THERMODYNAMICS OF AN IDEAL FERROMAGNETIC SUBSTANCE

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A diagram technique is proposed for a system of interacting spins which permits one to study the thermodynamics of a Heisenberg ferromagnet with arbitrary spin S at any temperature T or magnetic field strength H. The relevant high-temperature expansions are presented. Expressions for the thermodynamic quantities which are valid everywhere except in a narrow region near the transition point $T = T_{cr}$, $H = 0$ are derived for a ferromagnet with a large radius of interaction $r_0$. Corrections to the phenomenological phase transition theory are found in this case, and it is shown that the theory is valid for $|T - T_{cr}| \gg T_{cr}r_0^6$ and $\mu HS \gg T_{cr}r_0^9$. Low-temperature expansions of the thermodynamic quantities are presented. In this region the results for any spin are the same as those of Dyson, but have been obtained by a more simple and standard method. It is shown that for large spin S the Dyson expansion is correct only for $T \ll T_{cr}S^{-1}$. The thermodynamics is also derived in the region $T_{cr}S^{-1} \ll T \ll T_{cr}$ when $S \gg 1$.

1. INTRODUCTION

Matsubara's diagram technique\textsuperscript{[1]} which has been worked out in detail is available for studying the temperature behavior of ordinary Fermi and Bose systems. This technique permits one to find the thermodynamic and kinetic properties of systems in the presence of any small parameter. In the theory of magnetism it is accepted practice to use Hamiltonians containing products of spin operators of various atoms. An example is the well-known Heisenberg model of a ferromagnet. A consistent method for describing such systems has been worked out only for low temperatures. Even in this case rigorous results are obtained by a very cumbersome and nonstandard method,\textsuperscript{[2,3]} while the simple Holstein-Primakoff formalism is suitable only for large values of the spin S of the atom.\textsuperscript{[4]}

In order to describe a ferromagnet at arbitrary temperatures, use has been made of the molecular-field method,\textsuperscript{[5]} and of various methods of “chain decoupling” in the equations for the Green’s functions.\textsuperscript{[6]} However, the results obtained by these methods do not agree with each other, and for low or high temperatures they do not go over into the exact low- and high-temperature expansions, so that none of these methods yields a consistent method of calculation.

In this paper we present a diagram technique for describing systems with spin-spin interaction; the technique is analogous to that of Matsubara and constitutes a series of successive approximations of the self-consistent field method. This method is suitable in all cases when the deviations of field acting on the particle from the average field are small, i.e., for a large radius of interaction $r_0$, as well as at low and high temperatures. The formal expansion parameter in this method is the reciprocal interaction volume $r_0^3$, in analogy with the fact that in Matsubara’s method the expansion is in powers of the interaction. For low and high temperatures the results are obtained without assuming $r_0$ to be large.

We consider an ideal ferromagnet, i.e., the Heisenberg model with an arbitrary exchange interaction between the spins. At low temperatures we obtain expansions of the thermodynamic quantities in powers of the temperature that coincide with Dyson’s results.\textsuperscript{[2,9]} It has been found that for large spin S Dyson’s results are only valid in a narrow temperature range $T \ll T_{cr}S^{-1}$ where $T_{cr}$ is the Curie temperature. Expressions are obtained for the thermodynamic quantities in a broader range $T \ll T_{cr}$. For high temperatures the method yields an expansion in terms of $T_{cr}/T$. Expansions are presented of thermodynamic quantities up to the fourth order in $T_{cr}/T$, which coincide in particular cases with those obtained previously.\textsuperscript{[7]} If the radius of interaction $r_0$ is large, then for large S the obtained results are valid everywhere except in the direct vicinity of the transition point.

For this case we present expansions of the thermodynamic quantities near $T_{cr}$ which are valid in
the range $T\text{cr} \gg |T - T\text{cr}| \gg T\text{cr}r_0^2$ or $T\text{cr} \gg \mu HS \gg T\text{cr}r_0^2$, where $\mu S$ is the magnetic moment and $H$ is the external field. The first terms of these expansions correspond to the molecular-field approximation and to the results of the phenomenological theory. The connection with other methods, in particular with the methods of decoupling the equations for the Green's functions is discussed in Sec. 8. It is shown that they correspond to an interpolation form of the zeroth self-consistent field approximation. The problem of the applicability of the results to real ferromagnets is discussed in the Conclusion.

2. DIAGRAM TECHNIQUE FOR SYSTEMS WITH SPIN-SPIN INTERACTION

The Hamiltonian of the model under consideration is of the form

$$\hat{H} = -\mu H \sum_\mathbf{r} S_\mathbf{r}^z - \frac{1}{2} \sum_{\mathbf{r} \neq \mathbf{r}'} V(\mathbf{r} - \mathbf{r}') S_\mathbf{r} S_{\mathbf{r}'}. \quad (1)$$

Here $S_\mathbf{r}$ is the spin operator of the atom which is considered fixed at the site of the crystal lattice, $\mathbf{r}$ is the coordinate of the site, $V(\mathbf{r} - \mathbf{r}')$ is the effective interaction potential between the spins, $H$ is the external magnetic field directed along the axis, and $\mu S$ is the magnetic moment of the atom.

In order to obtain successive approximations, it is convenient to separate in (1) the interaction with the average spin $\langle S \rangle$. The free energy then takes on the form

$$-\beta F = \frac{1}{N} \ln \text{Sp} \exp\left[ - \frac{N\beta V_S\langle S \rangle^2}{2} + \beta \sum_\mathbf{r} V_0(\langle S \rangle + \mu H) S_\mathbf{r} \right] + \frac{\beta}{2} \sum_{\mathbf{r} \neq \mathbf{r}'} \sum_\mathbf{S} \langle V(\mathbf{r} - \mathbf{r}') (S_\mathbf{r} - \langle S \rangle) (S_{\mathbf{r}'} - \langle S \rangle) \rangle, \quad (2)$$

where $N$ is the number of sites, $\beta = 1/T$, and $V_0 = \Sigma \mathbf{r} V(\mathbf{r})$.

The zeroth self-consistent field approximation, referred to as the molecular-field approximation, is obtained when the last term in (2) is neglected. In this case the free energy is given by the expression

$$\beta F^0 = \frac{(y - \beta \mu H)}{2V_0} - \frac{\ln \text{sh}(y + 1/2)}{\text{sh}(y/2)},$$

$$y = \beta (V_0\langle S \rangle + \mu H). \quad (3)$$

The average spin $\langle S^2 \rangle$ is obtained from the condition that the free energy be a minimum, $\partial F / \partial y = 0$:

$$\langle S^2 \rangle = \frac{y - \beta \mu H}{\beta V_0} = b(y). \quad (4)$$

Here $b(y)$ is a function which is simply related with the well-known Brillouin function $B_S(y)$:

$$b(y) = \frac{\text{Sp} S^2 \exp\left[ y \right]}{\text{Sp} \exp\left[ y \right]} = \frac{1}{2} \text{cth} \left( \frac{1}{2} y \right)$$

In the absence of a magnetic field $H = 0$, it follows from (4) that a second-order phase transition into a ferromagnetic state takes place in the system at a temperature $T_c$

$$T_c = V_0\langle S \rangle + 1/3. \quad (5)$$

According to (3)-(5), the thermodynamic quantities vary in the vicinity of $T_c$ in accordance with the phenomenological theory; in particular, for $H = 0$ $y$ increases like $(T_c - T)^{1/2}$.

In order to set up a diagram technique we make use of a method which has previously been used in considering anharmonic vibrations in crystals and which is analogous to that proposed by Abrikosov for describing the Kondo effect in metals. The usual Matsubara diagram technique has been worked out for systems of Fermi and Bose particles; we transform, therefore, the Hamiltonian (1) to the usual fermion (or boson) form. We introduce the operators $\hat{a}_{\mathbf{r} \lambda}$ and $\hat{a}_{\mathbf{r} \lambda}^\dagger$ of the production and absorption of a particle in a state with a coordinate $\mathbf{r}$ and a spin projection $\lambda$, and take into account the fact that one and only one such particle is always present in each site $\mathbf{r}$. Then the Hamiltonian can be rewritten in the form

$$\hat{H} = -\sum_{\mathbf{x},\mathbf{x}',\lambda} \mu H a_{\mathbf{x} \lambda}^+ S_{\mathbf{x} \lambda} a_{\mathbf{x}' \lambda'} - \frac{1}{2} \sum_{\mathbf{r} \neq \mathbf{r}'} V(\mathbf{r} - \mathbf{r}') (a_{\mathbf{r} \lambda}^+ S_{\mathbf{r} \lambda} a_{\mathbf{r}' \lambda'}) \sum_{\mathbf{x},\mathbf{x}',\lambda} (a_{\mathbf{x} \lambda}^+ S_{\mathbf{x} \lambda} a_{\mathbf{x}' \lambda')^\dagger + g \sum_{\mathbf{r}} \left( \sum_{\lambda} a_{\mathbf{r} \lambda}^+ a_{\mathbf{r} \lambda} - 1 \right)^2, \quad (7)$$

where the auxiliary constant $g$ will tend to infinity in the answers, and therefore the remaining states in which the number of “particles” in one site differs from unity will make no contribution to the statistical properties.

The Hamiltonian (7) is of the usual form so that one can make use of the well-known rules of the Matsubara diagram technique. Each diagram is proportional to certain powers of the interaction $V$ and $g$. Since $g$ tends to infinity, it is convenient to collect for each power of the interaction $V$ diagrams of all orders in $g$. It is important that the last term in (7) is of the form of the interaction of particles located in a single unit cell. Therefore each connected diagram can be represented in the form of single-cell diagrams connected by lines of interaction $V(\mathbf{r} - \mathbf{r}')$. Each line of interaction con-
nects vertices of different blocks, either $S^2$ with $S^2$, or $S^+$ with $S^-$ where $S^\pm = (S^x \pm iS^y)/2^{1/2}$. Since $g$ tends to infinity, in calculating a single-cell block the problem reduces to the calculation of the statistical average of the $T$-product of a certain number of single-particle spin operators of the form
\[ S^\alpha(t) = e^{\alpha \tau(t)}e^{-\alpha \tau(t)}, \tag{8} \]
where $\alpha = -yS^\alpha$ corresponds to the zeroth self-consistent field approximation (3)–(5).

The Fourier component of a single-cell block with $n$ outgoing lines of interaction $V$ is given by the expression
\[ \Gamma_n^{\alpha_1\ldots\alpha_n}(\omega_1, \omega_2, \ldots, \omega_n) = \frac{1}{\mathcal{T}} \sum_{m_1+m_2+\ldots+m_n=n} \Lambda^{\alpha_1\ldots\alpha_n}_{m_1\ldots m_n}, \tag{9} \]
where $\mathcal{T}$ is the $T$-ordering symbol, $\omega_{in} = 2\pi m T$ are the imaginary frequencies of the temperature diagram technique, the average $\langle \ldots \rangle$ denotes the sum of all possible blocks of lower rank. This is connected with the circumstance that in the Matsubara technique a block may include only singly-connected diagrams. One must therefore subtract from the average of the $T$-product the contribution of all unconnected diagrams.

Let us formulate the graphical rule for calculating the blocks; its derivation is based on the use of transposition relations among the spin operators and is presented in the Appendix. The block $\Gamma_n$ is represented by the aggregate of all diagrams with $m$ vertices $S^+$, $m$ vertices $S^-$, and $n-2m$ vertices $S^0$. Each $S^+$ vertex has one outgoing line, each $S^-$ vertex either one incoming or two incoming and one outgoing line. Each $S^0$ vertex has either one incoming or one outgoing line or no line at all. To each line there corresponds a Green’s function
\[ G(\omega_n) = \frac{1}{y - i\omega_n}, \tag{10} \]
for the sum of the incoming frequencies is equal to the sum of the outgoing ones. If the diagram splits into $N$ singly-connected diagrams, the total number of triple $S^+$ vertices and $S^0$ vertices on the continuous lines being $l$, then the common factor of this diagram is $(-1)^l b^{(N-1)}$ where $b^{(N-1)}$ is the $(N-1)$st derivative of the function $b(y)$ introduced in (5) with respect to $y$.

We present the analytic expressions for the simplest vertices illustrated in Figs. 1, a–e:

\begin{alignat*}{2}
\text{a)} 
\Gamma_{i0}^{i0}(1,2) &= b\delta_1\delta_2, &
\text{b)} 
\Gamma_{i0}^{i0}(1,2) &= bG_1\delta(1-2), &
\text{c)} 
\Gamma_{i0}^{i0}(1,2,3) &= -bG_1G_2\delta_{1+2-3} + b'G_1\delta_{1+2-3}, &
\text{d)} 
\Gamma_{i0}^{i0}(1,2,3,4) &= bG_1G_2G_3G_4\delta_{1+2+3+4} \\
& & & - bG_1G_2\delta_{1+3+4} + b'G_1\delta_{1+3+4}, &
\text{e)} 
\Gamma_{i0}^{i0}(1,2,3,4) &= -bG_1G_2G_3G_4\delta_{1+2+3+4} \\
& & & + b'G_1G_2\delta_{1+2+3+4} + b''G_1\delta_{1+2+3+4}. &
\end{alignat*}

Here $\Gamma_n(1, 2, \ldots, n) = \Gamma_n(\omega_1, \omega_2, \ldots, \omega_n)$, $\delta_{1-k} = \delta(\omega_1 - \omega_k)$ is the Kronecker symbol of the corresponding frequency difference, and $G_i = G(\omega_i)$. As an example of more complicated blocks Fig. 11 shows the diagrams for $\Gamma^{i+i+i+i+i+i}$.

We define the temperature correlation functions of the spins in the usual way:
\[ K_{\alpha\beta}(k, \omega_n) = \frac{1}{2\beta^{-1}} \langle e^{\omega_n} \frac{1}{\mathcal{T}} \sum_{\tau_1} \frac{\delta(\omega_n - \omega_{\tau_1})}{\langle \Sigma_{\tau_1}\rangle} \rangle. \tag{12} \]

The function $K_{\alpha\beta}(k, \omega_n)$ is represented by the aggregate of all singly-connected diagrams with two vertices. We denote by $\Sigma_{\alpha\beta}(k, \omega_n)$ the aggregate of all irreducible diagrams. Then the correlation functions can be written in the form (see, for example, (12))
\[ K_{\alpha\beta}(k, \omega_n) = \frac{\Sigma_{\alpha\beta}(k, \omega_n)}{1-\beta V_k \Sigma_{\alpha\beta}(k, \omega_n)}; \]
\[ K_{+\alpha}(k, \omega_n) = \frac{\Sigma_{+\alpha}(k, \omega_n)}{1-\beta V_k \Sigma_{-\alpha}(k, \omega_n)}. \tag{13} \]

As has been shown below, in the case of a large radius of interaction and also for low or high temperatures it is sufficient to restrict oneself in $\Sigma_{\alpha\beta}$ to the simplest diagrams shown in Figs. 1, a and b. Substituting for $\Sigma_{\alpha\beta}$ expressions (11a and b), we obtain for the correlation functions in this approximation
\[ K_{\alpha\beta}(k, \omega_n) = \delta_{\alpha\beta} \frac{b'}{1-\beta V_k G(\omega_n)}, \tag{14a} \]
\[ K_{+\alpha}(k, \omega_n) = \frac{bG(\omega_n)}{1-\beta V_k \delta bG(\omega_n)} = \frac{b}{y - \beta V_k b - \beta\omega_n}. \tag{14b} \]

The average temperature correlation function
\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Fig. 1.}
\end{figure}
It has been shown previously\cite{13} that the molecular-field approximation (3) represents for a large radius of interaction $r_0$ the main term of the expansion of the free energy $F$ in powers of $r_0^{-3}$. It does not however take into account spin correlation effects, in particular the presence of such correlations in the high-temperature region and their increase near the transition temperature $T_{Cr}$. For small $T$ expression (3) yields an exponential dependence of the thermodynamic quantities on the temperature, whereas the following terms which take into account the particle correlation yield for small $T$ an expression that the free energy is a minimum, $8F/8y = 0$\(\)\cite{14,19} in the approximation under consideration we have

$$\langle S^z \rangle = \frac{y - \beta\mu H}{8V_0} = b + \frac{\nu''}{2} \sum_k \frac{\beta V_k}{1 - \beta V_k b'}$$

\begin{align}
\langle S^z \rangle &= \frac{y - \beta\mu H}{8V_0} = b + \frac{\nu''}{2} \sum_k \frac{\beta V_k}{1 - \beta V_k b'} \\
&= \sum_k \left[ \nu_k (1 - \beta V_k b') - n_0 \right].
\end{align}

A formula for $K_{zz}(k)$ has been previously obtained by deGennes and Villain.\cite{12}

$$K_{zz}(k) = K_{zz}(k, \omega) = 8V_0 \sum_{\omega_n} \frac{1}{\omega_n - \epsilon(k)}.$$

In the approximation under consideration we have

$$\langle S^z \rangle = \frac{y - \beta\mu H}{8V_0} = b + \frac{\nu''}{2} \sum_k \frac{\beta V_k}{1 - \beta V_k b'}$$

and

$$\langle S^z \rangle = \sum_k \left[ \nu_k (1 - \beta V_k b') - n_0 \right].$$

In diagrams 2a and 2b there is single integration over the momenta, in diagrams 2c-g double integration. Therefore the first two diagrams of Fig. 2 are of the order of $r_0^{-3}$, the remaining--of the order of $r_0^{-6}$\cite{13} More complicated diagrams contain a larger number of integrations over the momenta and correspondingly higher powers of $r_0^{-3}$. In writing down the diagrams analytically it must be kept in mind that each vertex point in diagrams 2c-g is the sum of several terms shown in Fig. 1. Thus, for example, the diagram 2g is given in detailed notation by the sum of the three terms shown in Fig. 2g.

In accordance with the general rule for writing down diagrams,\cite{14} the nth term of the expansion of diagrams 2a and 2b in powers of $V$ contains the factor $1/n$; for this reason one obtains instead of geometric progressions of the type (14) and (16) logarithmic expansions:\cite{13}

$$\beta F^{(n)} = \frac{1}{2} \sum_k \ln (1 - \beta V_k b') + \sum_k \ln (1 - \beta V_k b' G(\omega_n))$$

$$= \frac{1}{2} \sum_k \ln (1 - \beta V_k b') + \sum_k \ln [1 - \exp (\beta V_k b - y)]$$

$$- \ln (1 - e^{-\gamma})$$

The first term in (17) describes the thermodynamic contribution of the fluctuation of the $z$ components of the spins. The second term takes on in conjunction with the self-consistency condition (4) the form of the free energy of an ideal Bose gas of spin waves with a spectrum given by formula (15) and depending on the temperature.

The value of $y$ is determined from the condition that the free energy is a minimum, $8F/8y = 0$\(\)\cite{14} In the approximation under consideration we have

$$\langle S^z \rangle = \frac{y - \beta\mu H}{8V_0} = b + \frac{\nu''}{2} \sum_k \frac{\beta V_k}{1 - \beta V_k b'}$$

\begin{align}
\langle S^z \rangle &= \frac{y - \beta\mu H}{8V_0} = b + \frac{\nu''}{2} \sum_k \frac{\beta V_k}{1 - \beta V_k b'} \\
&= \sum_k \left[ \nu_k (1 - \beta V_k b') - n_0 \right].
\end{align}
Here
\[ n_k = \left[ \exp(y - \beta V_k b) - 1 \right]^{-1}, \quad n_y = (e^y - 1)^{-1}. \]

In the first-order terms in (18), as in (17), one must substitute in accordance with the method of successive approximations \( y = y_0(T, H) \) obtained from the zeroth approximation (4).

In (18) the main, first term corresponds to the molecular-field approximation. The second term describes the contribution of the fluctuations \( S^2 \), and the third corresponds to the spin waves. For a large radius of interaction \( r_0 \) the last terms are small corrections of the order of \( r_0^{-3} \) to the first term. However, for small \( T \) the entire temperature dependence is determined by the Bloch spin-wave term in (18).

Taking into account the fact that \( \partial F/\partial y \big|_{y=y_0} = 0 \), one can readily show that an account of the first correction to \( y \) given by (18) results in the appearance of a second-order term in \( r_0^{-3} \) which is
\[
\delta F^{(2)} = \left( \frac{\partial^2 F^{(0)}}{\partial y^2} \right) \left( \frac{\partial^2 F^{(0)}}{\partial y^2} \right)^{-1} \delta F^{(0)} = \frac{-B\beta V_0}{2(1 - B\beta \alpha_0)} \left[ b'' \sum_k \frac{B\beta V_k}{1 - B\beta V_k b'} - \sum_k (n_k(1 - B\beta V_k b') - n_y) \right]^2.
\]

Graphically this term is shown by the sum of pairs of single loops joined by one dashed line. Together with other second-order terms which are represented by diagrams 2c–g and in which one must substitute \( y \) from the zeroth approximation (4), we obtain for the total free energy in the second approximation
\[
\beta F = \frac{(y - \beta \mu H)^2}{2\alpha_0} - \frac{\ln(sh(S+1/2)y)}{\ln(sh(y/2))} + \frac{1}{\alpha_0} \sum_k \ln(1 - a_k b')
+ \frac{1}{8} \sum_k \ln[1 - \exp(a_k b - y)] - \ln(1 - e^{-y})
+ \frac{1}{12} \left[ b'' \sum_{k,q} \frac{a_q}{1 - b' a_q} \right]^2 \left( \frac{b'}{4 - b'a_q} \right)^2
+ \frac{1}{12} \sum_{k,q} \frac{1}{1 - b' a_q} \left( \frac{a_k}{1 - b' a_k} - \frac{a_{k+q}}{1 - b' a_{k+q}} \right)
+ \frac{b'}{2} \frac{\sum_{k,q} \frac{a_k}{1 - b' a_k} (n_k - n_q)}{\sum_{k,q} \frac{a_k^2}{1 - b' a_k}}
+ \frac{b' \partial y}{2} \frac{\sum_{k,q} \frac{a_k^2}{1 - b' a_k}}{\sum_{k,q} \frac{a_k^2}{1 - b' a_k}}
\]

Here we have introduced the notation \( \alpha_k = \beta V_k \), \( c_k = y - \beta \alpha_k b' \), and \( y \) is understood everywhere to be its "zeroth" value given by Eq. (4). In deriving (20) we used the identity
\[
\sum_k a_k = \beta V(r = 0) = 0.
\]

The terms of the second approximation in (20) have a simple physical meaning which is obvious from the diagrams of Fig. 2. Thus the first and second terms correspond to the contribution of the correlated fluctuations of \( S^2 \); the third and fifth terms correspond to correlated fluctuations of longitudinal and transverse components, in particular to scattering of spin waves by fluctuations of \( S^2 \). Finally, the two last terms describe the interaction of transverse fluctuations, including the kinematic and dynamic interactions of spin waves.\([12,31]\)

It is seen that for small values of the wave vector the interaction of the spin waves, both with one another and with the fluctuations of \( S^2 \), vanishes at all temperatures.

In the following treatment of various limiting cases it often turns out to be convenient not to determine \( y \) from the zeroth approximation (4), but directly from the condition that the free energy is a minimum. In this case one need not add in expression (20) the term (19), i.e., one sets formally in all terms of the second approximation (2) \( \alpha_0 = 0 \), and \( y \) is obtained from the condition \( \partial F/\partial y = 0 \).

4. HIGH TEMPERATURES

Let us consider the range of high temperatures \( T \gg T_{cr} \) and weak magnetic fields \( \beta \mu H \ll 1 \). In this case the value of \( y \) will according to (4) also be small, and the function \( b(y) \) can be expanded in a series in powers of \( y \):
\[
b(y) = ay - cy^3/3 + \ldots,
\]
\[
a = \frac{S(S + 1)}{3}, \quad c = \frac{S(S + 1)(S^2 + S + 1/2)}{15} = \frac{3}{5} a^2 + \frac{a}{10}.
\]

According to (6) the transition temperature \( T_{cr} \) is of the order of \( a V_0 \). Therefore for \( T \gg T_{cr} \) the quantities \( b' \alpha_k \), and \( b' \alpha_k b' \approx a V_k \) in (20) are small, and the self-consistent field expansion goes over into the perturbation-theory series in powers of \( \alpha_k \). In an actual calculation it is more convenient
to expand in (20) formally in powers of $\alpha_k$, and only then expand $b(y)$ and $b'(y)$ in $y$. As a result we obtain for the free energy

$$\beta F = -\ln(2S + 1) - \frac{3}{4} a^2 \sum_k a_k^2 - \frac{a^2}{2} \sum_k a_k^3$$

$$+ \frac{a^2}{8} \sum_{k,q} a_k a_q a_{k+q} - \frac{a(\beta \mu H)^2}{2(1 - a\alpha_0)} + \frac{a^2(\beta \mu H)^2}{2(1 - a\alpha_0)^2}$$

$$\times \left[ \left( a + \frac{4}{3} \right) \sum_k a_k^2 + \left( a^2 + \frac{4}{9} \right) \sum_k a_k^3 \right]$$

$$- \frac{2}{5} a^2 + \frac{3}{10} a + \frac{1}{15} \sum_{k,q} a_k a_q a_{k+q} \right]. \quad (22)$$

For the sake of conciseness and clarity we retained in (22) in the denominators the expressions $\alpha_0$ resulting from the zeroth approximation (4) for $y$, although for large $T$ these denominators should also be expanded in $\alpha_0$.

By differentiating (22) with respect to $T$ or $H$ we obtain high-temperature expansions of various thermodynamic quantities. Thus, for example, we obtain from (22) for the isothermal susceptibility $\chi_T$

$$\chi_T = -\frac{\partial F}{\partial H^2} \bigg|_T = \mu^2 a \left[ 1 - a\alpha_0 + a^2 \alpha_0^2 - a \left( a + \frac{1}{3} \right) \sum_k a_k^2 \right]$$

$$+ a^2 \alpha_0^2 - 2a \left( a + \frac{1}{3} \right) a_0 \sum_k a_k^2 - a \left( a + \frac{1}{6} \right) \sum_k a_k^3$$

$$- a \left( \frac{2}{5} a^2 + \frac{3}{10} a + \frac{1}{15} \right) \sum_{k,q} a_k a_q a_{k+q} \right]. \quad (23)$$

For the case of nearest-neighbor interaction in cubic lattices (23) goes over into the results of Brown and Luttinger.[9]

In the high-temperature case under consideration successive approximations in $F$ are comparatively simple to calculate. Therefore the proposed diagram technique can be used to set up the high-temperature expansions, in particular in computer calculations of the Heisenberg model for arbitrary spin $S$.[11] In the case of the Ising model there are no diagrams with transverse interaction (16b), and the diagram technique is even further simplified.

5. THE REGION NEAR THE TRANSITION

For temperatures close to $T_C$ and low magnetic fields $\beta \mu H \ll 1$ the value of $y = \beta(V_0/S^2) + \mu H$ is small as before, and one can use for $b(y)$ expansion (21). However, in expanding the free energy (20) in powers of $y$ and $T - T_C$, integrals appear which diverge for small momenta $k$. These divergences indicate that $F$ is nonanalytic at the transition point; this nonanalyticity reflects the increase in the long-wave correlations near $T_C$.

The divergences should be removed in the same way as in [3]: in the denominators and under the logarithm sign one must retain along with $V_0 - V_k$ term expressions of the order $y^2$ and $T - T_C$.

Thus the correlation function of the first approximation (14a) entering in (20) takes on for small $k$ the form

$$K_{\tau}(k, 0) = a \left[ \frac{T}{T_C} - 1 + \frac{cy^2}{a} + \frac{V_0 - V_k}{V_0} \right]$$

$$= a \left[ \frac{T - T_C}{T_C} + \frac{cy^2}{a} + \frac{1}{2} \sum_{i=1}^3 k_i^2 x_{0i}^2 \right]. \quad (24)$$

In (24) $x_{0i}^2$ denote the principal values of the tensor $\Sigma x_{\alpha \beta} x_{\gamma \delta} V(\tau)V_0^{-1}$, and $k_i$ are the projections of $k$ on its principal axes. For cubic lattices $x_{0i}^2 = R_0^2/3$ where $R_0$ is the mean square of the radius of interaction. The values of $y$ and $T_C$ in (24) are determined by the zeroth approximation (4) and (6). In accordance with (4) in the absence of a magnetic field $y = 0$ for $T > T_C$ and $cy^2 = 3a(T_C - T)$ for $T < T_C$ so that (24) is of the form of the Ornstein-Zernike equation.

Just as in the previous paper,[3] in finding the second-order terms in (20), it is essential to take into account the renormalization of $T_C$ which can be obtained with the aid of the first-order approximation (18). Instead of using the general expression (20), it is more convenient in the calculations to expand each diagram $2c-g$ separately in $y$ and $T - T_C$, since this results in considerable cancellation. Retaining in each order only the most singular terms, we obtain

$$\beta F = -\ln(2S + 1) - \frac{\beta \mu H^2}{2V_0} - a y h + \frac{a^2 h^2}{2} + \frac{cy^2}{12}$$

$$- \frac{y^2}{3c} (u^0 + 2\beta h) + \frac{y^2 a^2}{3c} \ln \left( 1 + \frac{4}{9} \frac{\ln \left( 1 + \frac{4}{9} \right)}{u} \right)$$

$$- \left( 1 + \frac{2V}{u} \right) + \left( 1 + \frac{2V}{u} \right)^2 + A]. \quad (25)$$

Here

$$h = \mu H/T_C, \quad \tau = \frac{T - T_C}{T_C}, \quad u = \frac{cy^2}{a} + \tau, \quad v = \frac{cy^2}{3a} + \tau;$$

$$\gamma = c \frac{3\sqrt{6}}{a^2 2\pi a^2} = \frac{3}{5} \left( 1 - \frac{1}{2} \frac{1}{S(S + 1)} \right) \frac{3\sqrt{6}}{2\pi a^2};$$

$$T_c = a V_0 \left[ 1 - \frac{5c}{3a^2} \sum_k \frac{V_k}{V_0 - V_k} - \frac{1}{12a^2} \sum_k \frac{V_k^2}{V_0 - V_k} \right]. \quad (26)$$

A denotes an immaterial constant of the order of unity which can be included in the renormalization of $T_C$.

In (25) and (26) $y$ denotes a quantity determined
by the zeroth approximation (4) which is near the transition of the form \( cv^3 + 3ay^3 - 3ah = 0. \) We present the explicit form of the dependence of \( y \) on \( h \) and \( \tau \):

\[
y = \left( \frac{3ah}{2c} \right)^{1/6} \begin{cases} 
(1 + \gamma^I + 4ar^2/9ch^2)^{1/6} + (1 - \gamma^I + 4ar^2/9ch^2)^{1/6} & \text{for } 1 + 4ar^2/9ch^2 > 0 \\
(1 + e^{in\gamma} - 1 - 4ar^2/9ch^2)^{1/6} + (1 + e^{-in\gamma} - 1 - 4ar^2/9ch^2)^{1/6} & \text{for } 1 + 4ar^2/9ch^2 < 0.
\end{cases}
\]  

(27)

The quantity \( r_0^3 \) entering in the formula for \( \gamma \) in (26) is defined in the general case as

\[
r_0^3 = \frac{1}{\nu_c} \text{Det} \frac{3}{V_0} \sum_{x_0} x_0 x_0 \nu_c
\]  

(28)

where \( x_0 \) are the same as in (24), and \( \nu_c \) is the volume of the cell. For cubic lattices this is simply the ratio \( r_0^3/V \); in the general case \( r_0^3 \) also characterizes the relative volume of interaction.

The equations of this Section, including (24), have a region of applicability only for \( r_0^3 \gg 1 \). For the usually considered simple, face-centered, and body-centered cubic lattices with nearest-neighbor interaction \( r_0 = 1, \sqrt{2}, \) and \( \sqrt{3} \) respectively, so that the self-consistent field approximation is in these instances unsuitable for describing the region near the transition.

It is seen from (25) and from Eqs. (29) presented below that the expansion parameter near the transition is \( \gamma u^{-1/2} \sim r_0^{-3} u^{-1/2} \). Therefore even for large \( r_0 \) the expansion used becomes inapplicable for \( |r_0| < r_0^3 \). In this connection it is also impossible to obtain the value of the transition temperature \( T_{cr} \) with an accuracy greater than given by the first-approximation formula (26).

From (25) one can find the behavior of all thermodynamic quantities close to the transition. Thus we have the average moment \( \langle S^z \rangle \) and the specific heat \( C_H \) in various regions of variation of the temperature and magnetic field:

a) \( \tau = \frac{(T - T_c)}{T_c} > 0, \quad \text{cH}/\alpha \approx 1 \):

\[
\langle S^z \rangle = \frac{4}{3} \frac{Y}{\tau^2} \left[ 1 + \frac{5}{3} \frac{\gamma}{\tau^2} + \frac{\gamma^2}{(3\ln 4 - 2\ln 3 + 7/3)} \right] - \frac{\text{ch}^2}{\alpha^2} \left[ 1 + \frac{29}{18} \frac{\gamma}{\tau^2} + \frac{20}{27} \frac{\gamma^2}{\ln 4 - 16} \frac{1}{17} \ln 3 + 5 \frac{1}{35} \right] \bigg];
\]

\[
C_H = \frac{a^2 \tau^3}{c} \left[ \frac{3}{2} \gamma + \frac{\text{ch}^2 + 3}{6 \gamma^2} + \frac{25}{8} \frac{\gamma}{\tau^2} + \frac{\gamma^2}{\ln 4 - 2\ln 3 + 7/18} \right].
\]  

(29a)

b) \( \text{ch}^2/\alpha \tau^2 \gg 1 \):

\[
\langle S^z \rangle = \left( \frac{3ah}{c} \right)^{1/6} \left[ 1 + \left( \frac{\gamma a}{9ch^2} \right)^{1/6} \left( 1 + \frac{2}{\gamma^3} \right) \right]
\]

Equations (29) illustrate the structure of the asymptotic expansions near the transition.

The susceptibility \( \chi^2 \) is proportional to the derivative of \( \langle S^2 \rangle \) with respect to \( H \). We see from (29c) that below \( T_{cr} \) the susceptibility in a weak magnetic field tends to infinity as \( H^{-1/2} \), a fact which is connected with the existence of spin waves in this region.

6. LOW TEMPERATURES

At low temperatures the quantity \( y \), equal to \( \beta(V_0(\langle S^2 \rangle + \mu H)) \) tends to infinity. We therefore have with an accuracy up to exponentially small terms

\[
b = S, \quad b' = 0, \quad n_y = 0.
\]  

(30)

Equation (20) takes on the form
where \( \varepsilon_k = S(V_0 - V_k) + \mu H \). The third term in this formula represents the Bloch free energy of an ideal Bose gas of spin waves, and its expansion in powers of the temperature has the well-known form:

\[
- \frac{1}{2} \sum_{k, q} \left( V_0 - V_k - V_q + V_{k-q} \right) n_k n_q, \tag{31}
\]

where

\[
Z_a(x) = \sum_{n=1}^{\infty} n^{-a} e^{-nx},
\]

and the constants \( \lambda_1 \) and \( \lambda_2 \) depend on the type of lattice and are expressed for cubic lattices in terms of the radii of interaction in the following form:

\[
\lambda_1 = \frac{3}{2} / w, \quad \lambda_2 = \frac{1}{2 \sqrt{3}} (20\pi^2 - 44\pi + 45\pi^2 - 8\pi),
\]

\[
v = \sum \tau^s V(\tau) / R^s V_0, \quad v_1 = 3 \sum \tau^s V(\tau) / R^s V_0,
\]

\[
\rho = \sum \tau^s V(\tau) / R^s V_0.
\]

Thus in the case of nearest-neighbor interaction in a simple cubic lattice

\[
v = v_1 = \rho = 1, \quad \lambda_1 = 3 / \pi, \quad \lambda_2 = 33 / 32.
\]

The last term in (31) describing the interaction of spin waves is proportional to \( T^3 k_0^3 \). It is equal to the Born approximation for the analogous term obtained by Dyson.\(^{17,11}\) The main contribution corresponds to the ideal gas and is given by the third term of (31). The following term describing the interaction of two spin waves is of the same form as the last term in (31), however instead of the Born amplitude \( V_0 - V_k - V_q + V_{k-q} \) one must write the exact two-particle amplitude. Neglecting higher powers of the density, i.e., of the temperature, one can use the ladder approximation to determine this amplitude.\(^{17,11}\)

The equation for the amplitude is shown graphically in Fig. 4. It is of the form

\[
A(p_1, p_2, p_3, p_4) = \sum (V_{p_1 - p_2 - q} - V_q) \delta_{p_1 - q} + \delta_{p_2 - q} + G_1 G_2 (A(q, p_1 + p_2 - q, p_3, p_4) + A(p_1 + p_2 - q, q, p_3, p_4)), \tag{34}
\]

where \( p_1 \) and \( q \) are the “four-dimensional” momenta (\( p_1, \omega_1 \)). The amplitude \( A \) depends parametrically only on the sum of the frequencies of the colliding spin waves \( \omega_1 + \omega_2 = \omega_3 + \omega_4 \). Summing the kernel of Eq. (34) over \( \omega_1 \), we obtain

\[
\sum_{\omega_1} = \frac{1}{2} \left( x + x^4 + x^2 + x^3 - x^4 + x^2 + x^3 + x + x^4 \right)
\]

FIG. 3.

\[
G_k = \beta (G(\omega_n) + G(\omega_n) \beta V_k b G(\omega_n) + G(\omega_n) (\beta V_k b G(\omega_n))^2 + \ldots) = 1 / (\varepsilon_k - i \omega_n), \tag{33}
\]

where \( \varepsilon_k \) is the same as in (31).

The resulting diagram technique coincides with that of Dyson. It describes a Bose gas of interacting spin waves, and is analogous to the technique for the usual nonideal Bose gas.\(^{17,11}\) At low temperatures the density of spin waves is low, and in calculating the thermodynamic functions one can make use of the gas approximation.\(^{17,11}\) The presented diagram technique permits one to obtain Dyson's low-temperature expansions also without assuming \( r_0^3 \) to be large. Condition (30) permits one to take into account in the vertex blocks (9) and (11) only singly-connected diagrams, since the multiply-connected vertex diagrams are proportional to the derivatives of \( b(\nu) \). It is therefore now possible not to split the diagrams into single-cell blocks connected by lines (16b), but instead to draw directly lines representing sums of single-cell diagrams with analogous multi-cell ones. This is illustrated by the diagrams of Fig. 3 in which the dotted line represents the initial interaction \( V \). It is seen that the lines \( G(\omega_n) \) coming into each single-cell block are replaced after summing by thick lines which we shall denote by \( TG_k \):

\[
G_k = \beta [G(\omega_n) + G(\omega_n) \beta V_k b G(\omega_n) + G(\omega_n) (\beta V_k b G(\omega_n))^2 + \ldots] = 1 / (\varepsilon_k - i \omega_n), \tag{33}
\]

where \( \varepsilon_k \) is the same as in (31).
At low temperatures one can neglect in the numerator the important frequencies \( \omega_1 + \omega_2 \sim T \ll \epsilon_0 \approx V_0 S \). One can, therefore, ignore in the denominator of the kernel the term \( \epsilon_0 \) and \( \epsilon_{p_1 + p_2 - q} \sim V_0 S \). However, for large \( S \) the region of applicability of the low-temperature expansion turns out to be very narrow. Indeed, as has been shown in Secs. 2 and 5, the transition temperature is for large \( S \) of the order of \( V_0 S^2 \), and in the derivation of (31) and (32) we have used the fact that \( y \gg 1 \), i.e., \( T \ll V_0 S \sim T_{cr} S^{-1} \). Equation (32) is in this case an expansion in the parameter \( S T_{cr} \) and becomes inapplicable for \( T \gtrsim T_{cr} S^{-1} \).

7. REGION OF LARGE SPINS \( S \) AND TEMPERATURES \( T_{cr}/S \ll T \ll T_{cr} \)

The general method presented in Sec. 3 permits one to obtain for large \( S \) an expression for the free energy also in the region \( T \sim T_{cr} S^{-1} \) without assuming \( r_0 \) to be large. In this region we have with an accuracy up to small exponential terms of the order of \( e^{-Sy} \sim e^{-T_{cr}/T} \)

\[
b(y) = S - n_y. \tag{36}
\]

Therefore in all diagrams, except those collecting in \( V^* \) (16b), the expansion in the diagram technique is in the parameter \( \beta V_q \) and \( \beta V_k \ll 1/S \).

Substituting (36) in Eq. (20) and expanding in powers of \( 1/S \), we find that the quantity \( n_y \) entering in \( b(y) \) and in other parts of the formula cancels, so that the expression for the free energy is as before with an accuracy up to higher powers of \( 1/S \) of the form (31). But whereas for \( T \ll T_{cr} S^{-1} \) the free energy was determined by the long-wave portion of the spin-wave spectrum, in the region \( T \sim T_{cr} S^{-1} \) the short-wave portion of the spectrum becomes important; therefore the temperature dependence of the free energy depends on the type of crystal lattice and the explicit form of the interaction \( V(r) \).

An interesting result is obtained in the other limiting case \( V_0 S \ll T \ll V_0 S^2 \). From (31) we again obtain a power expansion, but now in powers of \( T_{cr}/S \) and \( T_{cr}^{-1} \):

\[
F = - \frac{V_0 S^2}{2} - S \mu H - T \sum_k \left( \ln \frac{T}{\epsilon_k} + \frac{\epsilon_k}{2T} + \frac{\epsilon_k^2}{24T^2} \right) - \frac{T^2}{2} \sum_{k,q} \frac{V_0 - V_k - V_q + V_{k-q}}{\epsilon_k \epsilon_q} \tag{37}
\]

Hence we obtain for the spontaneous moment and the specific heat

\[
\langle S^z \rangle = S \left[ 1 - \frac{T}{V_0 S^2} \left( c_1 + \frac{V_0 S}{T} + \frac{V_0^2 S^2}{12T^2} \right) - c_2 \left( \frac{T}{V_0 S^2} \right)^2 \right]. \tag{38}
\]

The constants \( c_1 \) depend on the type of lattice and are determined as follows:

\[
c_1 = \sum_k \frac{V_0}{V_0 - V_k}, \quad c_2 = \sum_{k,q} \frac{V_0(V_0 - V_k - V_q + V_{k-q})}{(V_0 - V_k)(V_0 - V_q)}, \quad c_3 = \frac{1}{12} \left( 1 + \sum_k \frac{V_k^2}{V_0^2} \right). \tag{39}
\]

Thus for a simple cubic lattice with nearest-neighbor interaction

\[
c_1 = 1.516, \quad c_2 = 1, \quad c_3 = 7/72.
\]

The results (38) have a simple physical meaning. For large \( S \) the temperature \( T_{cr} \sim V_0 S^2 \) will be much higher than the energy of the spin waves for all \( k \): \( \epsilon_k \ll V_0 S \ll V_0 S^2 \). Therefore for \( V_0 S \ll T \) the occupation numbers of spin waves \( n_y = (e^{\beta \epsilon_k} - 1)^{-1} \sim T_{cr}^{-1} \) are large for all \( k \). On the other hand, the interaction of spin waves with one another is proportional to \( T(V_0 S^2)^{-1} \sim T_{cr}^{-1} \), and the thermodynamic contribution of the fluctuations of the moment is proportional to \( e^{-\beta T_{cr}} \). Thus we have in the range \( T_{cr} S^{-1} \ll T \ll T_{cr} \) in the first approximation only a classical ideal gas of spin waves. Therefore the main term in the specific heat is equal to unity and does not depend on the type of lattice and the form of the interaction, in analogy with the law of Dulong and Petit in the case of phonons. The following term, proportional to the temperature, in the specific heat is due to the interaction of spin waves and is analogous to the term due to the anharmonicity of the lattice vibrations.
8. COMPARISON WITH OTHER METHODS

At low temperatures the method which has been presented leads to the same results as the methods of Dyson\(^{14,15}\) and Holstein and Primakoff.\(^{18,4}\) However, Dyson's method is very cumbersome, while the Holstein-Primakoff method is only applicable for large S. In addition, in the Holstein-Primakoff method one must make approximations in the initial Hamiltonian and it is difficult to estimate their accuracy. Thus the new results of Sec. 7 on the thermodynamics in the range \(T \ll T_{cr}\) could have also been obtained by the Holstein-Primakoff method, but it is not clear whether this method is applicable in this range. The diagram technique presented above, as the method of Matsubara, permits one to obtain a general diagram expression for the free energy, and only then discard diagrams which are small in any parameter, for example \(TT_{cr}^{-1}\).

For \(T \sim T_{cr}\) the thermodynamics of a ferromagnet has been described by the molecular-field method, or by the methods of Tyablikov, or Callen, et al.\(^{6,3}\) by decoupling chains of equations for Green's functions. All these methods are applicable only for large \(r_0\); in this case they yield coinciding results corresponding the zeroth self-consistent field approximation (3)-(6).

Let us consider, for instance, the Bogolyubov-Tyablikov equation for the average moment with spin \(S = \frac{1}{2}\) which is in our notation of the form\(^{16}\)

\[
1 = 2 \langle S^+ \rangle \sum_k \text{cth} \left( \frac{\beta(V_0 - V_k)\langle S^+ \rangle + \beta \mu H}{2} \right)
\]
or

\[
y - \beta \mu H = \frac{1}{2} \text{th} \left[ \frac{y}{2} \left( 1 + 2 \text{th} \left( \frac{y}{2} \sum_k (n_k - n_0) \right) \right) \right]
\]

In the case of a large radius of interaction the quantity \(V_k\) decreases rapidly for \(k \gg r_0^{-1}\), so that (40) goes over into (4) with accuracy up to terms \(\sim r_0^{-3}\). As can be seen, for example, from a comparison of (40) and (18), in the decoupling methods the terms after \(r_0^{-3}\) are taken into account incorrectly. However, at low temperatures of all correction terms in (18) only the Bloch component \(\Xi_k n_k\), corresponding to the contribution of free spin waves, contributes a nonexponentially small contribution. Comparing with (40), we see that in this region the first correction term of (40) also coincides with (18). Therefore the decoupling method is actually a sensible interpolation form of the zeroth self-consistent field approximation.

We note, however, that the usual application of this method to the case of temperatures that are not low and to nearest-neighbor interaction can, as has been shown in this paper, yield only a qualitative description. In addition, in the decoupling methods there is no clear-cut scheme of constructing successive approximations. Therefore in proceeding to terms of subsequent orders which describe in particular the interaction of spin waves well-known difficulties appear even in the low-temperature range.\(^{6}\) Thus, for example, for spin \(\frac{1}{2}\) for small \(T\) one obtains a contribution proportional to \(T^3\) to the average moment instead of the Dyson term \(\sim T^4\) found in Sec. 6.

At the transition point both the decoupling methods as well as the molecular-field methods lead to a jump in the specific heat and give no indications of the existence of a stronger singularity; as has been shown in Sec. 5, such indications appear when consistent account is taken of the following self-consistent field approximations. Analogous difficulties of the decoupling methods in describing the dynamics of spin waves are discussed in\(^{14}\).

9. CONCLUSION

This paper is basically of a methodological nature. The physical results are therefore for the most part not qualitatively new. Thus the results of Secs. 4 and 6 represent a generalization of well-known high- and low-temperature expansions to the case of arbitrary lattices and interaction of not only the nearest neighbors. The results of Sec. 5 are valid only for a large radius of interaction and contain corrections to the phenomenological theory of phase transitions. Qualitative results refer only to the region of large \(S\) and small \(T\) considered in Sec. 7. Taking into account the statements of Secs. 6 and 7, the temperature dependence of the specific heat \(C_H(T)\) for large spin should be peculiar. Following a rapid increase in the region of low temperatures in accordance with a \((ST/T_{cr})^{3/2}\) law, the specific heat reaches in the region \(T_{cr}/S \ll T \ll T_{cr}\) in the case of all lattices a plateau \(C_H = 1\), and the subsequent growth of \(C_H\) starts only at \(T \sim T_{cr}\).

The weak-field susceptibility is anomalously large \(\sim H^{-1/2}\) throughout the region below the transition. Applied to real ferromagnets this result is valid for sufficiently strong fields, since it is sensitive to the anisotropy field and to the magnetic interaction. These interactions are relativistic and for the majority of ferromagnets they are small compared with the exchange interaction which has been taken into account above. Therefore the basic thermodynamic properties will change little when
these interactions are taken into account. However, the magnetic interaction and the anisotropy field are important for describing the susceptibility in a weak field, as well as the domain structure and hysteresis; they can be taken into account by the method described above.

In order to apply the results to ferromagnetic metals, one must take into account the exchange interaction of the spins, i.e., of the electrons of the filled bands with the conduction electrons. It can be expected that taking this into account will reduce to a change in the effective interaction, and will not affect the magnetic part of the thermodynamic quantities. In ferrodielectrics the radius of interaction is usually small; therefore the results apply to them basically at high and low temperatures. We considered above only ferrodielectrics with a cell containing one magnetic atom, like for example, EuO. The majority of ferrodielectrics are antiferromagnets with uncompensated spins (ferrites). The obtained results apply to these without appreciable changes. Excitations and fluctuations with small \( k \) in which the averaged characteristics of the cell are thus important at low temperatures and near the transition.

The authors are grateful to M. Sh. Gitterman for a useful discussion of the results.

**APPENDIX**

We present the proof of the rule for writing down the vertex blocks \( \Gamma_n \) which we formulated above [see formula (9)].

Let us first calculate the first term of (9) which represents the average of some number of operators \( S^+\)(t). Let us first consider the case when we have on the left the operator \( S^+ \): 

\[
\langle S^+ S^z \ldots S^- \rangle = \rho_0 S^+ S^z \ldots S^-.
\]

We make use of the assumption employed by Luttinger to prove the Wick theorem for Bose and Fermi operators in statistics, 190 and find the average of the commutator

\[
[S^+, S^-] = -S^+ + S^z \ldots [S^+, S^-] = -S^+ + S^z \ldots [S^+, S^-].
\]

On the other hand, in the second term of the left-hand side of (A.1) one can carry out a cyclic transposition of the operators, and use the relation: 

\[
S^+ \rho_0 = e^{y} \rho_0 S^+ \quad \text{as a result the left-hand part of (A.1) takes on the form (1 - e^{y})} S^+ S^z \ldots S^-.
\]

Taking into account that \([S^+, S^-] = -S^+\), and \([S^+, S^z] = S^z\), we obtain from (A.1)

\[
\langle S^+ S^z \ldots S^- \rangle = \rho_0 \{e^y \langle S^+ S^z \ldots S^- \rangle - e^y \langle S^+ \rangle \}.
\]

The authors are grateful to M. Sh. Gitterman for a useful discussion of the results.

Thus the average of the product has been reduced to a sum of averages of products of a smaller number of operators. The left-hand operator \( S^+ \) has disappeared in each product, and one of the operators \( S^- \) or \( S^z \) has been replaced by \( S^+ \) or \(-S^+\) respectively.

In the case when the operator \( S^+ \) is not on the left the average of the product is calculated analogously. In this case \( S^+ \) is first transposed to the left, commutations with \( S^z \) and \( S^- \) resulting in terms of the same form as in (A.2) but with a factor +1 and -1 for \( S^z \) and \( S^- \) respectively. As a result

\[
\langle S^+ \ldots S^z \ldots S^- \rangle = (n_y + 1) \langle S^+ \ldots S^- \rangle + \ldots
\]

\[
- n_y \langle S^+ \ldots S^- \rangle.
\]

Terms obtained by contraction of the operator \( S^+\) with operators on its left enter with a factor \( n_y + 1 \), and those on the right with a factor \( n_y \). Taking into account that the time dependence of the operators is given by

\[
S^+ (t) = e^{yT} S^+ e^{-yT} = e^{yT} S^+; \quad S^- (t) = e^{yT} S^-; \quad S^z (t) = S^z,
\]

we obtain

\[
\langle \tilde{T} S^+ (t_1) S^+ (t_2) \ldots S^- (t_n) \rangle = G(t_1 - t_2) \langle \tilde{T} S^+ (t_2) \ldots S^- (t_n) \rangle
\]

\[
G (t) = e^{yT} \begin{cases} n_y & t > 0 \\ n_y + 1 & t < 0 \end{cases}
\]

Continuing this process, we finally find that the averaging sign will include one or several operators \( S^z \).

In the graphical representation of vertex blocks by diagrams of the type of Fig. 1 the number of lines representing \( G \) functions in singly-connected diagrams will only be one less than the number of vertices. These diagrams correspond to cases when only one operator \( S^z \) remains and therefore the expression represented by them contains the factor \( \langle S^z \rangle = b(y) \). A diagram that splits into \( N \) singly-connected diagrams is proportional to \( \langle S^z \rangle^N \). In the second term of (9) one will then obtain expressions which are represented by the same diagram and contain the same kind of products \( G(\omega_i) \) and \( \delta(\omega_i) \). Each vertex splits into an aggregate of singly-connected diagrams in all possible ways.

We shall prove that in this case the difference in (9) is proportional to \( b^{N-1}(y) \). We assume that this rule is obeyed for \( M < N \). The subtracted terms are then proportional to
\[
\sum_{m_i} \prod_{i} \frac{(b[M_i-1]m_iN_i)}{M_i m_i!} = \sum_{m_i} \prod_{i} \frac{(b[M_i-1]m_iN_i)}{M_i m_i!} - b[N-1]. \tag{A.6}
\]

In order to express \(\langle S_z^2 \rangle^N \rangle\) in terms of the function \(b(y)\) and its derivatives, we use the equations

\[
\langle S_z^2 \rangle^N = \frac{z^{(N)}}{z}; \quad b = \frac{z'}{z}; \quad z = \exp(z). \tag{A.7}
\]

Using Leibnitz's rule, we obtain

\[
\langle S_z^2 \rangle^N = \frac{1}{z} (bz)^{[N-1]} = \sum_{n} \frac{(N-1)!}{n! (N-1-n)!} b^n \langle S_z^2 \rangle^{N-n}. \tag{A.8}
\]

We assume that each average \(\langle S_z^2 \rangle^{N-n}\) entering in the right-hand side of (A.8) is given by the first term of the right-hand side of (A.6) with the replacement \(N \rightarrow N - n\). Substituting in (A.8) the expressions \(\langle S_z^2 \rangle^{N-n}\), we convince ourselves that the same assumption is also correct for \(\langle S_z^2 \rangle^N\) and for \(N = 1\) the average \(\langle S_z^2 \rangle = b\) according to definition (5).

Thus after the subtraction (A.6) the coefficient for the \(N\)-connected diagram in (9) is \(b^{(N-1)}(y)\). Carrying out a Fourier transformation over the times \(t_1, t_2, ..., t_n\) and using for the Fourier components of the Green's function \(G(t)\) of (A.5) the well-known expression (10), we obtain the rule formulated in the paper.

2. F. J. Dyson, Phys. Rev. 102, 1217 (1956).
19. J. M. Luttinger, Lectures presented at the Physics Faculty of the Moscow State University in 1961; S. V. Tyablikov, Metody kvantovoǐ teorii magnetizma (Methods of the Quantum Theory of Magnetism), Nauka, 1965, Sec. 10.

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