta(t|b)|m\rangle. \tag{II.5}$$

In this formula we have formally introduced the following quantity, closely related to a density matrix:

$$\rho^\beta(t|b)=\exp(-iHt)S_b{}^\beta\rho^{\rm eq}\exp(iHt) \tag{II.6}$$

with

$$\rho^{\rm eq}=e^{-\beta H}/{\rm Tr}e^{-\beta H}. \tag{II.7}$$

From Eq. (II.6) we see at once that $\rho^\beta(t|b)$ obeys the von Neumann equation which is written in the $|m\rangle$ representation

$$i\partial_t\langle m|\rho^\beta(t|b)|m'\rangle=\lambda\langle m|[H,\rho^\beta(t|b)]|m'\rangle. \tag{II.8}$$

(We have introduced a counting parameter $\lambda$, which we shall set equal to 1 at the end of the calculation.) Equation (II.8) is subject to the initial condition

$$\langle m|\rho^\beta(0|b)|m'\rangle=\langle m|S_b{}^\beta\rho^{\rm eq}|m'\rangle. \tag{II.9}$$

We now rewrite Eq. (II.8) using the following definition valid for any operator $A$ (see also Ref. 8):

$$\langle m|A|m'\rangle\equiv A_{m-m'}(\tfrac{1}{2}(m+m'))=A_\mu(M). \tag{II.10}$$

Here

$$\begin{aligned}\mu&=m-m',\\ M&=\tfrac{1}{2}(m+m'),\end{aligned} \tag{II.11}$$

define a new set of variables for each spin $j$ ($M=(M_1\cdots M_j\cdots M_n)$; $\mu=(\mu_1\cdots\mu_j\cdots\mu_n)$). It is then an easy matter to express Eq. (II.8) in terms of these variables; we obtain

$$\begin{aligned}&i\partial_t\rho_\mu{}^\beta(M;t|b)\\ &=\lambda\sum_{\mu'}[H_{\mu-\mu'}(M+\tfrac{1}{2}\mu')\rho_{\mu'}{}^\beta(M+\tfrac{1}{2}(\mu'-\mu);t|b)\\ &\quad-H_{\mu-\mu'}(M-\tfrac{1}{2}\mu')\rho_{\mu'}{}^\beta(M-\tfrac{1}{2}(\mu'-\mu);t|b)],\end{aligned} \tag{II.12}$$

where the summation over $\mu'$ runs over all possible values 1, 0, −1 (indeed, $\mu_j'=m_j'-m_j''=1,0,-1$).

If we now introduce a displacement operator $\eta^{\pm\mu}$ which acts on an arbitrary function of $M$ in the following way

$$\eta^{\pm\mu}f(M)=f(M\pm\mu/2), \tag{II.13}$$

we can cast Eq. (II.12) into the following form

$$i\partial_t\rho_\mu{}^\beta(M;t|b)=\lambda\sum_{\mu'}\langle\mu|\mathcal{H}(M)|\mu'\rangle\rho_{\mu'}{}^\beta(M;t|b), \tag{II.14}$$

where the "Liouville–von Neumann" operator is defined by

$$\begin{aligned}&\langle\mu|\mathcal{H}(M)|\mu'\rangle\\ &\quad=\eta^{\mu'}H_{\mu-\mu'}(M)\eta^{-\mu}-\eta^{-\mu'}H_{\mu-\mu'}(M)\eta^{\mu}.\end{aligned} \tag{II.15}$$

In the case of a quantum gas, it has been shown that (II.14) is the strict quantum analog of the classical Liouville equation[8]; here, we have of course no such analogy, but it remains nevertheless very useful to use the compact form (II.14) instead of the explicit commutator involved in (II.8); as we shall see later, many properties which depend explicitly upon the fact that we are interested in the density matrix (and not in the wave function) are easily established in this formalism.

Using Eqs. (II.1), (II.2), (II.3), and (II.10), it is a matter of elementary algebra to obtain the expression for the matrix elements (II.15)

$$\langle\mu|\mathcal{H}(M)|\mu'\rangle=\sum_{i\neq j}\langle\mu|\mathcal{H}_{ij}(M)|\mu'\rangle,$$

where we can split the two-spin operator $\mathcal{H}_{ij}$ into a transverse and a longitudinal part

$$\begin{aligned}&\langle\mu|\mathcal{H}_{ij}(M)|\mu'\rangle\\ &\quad=\langle\mu|\mathcal{H}_{ij}{}^{+-}(M)|\mu_i-1,\mu_j+1,\{\mu\}'\rangle\\ &\qquad\times\delta^{\rm Kr}{}_{\mu_i-1,\mu_i'}\delta^{\rm Kr}{}_{\mu_j+1,\mu_j'}\delta^{\rm Kr}{}_{\{\mu\}',\{\mu'\}'}\\ &\qquad+\langle\mu|\mathcal{H}_{ij}{}^{zz}(M)|\mu\rangle\delta^{\rm Kr}{}_{\mu_i,\mu_i'}\delta^{\rm Kr}{}_{\mu_j,\mu_j'}\delta^{\rm Kr}{}_{\{\mu\}',\{\mu'\}'},\end{aligned} \tag{II.16}$$

with

$$\begin{aligned}&\langle\mu|\mathcal{H}_{ij}{}^{+-}(M)|\mu_i-1,\mu_j+1,\{\mu\}'\rangle\\ &\quad=-J(i-j)[\eta^{\mu_i-1}\eta^{\mu_j+1}\delta^{\rm Kr}{}_{M_i,0}\delta^{\rm Kr}{}_{M_j,0}\eta^{-\mu_i}\eta^{-\mu_j}\\ &\qquad-\eta^{-\mu_i+1}\eta^{-\mu_j-1}\delta^{\rm Kr}{}_{M_i,0}\delta^{\rm Kr}{}_{M_j,0}\eta^{\mu_i}\eta^{\mu_j}]\end{aligned} \tag{II.17}$$

and

$$\langle\mu|\mathcal{H}_{ij}{}^{zz}(M)|\mu\rangle=-J(i-j)[\mu_iM_j+\mu_jM_i]. \tag{II.18}$$

Equation (II.17) expresses the fact that the transverse part of the Heisenberg Hamiltonian describes a "flip-flop" process, where the quantum numbers of spins $i$ and $j$ respectively change by −1 and +1, while in Eq. (II.18) the absence of displacement operators exhibits the diagonal character of the longitudinal part of the Heisenberg Hamiltonian.

Since we are interested in a system with spin $|S|=\frac{1}{2}$, the only possible values of $\mu$ are $\mu=-1,0,+1$; thus, the only nonvanishing matrix elements in (II.17) are of the following type:

$\mu_i=0,\ \mu_j=0$:

$$\begin{aligned}&\langle 0_i,0_j,\{\mu\}'|\mathcal{H}_{ij}{}^{+-}|-1_i,1_j,\{\mu\}'\rangle\\ &\qquad=-J(i-j)\eta_{ij}\delta^{\rm Kr}{}_{M_i,0}\delta^{\rm Kr}{}_{M_j,0},\end{aligned} \tag{II.19a}$$

$\mu_i=1,\ \mu_j=-1$:

$$\begin{aligned}&\langle 1_i,-1_j,\{\mu\}'|\mathcal{H}_{ij}{}^{+-}|0_i,0_j,\{\mu\}'\rangle\\ &\qquad=-J(i-j)\delta^{\rm Kr}{}_{M_i,0}\delta^{\rm Kr}{}_{M_j,0}\eta_{ij},\end{aligned} \tag{II.19b}$$

$\mu_i=1,\ \mu_j=0$:

$$\begin{aligned}&\langle 1_i,0_j,\{\mu\}'|\mathcal{H}_{ij}{}^{+-}|0_i,1_j,\{\mu\}'\rangle\\ &\qquad=-J(i-j)\delta^{\rm Kr}{}_{M_i,0}\eta_{ij}\delta^{\rm Kr}{}_{M_j,0},\end{aligned} \tag{II.19c}$$

$\mu_i=0,\ \mu_j=-1$:

$$\begin{aligned}&\langle 0_i,-1_j,\{\mu\}'|\mathcal{H}_{ij}{}^{+-}|-1_i,0_j,\{\mu\}'\rangle\\ &\qquad=-J(i-j)\delta^{\rm Kr}{}_{M_j,0}\eta_{ij}\delta^{\rm Kr}{}_{M_i,0},\end{aligned} \tag{II.19d}$$

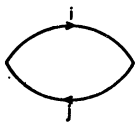


FIG. 1. A simple second-order term.

where we have used the shortened notation

$$\eta_{ij}=\eta^{-1_i}\eta^{+1_j}-\eta^{+1_i}\eta^{-1_j}. \tag{II.20}$$

It should be noted that the only difference between the four matrix elements of Eqs. (II.19a)–(II.19d) is the position of the Kronecker delta functions $\delta^{\mathrm{Kr}}{}_{M_i,0}$ and $\delta^{\mathrm{Kr}}{}_{M_j,0}$: the rule is that each of these functions appears on the side where the corresponding $\mu$ number is not vanishing.

The formal solution of Eq. (II.14) is easy to obtain; because the Heisenberg Hamiltonian is time-independent, the time integrals are trivial to perform, and it is thus convenient to keep the time-dependent formalism; we get

$$\rho_\mu{}^\beta(M;t|b)=\sum_{n=0}^{\infty}\left(\frac{\lambda}{-i}\right)^n\int_0^t d\tau^n \times\sum_{\mu'}\langle\mu|[\mathfrak{IC}(M)]^n|\mu'\rangle\rho_{\mu'}{}^\beta(M;0|b). \tag{II.21}$$

We have introduced the symbol

$$\int_0^t d\tau^n f(\tau_1\cdots\tau_n) \equiv\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{n-1}}d\tau_n f(\tau_1\cdots\tau_n); \tag{II.22}$$

with $f(\tau_1\cdots\tau_n)=1$, we have thus

$$\int_0^t d\tau^n=t^n/n!. \tag{II.22'}$$

Equation (II.21) will be the starting point of our analysis of the spin autocorrelation function. However, before attacking this problem, we wish to close this section with a few general results which will be useful in the following.

First, we recall the well-known fact that in the absence of external field and above the critical point, the symmetry of rotation of the system implies that

$$\Gamma_{ab}{}^{+-}(t)=2\Gamma_{ab}{}^{zz}(t)=\tfrac{1}{2}\Gamma_{ab}(t), \tag{II.23}$$

where

$$\Gamma_{ab}(t)=[\Gamma_{ab}{}^{+-}(t)+\Gamma_{ab}{}^{zz}(t)]/S(S+1). \tag{II.24}$$

Equation (II.23) is a useful relation connecting the longitudinal and transverse components of the autocorrelation functions.

Second, we remark that all we really need is a *reduced* density matrix; indeed, using the notation (II.10), Eq. (II.5) may be written

$$\Gamma_{ab}{}^{zz}(t)=\sum_{\{M\}}M_a\rho_0{}^z(\{M\};t|b) \tag{II.25}$$

for the longitudinal component, and

$$\Gamma_{ab}{}^{+-}(t)=\sum_{\{M\}}\delta^{\mathrm{Kr}}{}_{M_a,0}\rho^{-}{}_{-1_a}(\{M\};t|b), \tag{II.26}$$

for the transverse component.

In Eq. (II.25), each $M_i$ only takes the values $+\frac{1}{2}$ and $-\frac{1}{2}$ [indeed, since $\mu_i=0$, $m_i=m_i'$, and thus $M_i=\frac{1}{2}(m_i+m_i')=\pm\frac{1}{2}$]; we have thus

$$\Gamma_{ab}{}^{zz}(t)=\tfrac{1}{2}[\rho^z(\tfrac{1}{2};t|ab)-\rho^z(-\tfrac{1}{2};t|ab)], \tag{II.27}$$

where the one-spin density matrix

$$\rho^z(M_a;t|ab)=\sum_{\{M_i\neq a\}}\rho_0{}^z(\{M\};t|b) \tag{II.28}$$

is obtained by taking the trace over each spin except $a$. Similarly, we get from Eq. (II.26)

$$\Gamma_{ab}{}^{+-}(t)=\rho^-(0;t|ab), \tag{II.29}$$

where the reduced density matrix $\rho^-$ is defined by

$$\rho^-(M_a;t|ab)=\sum_{\{M_i\neq a\}}\rho^{-}{}_{-1_a}(\{M\};t|b). \tag{II.30}$$

As we shall need this result in Sec. IV, let us finally write this function in a more explicit form; using Eqs. (II.9) and (II.21) we get

$$\rho^-(M_a;t|ab)=\sum_{\{M_i\neq a\}}\sum_{n=0}^{\infty}\left(\frac{\lambda}{-i}\right)^n\int_0^t d\tau^n \times\sum_{\{\mu'\}}\langle-1_a,\{0\}'|[\mathfrak{IC}(M)]^n|-1_b+\mu_b',\{\mu'\}'\rangle \times\delta^{\mathrm{Kr}}{}_{M_b,-\frac{1}{2}\mu' b}\rho\{\mu'\}^{\mathrm{eq}}(M_b+\tfrac{1}{2},\{M\}'). \tag{II.31}$$

## III. DIAGRAM TECHNIQUE–GENERAL THEOREMS IN THE HIGH-TEMPERATURE LIMIT

In order to analyze the formal expansion (II.21), it is very useful to have a diagrammatic representation for each contribution. Let us consider for instance the second-order contribution with $\mu'=0$ and $\alpha=z$:

$$\rho_0{}^{z(2)}(M;t|b)=\left(\frac{\lambda}{-i}\right)^2\sum_{i\neq j}\int_0^t d\tau^2 \times\sum_{\mu}\langle 0|\mathfrak{IC}_{ij}|\mu\rangle\langle\mu|\mathfrak{IC}_{ij}|0\rangle\rho_0{}^z(M;0|b). \tag{III.1}$$

From the rule (II.16), we see that only the transverse interactions contribute:

$$\rho_0{}^{z(2)}(M;t|b)=\left(\frac{\lambda}{-i}\right)^2\sum_{i\neq j}\int_0^t d\tau^2\langle 0|\mathfrak{IC}_{ij}{}^{+-}|-1_i,+1_j\rangle \times\langle-1_i,+1_j|\mathfrak{IC}_{ji}{}^{+-}|0\rangle\rho_0{}^z(M;0|b). \tag{III.2}$$

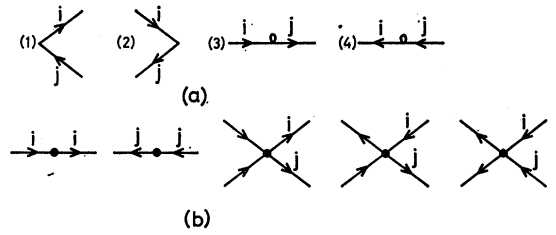


FIG. 2. The elementary vertices: (a) transverse vertices; (b) longitudinal vertices.

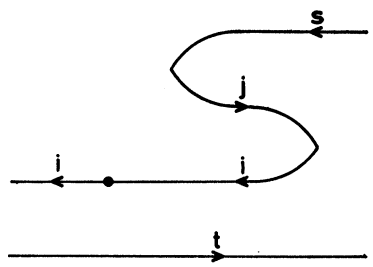


FIG. 3. A typical graph of order $\lambda^3$ ($\{\mu'\}=1_s,-1_t,\{0\}'$).

Reading this contribution from right to left, we thus start from a diagonal state $\mu=0$; a first transition brings the system to a nondiagonal state $\mu_i=-1$, $\mu_j=+1$ and a second transition brings it back to the diagonal state. We shall represent a state with $\mu_i=\pm1$ by a plain line with an arrow pointing to the left if $\mu_i=+1$ or to the right if $\mu_i=-1$; the contribution (III.2) will thus be represented by the graph of Fig. 1. The contribution associated with this graph is, using (III.2) and (II.19),

$$\rho_0{}^{z(2)}(M;t|b)=\left(\frac{\lambda}{-i}\right)^2\sum_{i\neq j}\int_0^t d\tau^2[-J(i-j)]^2 \times(\eta_{ij}\delta^{\mathrm{Kr}}{}_{M_i,0}{}^2\delta^{\mathrm{Kr}}{}_{M_j,0}{}^2\eta_{ji})\rho_0{}^z(M;0|b). \quad \text{(III.3)}$$

An important point should be stressed: because of the structure of the matrix elements (II.19), we see that the $\delta^{\mathrm{Kr}}{}_{M_i,0}$ functions are situated between the two $\eta_{ij}$ operators precisely as the plain lines are between the two vertices; we can thus put each plain line in one-to-one correspondence with a factor $\delta^{\mathrm{Kr}}{}_{M_i,0}$. This property is quite general.

In more complicated cases, we shall have in Eq. (II.21) a series of transitions which bring the system through the states $|\mu'\rangle\rightarrow|\mu''\rangle\rightarrow\cdots\rightarrow|\mu\rangle$. Correspondingly, we shall represent the initial state by a certain number of arrowed lines corresponding to the different $\mu_i'\neq0$ and then each interaction will be represented by a vertex, either transverse or longitudinal, as shown in Fig. 2. The difference between the loop (transverse vertex) and the dots (longitudinal vertex) should be noticed. An example of a more complicated graph is given in Fig. 3. It is readily realized that there exists a one-to-one correspondence between each diagram and a term in Eq. (II.21). However, we shall not, at this stage, give the rules to compute the contribution associated with a diagram because we want first to take advantage of the fact that we are interested only in a reduced density matrix, as was stressed at the end of Sec. II.

As an example, let us construct the reduced density matrix (II.27) corresponding to the contribution (III.1) or (III.3). We get

$$\rho^{z(2)}(M_a;t|ab)=\sum_{\{M_{s\neq a}\}}\left(\frac{\lambda}{-i}\right)^2\int_0^t d\tau^2 \times\sum_{i\neq j}[-J(i-j)]^2(\eta_{ij}\delta^{\mathrm{Kr}}{}_{M_i,0}\delta^{\mathrm{Kr}}{}_{M_j,0}\eta_{ji})\rho_0{}^z(M;0|b). \quad \text{(III.4)}$$

We see at once that this expression vanishes if both indices $i$ and $j$ are different from $a$; indeed, leaving out unimportant factors and using (II.13) and (II.20) we have then

$$\begin{aligned}&\sum_{M_i}\sum_{M_j}\eta_{ij}\delta^{\mathrm{Kr}}{}_{M_i,0}\delta^{\mathrm{Kr}}{}_{M_j,0}\eta_{ji}\rho_0{}^z(M;0|b)\\&=\sum_{M_i}\sum_{M_j}(\eta^{-1i}\eta^{1j}-\eta^{1i}\eta^{-1j})\delta^{\mathrm{Kr}}{}_{M_i,0}\delta^{\mathrm{Kr}}{}_{M_j,0}\eta_{ji}\rho_0{}^z(M;0|b)\\&=\sum_{M_i}\sum_{M_j}[\delta^{\mathrm{Kr}}{}_{M_i-\frac{1}{2},0}\delta^{\mathrm{Kr}}{}_{M_j+\frac{1}{2},0}\eta_{ji}\rho_0{}^z(M-1_i/2+1_j/2;0|b)-\delta^{\mathrm{Kr}}{}_{M_i+\frac{1}{2},0}\delta^{\mathrm{Kr}}{}_{M_j-\frac{1}{2},0}\eta_{ji}\rho_0{}^z(M+1_i/2-1_j/2;0|b)]\\&=[\eta_{ji}\rho_0{}^z(M;0|b)]_{M_i=0,M_j=0}-[\eta_{ji}\rho_0{}^z(M;0|b)]_{M_i=0,M_j=0}=0.\end{aligned} \quad \text{(III.5)}$$

We have given this calculation in detail because it illustrates, in a very simple case, the algebra that is involved in the present formalism. In the following, we shall be much briefer, since the technique will always be similar.

Of course, we have not the same results if either $i$ or $j$ is identical to $a$, because then no summation appears over $M_i$ (or $M_j$); we are thus left with

$$\rho^{z(2)}(M_a;t|ab)=\sum_{\{M_{s\neq a}\}}\left\{\left(\frac{\lambda}{-i}\right)^2\sum_{i\neq a}\int_0^t d\tau^2[J(i-a)]^2[\eta_{ia}\delta^{\mathrm{Kr}}{}_{M_i,0}\delta^{\mathrm{Kr}}{}_{M_a,0}\eta_{ai}] +\left(\frac{\lambda}{-i}\right)^2\sum_{j\neq a}\int_0^t d\tau^2[J(j-a)]^2[\eta_{aj}\delta^{\mathrm{Kr}}{}_{M_j,0}\delta^{\mathrm{Kr}}{}_{M_a,0}\eta_{ja}]\right\}\rho_0{}^z(M;0|b). \quad \text{(III.6)}$$

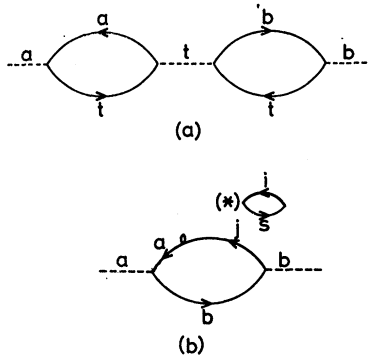


FIG. 4. Examples of graphs with semiconnection bonds.

This result can be generalized in a theorem:

*Theorem I* (theorem of the trace): *If any vertex in the expansion (II.21) involves two spins which are both different from a and which do not appear again on the left of this vertex, the corresponding contribution vanishes identically.*

The proof of this theorem is trivial and follows exactly the steps indicated in Eq. (III.5).

We see, thus, that it is extremely important to know whether a spin $i$ which appears at a given vertex will still interact at other vertices, even if in some intermediate state it has a vanishing $\mu_i$. In order to introduce this idea into the diagram technique, let us define a *semiconnection bond:* it will be represented by a dashed line and will appear whenever a spin is in a state $\mu=0$, between two states where it interacts. An exception will be made for spins $b$ and $a$ which will respectively start (at $t=0$) and end (at time $t$) with such a dashed line. Examples will be found in Fig. 4.

Theorem I finds then a very simple translation in terms of diagrams: any graph which contains a vertex which is neither connected nor semiconnected to its left vanishes identically. This is the case for the diagram of Fig. 4(b) where the starred vertex is of a vanishing type.

Although we shall soon find stronger restrictions on the possible graphs for the high-temperature case, let us now state the rules which allow us to establish the connection between a given graph and its contribution to the reduced density matrix (II.27):

(1) Draw all possible different graphs ending with a dotted line $a$, consistent with the initial condition (II.9) and with the various elementary vertices of Fig. 2, and including all possible semiconnection bonds. Each vertex should be either connected or semiconnected on its left.

(2) For each graph, associate a factor $\delta^{\mathrm{Kr}}{}_{M_i,0}$ to each plain line.

(3) Associate an operator $-J(i-j)\eta_{ij}$ to each transverse vertex, and a factor $-2J(i-j)[\mu_i M_j+\mu_j M_i]$ to each longitudinal vertex.[9] The operators and the Kronecker delta functions are ordered as they appear in the graph.

(4) Multiply on the right by the initial condition $\rho_\mu{}^z(M;0|b)$.

(5) Multiply by $(\lambda/i)^n\int_0^t d\tau^n$ for a graph of order $n$.

(6) Take the trace $(\sum_{M_i}\cdots)$ over all spins different from $a$.

(7) Sum over all possible indices different from $a$ and $b$.

As an example, we give the contribution corresponding to Fig. 4(a):

$$\rho^{z(4a)}(M_a;t|ab)=\sum_{\{M_{s\neq a}\}}\left(\frac{\lambda}{i}\right)^4\int_0^t d\tau^4 \times\sum_t(-J_{ta})^2[\eta_{ta}\delta^{\mathrm{Kr}}{}_{M_t,0}\delta^{\mathrm{Kr}}{}_{M_a,0}\eta_{at}](-J_{tb})^2 \times[\eta_{bt}\delta^{\mathrm{Kr}}{}_{M_t,0}\delta^{\mathrm{Kr}}{}_{M_b,0}\eta_{tb}]\rho_0{}^z(\{M\};0|b). \quad \text{(III.7)}$$

The results we have obtained up to now are quite general; in fact Theorem I is the analog in the spin case of a similar result in gases,[10] and the rules given above would only be slightly modified in the presence of a magnetic field.

We shall now be more specific and establish a few other theorems which are valid only in the absence of external field and above the critical point. We shall even be more specific by taking immediately the high-temperature limit $\beta ZJ=0$ which we want to consider in detail later. In this limit, the equilibrium distribution (II.7) becomes simply

$$\rho^{\mathrm{eq}}=(\tfrac{1}{2})^N, \quad \text{(III.8)}$$

and we thus obtain for the initial condition (II.9) when $\alpha=z$:

$$\rho_\mu{}^z(M;0|b)=M_b(\tfrac{1}{2})^N\delta^{\mathrm{Kr}}{}_{\mu,0}. \quad \text{(III.9)}$$

*Theorem II: In the high-temperature limit, the graphs which give a nonvanishing contribution contain only*

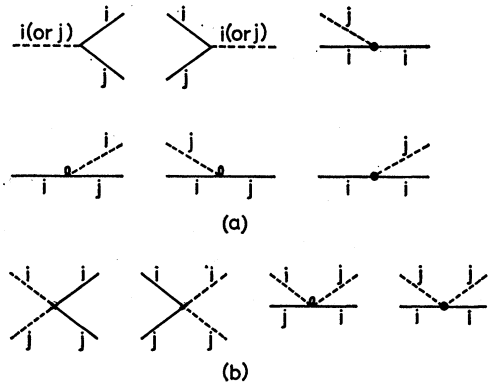


FIG. 5. Nonvanishing elementary vertices in the high-temperature limit: (a) vertices with one semiconnection bond; (b) vertices with two semiconnection bonds.

[9] The factor 2 in front comes from the two possibilities of a longitudinal interaction between the same pair of spins in Eq. (II.18).

[10] I. Prigogine and R. Balescu, Physica **25**, 281 (1959); **25**, 302 (1959).

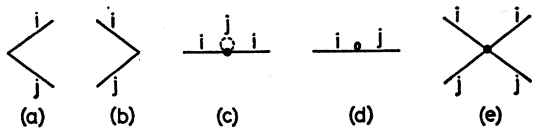


FIG. 6. Vertices not contributing in the high-temperature limit.

*vertices which are at least once semiconnected to the rest of the diagram.*

In other words, if we explicitly draw the semiconnection bonds, the only elementary vertices which have to be retained are those of Figs. 5(a), 5(b) where, for simplicity, we have not drawn the arrows on the plain lines. On the contrary, all graphs involving at least one vertex of the type shown in Fig. 6 vanish identically. This theorem is established by showing that whenever a vertex of the type indicated in Fig. 6 appears in a graph, the corresponding contribution vanishes identically. For Fig. 6(a), this is merely a restatement of Theorem I; the other cases are briefly discussed in Appendix A, where the calculations are always based on identities of the type (III.5). Physically, the theorem expresses the fact that in the absence of total magnetization, a given spin gives no global effect when it interacts only once with the rest of the system.

Of major importance in the further developments of the theory are the following corollaries of Theorem II:

(1) *Corollary I:* All nonvanishing contributions are of even order in $n$.

(2) *Corollary II:* In the limit where the number of neighbors becomes large ($Z\to\infty$), the dominant terms in $\lambda^{2n}$ are of order $\lambda^2(\lambda^2 Z)^{n-1}$ for the indirect autocorrelation function ($a\neq b$) and of order $(\lambda^2 Z)^n$ for the direct autocorrelation function ($a=b$).

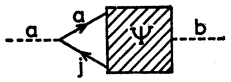


FIG. 7. Schematic picture of the contributions to $\rho^z(M_a;t|ab)$.

The formal proof of these properties is given in Appendix B; the result is however quite obvious once it is noticed that each spin must at least interact twice in any nonvanishing graph.

(3) *Corollary III:* The two diagonal matrix elements of the reduced density matrix (II.27) are connected by the very simple relation:

$$\rho^z(\tfrac{1}{2};t|ab)=-\rho^z(-\tfrac{1}{2};t|ab)=\Gamma_{ab}{}^{zz}(t)\,. \quad \text{(III.10)}$$

We only have to establish the first equality; the second then follows immediately from Eq. (II.26). We first notice that the first vertex on the left in any graph is necessarily of the type shown in Fig. 7; indeed the only possible transitions having $\{\mu\}=\{0\}$ on their left have to involve the dashed line corresponding to particle $a$ (for simplicity, we choose one direction of the arrows). No specification whatsoever is made about the remaining interactions which are schematized by a box. When all the operations involved in this box are performed, the result is a function of the set of numbers $\{M\}$; we denote it by $\Psi(\{M\})$. Thus, using Eq. (II.19a) and leaving aside the unimportant time factors, we find

$$\rho^z(M_a;t|ab)\sim\sum_{\{M_{s\neq a}\}}\sum_j[-J(a-j)]\eta_{aj}\delta^{\mathrm{Kr}}{}_{M_a,0}\delta^{\mathrm{Kr}}{}_{M_j,0}\Psi(\{M\})\,. \quad \text{(III.11)}$$

Using (II.20) and performing explicitly the displacement operations, we get

$$\rho^z(M_a;t|ab)\sim\sum_{\{M_{s\neq a}\}}\sum_j[-J(a-j)]\{\delta^{\mathrm{Kr}}{}_{M_a+\frac{1}{2},0}\delta^{\mathrm{Kr}}{}_{M_j-\frac{1}{2},0}\Psi(M_1,\cdots,M_a+\tfrac{1}{2},\cdots,M_j-\tfrac{1}{2},\cdots M_N)$$
$$-\delta^{\mathrm{Kr}}{}_{M_a-\frac{1}{2},0}\delta^{\mathrm{Kr}}{}_{M_j+\frac{1}{2},0}\Psi(M_1,\cdots,M_a-\tfrac{1}{2},\cdots,M_j+\tfrac{1}{2},\cdots M_N)\}\,. \quad \text{(III.12)}$$

If $M_a=+\frac{1}{2}$, only the second term in (III.12) survives; on the other hand, if $M_a=-\frac{1}{2}$, only the first term remains; as they are equal and of opposite sign, Eq. (III.10) is true.

This demonstration shows very clearly the advantage we have gained in using a formalism in which the commutators are treated in a compact manner; indeed, the property (III.10) is typically a result valid only for the reduced density matrix, and which would be more difficult to prove in a formalism based on the Schrödinger equation.

## IV. REORGANIZATION OF THE PERTURBATION SCHEME

Even in the Weiss limit, it is of course an impossible task to sum all the graphs contributing to the autocorrelation function (I.1). Only in the limit of short times can we get a simple exact result; indeed, as is apparent from Eq. (II.22), each $\lambda$ factor is accompanied by a $t$ factor, and provided that

$$\lambda^2 Z t^2\ll 1\,, \quad \text{(IV.1)}$$

the series (II.21) converges term by term. For instance, the first contribution to $\Gamma_{ab}{}^{zz}(t)$ is given by the graph of Fig. 8 and behaves like $\lambda^2 t^2$. However, for times such that

$$\lambda^2 Z t^2\gtrsim 1 \quad \text{(IV.2)}$$

the series (II.21) is no longer converging, and we have then to perform some kind of partial "resummation" in order to get an asymptotic series which remains meaningful in this limit (IV.2). In order to get some hint of an adequate resummation procedure, let us compare

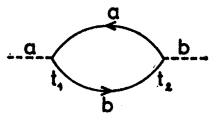


FIG. 8. The simplest contribution to $\Gamma_{ab}^{zz}(t)$.

the Born approximation as pictured in Fig. 8 with the corresponding Born approximation in the case of a dilute gas, where the Boltzmann equation is known to hold.[8] In this latter case, the transition probability in a two-particle collision is of the form

$$P^{\text{gas}}\sim\lambda^2 t 2\pi\delta(E_i-E_f)\,, \tag{IV.3}$$

$E_i$ and $E_f$ being, respectively, the energies of the two particles before and after the collision process. Clearly, the delta function expressing the conservation of energy plays the role of a collision time $\tau_c\sim(E_i-E_f)^{-1}$, and we thus have

$$P^{\text{gas}}\sim\lambda^2 t\tau_c\,. \tag{IV.4}$$

In contrast, in the spin problem we find

$$P^{\text{spin}}\sim\lambda^2 t^2\,. \tag{IV.5}$$

Comparing Eqs. (IV.4) and (IV.5), we see that the $t^2$ factor in the spin transition probability corresponds to the fact that the duration of the collision between the two neighboring spins is arbitrarily large; indeed, two spins fixed on neighboring lattice sites remain there forever and can thus interact at any time. On the contrary, in the case of a gas, two colliding molecules will separate after a short time $\tau_c$ and will not interact with each other later on.

Yet, it is not physically satisfactory to consider two given spins as completely isolated from the rest of the system for such a long time $t$; we expect rather that during the time interval $(t_1-t_2)$ both spins $a$ and $b$ will interact with the "bath" made of the remaining spins. By this mechanism, the information that was put on spins $a$ and $b$ at time $t_2$ will dissipate in the bath; if the time interval $(t_1-t_2)$ is larger than some time $\tau_d$, characteristic of this dissipation, the interaction between spins $a$ and $b$ at time $t_1$ will become completely inefficient, leaving thus an "effective" transition probability of the form

$$\tilde{P}^{\text{spin}}\sim\lambda^2 t\tau_d\,. \tag{IV.6}$$

In other words, we expect that, in the real physical process involving the two given spins $a$ and $b$, the "free spin propagator," as represented by the plain lines of Fig. 8 should be replaced by the *direct* correlation function $\Gamma_{aa}{}^{+-}(t_1-t_2)$ [or $\Gamma_{bb}{}^{+-}(t_1-t_2)$] which is precisely the quantity measuring the dissipation of the information put on spin $a$ [or $b$] at time $t_2$. This physically appealing assumption can be formalized in a theorem: let us define the "skeleton" of a given graph as the diagram which is obtained by cutting off all the "self-energy insertions" on the plain lines; a self-energy insertion is defined as a part of graph which starts with one plain line and ends with the *same* plain line[11] (the same spin index should appear on the ingoing and outgoing plain lines). An example is shown in Fig. 9(a); in contrast, the starred part in Fig. 9(b) is not a self-energy part because $i\neq a$.

We have then

*Theorem III: In the high temperature region ($\beta ZJ\to 0$) and in the Weiss limit ($Z\to\infty$), the whole series of graphs giving the expansion (II.21) may be obtained by taking the sum of all skeleton graphs, where every plain line should be replaced by a heavy line, representing the sum of all possible self-energy parts. The corresponding analytical contribution is obtained by applying the rules of Sec. III to these skeletons, with the sole exception that to each heavy line starting at $t=t_1$ and ending at $t=t_2$, we now associate a factor $\Gamma(t_1-t_2)\delta^{\text{Kr}}{}_{M_a,0}$ [cf. Eq. (II.23)] instead of the factor $\delta^{\text{Kr}}{}_{M_a,0}$ associated with a plain line.*

The demonstration of the first part of the theorem, which is of purely topological character, is trivial once it is recognized that, in the Weiss limit, the contributions where one spin appearing in the self-energy also appears elsewhere (and vice versa) are of order $Z^{-1}$ and may thus be neglected. For instance, with the heavy line of Fig. 10(a) inserted in Fig. 10(b) we obviously generate an infinite class of graphs appearing in the initial perturbation expansion.

The second part of the theorem is more subtle because the heavy line, when computed according to the rules of Sec. III, is in principle an *operator*, which, when inserted in a skeleton, acts on whatever stands on its right. In order to prove that it may be replaced by $\Gamma(t_1-t_2)\delta^{\text{Kr}}{}_{M_a,0}$, let us provisionally neglect the time-dependent factors and concentrate on the matrix elements.

The general structure of the contribution of a heavy line (which we shall also call a "renormalized propagator"; see footnote 11), may be calculated according to the rules of Sec. IV; leaving out the time factors, it is an operator which we may write formally, in the case

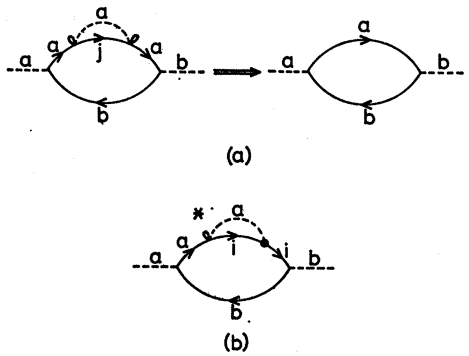


FIG. 9. Examples of skeleton: (a) a graph and its skeleton; (b) a graph which is its own skeleton.

[11] Although we clearly expect the self-energy parts to be purely dissipative, we shall nevertheless use the usual nomenclature of the $N$-body problem.

$\mu_a=-1$, as

$$\delta^{\mathrm{Kr}}{}_{M_a,0}\bar{\Psi}(M_a,\{M_{i_a}\})\delta^{\mathrm{Kr}}{}_{M_a,0}, \qquad \text{(IV.7)}$$

where

$$\bar{\Psi}(M_a,\{M_{i_a}\})=\sum_{n=0}^{\infty}\binom{\lambda}{i}^n \times\langle -1_a,\{0\}'|[\mathfrak{K}(M_a,\{M_{i_a}\})]^n|-1_a,\{0\}'\rangle. \qquad \text{(IV.8)}$$

We have factored out in (IV.7) two Kronecker functions because any renormalized propagator has to start and to end with a plain line $a$; moreover, in Eq. (IV.8), $M_{i_a}$ denotes the quantum number of any spin $i_a$ that explicitly appears in the self-energy insertion. If we now consider the effect of inserting such a renormalized propagator in an arbitrary skeleton, we may express the corresponding contribution in the very schematic fashion:

$$C=\sum_{\cdots}\sum_{M_a}\sum_{\{M_{i_a}\}}\cdots[\delta^{\mathrm{Kr}}{}_{M_a,0}\bar{\Psi}(M_a,\{M_{i_a}\})\delta^{\mathrm{Kr}}{}_{M_a,0}]\cdots \rho_0{}^{\mathrm{eq}}(\{M\}), \qquad \text{(IV.9)}$$

where the dots indicate the part of the contribution $C$ which is not the particular insertion under consideration.

In (IV.9) we know that spins $i_a$ do not appear either on the right or on the left of $\bar{\Psi}$ because this would lead to negligible contributions in the Weiss limit. We may thus shift the summation over $\{M_{i_a}\}$ immediately after the first $\delta^{\mathrm{Kr}}{}_{M_a,0}$; similarly the initial condition $\rho_0(\{M_{i_a}\})$ may be factored out and put on the left of the second Kronecker delta:

$$C=\sum_{\cdots}\sum_{M_a}\cdots[\delta^{\mathrm{Kr}}{}_{M_a,0}\sum_{\{M_{i_a}\}}\bar{\Psi}(M_a,\{M_{i_a}\}) \times\rho_0{}^{\mathrm{eq}}(\{M_{i_a}\})\delta^{\mathrm{Kr}}{}_{M_a,0}]\cdots\rho_0{}^{\mathrm{eq}}(\{M_{j\neq i_a}\}). \qquad \text{(IV.10)}$$

Using the property Eq. (A3) of Appendix A, it is easily seen that the operator $\bar{\Psi}$, being on the left of $\delta^{\mathrm{Kr}}{}_{M_a,0}$, does not act on the dotted part on the right. Also the operators involving spin $a$ which are on the left of the first $\delta^{\mathrm{Kr}}{}_{M_a,0}$ do not act on $\bar{\Psi}$. The bracketed quantity behaves thus like *a pure number*, which is

$$\Psi_a=\delta^{\mathrm{Kr}}{}_{M_a,0}\sum_{\{M_{i_a}\}}\bar{\Psi}(M_a,\{M_{i_a}\}) \times\delta^{\mathrm{Kr}}{}_{M_a,0}\rho^{\mathrm{eq}}(\{M_{i_a}\}). \qquad \text{(IV.11)}$$

Comparing Eqs. (IV.11) and (IV.8) with the high-temperature limit of Eq. (II.31) (in which case only the term $\mu'\equiv 0$ survives), we see that $\Psi_a$ differs from $\rho^{-}(0;t|aa)$ by only a factor $\rho^{\mathrm{eq}}(M_a+\frac{1}{2})\equiv\frac{1}{2}$.

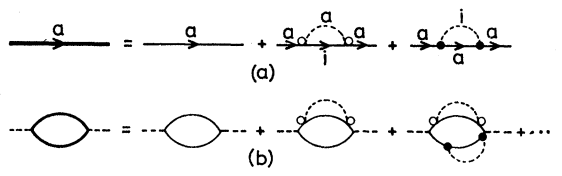


FIG. 10. An example illustrating Theorem III: (a) the meaning of a heavy line; (b) example of self-energy insertions.

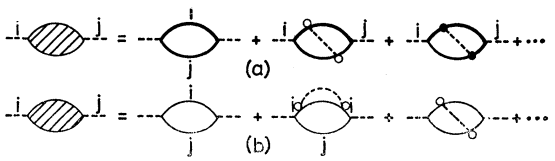


FIG. 11. Irreducible renormalized skeleton part for $i\neq j$: (a) compact form; (b) expanded form.

Of course, we should still prove that the time factors that appear in $\Psi_a(t_1-t_2)$ are the same as those of $\rho^{-}(0;t_1-t_2|aa)$; however, very similar properties have been demonstrated in a different context[12] and we shall not reproduce that part of the demonstration here. Using Eq. (II.29) we thus have

$$\Psi_a(t_1-t_2)=2\Gamma_{aa}{}^{+-}(t_1-t_2)\equiv\Gamma(t_1-t_2), \qquad \text{(IV.12)}$$

where explicit account has been taken of the fact that the direct autocorrelation function does not depend on the particular spin we consider.

The results of this section may be summarized as follows: the complete perturbation series for the autocorrelation function may be rewritten in terms of skeletons only, but with renormalized propagators as given by (IV.12).

Of course, we are not able to prove strictly that, in this new classification, the renormalized graph of Fig. 10(b) behaves as is indicated on Eq. (IV.6); indeed, the function $\Gamma(t)$ itself is an unknown of the problem. Nevertheless, it seems clear that with such renormalized skeletons the spin problem becomes very similar to the case of a gas, and we shall now derive exact kinetic equations following the scheme that has proved fruitful in quantum gases (see Ref. 8).

## V. DERIVATION OF THE KINETIC EQUATIONS

Let us define the contribution corresponding to an *irreducible renormalized skeleton part*; it is the operator given by

$$\bar{G}_{ij}(t_1-t_2;M_i,M_j\{M_{a_{ij}}\}|\Gamma(t'')) =\sum(\text{contribution of all renormalized skeleton parts starting at } t=t_2 \text{ with a dashed line } j \text{ and ending at } t=t_1 \text{ with a dashed line } i, \text{ without any intermediate state involving only one such line}). \qquad \text{(V.1)}$$

This definition also holds when $i=j$; moreover, the functional dependence on $\Gamma$, as expressed by Theorem IV, has been explicitly indicated. We should stress that $\bar{G}_{ij}$ corresponds only to the operator part of the graphs under consideration; no trace is taken over the quantum numbers $M_i$, $M_j$, $\{M_{a_{ij}}\}$, and the state over which $\bar{G}_{ij}$ acts is not specified; it is thus not given by

[12] P. Résibois, Phys. Fluids 6, 817 (1963).

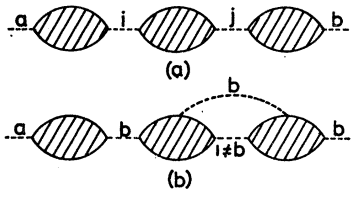


FIG. 12. General structure of $\Gamma_{ab}{}^{zz}(t)$: (a) typical term; (b) a negligible contribution in the Weiss limit.

direct application of the rules of Sec. III; perhaps the simplest formal way to define it in analytical form is to use the complete perturbation expansion for each renormalized propagator, in which case it becomes simply

$$\bar{G}_{ij}(t_1-t_2; M_i, M_j, \{M_{\alpha ij}\}|\Gamma(t'')) = \sum_{n=0}^{\infty}\binom{\lambda}{-i}^n \int_{t_2}^{t_1} d\tau^{n-2}\langle 0|[\mathfrak{IC}(M)]^n|0\rangle_{\text{irr } ij}, \quad \text{(V.2)}$$

where "irr $ij$" means the irreducible contribution (i.e., no intermediate state $\mu=0$) involving spin $i$ at the first vertex and spin $j$ at the last vertex. Illustration of these two definitions is given in Fig. 11.

It should, however, be clear from the discussion of Sec. IV that Eq. (V.2) is purely formal and that only the compact form (V.1) is useful in analyzing the long-time behavior of the system. We shall be content here with the formal analytical expression (V.2) and we shall give later, at the end of this section, the prescriptions for calculating a quantity closely connected to $\bar{G}_{ij}$ in a form involving explicitly the functional $\Gamma$ dependence. With the definition (V.2), it is readily seen that the most general graph contributing to $\Gamma_{ab}{}^{zz}(t)$ has the structure indicated in Fig. 12(a). We may write the corresponding analytical contribution as [see also Eq. (III.10)]:

$$\Gamma_{ab}{}^{zz}(t)\equiv\rho^z(\tfrac{1}{2}; t|ab)=\sum_{m=0}^{\infty}\sum_{j,s\cdots l}\sum_{\{\alpha_{aj}\}\{\alpha_{js}\}\cdots\{M_{i\neq a}\}}\int_0^t dt_1\int_0^{t_1} dt_2\cdots\int_0^{t_{2m-1}} dt_{2m}\bar{G}_{aj}(t_1-t_2; M_a=\tfrac{1}{2}, M_j, \{M_{\alpha aj}\}|\Gamma)$$
$$\times\bar{G}_{js}(t_3-t_4; M_j, M_s, \{M_{\alpha js}\}|\Gamma)\cdots\bar{G}_{lb}(t_{2m-1}-t_{2m}; M_l, M_b, \{M_{\alpha lb}\}|\Gamma)M_b\rho_0{}^{\text{eq}}(\{M\}). \quad \text{(V.3)}$$

Note that in Eq. (V.3) no exclusion has been indicated on the various indices $j$, $s,\cdots l$; this amounts to including not only the dominant structures, as given for instance in Fig. 12(a), but also some contributions of the type of Fig. 12(b), where more than one semiconnection bond appear between two irreducible parts. In the Weiss limit, these terms are, however, negligible with respect to the dominant ones and may thus be added whenever it is convenient. We immediately see that $\bar{G}_{ij}$ defined by (V.1) is such that no other spin than $j$ in the set $(i,j,\{\alpha_{ij}\})$ reappears in any other irreducible part on its right; this allows us to rewrite Eq. (V.3) as

$$\rho^z(\tfrac{1}{2}; t|ab)=\rho^z(\tfrac{1}{2}; 0|ab)+\int_0^t dt_1\int_0^{t_1} dt_2\sum_j\sum_{M_j}\bar{G}_{aj}{}^{\Sigma}(t_1-t_2; M_a=\tfrac{1}{2}, M_j|\Gamma)\times\rho^z(M_j; t_2|jb), \quad \text{(V.4)}$$

where

$$\bar{G}_{aj}{}^{\Sigma}(t_1-t_2; M_a=\tfrac{1}{2}, M_j|\Gamma)=\sum_{\{\alpha_{aj}\}}\sum_{\{M_{\alpha_{aj}}\}}\bar{G}_{aj}(t_1-t_2; M_a=\tfrac{1}{2}, M_j, \{M_{\alpha aj}\}|\Gamma)\times\rho_0{}^{\text{eq}}(\{M_{\alpha aj}\}). \quad \text{(V.5)}$$

From the formal expansion (V.2), we notice that $\bar{G}$ necessarily ends with a vertex of the type (II.19b); accordingly $\bar{G}^{\Sigma}$ has the structure

$$\bar{G}_{aj}{}^{\Sigma}=\sum_{\{\alpha_{aj}\}}\sum_{\{M_{\alpha_{aj}}\}}[\cdots]\delta^{\text{Kr}}{}_{M_{\alpha_{j,0}}}\delta^{\text{Kr}}{}_{M_{j,0}}\times[-J(\alpha_j-j)]\eta_{j\alpha_j}\rho_0{}^{\text{eq}}(\{M_{\alpha aj}\}), \quad \text{(V.6)}$$

where $\alpha_j$ is any spin in the set $(a,\{\alpha_{aj}\})$. Here again, the bracketed dots denote all contributions to $\bar{G}^{\Sigma}$ which are on the left of the last vertex; they are left unspecified. Precisely as in Eq. (IV.9), the $\delta^{\text{Kr}}{}_{M_{j,0}}$ insures that all the operators which depend on $j$ and which appear in the bracket do not operate on the right of this delta function. Moreover, let us define a quantity $\Delta$ by

$$\Delta\equiv\delta^{\text{Kr}}{}_{M_{j,0}}\delta^{\text{Kr}}{}_{M_{\alpha_{j,0}}}\eta_{j\alpha_j}\rho_0{}^{\text{eq}}(\{M_{\alpha_{aj}}\})\rho^z(M_j; t_2|jb). \quad \text{(V.7)}$$

We then perform explicitly the displacement operations implied by Eq. (II.20) and get

$$\Delta=\delta^{\text{Kr}}{}_{M_{j,0}}\delta^{\text{Kr}}{}_{M_{\alpha_{j,0}}}\rho_0{}^{\text{eq}}(\{M_{\alpha_{aj}}\})\times[\rho^z(\tfrac{1}{2}; t_2|jb)-\rho^z(-\tfrac{1}{2}; t_2|jb)]. \quad \text{(V.8)}$$

Using the important property (III.10) and the identity $2\rho_0{}^{\text{eq}}(M_j)=1$, we may put (V.8) in the form

$$\Delta=4\delta^{\text{Kr}}{}_{M_{j,0}}\delta^{\text{Kr}}{}_{M_{\alpha_{j,0}}}\eta_{j\alpha_j}\times M_j\rho_0{}^{\text{eq}}(M_j)\rho_0{}^{\text{eq}}(\{M_{\alpha_{aj}}\})\Gamma_{jb}{}^{zz}(t_2). \quad \text{(V.9)}$$

Combining Eqs. (V.4) to (V.8), and taking the derivative of $\Gamma_{ab}{}^{zz}(t)$ with respect to $t$, we obtain then easily the following equation for $\Gamma_{ab}(t)$ introduced in (II.23):

$$\partial_t\Gamma_{ab}(t)=\sum_j\int_0^t G_{aj}(t-t'|\Gamma)\Gamma_{jb}(t')dt', \quad \text{(V.10)}$$

where $G_{aj}(t-t'|\Gamma)$ is now an ordinary function, and not an operator, defined by

$$G_{aj}(t|\Gamma)=4\sum_{\{\alpha_{aj}\}}\sum_{\{M_{\alpha_{aj}}\}}\sum_{M_j}\bar{G}_{aj}(t; M_a=\tfrac{1}{2}, M_j, \{M_{\alpha aj}\}|\Gamma)\times M_j\rho_0{}^{\text{eq}}(M_j,\{M_{\alpha aj}\}). \quad \text{(V.11)}$$

Equation (V.10) is the exact kinetic equation for the spin autocorrelation function of a Heisenberg system valid in the high-temperature region and in the Weiss limit. It shows that the evolution of $\Gamma_{ab}(t)$ is entirely determined by the kernel $G_{aj}(t|\Gamma)$, which itself is a nonlinear functional of the direct autocorrelation

$$\Gamma(t)\equiv\Gamma_{aa}(t).$$

As this kernel plays a central role in the application of the theory, it is convenient to know the prescriptions needed to calculate it directly, without use of the auxiliary operator $\tilde{G}_{aj}$. Such prescriptions are, however, very easy to obtain once the formal similarity between Eq. (V.11) combined with (V.2) and the *irreducible* contributions to $\Gamma_{aj}{}^{zz}(t)$ itself—when expressed in terms of renormalized propagators—has been recognized; except for a numerical factor 4 and for a double time integral,[13] $G_{aj}(t_1-t_2|\Gamma)$ is in fact identical to the irreducible part of $\Gamma_{aj}{}^{zz}(t|\Gamma)$; this is most easily seen from (V.11) and the graphic definition of $\tilde{G}$, as given by Fig. 11. For the convenience of the reader, we have nevertheless summarized the rules for the calculation of $G_{aj}$ in Appendix C.

Equation (V.10) takes a very simple form when expressed in Fourier space; let us define

$$\Gamma_q=\sum_a \Gamma_{ab}e^{iq(ab)}, \tag{V.12}$$

$$\tilde{G}_q=\sum_{a\neq b} G_{ab}e^{iq(ab)}. \tag{V.13}$$

We introduce (V.12) and (V.13) into (V.10), and we use the property

$$G_{aa}=-\sum_{a\neq b} G_{ab}. \tag{V.14}$$

This latter condition is an easily demonstrated consequence of the well-known sum rule

$$\Gamma_{aa}(t)=1-\sum_{a\neq b}\Gamma_{ab}(t). \tag{V.15}$$

We get then

$$\partial_t\Gamma_q(t)=\int_0^t[\tilde{G}_q(t'|\Gamma)-\tilde{G}_0(t'|\Gamma)]\Gamma_q(t-t')dt' \tag{V.16}$$

which is the final form for our kinetic equation.

However, because we have

$$\Gamma(t)=\Gamma_{aa}(t)=(1/N)\textstyle\sum_{q'}\Gamma_{q'}(t), \tag{V.17}$$

Eq. (V.16) is still in principle a very complicated integral equation because all Fourier components are mixed by Eq. (V.17). There is, however, a simpler method that may be used, which amounts to writing down a separate equation for $\Gamma(t)$; indeed, we have mentioned after Eq. (V.3) that we had not taken any exclusion into account because we found it more convenient; this leads, in (V.3), to free summations over $j, s, \cdots l$. However, in the particular case $a=b$, it is extremely simple to take these exclusions into account because all dominant graphs are of the type of Fig. 13, where each intermediate state is equal to $a$. All the other terms, $i, j, s, l\cdots\neq a$, which have been formally introduced in Eq. (V.3) are negligible in the Weiss limit. We may thus as well write, in this particular case,

FIG. 13. Dominant graphs for $\Gamma_{aa}{}^{zz}(t)$.


$$\Gamma_{aa}{}^{zz}(t)=\rho^z(\tfrac{1}{2};t|aa)$$
$$=\sum_{n=0}^{\infty}\sum_{\{\alpha_{aa}\}}\cdots\sum_{\{M_{\alpha_{aa}}\}}\cdots\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{2n-1}}dt_{2n} \tag{V.3'}$$
$$\tilde{G}_{aa}(t_1-t_2;M_a,\{M_{\alpha_{aa}}\}|\Gamma)_{M_a=1/2}$$
$$\times\tilde{G}_{aa}(\cdots)\cdots M_a\rho_0{}^{eq}(\{M\}).$$

Following the same steps as before, we obtain immediately

$$\partial_t\Gamma_{aa}{}^{zz}(t)=\int_0^t G_{aa}(t'|\Gamma)\Gamma_{aa}{}^{zz}(t-t')dt'. \tag{V.18}$$

Using Eqs. (V.13) and (V.14), together with the definition $\Gamma_{aa}{}^{zz}(t)\equiv 4\Gamma(t)$, we get finally

$$\partial_t\Gamma(t)=-\int_0^t\tilde{G}_0(t'|\Gamma)\Gamma(t-t')dt'. \tag{V.19}$$

The considerable simplification brought by the auxiliary equation (V.19) will be appreciated; indeed, once the single nonlinear equation for $\Gamma(t)$ has been solved, all other Fourier components, which are determined by (V.16), now obey a linear non-Markoffian equation which can generally be solved quite easily.

Finally, we would like to remark that, although we have no general proof of this property, we expect, of course, that

$$\Gamma(t)\to 0, \quad t\gg\tau_d \tag{V.20}$$

which implies in turn that

$$\tilde{G}_q(t|\Gamma)\to 0, \quad t\gg\tau_d. \tag{V.21}$$

We see thus that the reclassification of the perturbation series in terms of irreducible renormalized skeletons allows us to obtain kinetic equations in which all quantities are well-behaved in the long time limit; this is a considerable improvement over the initial perturbation form (II.21). It is the keystone to the possibility of getting approximate expressions for $\Gamma_q(t)$ and $\Gamma(t)$ valid for both short and long times. The derivation of such expressions will be considered in the following paper of this series.

[13] The time factor is here $\int_{t_1}^{t_2}d\tau^{n-2}$ because we consider the first and the last vertices as, respectively, fixed at times $t_1$ and $t_2$.

## ACKNOWLEDGMENTS

It is gratefully acknowledged that preliminary calculations to the present work were done in collaboration with Dr. R. Dagonnier. We also wish to express our gratitude to Professor I. Prigogine for his interest in the problem.

## APPENDIX A: DEMONSTRATION OF THEOREM II

As an example, we shall show here that the presence of a vertex of the type given in Fig. 6(d) gives a vanishing contribution to the corresponding graph.

Using again the schematic notation used in Fig. 7, we have pictured a graph of this type in Fig. 14. Be-

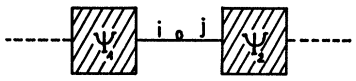


FIG. 14. Schematic representation of a graph involving the vertex (d) of Fig. 6.

cause of the absence of any semiconnection bond, we know that the operators in $\Psi_1$ do not involve spin $j$; let us denote by $\bar{\Psi}_1(\{M_{s\neq j}\})$ the operator corresponding to this box. Similarly in the box $\Psi_2$, spin $i$ cannot appear. We denote by $\bar{\Psi}_2(\{M_{s\neq i}\})$ the corresponding operator, and by $\Psi_2(\{M_{s\neq i}\})$ the function of the different $M_{s\neq i}$ that results when the displacement operations are performed.

Using (II.19c) and leaving out the unimportant time factors, we have, for this contribution,

$$C\sim \sum_{\{M_{s\neq a}\}} \bar{\Psi}_1(\{M_{s\neq j}\})[-J(i-j)] \times\delta^{\mathrm{Kr}}{}_{M_i,0}\eta_{ij}\delta^{\mathrm{Kr}}{}_{M_j,0}\Psi_2(\{M_{s\neq i}\}) \quad \text{(A1)}$$

or

$$C\sim \sum_{\{M_{s\neq a}\}} \bar{\Psi}_1(\{M_{s\neq j}\})[-J(i-j)] \times\delta^{\mathrm{Kr}}{}_{M_i,0}[\eta^{-1i}-\eta^{+1i}]\delta^{\mathrm{Kr}}{}_{M_j,0}\Psi_2(\{M_{s\neq i}\}). \quad \text{(A2)}$$

Using then the basic property

$$\eta^{\mu}\delta^{\mathrm{Kr}}{}_{M,0}\Psi(M)=\eta^{\mu}\delta^{\mathrm{Kr}}{}_{M,0}\Psi(0), \quad \text{(A3)}$$

an immediate consequence of the definition of the Kronecker function, we have

$$C\sim \sum_{\{M_{s\neq a}\}} \bar{\Psi}_1(\{M_{s\neq j}\})[-J(i-j)] \times\delta^{\mathrm{Kr}}{}_{M_i,0}[\delta^{\mathrm{Kr}}{}_{M_j-\frac{1}{2},0}-\delta^{\mathrm{Kr}}{}_{M_j+\frac{1}{2},0}] \times\Psi_2(\{M_{s\neq i,j}\}, M_j=0). \quad \text{(A4)}$$

Among the sums over $M_{s\neq a}$, we may of course commute the sum over $M_j$ with the operator $\bar{\Psi}_1$, where spin $j$ does not appear; we get then

$$C\sim \sum_{\{M_{s\neq a,i}\}} \bar{\Psi}_1(\{M_{s\neq j}\})[-J(i-j)] \times\delta^{\mathrm{Kr}}{}_{M_i,0}\sum_{M_j}[\delta^{\mathrm{Kr}}{}_{M_j-\frac{1}{2},0}-\delta^{\mathrm{Kr}}{}_{M_j+\frac{1}{2},0}] \times\Psi_2(\{M_{s\neq i,j}\}, M_j=0)\equiv 0 \quad \text{(A5)}$$

which is the required result. The other cases are treated similarly.

## APPENDIX B: DEMONSTRATION OF COROLLARIES I AND II OF THEOREM II

The demonstration of Corollary I is almost trivial; to any given graph we may associate the "conjugate" graph obtained by reversing the direction of the arrow on each plain line. In this transformation, one sees immediately from (II.17) and (II.18) that we change the sign of each matrix element, either longitudinal or transverse. We get thus a vanishing total result if the graph is of odd order in $n$.

The proof that for large $Z$, the indirect correlation function is of order $\lambda^2(\lambda^2 Z)^{n-1}$ is more elaborated.

Let us define the *topological index* of a vertex: It is equal to the number of spins over which we may sum freely at this vertex, reading the graph from left to right. If we take into account that the number of neighbors is $Z$ ($Z\gg 1$), this index is $Z$ or zero as indicated on Fig. 15. The only exception is the last vertex on the right of each graph, where we have to introduce the index $Z^{-1}$ because we impose the condition that one of the plain lines is necessarily $b$.

Let us then consider an arbitrary graph of order $2n$, with $m_1$ vertices of the type indicated in Fig. 15(1), $m_2$ vertices of type Fig. 15(2), $\cdots m_7$ vertices of type Fig. 15(7). We have the following identities:

(a) The graph is of order $2n$:

$$\sum_{i=1}^{7} m_i=2n. \quad \text{(B1)}$$

(b) As the graph starts with a dashed line and ends with a dashed line, the number of vertices that create

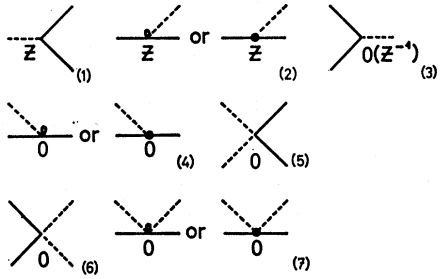


FIG. 15. Topological index of the elementary vertices.

two plain lines is equal to the number of vertices that absorb two plain lines; we have thus

$$m_1+m_5=m_3+m_6. \tag{B2}$$

(c) Each created semiconnection line has to be absorbed later on

$$m_2+m_3+2m_6+m_7=m_1+m_4+2m_5+m_7. \tag{B3}$$

(d) The order of the graph is

$$O=\lambda^{2n}Z^{m_1+m_2-1}. \tag{B4}$$

Solving (B1), (B2), and (B3) for $m_1+m_2$, we get

$$m_1+m_2=n-\tfrac{1}{2}(m_5+m_6+m_7). \tag{B5}$$

As $m_1$, $m_2$, $m_3\cdots m_7$ are by definition positive numbers, we see that the maximum order

$$O_{\max}=\lambda^{2n}Z^{n-1}, \tag{B6}$$

provided it is possible to take $m_5=m_6=m_7=0$, i.e. to neglect all graphs with more than one dashed line on any vertex. It is easily verified that such a choice is indeed consistent with conditions (B1)–(B3); Corollary II is thus demonstrated for the indirect case ($a\neq b$). A similar proof can be given for the direct correlation function ($a=b$).

## APPENDIX C: RULES FOR CALCULATING $G_{ab}(t|\Gamma)$

As indicated in Sec. IV, the rules for computing $G_{ab}(t|\Gamma)$ in terms of renormalized propagators are easily obtained from those for $\Gamma_{ab}(t)$. However, before giving these prescriptions, let us remark that we may perform without any difficulty the renormalization of all the internal *dashed* lines of a given irreducible skeleton part; this will reduce considerably the number of graphs and will also insure a faster convergence of the expansion for the kernel $G_{ab}(t|\Gamma)$.

Indeed, let us define a *basic* irreducible skeleton part as an irreducible skeleton part with no self-energy parts on the dashed lines. We have then the analog of Theorem III, which is

*Theorem III′:* The sum of all irreducible skeleton parts is obtained from all basic irreducible skeleton parts by replacing each dashed line with the renormalized dashed line of Fig. 16(a). The corresponding analytical contribution is obtained by associating a factor $\Gamma(t_1-t_2)$ to each renormalized dashed line starting at $t_2$ and ending at $t_1$.

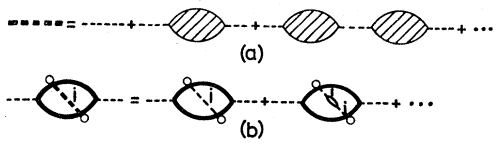


FIG. 16. Renormalization of the internal dashed line in a basic irreducible skeleton part: (a) renormalized dashed lines; (b) renormalized basic irreducible skeleton part.

The demonstration of this theorem follows exactly the proof of Theorem III, Sec. IV, and will not be reproduced here. An example of application is given in Fig. 16. Using this theorem and the results of Sec. V, we obtain the following rules for calculating $G_{ab}(t_1-t_2|\Gamma)$.

(1) Draw all possible renormalized basic irreducible skeleton parts starting with a dashed line $b$ and ending with a dashed line $a$.

(2) Associate a factor $\Gamma(t_1-t_2)\delta^{\mathrm{Kr}}{}_{M_i,0}$ to a heavy line with index $i$ starting at $t=t_2$ and ending at $t=t_1$; similarly, associate a factor $\Gamma(t_1-t_2)$ to an internal renormalized dashed line.

(3) Associate a factor $[-J(i-j)\eta_{ij}]$ to each transverse vertex and a factor $[-2J(i-j)(\mu_iM_j+\mu_jM_i)]$ to each longitudinal vertex. The operators $\eta_{ij}$ and the Kronecker deltas are ordered as they appear in the graph.

(4) Multiply on the right by

$$M_0\rho_0{}^{\mathrm{eq}}(\{M\})[\rho_0{}^{\mathrm{eq}}(M_i)=\tfrac{1}{2},\ (i=1\cdots N)].$$

(5) Multiply on the left by

$$4(-\lambda^2)^n\int_{t_1}^{t_2}d\tau^{n-2}$$

for a graph with $2n$ vertices.

(6) Take the trace ($\sum_{M_i}\cdots$) over all spins different from $a$.

(7) Sum over all indices different from $a$ and $b$.