present paper is achieved. We have a starting point for detailed calculations of the thermodynamic effects of spin-wave interactions. Such calculations will be carried through, and quantitative results obtained, in a following paper.

ACKNOWLEDGMENTS

This work was done at the University of California; the author wishes to thank the Berkeley Physics Department for its hospitality, and Professor Kittel for supplying the initial stimulus.

PHYSICAL REVIEW VOLUME 102, NUMBER 5 JUNE 1, 1956

Thermodynamic Behavior of an Ideal Ferromagnet*

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(Received February 2, 1956)

The free energy of an ideal Heisenberg-model ferromagnet is calculated as a power series in the temperature T, using the mathematical machinery developed in an earlier paper. The spontaneous magnetization in zero external field is given by

$$[M(T)/M(0)]=S-a_0\theta^{3/2}-a_1\theta^{5/2}-a_2\theta^{7/2}-a_3S^{-1}\theta^4+O(\theta^{9/2}).$$

Here θ is the temperature in dimensionless units, and a_0, a_1, a_2, a_3 are positive numerical coefficients which are computed for the three types of cubic crystal lattice. The first two terms are the result of the simple Bloch theory in which spin waves are treated as noninteracting Bose particles with constant effective mass. The a_1 and a_2 corrections come from the variation of effective mass with velocity. The a_3 term is the lowest order correction arising from interaction between spin waves. This result is in violent contradiction to earlier published calculations which gave interaction effects proportional to $T^{7/4}$ and T^2.

The smallness of the thermodynamic effects of spin-wave interactions is discussed in physical terms, and partially explained, in the introduction of this paper. A general proof is given that the thermodynamic effects of the "exclusion principle," which forbids more than $(2S)$ spin deviations to occupy the same atom, are of order $\exp(-a\theta^{-1})$ and give zero contribution to any finite power of θ. The residual dynamical interaction between 2 spin waves gives rise to a second virial coefficient b_2' which is calculated and shown to be of order $T^{5/2}$. The a_3 term in the magnetization is proportional to b_2'. Effects of interaction of 3 or more spin waves are estimated and found to be of order θ^5 or higher.

1. INTRODUCTION

In the preceding paper,[1] a mathematical formalism was constructed to describe the motions of spin waves in an ideal ferromagnetic lattice. In particular, an exact formula (I, 157) was derived for the free energy of such a lattice. In this paper the free energy will be evaluated as a series expansion in powers of the temperature T. The results may be expected to provide an accurate description of the thermodynamics of the model in the range of low temperatures, say below one quarter of the Curie temperature. The notations and definitions of the earlier paper will be used without further explanation.

The quantity which is of the greatest practical interest is the spontaneous magnetization $M(T)$ of the lattice in zero external field. In the linear approximation of the Bloch spin-wave theory,[2] this magnetization is given by the formula

$$[M(T)/M(0)]=S-\zeta(\tfrac{3}{2})\theta^{3/2}. \tag{1}$$

Here $\zeta(a)=\sum_1^\infty n^{-a}$ is the Riemann zeta function, S is the spin of each atom, and θ is the dimensionless temperature defined by Eq. (I, 108). Considerable uncertainty has existed concerning the accuracy of this formula. Kramers and Opechowski[3] have calculated additional terms in an expansion in ascending powers of θ, and find the next term to be of order θ^2. However, Schafroth,[4] using the spin-wave formalism of Holstein and Primakoff,[4] finds a term in $\theta^{7/4}$ with a positive coefficient, which would interfere seriously with the $\theta^{3/2}$ term in the temperature range of current experiments.[5] Van Kranendonk[6] by another method arrives at a term in $\theta^{7/4}$ with a different coefficient. There is a clear disagreement between these three published results. The starting point of the present investigation was an attempt to decide which of them is correct.

The Bloch formula (1) is obtained by assuming that spin waves do not interact with one another, and that the energy of a spin wave is proportional to λ^{-2}, where λ is the wavelength. The theoretical deviations arise from three causes: (a) deviation of the energy spectrum from the λ^{-2} law; (b) true dynamical interaction between spin waves; (c) kinematical interaction between spin waves due to the fact that a single atom cannot carry more than $2S$ units of reversed spin simultane-

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* Research supported by the National Science Foundation.

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ously. The exact definitions of dynamical and kinematical interaction are given in Sec. (I, 3). Effect (a) is simple to calculate and adds to Eq. (1) terms in $\theta^{5/2}, \theta^{7/2}, \cdots$ which are exhibited in Sec. 5 of this paper. Effect (b) is also straightforward and is calculated in Secs. 6–9; the leading term is given by Eq. (122) and is of order θ^4. The major difficulty of the problem lies in the treatment of (c).

We shall prove in Secs. 2–4 that the contribution of (c) to the free energy is less than $\exp[-aT_c/T]$, where T_c is the Curie temperature[7] and a is a numerical coefficient of the order of unity and independent of temperature. The effects of (c), although they are certainly important in the neighborhood of the Curie point, give rigorously zero contribution to the coefficients in the low-temperature expansion of the free energy in powers of θ. The lowest order correction to Eq. (1) arising from spin-wave interactions is the θ^4 term from effect (b). In particular, it is established that neither θ^2 nor $\theta^{7/4}$ corrections exist. The corrections are all so small that experimental departures from the Bloch formula can be reliably attributed to physical effects not included in the model.

The large corrections found by earlier investigators[3,4,6] arose from insufficiently exact treatments of the kinematical interaction (c). This interaction produces effects which appear to be large, but which upon closer examination cancel each other almost exactly. It is easy to be misled, because an approximation which looks harmless can destroy the cancellation and produce a result much larger than the true one. The present author once fell into the same trap and announced a correction to Eq. (1) of order $\theta^{9/4}$, in a letter which was circulated but fortunately not published. The $\theta^{9/4}$ term was obtained by calculating the terms in Eq. (I, 157) which involve the kinematical interaction but not the dynamical interaction. Since the terms involving the dynamical interaction alone are of order θ^4, it seemed safe to assume that terms involving both interactions simultaneously would be of higher order than $\theta^{9/4}$. However, it turned out that the leading term involving both interactions is of order $\theta^{9/4}$ and precisely cancels the leading kinematical term. The analysis of Secs. 2–4 will show that the cancellation is by no means accidental and extends to all powers of θ.

The main result of this paper is therefore a negative one, that there is no thermodynamical effect of the kinematical spin-wave interaction in any series expansion in powers of θ. In other words, the spin waves can be considered as a Bose gas of ordinary particles subject to no "exclusion principle" but only to the weak dynamical interaction. The basic physical reason for this result seems to be the following. A spin wave of long wavelength is a rotation of the total spin of a *large* number of aligned atoms through a *small* angle. Such small rotations do not have any significant tendency to exclude each other.

The picture of a spin wave as a coherent rotation of a large number of atomic spins through a small angle provides a qualitative explanation for the smallness of both kinematical and dynamical interactions. In this picture the kinematical interaction is the limitation in the number of available states, due to the fact that rotation angles have a range of variation which is not infinite but equal to 2π. This limitation will become important only when rotation angles of the order of a radian are actually excited, which is the case at temperatures in the neighborhood of the Curie point. At low temperatures, the probability of a rotation angle exceeding a radian decreases exponentially with decreasing temperature, and the effects of kinematical interaction are correspondingly small.

In the same picture, the dynamical interaction between spin waves arises in the following way. When two long-wavelength spin waves are superposed in the same region of the lattice, they will interfere with each other to the extent that the two corresponding rotations of the total spin of the region fail to commute. The noncommutativity causes a mutual disturbance which is the dynamical interaction.[8] Since any two rotations through small angles almost commute, the dynamical interaction is always weak and grows rapidly weaker at longer wavelengths.

The explanation of the smallness of both kinds of interaction effects lies in the fact that a spin wave of long wavelength is a basically nonlocal phenomenon. Because each spin wave is a coherent movement of a great number of atomic spins, the quantum effects of the individual spins are very largely suppressed. For this reason it seems that the spin-wave picture is more appropriate than the Van Kranendonk picture[6] of a gas of spin deviations attached to individual lattice sites, for describing the state of a ferromagnet at low temperatures. At higher temperatures, and especially in the neighborhood of the Curie point, the situation is reversed; the spin-wave picture becomes meaningless while the Van Kranendonk picture remains valid and useful.

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[7] The relation between the Curie temperature and the exchange integral J is not known precisely. For convenience we define an "approximate Curie temperature" T_c by the equation $kT_c = \frac{1}{3}JS\gamma_0\nu$, which gives the convenient relation $(T/T_c) = 2\pi\theta$ to define the dimensionless variable θ. Various approximate calculations, reported by C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 163, give values for the Curie temperature equal to T_c within the theoretical uncertainty. More recent calculations by G. S. Rushbrooke and P. J. Wood, Proc. Phys. Soc. (London) **A68**, 1161 (1955), indicate that for all three types of cubic lattice, with $S=\frac{1}{2}$, the true Curie temperature is about $0.9T_c$. Note that the J in the quoted references is equal to $\frac{1}{2}J$ in the notations of the present paper.

[8] Strictly speaking, if two degrees of freedom of a system are associated with coordinates x, y, the extent to which the two coordinates fail to be dynamically independent is measured not by the commutator $[x,y]$ but by the double commutator $[\dot{x},y] = (i/\hbar)[[\mathcal{H},x],y]$. Accordingly it is the double commutator of the Hamiltonian with two rotations [see Eq. (I, 22)] which determines the magnitude of the dynamical interaction.

2. PHYSICAL AND IDEAL SPIN-WAVE MODELS

We now begin the analysis of thermodynamic effects of the kinematical interaction, which will occupy Secs. 2–4. The first step is to reformulate the properties of the physical and ideal spin-wave models which were discussed in Sec. (I, 5). The reformulation will supplement and simplify, but not supersede, the results obtained in I.

We introduce an operator F, operating in the Hilbert space of the ideal spin-wave model. Between two states $|u)$, $|v)$ of the ideal model, defined by Eq. (I, 43), the matrix element of F is

$$(v|F|u)=F_u\delta_{uv}, \tag{2}$$

with F_u given by Eqs. (I, 31) and (I, 32). Then according to Eq. (I, 31)

$$(v|F|u)=\langle v|u\rangle. \tag{3}$$

An ideal state $|u)$ is called "proper" if there exists a physical state $|u\rangle$ corresponding to it, which is the case if each u_j does not exceed $2S$. Otherwise the state $|u)$ is called "improper." The meaning of Eq. (3) is that the two sides of the equation are equal when $|u)$ and $|v)$ are proper states, and the left side is zero if one or both states are improper.

The Hamiltonian $\mathcal{H}$ is transferred from the physical to the ideal model by means of the parallel equations (I, 26) and (I, 47). In consequence of Eq. (3), the definition of the transferred Hamiltonian may be written

$$(v|F\mathcal{H}|u)=\langle v|\mathcal{H}|u\rangle. \tag{4}$$

This equation, like Eq. (3), means that the two sides are equal when $|u)$ and $|v)$ are proper, while the left side is zero otherwise. In particular, Eq. (4) implies that all matrix elements of $\mathcal{H}$ from an improper state $|u)$ to a proper state $|v)$ are zero. But the matrix elements into an improper state $|v)$ need not be zero, because the left side of Eq. (4) is automatically zero when $|v)$ is improper. The matrix elements of $\mathcal{H}$ into improper states are left completely undetermined by Eq. (4).

The choice of Eq. (I, 48) for the Hamiltonian of the ideal model is not uniquely determined by Eq. (I, 47). We may add to the Hamiltonian (I, 48) any operator which has zero matrix elements into proper states $|v)$, and all the results obtained in I will remain valid. We shall take advantage of this freedom to modify $\mathcal{H}$ in the next section.

A convenient language in which to speak of the ideal spin-wave model is to call the operator F an "indefinite metric tensor." Thus every state $|u)$ has an adjoint defined by

$$(\bar{u}|=(u|F. \tag{5}$$

Every operator O of the physical model is transferred to the ideal model by the definition

$$(\bar{v}|O|u)=(v|FO|u)=\langle v|O|u\rangle, \tag{6}$$

of which Eqs. (3) and (4) are special cases. If O is Hermitian in the physical model, it satisfies in the ideal model the condition

$$FO=O^*F, \tag{7}$$

that is to say it is self-adjoint with respect to the metric F. In particular $\mathcal{H}$ is self-adjoint in this sense. In general, all physically observable quantities such as probabilities and eigenvalues are unchanged when we pass from the physical to the ideal model, provided that conjugate states are replaced by adjoints.[9]

The interpretation of F as an indefinite metric makes clearer the physical meaning of the eigenstates of the Hamiltonian $\mathcal{H}$ which were studied in Sec. (I, 6). These were states $|\psi)$ of the ideal model satisfying the equation

$$\mathcal{H}|\psi)=\epsilon|\psi). \tag{8}$$

Let P be the projection operator onto the proper states of the ideal model; this has matrix elements

$$(v|P|u)=E_u\delta_{uv}, \tag{9}$$

with E_u given by Eq. (I, 56). The fact that $\mathcal{H}$ has zero matrix elements from improper to proper states is expressed by the identity

$$P\mathcal{H}=P\mathcal{H}P. \tag{10}$$

Thus Eq. (8) implies

$$F\mathcal{H}P|\psi)=\epsilon F|\psi). \tag{11}$$

If $|\psi\rangle$ is the physical state corresponding to the proper part $P|\psi)$ of $|\psi)$, than Eq. (11) is equivalent to the statement

$$\mathcal{H}|\psi\rangle=\epsilon|\psi\rangle. \tag{12}$$

Thus every solution of Eq. (8) for which $P|\psi)\neq 0$ gives rise to a physical eigenstate of the Hamiltonian in the physical model.

Conversely, let $|\psi\rangle$ be any physical eigenstate satisfying Eq. (12). Then the corresponding proper ideal state $P|\psi)$ satisfies Eq. (11), from which

$$P\mathcal{H}P|\psi)=\epsilon P|\psi) \tag{13}$$

follows. Thus Eqs. (12) and (13) are equivalent, and there is a one-to-one correspondence between the physical eigenstates $|\psi\rangle$ and the ideal eigenstates $P|\psi)$, corresponding eigenvalues being equal. The deduction of Eq. (8) from (13) is, however, not trivial. For Eq.

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[9] The Holstein-Primakoff method (see reference 4) associates with each physical state $|u\rangle$ the ideal state $|u)_{HP}=F^{\frac{1}{2}}|u)$. Thus Eqs. (3) and (6) are replaced by $(u|v)_{HP}=\langle u|v\rangle$, $(u|O_{HP}|v)_{HP}=\langle u|O|v\rangle$, with a transformed operator O_{HP} defined by $O_{HP}=F^{\frac{1}{2}}OF^{-\frac{1}{2}}$. In particular, the transformed Hamiltonian $\mathcal{H}_{HP}=F^{\frac{1}{2}}\mathcal{H}F^{-\frac{1}{2}}$ is Hermitian in the ideal model. By using the basic states $|u)_{HP}$, which are orthogonal and correctly normalized, the method avoids the conceptual difficulties associated with indefinite metric and non-Hermitian Hamiltonian. But the metric tensor F takes its revenge by appearing in $\mathcal{H}_{HP}$ with a square root; for any practical calculation of spin-wave interaction effects, the Hamiltonian $\mathcal{H}_{HP}$ is useless because of the dominating nonlinear behavior of the square roots.

(8) to hold, the improper part $|\psi')$ of $|\psi)$ must be determined by

$$(\mathcal{H}-\epsilon)|\psi')=(1-P)\mathcal{H}P|\psi). \tag{14}$$

This can be solved for $|\psi')$ and gives a unique state $|\psi)$ satisfying Eq. (8), provided that there does not exist a purely improper eigenstate of $\mathcal{H}$ with the same eigenvalue ϵ. For Eqs. (8) and (12) to be equivalent, it is thus sufficient that ϵ should not be the eigenvalue of a purely improper state.

We shall investigate whether ϵ may be an improper eigenvalue, in the case of the two-particle states constructed in Sec. (I, 6). When $S>\frac{1}{2}$, two-particle states have no improper components and so the question does not arise. So we suppose $S=\frac{1}{2}$. Then any improper two-particle state $|\psi')$ is of the form

$$|\psi')=\sum_j\psi(\mathbf{j},\mathbf{j})\eta_j^{*2}|0), \tag{15}$$

and the Hamiltonian (I, 57) operating on it gives

$$\mathcal{H}|\psi')=(E_0+2L+\gamma_0J)|\psi'). \tag{16}$$

Every improper two-particle state is an eigenstate with the same eigenvalue given by Eq. (16). The eigenvalue of the physical scattering state of two spin waves with momenta $\boldsymbol{\sigma}$, $\boldsymbol{\tau}$ is

$$\epsilon=E_0+2L+\tfrac{1}{2}J[2\gamma_0-\gamma_\sigma-\gamma_\tau]. \tag{17}$$

This can indeed become degenerate with Eq. (16) when the two spin waves have energies of the order of $\frac{1}{2}\gamma_0J$. But whenever the wavelengths are long compared with δ, the energies are small compared with γ_0J, and there is a clear separation between proper and improper eigenvalues. In the case of long wavelengths, the eigenstates of Eq. (8) are in one-to-one correspondence with the physical states satisfying Eq. (12).

To conclude this section, we observe that the identity (10) leads to a very simple derivation of the formula (I, 55) for the partition function of the lattice. By using Eq. (10) repeatedly, it is easy to prove

$$\exp(-\beta P\mathcal{H}P)=P\exp(-\beta\mathcal{H}). \tag{18}$$

We have seen that the eigenstates of $(P\mathcal{H}P)$ in the ideal model are in one-to-one correspondence with the eigenstates of $\mathcal{H}$ in the physical model. Therefore the partition-function Z is the trace of the left side of Eq. (18), taken in the ideal model. But the trace of the right side of Eq. (18) is identical with the right side of Eq. (I, 55), and this completes the proof.

3. CONSTRUCTION OF A POSITIVE HAMILTONIAN

The Hamiltonian (I, 57) may conveniently be written

$$\mathcal{H}=E_0+Lq+JS\sum_{j\delta}[\eta_j^*f(u_{j+\delta})(\eta_j-\eta_{j+\delta})], \tag{19}$$

with

$$f(u)=1-(u/2S). \tag{20}$$

Here q is the total number of particles, which is a constant of the motion and may be treated as a c-number, and u_j is the occupation number at lattice site $\mathbf{j}$. The eigenvalues of this Hamiltonian corresponding to proper eigenstates all lie above E_0, by a theorem of Teller.[10] However, the third term in Eq. (19) is not positive-definite for improper states. Consider for example the state

$$(\eta_j^*)^X(\eta_{j+\delta}^*)^Y|0). \tag{21}$$

In this state, Eq. (19) has the expectation value

$$\langle\mathcal{H}\rangle=E_0+L(X+Y)+JS[Xf(Y)+Yf(X)], \tag{22}$$

which certainly lies below E_0 if X and Y are both large. Thus the Hamiltonian is not only not positive-definite, but even has no lower bound to its eigenvalues, when improper states are included.

The improper eigenvalues are a purely artificial creation and must disappear automatically from any physically observable quantity. For example, they are excluded from the partition function (I, 55) by the factor E_u which is zero for improper states. However, our method of calculation is based on the identity

$$Z=Z_T-Z_I, \tag{23}$$

where

$$Z_T=\text{Spur}[\exp(-\beta\mathcal{H})] \tag{24}$$

is a sum extended over all eigenstates of $\mathcal{H}$ in the ideal model, and Z_I is the same sum extended over improper eigenstates. The exact formula (I, 157) for the free energy is obtained by taking the logarithm of Eq. (23). The terms in Eq. (I, 157) involving no Δ_j with $j>1$ are

$$A_T=-(kT/N)\log Z_T, \tag{25}$$

and the terms involving some Δ_j with $j>1$ are corrections which subtract away the nonphysical effects of the improper states in Z_I. In other words, A_T is the free energy of a Bose gas with dynamical interaction but no kinematical interaction, and the kinematical corrections to A_T consist in the removal of the contributions arising from improper states.

If we use this method of calculation, it is essential that the eigenvalues of $\mathcal{H}$ should be bounded below, in order that A_T should even exist. We are therefore forced to modify the Hamiltonian. The desired result is obtained by a very simple modification, keeping Eq. (19) unchanged but using instead of Eq. (20)

$$\begin{aligned} f(u)&=1-(u/2S), & u&=0,1,\cdots,2S,\\ f(u)&=0, & u&>2S. \end{aligned} \tag{26}$$

This change is allowed by the argument of Sec. 2, because it adds to the Hamiltonian an operator which has zero matrix elements into all proper states. The added term also has zero matrix elements between states containing less than $(2S+2)$ particles, so that the previous discussion of 2-particle eigenstates is not affected by the change. The dynamical spin-wave inter-

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[10] E. Teller, Z. Physik **62**, 102 (1930). A proof of this theorem is incidentally provided by Eq. (40).

action will be modified by the addition of terms representing the direct interaction of $(2S+2)$ or more particles. The Green's functions Γ_j defined in Sec. (I, 9) will be unchanged for $j=1, 2, \cdots, 2S+1$, but changed for $j\geq 2S+2$.

An important property of the modified Hamiltonian is that it still contains the factor $(\eta_j-\eta_{j+\delta})$ operating to the right. This means that the new dynamical interactions introduced by the change have the property of being uniformly small when operating on a state composed of spin waves with long wavelengths.

We now proceed to the proof that the eigenvalues of the modified Hamiltonian all lie above E_0. Let g be any set consisting of a finite number of lattice points $\mathbf{j}$. Let (M) be a set of integers M_j, one corresponding to every $\mathbf{j}$ in g, satisfying

$$M_j\geq 2S+1, \quad \mathbf{j}\in g. \tag{27}$$

Let Q_M be the space composed of linear combinations of those states of the ideal model for which

$$\begin{aligned} u_j&=M_j, & \mathbf{j}&\in g,\\ u_j&\leq 2S, & \mathbf{j}&\in \bar{g}. \end{aligned} \tag{28}$$

Here $\bar{g}$ means the set of lattice points $\mathbf{j}$ not in g. Let P_M be the projection operator onto the space Q_M. In particular, when g is the empty set, Q_M is the space of proper states and P_M is the projection operator P defined by Eq. (9). When g is not empty, Q_M is the space of states which are improper with respect to a fixed set of lattice points at which fixed numbers of particles are located.

Let $|u)$ and $|v)$ be any two states, and $\mathbf{j}$ any lattice-site for which $u_j<v_j$. The matrix element $(u|\mathcal{H}|v)$ according to Eq. (19) contains a factor $f(u_j)$, which is zero by Eq. (26) when $u_j\geq 2S$. If then the state $|v)$ lies in Q_M, nonzero matrix elements of $\mathcal{H}$ lead only to states $|u)$ with

$$u_j\geq M_j, \quad \mathbf{j}\in g. \tag{29}$$

In other words, $\mathcal{H}$ has matrix elements from a state of Q_M to a state of $Q_{M'}$ only if the conditions

$$\begin{aligned} &g'\supset g,\\ &M_j'\geq M_j, \quad \mathbf{j}\in g, \end{aligned} \tag{30}$$

hold. The conditions (30) will be expressed for brevity by the notation $(M')\geq(M)$. The important point is that the relation $(\geq)$ is transitive, that is to say $(M'')\geq(M')$ and $(M')\geq(M)$ imply $(M'')\geq(M)$, and asymmetric, that is to say $(M')\geq(M)$ and $(M)\geq(M')$ imply $(M')=(M)$. Hence, if a cycle of nonzero matrix elements $(u_1|\mathcal{H}|u_n)$, $(u_n|\mathcal{H}|u_{n-1})$, $\cdots$, $(u_2|\mathcal{H}|u_1)$ exists with each $|u_i)$ belonging to Q_{M_i}, all the (M_i) must be identical. From this follows the identity

$$P_M[\exp(-\beta\mathcal{H})]P_M=\exp(-\beta P_M\mathcal{H}P_M), \tag{31}$$

of which Eq. (18) is the special case $g=0$.

Taking the spur of Eq. (31) and summing over (M), we obtain Z_T given by Eq. (24). Thus

$$Z_T=\textstyle\sum_M \operatorname{Spur}[\exp(-\beta P_M\mathcal{H}P_M)]. \tag{32}$$

Equation (32) states that to find all the eigenvalues of $\mathcal{H}$ it is sufficient to examine the projections of $\mathcal{H}$ in each subspace Q_M separately.

When $\mathcal{H}$ is operating between two states of the subspace Q_M, Eq. (19) may be written

$$\begin{aligned}\mathcal{H}=E_0+Lq+JS\textstyle\sum_1[\eta_j^*f(u_{j+\delta})(\eta_j-\eta_{j+\delta})]&\\ +JS\textstyle\sum_2 M_jf(u_{j+\delta}).&\end{aligned} \tag{33}$$

Here the sum $\sum_1$ extends over points $(\mathbf{j}, \mathbf{j}+\boldsymbol{\delta})$ both belonging to $\bar{g}$, while $\sum_2$ extends over $\mathbf{j}$ belonging to g with $(\mathbf{j}+\boldsymbol{\delta})$ belonging to $\bar{g}$. In Eq. (33) the operators η_j, η_j^*, with $\mathbf{j}$ in g, no longer appear; the degrees of freedom of the system corresponding to these variables are suppressed by Eq. (28). Therefore $\mathcal{H}$ may be considered as operating between states $|u)$ and $|v)$ defined by occupation-numbers u_j and v_j at points $\mathbf{j}$ in $\bar{g}$ alone. When defined in this way the states $|u)$ and $|v)$ are proper, corresponding to physical states $|u\rangle$ and $|v\rangle$ of the spin system which remains after the atoms at points $\mathbf{j}$ in g are removed from the lattice.

By following the argument of Sec. 2 in the reverse direction, we may transfer $\mathcal{H}$ back into an operator operating on physical states $|u\rangle$. The eigenvalue problem

$$\mathcal{H}|u)=\epsilon|u), \tag{34}$$

with $\mathcal{H}$ given by Eq. (33) and the state $|u)$ in Q_M, is then equivalent to the problem

$$\mathcal{H}|u\rangle=\epsilon|u\rangle, \tag{35}$$

where $|u\rangle$ is a state of the spin system with atoms $\mathbf{j}$ in g removed, and $\mathcal{H}$ is given by

$$\begin{aligned}\mathcal{H}=E_0+Lq+\tfrac{1}{2}J\textstyle\sum_1[S^2-(\mathbf{S}_j\cdot\mathbf{S}_{j+\delta})]&\\ +\tfrac{1}{2}J\textstyle\sum_2 M_j(S-S_{j+\delta}^z).&\end{aligned} \tag{36}$$

There is a theorem, proved in Appendix I, which states that

$$S^2-\langle(\mathbf{S}_j\cdot\mathbf{S}_{j+\delta})\rangle\geq(8S)^{-1}[\langle S_j^z\rangle-\langle S_{j+\delta}^z\rangle]^2, \tag{37}$$

where the expectation values are taken with respect to any physical state whatever. When the expectation value of Eq. (36) is taken in the state $|u\rangle$ which satisfies Eq. (35), the theorem gives

$$\begin{aligned}\epsilon\geq E_0+Lq+(J/16S)\textstyle\sum_1[V_j-V_{j+\delta}]^2&\\ +\tfrac{1}{2}J\textstyle\sum_2 M_j[V_j-V_{j+\delta}],&\end{aligned} \tag{38}$$

with

$$\begin{aligned} V_j&=S+\langle S_j^z\rangle, & \mathbf{j}&\in\bar{g},\\ V_j&=2S, & \mathbf{j}&\in g. \end{aligned} \tag{39}$$

By means of Eqs. (27) and (39), the second sum in Eq. (38) may be crudely approximated and combined with the first to give

$$\epsilon \geq E_0 + Lq + (J/16S)\sum_{\mathbf{j}\boldsymbol{\delta}}[V_{\mathbf{j}} - V_{\mathbf{j}+\boldsymbol{\delta}}]^2, \tag{40}$$

where the sum is now over all $\mathbf{j}$ and $\boldsymbol{\delta}$.

To find a lower bound to Eq. (40), we return to the electrical network analog which was introduced after Eq. (I, 75). The sum

$$D = \tfrac{1}{2}\sum_{\mathbf{j}\boldsymbol{\delta}}[V_{\mathbf{j}} - V_{\mathbf{j}+\boldsymbol{\delta}}]^2 \tag{41}$$

is the energy dissipation in the network when each junction $\mathbf{j}$ is maintained at potential $V_{\mathbf{j}}$. The presence of the term Lq in Eq. (40) requires that q be finite and therefore the $V_{\mathbf{j}}$ tend to zero at large distances. The minimum of D is attained when current is fed into the network only at the junctions $\mathbf{j}$ of g at which the potential is $2S$, the current flowing out to zero potential at infinity. Thus

$$D \geq (2S)^2 R_g^{-1}, \tag{42}$$

where R_g is the resistance of the network between the junctions g and infinity. When one or more junctions are removed from g, the resistance R_g increases and the dissipation decreases. Therefore for any $g \neq 0$,

$$D \geq (2S)^2 R_1^{-1}, \tag{43}$$

where R_1 is the resistance between a single junction and infinity and is given by

$$R_1 = G_0(0) = \int\!\!\int\!\!\int_{-\pi}^{\pi} Q^{-1}dxdydz, \tag{44}$$

with G_0 and Q defined by Eqs. (I, 90, 91, 93, 96). We may write

$$R_1 = (1+\alpha)\gamma_0^{-1}, \quad 0 < \alpha < 1, \tag{45}$$

the numerical values of α for the three types of cubic lattice being, respectively,[11]

$$\alpha = 0.5164, \quad 0.3447, \quad 0.3932. \tag{46}$$

Combining Eqs. (40) and (43), we obtain the inequality

$$\epsilon \geq E_0 + Lq + [JS\gamma_0/2(1+\alpha)] > E_0 + Lq + \tfrac{1}{4}JS\gamma_0, \tag{47}$$

which holds for every eigenvalue of $\mathcal{H}$ operating within a subspace Q_M with $g \neq 0$. The only eigenvalues which are not subject to Eq. (47) are those belonging to proper eigenstates.

We have thus proved that the modified Hamiltonian defined by Eqs. (19) and (26) is positive definite. Further, there is a finite energy gap greater than $(\frac{1}{4}JS\gamma_0)$ between the lowest proper eigenstates and the lowest improper eigenstates. According to reference 7, this gap is of the order of (kT_c) at least.[12] In the partition function defined by Eq. (23), the contribution of an improper eigenstate to Z_I is smaller than Z_T by a factor

$$\exp[-\epsilon/kT] < \exp[-(3\pi\theta)^{-1}], \tag{48}$$

by virtue of Eqs. (I, 108) and (47). It is to be expected that the contribution from improper states to the free energy will remain of the order of magnitude (48), after summing over states and taking the logarithm of Eq. (23). This statement will be proved in the following section.

4. ELIMINATION OF THE KINEMATICAL INTERACTION

In the formula (I, 157) for the free energy, each momentum $\boldsymbol{\lambda}_r$ or $\boldsymbol{\mu}_r$ occurs just twice, once as argument of a Γ_i and once as argument of a Δ_i. Hence the whole expression is formally unchanged if we transform to configuration space, replacing each function Γ_i and Δ_i by its Fourier transform, and replacing each momentum variable $\boldsymbol{\lambda}_r$ or $\boldsymbol{\mu}_r$ by a position variable $\mathbf{j}_r$ or $\mathbf{k}_r$. By Eq. (I, 150), the transformed Δ_q is simply

$$\Delta_q(\mathbf{j}_1,\cdots,\mathbf{j}_q,\mathbf{k}_1,\cdots,\mathbf{k}_q) = e(q)\prod_{r=1}^{q}\delta(\mathbf{j}_r - \mathbf{k}_r)\prod_{r=2}^{q}\delta(\mathbf{j}_r - \mathbf{j}_1). \tag{49}$$

This means that in configuration space the effect of each Δ_q is only to make a set of $2q$ position variables occupy the same lattice point.

The Fourier transform of Γ_1 is, by Eq. (I, 135),

$$\Gamma_1(\mathbf{j},\mathbf{k}) = N^{-1}\sum_{\lambda}\exp[i\boldsymbol{\lambda}\cdot(\mathbf{j}-\mathbf{k}) - \beta(L+\epsilon_\lambda)]. \tag{50}$$

When we insert into Eq. (50) the quadratic approximation (I, 109) for ϵ_λ, the result is

$$\Gamma_1(\mathbf{j},\mathbf{k}) = \theta^{\frac{3}{2}}\exp[-\beta L - \pi\theta V^{-\frac{2}{3}}(\mathbf{j}-\mathbf{k})^2], \tag{51}$$

a Gaussian distribution representing the solution of a continuous diffusion problem. The exact Γ_1 given by Eq. (50) is the solution of the corresponding discrete random-walk problem, in which a particle jumps at random from a lattice point to any one of its nearest neighbors. The exact Γ_1 will behave like Eq. (51) at large separations $|\mathbf{j}-\mathbf{k}|$, decreasing exponentially with a finite range of the order of $\theta^{-\frac{1}{2}}V^{\frac{1}{3}}$.

The Green's functions Γ_q with $q > 1$ are solutions of multiple random-walk problems in which q particles diffuse simultaneously over the lattice with an interaction which acts only between particles which happen to occupy the same or nearest neighbor positions. Since the interaction has short range, the range of the diffusion of any one particle is determined by the function Γ_1. Since Γ_q is defined as a sum only over connected Feynman graphs, all of the q particles are connected with each other by interactions. Therefore the function Γ_q has a finite over-all range, and decreases exponentially as soon as the separation between any two of its arguments is large compared with $\theta^{-\frac{1}{2}}V^{\frac{1}{3}}$.

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[11] The integrals were computed analytically by G. N. Watson, Quart. J. Math. **10**, 266 (1939). For the body-centered case the result is particularly simple, namely $G_0(0) = [32\pi^3]^{-1}[\Gamma(\frac{1}{4})]^4$.

[12] More careful analysis could probably increase the gap by a factor of 2. According to Eq. (16) the gap is not greater than $2JS\gamma_0$ when $S = \frac{1}{2}$.

The general term in Eq. (I, 157) may be written schematically

$$I=N^{-1}\sum_{j_1\cdots j_p}\Big[\prod_i (n_i!)^{-1}\prod_1^{n_i}\Gamma_i(P\mathbf{j},Q\mathbf{j})\Big]. \tag{52}$$

There is one position variable $\mathbf{j}_r$ corresponding to each factor Δ_i in Eq. (I, 157), and this $\mathbf{j}_r$ occurs $(2i)$ times among the arguments of the Green's functions Γ_i. The sum I is precisely what is called a "cluster integral" in the statistical mechanics of imperfect gases. The structure of I depends on the following parameters: (a) the integers m_i which determine how many of the variables $\mathbf{j}_r$ occur $(2i)$ times, (b) the integers n_i which determine how many times each function Γ_i occurs, (c) the permutations P and Q which distribute the $\mathbf{j}_r$ among the Γ_i. The choice of these parameters is restricted only by the requirement that the expression must not break up into a product of two or more unconnected cluster integrals.

If the integers m_i are kept fixed and I is summed over all P and Q, the resulting sum is apart from a numerical factor equal to

$$\textstyle\sum(m_i)=\sum_u(u|\exp[-\beta(\mathcal{H}-E_0)]|u). \tag{53}$$

This is part of the partition function Z_T given by Eq. (24), but the states $|u)$ are restricted to those which contain m_1 positions $\mathbf{j}_r$ occupied singly, m_2 positions occupied doubly, and so on. In Eq. (53) contributions are included from values of n_i, P, and Q which make I disconnected. Such contributions will be of the form

$$\textstyle\sum(m_{1i})\sum(m_{2i})\cdots\sum(m_{si}), \tag{54}$$

where the m_{ji} are integers satisfying

$$\textstyle\sum_j m_{ji}=m_i. \tag{55}$$

The sum of all connected cluster integrals with given m_i will be

$$\textstyle\sum_c(m_i)=\sum(m_i)-\sum(m_{1i})\sum(m_{2i})+\cdots, \tag{56}$$

where each of the correction terms is a product of the form (54) with a numerical coefficient which need not be written out in detail. In fact Eq. (56) states just the identity of the free energy A with the logarithm of the partition function Z, when both quantities are expanded in series of cluster integrals.

Suppose that at least one m_i with $i>1$ is nonzero. By Eq. (I, 151), this means that one m_i with $i>2S$ is nonzero, and so all the states contributing to Eq. (53) are improper. Moreover, in every product which appears in Eq. (56) there is at least one factor $\sum(m_{ji})$ with the same property. By Eq. (48), every term on the right of Eq. (56) has then a factor which is exponentially small at low temperatures. However, it does not immediately follow that $\sum_c(m_i)$ is itself exponentially small, because the different terms on the right of Eq. (56) contain various powers of N. Some care is needed to prove that $[N^{-1}\sum_c(m_i)]$ remains small in the limit as $N\rightarrow\infty$.

To complete the proof, we choose a number M and write

$$\textstyle\sum_c(m_i)=\sum_{c1}+\sum_{c2}. \tag{57}$$

Here $\sum_{c1}$ consists of those terms of the sum $\sum_c(m_i)$ for which

$$|\mathbf{j}_r-\mathbf{j}_s|\leq Mp\theta^{-\frac{1}{2}}V^{\frac{1}{3}} \tag{58}$$

for each pair of variables $(\mathbf{j}_r,\mathbf{j}_s)$, and $\sum_{c2}$ contains the terms for which Eq. (58) is false for some (r,s). The number of sets of points $(\mathbf{j}_1,\cdots,\mathbf{j}_p)$ contributing to $\sum_{c1}$ is of the order of

$$[pM\theta^{-\frac{1}{2}}]^{3p-3}N. \tag{59}$$

Each set $(\mathbf{j}_1,\cdots,\mathbf{j}_p)$ separately gives a contribution which can be written in the form (56) and is bounded by Eq. (48). Hence $\sum_{c1}$ is bounded by

$$N[pM\theta^{-\frac{1}{2}}]^{3p-3}\exp[-(3\pi\theta)^{-1}]. \tag{60}$$

But $\sum_{c2}$ is of the order

$$N\exp(-M^2), \tag{61}$$

because each of the functions Γ_i in the cluster integral has a range limited by Eq. (51). Taking M to be of order $\theta^{-\frac{1}{2}}$, Eqs. (60) and (61) give

$$\textstyle\sum_c(m_i)<bN\exp(-a\theta^{-1}), \tag{62}$$

with coefficients a,b independent of N and θ. It is thereby proved that all terms in the series (I, 157) for the free energy are of order $\exp(-a\theta^{-1})$, except the terms with $m_1=q$, $m_i=0$ for $i>1$.

This result implies that, in developing a series expansion in powers of θ, all terms involving the kinematical interactions Δ_i with $i>1$ may be simply dropped from Eq. (I, 157). The resulting formula for the free energy is

$$A=(E_0/N)-(\beta N)^{-1}\sum_q\sum_{\lambda_1\cdots\lambda_q}\sum_P \times\sum_{n_1n_2\cdots}\Big[\prod_i(n_i!)^{-1}\prod_1^{n_i}\Gamma_i(P\boldsymbol{\lambda},\boldsymbol{\lambda})\Big], \tag{63}$$

representing a virial expansion of the free energy of a Bose gas with only the ordinary dynamical interaction. Each variable $\boldsymbol{\lambda}_r$ occurs just twice among the arguments of the Γ_i, and the permutations P are subject to the condition that every subset of the Γ_i contains at least one $\boldsymbol{\lambda}_r$ whose second occurrence is outside the subset.

The virial coefficients b_n are defined[13] as coefficients in the series

$$A=(E_0/N)-\theta^{\frac{3}{2}}kT\sum_{n=1}^{\infty}b_ne^{-n\beta L}. \tag{64}$$

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[13] The definition of b_q is taken from D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart, New York, 1953), Chap. 8.

Thus b_n is given directly by the terms in Eq. (63) which have $q=n$.

5. FREE ENERGY IN THE LINEAR APPROXIMATION

The leading terms in the virial expansion (63) are those with $n_1=q$, $n_i=0$ for $i>1$. The sum of these terms is the quantity A_B, given explicitly by Eq. (I, 158), which represents the free energy of a spin-wave gas without interaction. At low temperatures, significant contributions to A_B come only from spin-waves of long wavelength, for which the quadratic relation (I, 109) between energy and momentum is a good approximation. If the quadratic approximation for the energy ϵ_λ is substituted into Eq. (I, 158), the result is an elementary Gaussian integral which gives a free energy proportional to $T^{5/2}$, in agreement with Bloch.[2] If we expand the difference between ϵ_λ and the quadratic approximation in powers of $(\delta\lambda)$, and then substitute into Eq. (I, 158), we obtain an expansion of A_B in ascending powers of T. The higher terms in the expansion are corrections to the Bloch formula arising from the discreteness of the lattice, but having nothing to do with interactions between spin waves. These are the corrections which are called type (a) in Sec. 1.

An elementary calculation gives, for the first three terms of the expansion,

$$A_B=-kT[Z_{5/2}(\beta L)\theta^{3/2}+\tfrac{3}{4}\pi\nu Z_{7/2}(\beta L)\theta^{5/2} +\omega\pi^2\nu^2 Z_{9/2}(\beta L)\theta^{7/2}+O(\theta^{9/2})], \tag{65}$$

where

$$Z_n(x)=\sum_{1}^{\infty} q^{-n}e^{-qx}, \tag{66}$$

and ω is a numerical coefficient which takes the values

$$\omega=33/32,\quad 15/16,\quad 281/288,$$

for the three types of cubic lattice. The explicit definition of ω is

$$\omega=(25/32)+\tfrac{3}{4}\langle\cos^4\phi\rangle, \tag{67}$$

where ϕ is an angle between two nearest neighbor lattice vectors $(\boldsymbol{\delta},\boldsymbol{\delta}')$, and $\langle\cos^4\phi\rangle$ denotes an average over all $\boldsymbol{\delta}$ and $\boldsymbol{\delta}'$.

The specific heat and the magnetization per atom are respectively defined by

$$C=-k\frac{\partial}{\partial\theta}\left[\theta^2\frac{\partial}{\partial\theta}\right](\beta A), \tag{68}$$

$$M=-(\partial A/\partial H)=-(m/S)(\partial A/\partial L), \tag{69}$$

according to Eq. (I, 7). At zero magnetic field H, Eq. (64) gives for C and M the values

$$C_B=k[(15/4)\zeta(5/2)\theta^{3/2}+(105/16)\pi\nu\zeta(7/2)\theta^{5/2} +(63/4)\omega\pi^2\nu^2\zeta(9/2)\theta^{7/2}+O(\theta^{9/2})], \tag{70}$$

$$M_B=(m/S)[S-\zeta(3/2)\theta^{3/2}-\tfrac{3}{4}\pi\nu\zeta(5/2)\theta^{5/2} -\omega\pi^2\nu^2\zeta(7/2)\theta^{7/2}+O(\theta^{9/2})], \tag{71}$$

where $\zeta(n)=Z_n(0)$ is the Riemann ζ function. These corrections to the Bloch formula (1), arising merely from the discreteness of the lattice, are easy to calculate and are not of any theoretical interest.

6. VIRIAL SERIES

We now begin the analysis of the contributions to the free energy arising from dynamical spin-wave interactions. The sum of all such contributions is denoted by

$$A_D=A-(E_0/N)-A_B; \tag{72}$$

it is the sum of the terms in the virial series (63) containing at least one Γ_i with $i>1$.

Consider a particular term in A_D for which

$$\sum_{i>1} in_i=q-n_1=f. \tag{73}$$

The labeling of the variables $\boldsymbol{\lambda}_r$ can be arranged so that the factors Γ_1 take the form

$$\prod_{f+1}^{q}\Gamma_1(P\boldsymbol{\lambda}_r,\boldsymbol{\lambda}_r). \tag{74}$$

We call the Γ_i with $i>1$ the "nontrivial" Γ_i, and the $\boldsymbol{\lambda}_r$ with $1\leq r\leq f$ the "nontrivial" $\boldsymbol{\lambda}_r$. Since the permutation P links the arguments of all the Γ_i, every closed cycle of P must include at least one nontrivial $\boldsymbol{\lambda}_r$. The $\boldsymbol{\lambda}_r$ are therefore divided into nonoverlapping chains C_s, $s=1,\cdots,f$, defined as follows. We write

$$\boldsymbol{\lambda}_{s0}=\boldsymbol{\lambda}_s,\quad s=1,\quad\cdots,\quad f, \tag{75}$$

and

$$\boldsymbol{\lambda}_{s,\,i+1}=P^{-1}\boldsymbol{\lambda}_{si},\quad i=0,1,\cdots, \tag{76}$$

whenever $P^{-1}\boldsymbol{\lambda}_{si}$ is a trivial $\boldsymbol{\lambda}_r$. The chain C_s is composed of the variables

$$C_s=[\boldsymbol{\lambda}_{s0},\boldsymbol{\lambda}_{s1},\cdots,\boldsymbol{\lambda}_{sp(s)}], \tag{77}$$

breaking off at the first value of p for which $P^{-1}\boldsymbol{\lambda}_{sp}$ is nontrivial. The chain C_s contains one nontrivial variable followed by $p(s)$ trivial ones, where $p(s)$ may take any value including zero. Every $\boldsymbol{\lambda}_r$ belongs to precisely one C_s.

The product (74) may be written

$$\prod_{s=1}^{f}\prod_{i=1}^{p(s)}\Gamma_1(\boldsymbol{\lambda}_{s,\,i-1},\boldsymbol{\lambda}_{si}). \tag{78}$$

According to Eq. (I, 135), the function Γ_1 contains a δ-function factor, so that Eq. (78) is nonzero only when all $\boldsymbol{\lambda}_{si}$ in the chain C_s are equal to $\boldsymbol{\lambda}_{s0}=\boldsymbol{\lambda}_s$. The summation over the trivial $\boldsymbol{\lambda}_r$ in A_D is therefore indeed trivial. After summing over the trivial variables the product (78) becomes

$$\exp[-\beta\sum_{s=1}^{f}p(s)(L+\epsilon_{\lambda_s})], \tag{79}$$

by virtue of Eq. (I, 135).

The permutation P of all the λ_r induces a permutation Q of the nontrivial λ_s according to the scheme

$$Q^{-1}\lambda_s = P^{-1}\lambda_{sp(s)}, \quad s=1,\cdots,f. \tag{80}$$

Whenever P links all the Γ_i, Q will link the nontrivial Γ_i, and conversely. For given P, Eq. (80) determines Q uniquely, but to a given Q there corresponds a wide variety of P. Namely, when Q is fixed the choice of P is equivalent to choosing (a) the lengths $p(s)$ of the chains $C_1,\cdots,C_f$, and (b) the identification of each chain-position λ_{si}, $i=1,\cdots,p(s)$, with a particular λ_r, $r=f+1,\cdots,q$. The choice (b) can be made in $(q-f)!$ ways, and this cancels the factor $(n_1!)^{-1}$ in Eq. (63). The choice of the $p(s)$ is limited only by the condition

$$\sum_{s=1}^{f} p(s) = n_1, \tag{81}$$

therefore after summing over n_1 the $p(s)$ become independent variables.

Inserting Eq. (79) into Eq. (63) and carrying out the trivial summations, we obtain the formula for dynamical corrections to the free energy

$$A_D = -(\beta N)^{-1}\sum_f \sum_{\lambda_1\cdots\lambda_f} \Big[\prod_{s=1}^{f} Y(\lambda_s)\Big] \times \sum_Q \sum_{n_2 n_3\cdots} \Big[\prod_i (n_i!)^{-1} \prod_1^{n_i} \Gamma_i(Q\lambda,\lambda)\Big], \tag{82}$$

with

$$Y(\lambda) = \sum_{p=0}^{\infty} \exp[-\beta p(L+\epsilon_\lambda)] = \{1-\exp[-\beta(L+\epsilon_\lambda)]\}^{-1}. \tag{83}$$

The factors $Y(\lambda_s)$ in Eq. (82) represent the effect of eliminating from Eq. (63) the terms involving Γ_1.

The main advantage of Eq. (82) over Eq. (63) is that Eq. (82) is a series in which successive terms involve interactions of successively larger numbers of particles. Each factor Γ_i in Eq. (63) or (82) includes one δ function in the momentum variables, and between these δ functions there is one linear relation, namely

$$\sum_{r=1}^{q} (\lambda_r - P\lambda_r) = \sum_{s=1}^{f} (\lambda_s - Q\lambda_s) = 0; \tag{84}$$

no second linear relation can exist, because all the Γ_i are linked by P or Q. Therefore the number of independent momentum variables in a particular term of Eq. (63) or (82) is

$$F = \textstyle\sum_i (i-1)n_i + 1. \tag{85}$$

This F is the number of independent particles which are concerned in the interactions which the particular term describes. Obviously, F is independent of n_1, and so there is an infinite number of terms in Eq. (63) corresponding to each value of F. But in Eq. (82) only the n_i with $i\geq 2$ appear, and there is at most a finite set of terms with given F.

We shall see later that the functions $\Gamma_i(Q\lambda,\lambda)$ in general carry a factor

$$\exp(-\beta\epsilon_\lambda) \tag{86}$$

for each of their arguments λ. After integrating with respect to the F independent momentum variables (each with 3 components) in a particular term of Eq. (82), the factors (86) produce a result proportional to

$$T^{(\frac{3}{2})F}. \tag{87}$$

Actually, because the dynamical interaction vanishes at long wavelengths, the $\Gamma_i(Q\lambda,\lambda)$ carry positive powers of λ in addition to the factors (86), and so the λ integration gives a higher power of T than $\frac{3}{2}F$. But Eq. (87) is enough to indicate the essential point, that the terms of the series (82) belong to powers of T which increase with F. In order to calculate an asymptotic expansion of the free energy up to a given power of T, only a finite set of terms in Eq. (82) needs to be examined. The calculation from this point onward is therefore in principle straightforward.

The reason why the direct virial expansion Eq. (64) is not appropriate for our calculations is that the expansion parameter $\exp(-\beta L)$ becomes unity in the limit of zero external field. In other words, the Bose gas is precisely at the point of condensation when $L=0$. The coefficient b_q contains effects of the purely statistical correlations in the positions of q particles, and at the condensation point these correlations are important for large as well as small q. In Eq. (82), on the other hand, the higher terms represent particle correlations which arise from interactions and not from statistics, and when the interactions are weak these terms are correspondingly small. For a weakly interacting Bose gas at the point of condensation, the true virial expansion (63) converges very poorly, while the "interaction expansion" (82) converges well.

In the following sections we shall calculate all terms in Eq. (82) which might give contributions up to the order T^5. This will determine the magnetization up to order T^4.

7. LEADING DYNAMICAL CORRECTION, BORN APPROXIMATION

The leading term in the series (82) is the term $f=2$, $n_2=1$, $n_i=0$ for $i>2$. This term has $F=2$, and all others have $F\geq 3$, by Eq. (85). Since Γ_2 is a symmetric function, the two permutations Q in the leading term give equal contributions, and this term becomes

$$A_{LD} = -2(\beta N)^{-1}\textstyle\sum_{\sigma\tau} Y(\sigma)Y(\tau)\Gamma_2(\sigma\tau,\sigma\tau). \tag{88}$$

The function Γ_2 was defined by Eq. (I, 133) as a sum of contributions from Feynman graphs G with 2 initial and 2 final vertices. All such graphs belong to the sequence shown in Fig. 1, whose nth member we denote by G_n. The nth Born approximation to A_{LD} is the sum of the contributions from $G_1, \cdots, G_n$.

By following the rules of Sec. (I, 9), it is easy to write down the contribution from G_1,

$$A_{LD}^1 = -\tfrac{1}{2} J N^{-2} \sum_{\sigma\tau} \Gamma_{\sigma\tau}^0 Y(\boldsymbol{\sigma}) Y(\boldsymbol{\tau}) \times \exp[-\beta(\epsilon_\sigma + \epsilon_\tau + 2L)]. \quad (89)$$

When $\Gamma_{\sigma\tau}^0$ defined by Eq. (I, 23) is expanded in powers of $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$, the fourth-order term in $\sigma^2\tau^2$ is the first for which Eq. (89) does not vanish by symmetry. The fourth-order term gives

$$A_{LD}^1 = -(3\pi\nu/4S\beta)\theta^4[Z_{\frac{5}{2}}(\beta L)]^2, \quad (90)$$

an effect of order T^5. The vanishing of the lower-order terms at this point is the essential reason for the over-all smallness of the dynamical correction to the free energy. The vanishing is due to the algebraic structure of the $\Gamma_{\rho\sigma}^{\lambda}$, which in turn may be traced back to the origin of these coefficients in the double commutator (I, 22).

The next contribution to A_{LD} comes from G_2 and is

$$A_{LD}^2 = -(4\beta)^{-1} J^2 N^{-3} \sum_{\sigma\tau\rho\varphi} Y(\boldsymbol{\sigma}) Y(\boldsymbol{\tau}) \delta(\boldsymbol{\sigma}+\boldsymbol{\tau}-\boldsymbol{\rho}-\boldsymbol{\varphi}) \times \Gamma_{\sigma\tau}^{\rho-\tau} \Gamma_{\rho\varphi}^{\sigma-\varphi} \exp[-\beta(\epsilon_\sigma+\epsilon_\tau+2L)]\Phi(D), \quad (91)$$

with

$$\Phi(D) = D^{-2}[e^{-\beta D} - 1 + \beta D], \quad (92)$$

$$D = \epsilon_\rho + \epsilon_\varphi - \epsilon_\sigma - \epsilon_\tau. \quad (93)$$

An elementary calculation, neglecting terms of higher order in θ than those retained, gives the result

$$A_{LD}^2 = -(\pi\nu/4\beta S^2)\theta^4[Z_{\frac{5}{2}}(\beta L)]^2 \times [\alpha + 3X_1\Gamma_1 + 2X_2\Gamma_2]. \quad (94)$$

Here α is defined by Eq. (45), (46), the Γ_i by Eqs. (I, 85)–(I, 88), and the X_i by Eq. (I, 103). The contribution (94) is again of order T^5, and is smaller than Eq. (90) by a numerical factor which is approximately $(3S)^{-1}$ for the simple cubic lattice. Similarly the contributions from $G_3, G_4, \cdots$ will be of the same order, and the Born approximation series

$$A_{LD} = \sum_{n=1}^{\infty} A_{LD}^n \quad (95)$$

will converge only because of the numerical coefficients, which grow smaller in the higher terms according to the argument of Sec. (I, 8).

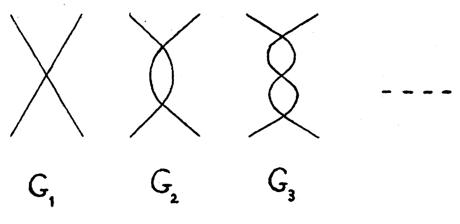

FIG. 1. Feynman graphs with 2 initial and 2 final vertices.

We have calculated the first two terms of the series (95), as a concrete example to show how accurate the successive Born approximations are. We see that the first Born approximation gives the correct order of magnitude of A_{LD}, but gives a wrong numerical coefficient. To obtain the exact value of A_{LD}, a calculation based on the series (95) is evidently clumsy and unsuitable. The advantage of the Born approximation is that it gives simple and rapid estimates of the orders of magnitude of the more complicated terms in the virial expansion (82). With the help of the apparatus of Feynman graphs, the calculation of Born approximations becomes a mechanical process which can be applied systematically to all such terms.

In the following section we abandon the Born approximation and calculate A_{LD} by an independent method which gives the coefficient of T^5 exactly. Equations (90) and (94) will be used only as a check on the results. However, when we consider in Sec. 9 the dynamical corrections to the free energy arising from interactions of more than two particles, the exact method will be impracticable and we shall return to Born approximation estimates.

8. LEADING DYNAMICAL CORRECTION, ACCURATE METHOD

The term A_{LD} defined by Eq. (88) is directly related to the second virial coefficient of the spin-wave gas. If we omit the factors $Y(\boldsymbol{\sigma})Y(\boldsymbol{\tau})$, Eq. (88) becomes

$$\begin{aligned} A_{LD}' &= -2(\beta N)^{-1} \sum_{\sigma\tau} \Gamma_2(\boldsymbol{\sigma\tau}, \boldsymbol{\sigma\tau}) \\ &= (\beta N)^{-1} e^{-2L\beta} \times \mathrm{Spur}[\exp(-\beta(H_1+H_2)) - \exp(-\beta H_1)], \end{aligned} \quad (96)$$

where the spur denotes a sum over states containing two spin waves only, and H_1 and H_2 are defined as in Eq. (I, 58). Equation (96) follows immediately from the definition of the function Γ_2 in Eqs. (I, 123) and (I, 133). The second virial coefficient of the spin-wave gas may be written in the form

$$b_2 = b_2^0 + b_2', \quad (97)$$

where b_2^0 is the coefficient for a perfect Bose gas without interactions. Then Eqs. (64) and (96) give

$$A_{LD}' = -e^{-2L\beta} b_2' \theta^{\frac{3}{2}} kT. \quad (98)$$

There is a well-known formula,[14]

$$b_2' = 2^{\frac{3}{2}} \pi^{-1} \sum_{l=0}^{\infty} (4l+1) \int_0^{\infty} \exp[-\mu\hbar^2 k^2/m] \times (d\eta_{2l}/dk)dk, \quad (99)$$

connecting b_2' with the phase shifts η_{2l} of the scattering states of two interacting Bose particles. Thus we may expect to be able to calculate b_2' exactly from the scattering wave functions which were explicitly con-

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[14] Reference 13, Eq. (8.631), p. 196.

structed in Sec. (I, 6). Because the lattice-space lacks both spherical symmetry and Galilean invariance, Eq. (99) does not apply directly to the spin-wave problem. It would not be difficult to construct a modified form of Eq. (99) which would be valid in a lattice space. We shall, however, take a short-cut and derive an approximate analog of Eq. (99) [namely Eq. (106)] which equates b_2' with an integral over the forward scattering amplitude. The approximation corresponds to replacing the angle η in Eq. (99) by the scattering amplitude ($e^{i\eta}\sin\eta$), and this is allowable in the spin-wave problem because[15] all the angles η go to zero with k at least as fast as k^3. In this way we avoid the need to introduce into the calculation any analysis of scattering states into partial waves.

The states

$$\Phi_{\sigma\tau}=N^{-1}\sum_{jk}\exp[i\boldsymbol{\lambda}\cdot(\mathbf{j}+\mathbf{k})] \times\cos[\boldsymbol{\mu}\cdot(\mathbf{j}-\mathbf{k})]\eta_j^*\eta_k^*|0), \quad (100)$$

with $\boldsymbol{\sigma}=\boldsymbol{\lambda}+\boldsymbol{\mu}$, $\boldsymbol{\tau}=\boldsymbol{\lambda}-\boldsymbol{\mu}$, form a complete orthonormal system[16] of states containing two spin waves. Therefore Eq. (96) may be written

$$\begin{aligned}A_{LD}'&=(\beta N)^{-1}e^{-2L\beta}\int_0^\beta d\beta'\,\mathrm{Spur}\{\exp[-(\beta-\beta')H_1]\\&\quad\times H_2\exp[-\beta'(H_1+H_2)]\}\\&=N^{-1}e^{-2L\beta}\,\mathrm{Spur}\Big\{H_2\exp(-\beta H_1)\\&\quad-\int_0^\beta[1-(\beta'/\beta)]d\beta' H_2\exp[-\beta'(H_1+H_2)]\\&\quad\times H_2\exp[-(\beta-\beta')H_1]\Big\}\\&=(2N)^{-1}\sum_{\sigma\tau}\exp[-\beta(\epsilon_\sigma+\epsilon_\tau+2L)]\\&\quad\times\Big\{\Phi_{\sigma\tau}^*\Big[H_2-\int_0^\beta[1-(\beta'/\beta)]d\beta' H_2\\&\quad\times\exp(-\beta'(H_1+H_2-\epsilon_\sigma-\epsilon_\tau))H_2\Big]\Phi_{\sigma\tau}\Big\}. \quad (101)\end{aligned}$$

This equation is still exact. We now make approximations based on the fact that the spin-wave interaction is *rapid*, that is to say the interaction is completed within a time short compared with $\beta\hbar$. According to the description given in Sec. (I, 8), the interaction consists of a short-range multiple scattering process, with a time scale of the order of $\hbar J^{-1}$ independent of temperature. In other words, the intermediate states which exist virtually between the two operators H_2 in the second term of Eq. (101) have mostly energies of the order of J which are large compared with $\beta^{-1}=kT$. Thus the values of β' which are important in Eq. (101) ($\beta'\hbar$ here represents the duration of the interaction) are small compared with β.

We make the approximation of dropping the term (β'/β) and extending the integration over β' to infinity, in the second term of Eq. (101). This gives

$$A_{LD}'=(2N)^{-1}\sum_{\sigma\tau}\exp[-\beta(\epsilon_\sigma+\epsilon_\tau+2L)] \times(\Phi_{\sigma\tau}^*H_2\Psi_{\sigma\tau}), \quad (102)$$

with

$$\Psi_{\sigma\tau}=[1-(H_1+H_2-\epsilon_\sigma-\epsilon_\tau)^{-1}H_2]\Phi_{\sigma\tau}. \quad (103)$$

This $\Psi_{\sigma\tau}$ is an eigenstate of (H_1+H_2) with eigenvalue $(\epsilon_\sigma+\epsilon_\tau)$. It is the scattering state with incoming particles described by the plane wave $\Phi_{\sigma\tau}$. It is therefore identical with the state

$$\Psi_{\sigma\tau}=N^{-1}\sum_{jk}\psi(\mathbf{j},\mathbf{k})\eta_j^*\eta_k^*|0), \quad (104)$$

in which $\psi(\mathbf{j},\mathbf{k})$ is given by Eq. (I, 71). The quantity

$$a_{\sigma\tau}=(\Phi_{\sigma\tau}^*H_2\Psi_{\sigma\tau}) \quad (105)$$

is precisely the forward scattering amplitude for two spin waves of momenta $\boldsymbol{\sigma}$, $\boldsymbol{\tau}$. Thus Eqs. (98) and (102) give

$$b_2'=-(2N)^{-1}\beta\theta^{-\frac{3}{2}}\sum_{\sigma\tau}\exp[-\beta(\epsilon_\sigma+\epsilon_\tau)]a_{\sigma\tau}, \quad (106)$$

which is the approximate analog of Eq. (99) for the spin-wave system.

The foregoing analysis can be equally well applied to A_{LD} given by Eq. (88), instead of to A_{LD}'. Instead of Eq. (102), we then find

$$A_{LD}=(2N)^{-1}\sum_{p,q=1}^{\infty}\sum_{\sigma\tau} \times\exp[-\beta p(\epsilon_\sigma+L)-\beta q(\epsilon_\tau+L)]a_{\sigma\tau}. \quad (107)$$

The amplitude $a_{\sigma\tau}$ can be expressed very simply in terms of the coefficients A_δ which appear in Eq. (I, 71). Eq. (105) with (I, 72) and (100) gives

$$a_{\sigma\tau}=-4SJN^{-1}\sum_\delta\cos(\boldsymbol{\mu}\cdot\boldsymbol{\delta})A_\delta. \quad (108)$$

We shall retain only the leading term in A_{LD} which is of order T^5. For this degree of accuracy, it is sufficient to calculate the summand in Eq. (108) as far as terms of fourth order in $(\boldsymbol{\sigma}\cdot\boldsymbol{\delta})$ and $(\boldsymbol{\tau}\cdot\boldsymbol{\delta})$. But Eq. (I, 79), which gives A_δ correct to second order in $(\boldsymbol{\sigma}\cdot\boldsymbol{\delta})$ and $(\boldsymbol{\tau}\cdot\boldsymbol{\delta})$, can only be used when A_δ is multiplied by a second-order quantity. The exact relation (I, 73) implies

$$\begin{aligned}2S\sum_\delta\cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})A_\delta&=\{\textstyle\sum_\delta\cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})[\cos(\boldsymbol{\mu}\cdot\boldsymbol{\delta})-\cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})]\}\\&\quad\times[1+\textstyle\sum_\delta A_\delta G(\boldsymbol{\delta})]. \quad (109)\end{aligned}$$

The first factor on the right of Eq. (109) is of second order; hence Eq. (I, 73) may be used in the second factor, and also $G(\boldsymbol{\delta})$ may be approximated by $G_0(\boldsymbol{\delta})$

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[15] According to Eq. (I, 102), η_0 is proportional to k^3, η_2 to k^5.

[16] The states with $\boldsymbol{\sigma}\neq\boldsymbol{\tau}$ have norm 1 while those with $\boldsymbol{\sigma}=\boldsymbol{\tau}$ have norm 2. In a sum over $\boldsymbol{\sigma}$, $\boldsymbol{\tau}$, the states with $\boldsymbol{\sigma}\neq\boldsymbol{\tau}$ are counted twice and those with $\boldsymbol{\sigma}=\boldsymbol{\tau}$ only once; this precisely compensates for the difference in normalization.

$=(\alpha/\gamma_0)$. Equation (109) then becomes

$$2S\sum_\delta \cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})A_\delta=\tfrac{1}{2}[\textstyle\sum_\delta(\boldsymbol{\sigma}\cdot\boldsymbol{\delta})(\boldsymbol{\tau}\cdot\boldsymbol{\delta})\cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})]\times[1+\alpha A'\delta^2(\boldsymbol{\sigma}\cdot\boldsymbol{\tau})]. \quad (110)$$

In Eq. (107) this quantity will be integrated over $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$; so we average Eq. (110) at once over the directions of $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$ and obtain

$$4S\sum_\delta \cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})A_\delta=(1/9)\gamma_0\delta^4\sigma^2\tau^2[-\tfrac{1}{4}+\alpha A']. \quad (111)$$

In the remaining sum

$$S_2=\sum_\delta[\cos(\boldsymbol{\mu}\cdot\boldsymbol{\delta})-\cos(\boldsymbol{\lambda}\cdot\boldsymbol{\delta})]A_\delta, \quad (112)$$

we may use Eq. (I, 73) directly and find, after averaging over the directions of $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$,

$$\begin{aligned}S_2&=\tfrac{1}{2}\textstyle\sum_\delta(\boldsymbol{\sigma}\cdot\boldsymbol{\delta})(\boldsymbol{\tau}\cdot\boldsymbol{\delta})A_\delta\\&=\tfrac{1}{2}\textstyle\sum_\delta[Z_1(\boldsymbol{\delta})+Z_2(\boldsymbol{\delta})+\tfrac{1}{3}(\boldsymbol{\sigma}\cdot\boldsymbol{\tau})\delta^2]\\&\qquad\times[A_1Z_1(\boldsymbol{\delta})+A_2Z_2(\boldsymbol{\delta})+A'(\boldsymbol{\sigma}\cdot\boldsymbol{\tau})\delta^2]\\&=[\gamma_0\delta^4\sigma^2\tau^2/54][3A_1X_1+2A_2X_2+3A']. \quad (113)\end{aligned}$$

With Eqs. (108) and (111), this gives

$$a_{\sigma\tau}=-QJN^{-1}[\gamma_0\delta^4\sigma^2\tau^2/36], \quad (114)$$

where the numerical coefficient Q is defined by

$$Q=8S(A_1X_1+\tfrac{2}{3}A_2X_2)+(\alpha/3S)-\tfrac{1}{3}. \quad (115)$$

After substituting Eq. (114) into (107), we carry out the summation over $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$ and obtain

$$A_{LD}=-Q[3\pi\nu/4S]\theta^4kT[Z_{\frac{5}{2}}(\beta L)]^2. \quad (116)$$

This result differs from the first Born approximation, Eq. (90), only by the factor Q. The expansion of Q in powers of S^{-1} is easily obtained from Eq. (I, 82). It begins

$$Q=1+(3S)^{-1}[3X_1\Gamma_1+2X_2\Gamma_2+\alpha]+\cdots, \quad (117)$$

in agreement with Eq. (94). The largest values of Q occur when $S=\frac{1}{2}$, in which case we have approximately

$$Q=1.68,\ 1.35,\ \text{and}\ 1.45, \quad (118)$$

for the simple, face-centered, and body-centered lattice, respectively.

The second virial coefficient is found from Eq. (106) and (114) and has the value

$$b_2'=[3\pi\nu Q/4S]\theta^{5/2}. \quad (119)$$

For an "ordinary" Bose gas, for example helium, the 2-particle interaction gives rise to an S-wave phase shift η_0 proportional to the momentum k at low energies, and Eq. (99) then gives

$$b_2'\sim T^{\frac{1}{2}} \quad (120)$$

at low temperatures. The spin wave b_2' is smaller by two powers of T than the normal order of magnitude[17] (120). Examination of the scattering-state wave function of Eq. (I, 102) shows that the D-wave and S-wave contributions to b_2' are both of order $T^{5/2}$. For the D-waves this is the normal behavior. The peculiarity of the spin-wave interaction lies in the fact that the amplitude of the outgoing S-wave in Eq. (I, 102) depends on the angle between the incoming particle momenta. Such an angle-dependence is not possible in a system possessing Galilean invariance. For this reason any approximation to the spin-wave interaction by means of ordinary potentials in a continuous space is certain to lead to erroneous results.[18] The S-wave phase shift is of order k^3, and if it were independent of angle it would give $b_2'\sim T^{\frac{3}{2}}$ according to Eq. (99). An additional power of T appears because the average of η_0 over angles is proportional to k^5.

The contributions of dynamical spin-wave interaction to the specific heat and magnetization are obtained by substituting Eq. (116) into (68) and (69). In zero external magnetic field these contributions become

$$C_{LD}=k[15\pi\nu Q/S][\zeta(5/2)]^2\theta^4, \quad (121)$$

$$M_{LD}=-(m/S)[3\pi\nu Q/2S]\zeta(5/2)\zeta(\tfrac{3}{2})\theta^4. \quad (122)$$

These are the leading correction terms which are to be added to the results (70) and (71) of the linear spin-wave theory. The correction to the magnetization is negative, indicating that the interaction between spin-waves is on the average attractive.

9. HIGHER-ORDER DYNAMICAL CORRECTIONS

There remains the task of estimating the order of magnitude of the higher terms in the virial series (82). It will be proved[19] in this section that all such terms are of higher order than T^5 and therefore negligible in comparison with Eq. (116). Exact values of these terms will not be calculated.

The change in the Hamiltonian from Eq. (20) to (26) has the effect of adding to Eq. (I, 58) a series of supplementary interactions between $(2S+2)$ or more particles. The first supplementary interaction, involving exactly $(2S+2)$ particles, is

$$H_{2S+2}=[\tfrac{1}{2}J/(2S+1)!]\times\textstyle\sum_{j\delta}\eta_j^*(\eta_{j+\delta}^*)^{2S+1}\eta_j^{2S+1}(\eta_j-\eta_{j+\delta}). \quad (123)$$

The others are of the same form and involve larger numbers of particles. All these interactions have matrix elements only between improper states.

Each Green's function Γ_i in the series (82) is a sum of contributions $\Gamma_i(G)$ from various Feynman graphs G. By dividing each Γ_i into its constituent $\Gamma_i(G)$, we

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[17] In this connection it may be of interest to observe that there is another well-known physical system which has an abnormally small b_2', namely the Maxwell field. For details see Appendix II.

[18] Van Kranendonk in Eq. (52) of the third paper quoted in reference 6 finds $\alpha_2'\sim T^{-1}$. His definition of the second virial coefficient α_2' differs from our b_2' by a factor $T^{-\frac{3}{2}}$. Thus his result is equivalent to Eq. (120), and the correct result is $\alpha_2'\sim T$.

[19] To avoid becoming immersed in what seem to be unimportant details, we do not attempt to maintain in this section the same standard of mathematical rigor as in Secs. 2–8.

divide the whole expression A_D into a sum of terms $T(G_1, \cdots, G_r)$. We call the term T "regular" if all the graphs $(G_1, \cdots, G_r)$ are constructed according to the rules of Sec. (I, 9) with the two-particle interaction H_2 alone. Other terms, in which one or more of the supplementary interactions such as H_{2S+2} are involved, are called "irregular."

Consider an irregular term in which H_{2S+2} occurs operating at a particular graph vertex to which is associated the integration variable β_1. To this term we add all the other terms which have H_{2S+2} operating at the same value of β_1 and which belong to the same value of f in the series (82). The sum of all such terms[20] is apart from numerical factors an expression of the form

$$\begin{aligned}\mathrm{Spur}\{\exp[-(\beta-\beta_1)(\mathcal{H}-E_0)]H_{2S+2}\\ \times\exp[-\beta_1(\mathcal{H}-E_0)]\},\end{aligned} \tag{124}$$

where the spur denotes a sum over states containing f particles. The summation over permutations Q in Eq. (82) is automatically included in Eq. (124) by the symmetry of the particle wave functions. Since $\mathcal{H}$ has zero matrix elements from improper to proper states, and H_{2S+2} operates only between improper states, the proper states make zero contribution to Eq. (124). The contribution of improper states is, by the argument of Sec. 3, of order $\exp[-a\theta^{-1}]$ at low temperatures. Therefore Eq. (124) gives zero contribution to the free energy[20] in any term of an expansion in powers of θ.

When we add together all irregular terms, the sum is not precisely Eq. (124). The terms including two irregular interactions are counted twice, and those including n irregular interactions are counted n times, in Eq. (124). From Eq. (124) we must therefore subtract a term of the form

$$\begin{aligned}\mathrm{Spur}\{\exp[-(\beta-\beta_1-\beta_2)(\mathcal{H}-E_0)]H_{2S+2}\\ \times\exp[-(\beta_1-\beta_2)(\mathcal{H}-E_0)]\\ \times H_{2S+2}\exp[-\beta_2(\mathcal{H}-E_0)]\},\end{aligned} \tag{125}$$

plus a similar term with H_{2S+2} appearing 3 times, and so on. But Eq. (125) is also of order $\exp[-a\theta^{-1}]$, by the same argument as before. In this way we arrive at the conclusion that the sum of all irregular contributions to the free energy is zero in any finite power of θ.

The elimination of the irregular terms rests on the assumption that the series,[21] of which Eqs. (124) and (125) are the first two terms, will be convergent. The assumption is not in fact valid. We have seen in Sec. (I, 3) that the Hamiltonian (H_1+H_2) has unbounded negative eigenvalues, and therefore the Born approximation series of the regular terms alone cannot converge. The irregular terms must to some extent compensate the divergence of the regular terms, because the modified Hamiltonian $\mathcal{H}$ is free from negative eigenvalues. It is possible that the divergences from regular and irregular terms can be made to cancel each other completely, so that the Born approximation series for the total free energy is convergent. We do not attempt here to prove the convergence, but leave the question open for future investigation. The convergence problem was already discussed qualitatively in Sec. (I, 8).

In this section we consistently use the Born approximation for estimating the magnitude of both regular and irregular contributions to the free energy. The estimates so obtained are not mathematically rigorous. But it seems unlikely that a more careful analysis would change the main conclusion that all terms other than A_{LD} are of higher order than T^5. A rigorous proof of this result would require a detailed investigation of the Green's functions Γ_i with $i\geq 3$, and such an investigation would need more time and effort than the problem is worth.

The result of the preceding analysis may then be stated as follows. So long as we are calculating the Born approximation series term by term, and grouping the terms suitably together, irregular terms make zero contribution to the free energy in any power of θ.

The regular terms can now be rapidly disposed of. According to Eq. (85), after the leading term A_{LD} which has $F=2$, the next terms of the series (82) which must be considered are those with $F=3$. There are two such terms, namely A_{D3} with $f=3$, $n_3=1$, $n_i=0$ for $i\neq 3$, and A_{D22} with $f=4$, $n_2=2$, $n_i=0$ for $i\neq 2$.

Let $\Gamma_3{}^R$ denote the Green's function for three particles, constructed with the regular interaction H_2 alone. The term A_{D3} is, apart from numerical factors,

$$A_{D3}=(\beta N)^{-1}\sum\nolimits_{\lambda\mu\nu}Y(\boldsymbol{\lambda})Y(\boldsymbol{\mu})Y(\boldsymbol{\nu})\Gamma_3{}^R(\boldsymbol{\lambda\mu\nu},\boldsymbol{\lambda\mu\nu}). \tag{126}$$

The summation variables $\boldsymbol{\lambda\mu\nu}$ are here independent, and the function $\Gamma_3{}^R$ carries a factor $\exp[-\beta(\epsilon_\lambda+\epsilon_\mu+\epsilon_\nu)]$ which has the effect of limiting each variable to values of the order of $[\theta^{\frac{1}{2}}V^{-\frac{1}{3}}]$. We express $\Gamma_3{}^R$ as a sum of contributions $\Gamma_3{}^R(G)$ from Feynman graphs G.

According to Eq. (I, 129), each $\Gamma_3{}^R(G)$ includes a factor

$$\Gamma_{\lambda_\rho}{}^{\tau} \tag{127}$$

corresponding to the incident particle with momentum $\boldsymbol{\lambda}$, and a similar factor for the other two incident particles with momenta $\boldsymbol{\mu}$, $\boldsymbol{\nu}$. By Eq. (I, 27), this $\Gamma_{\lambda_\rho}{}^{\tau}$ is proportional to $(\delta\lambda)$ for small $\boldsymbol{\lambda}$, and is to first approximation an odd function of $\boldsymbol{\lambda}$. After averaging over the direction of $\boldsymbol{\lambda}$, $\Gamma_{\lambda_\rho}{}^{\tau}$ becomes proportional to $(\delta\lambda)^2$. Thus the order of magnitude of Eq. (126) is at most

$$\begin{aligned}A_{D3}&\sim[N^{-1}\sum\nolimits_\lambda\exp(-\beta\epsilon_\lambda)Y(\boldsymbol{\lambda})(\delta\lambda)^2]^3\\ &\sim T^{15/2}[Z_{5/2}(\beta L)]^3.\end{aligned} \tag{128}$$

This is comfortably smaller than A_{LD}. The dependence

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[20] Strictly speaking, the sum is to be taken only over connected terms, while Eq. (124) includes contributions from disconnected terms also. A repetition of the argument of Sec. 4 shows that the disconnected terms can be subtracted, as in Eq. (56), without changing the conclusion that Eq. (124) is exponentially small.

[21] This series is not a Born approximation series, but can be regarded as obtained from the Born approximation series by a suitable grouping together of terms.

on L is such that the contribution of A_{D3} to the magnetization is a term of order $\theta^{13/2}$ which remains finite and nonsingular at zero external field.

Next we consider the term A_{D22} which is, apart from numerical factors,

$$A_{D22}=(\beta N)^{-1}\sum_{\lambda\mu\nu\rho} Y(\boldsymbol{\lambda})Y(\boldsymbol{\mu})Y(\boldsymbol{\nu})Y(\boldsymbol{\rho})$$
$$\times[\delta(\boldsymbol{\lambda}+\boldsymbol{\mu}-\boldsymbol{\nu}-\boldsymbol{\rho})\Gamma_2(\boldsymbol{\lambda}\boldsymbol{\mu},\boldsymbol{\nu}\boldsymbol{\rho})\Gamma_2(\boldsymbol{\nu}\boldsymbol{\rho},\boldsymbol{\lambda}\boldsymbol{\mu})$$
$$+\delta(\boldsymbol{\mu}-\boldsymbol{\rho})\Gamma_2(\boldsymbol{\lambda}\boldsymbol{\mu},\boldsymbol{\lambda}\boldsymbol{\mu})\Gamma_2(\boldsymbol{\nu}\boldsymbol{\rho},\boldsymbol{\nu}\boldsymbol{\rho})]. \quad (129)$$

The second term in the bracket in Eq. (129) carries a factor $\exp[-\beta(\epsilon_\lambda+\epsilon_\mu+\epsilon_\nu+\epsilon_\rho)]$, and a repetition of the previous argument shows that this term is again of the order (128). The first term in Eq. (129) is, however, larger, because not all the variables $\boldsymbol{\lambda}$, $\boldsymbol{\mu}$, $\boldsymbol{\nu}$, $\boldsymbol{\rho}$ are restricted to be small. The main contribution to Eq. (129) comes when either $(\boldsymbol{\lambda},\boldsymbol{\mu})$ are small and $(\boldsymbol{\nu},\boldsymbol{\rho})$ large or vice versa. Suppose for example that $(\boldsymbol{\nu},\boldsymbol{\rho})$ are large. Then the "intermediate state" consisting of the two particles with momenta $(\boldsymbol{\nu},\boldsymbol{\rho})$ can exist for a short "time" of order $(\hbar J^{-1})$ in both the functions $\Gamma_2(\boldsymbol{\lambda}\boldsymbol{\mu},\boldsymbol{\nu}\boldsymbol{\rho})$ and $\Gamma_2(\boldsymbol{\nu}\boldsymbol{\rho},\boldsymbol{\lambda}\boldsymbol{\mu})$. After some elementary calculation, the order of magnitude of the first term in Eq. (129) becomes

$$\begin{aligned}A_{D22}&\sim\beta^{-1}[N^{-1}\textstyle\sum_\lambda \exp(-\beta\epsilon_\lambda)Y(\boldsymbol{\lambda})(\delta\lambda)^2]^2\\&\sim T^6[Z_{\frac{5}{2}}(\beta L)]^2,\end{aligned} \quad (130)$$

and this gives a θ^5 contribution to the zero-field magnetization. A more detailed discussion indicates that the leading term in A_{D22} merely cancels out a term in A_{LD} involving (β'/β) which was omitted in passing from Eq. (101) to (102). In any case the entire contribution A_{D22} is of order T^6 or higher and will not be analyzed further.

The terms in the series (82) with $F\geq 4$ need not be discussed individually. The arguments which were used for $F=3$ can be applied to them, and it is clear that there will always be enough free momentum variables to make the terms of order T^6 at least. This completes our analysis of the higher order dynamical corrections.

10. SUMMARY OF QUANTITATIVE RESULTS

The results of this paper are all contained in the following formula for the free energy per atom at temperature T.

$$\begin{aligned}A=-\tfrac{1}{2}JS^2\gamma_0-LS-kT[&Z_{5/2}(\beta L)\theta^{3/2}\\&+C_1Z_{7/2}(\beta L)\theta^{5/2}+C_2Z_{9/2}(\beta L)\theta^{7/2}\\&+C_3S^{-1}[Z_{5/2}(\beta L)]^2\theta^4+O(\theta^{9/2})].\end{aligned} \quad (131)$$

To avoid numerous cross references, the notations will be recapitulated: S is the spin per atom; $(-JS^2)$ is the energy of two aligned nearest neighbor spins, γ_0 is the number of nearest neighbors per atom; L is the Zeeman splitting of the levels of a single atom in the external magnetic field; k is Boltzmann's constant; ν is the geometrical factor

$$\nu=1,\ 2^{\frac{1}{3}},\ \text{and}\ 3.2^{-4/3}, \quad (132)$$

for the simple, face-centered, and body-centered cubic lattices, respectively. Also

$$Z_n(x)=\sum_{j=1}^{\infty} j^{-n}e^{-jx}, \quad (133)$$

$$\beta=(kT)^{-1}, \quad (134)$$

$$\theta=3kT/(2\pi JS\gamma_0\nu)=T/(2\pi T_c), \quad (135)$$

where T_c is approximately equal to the Curie temperature, as explained in reference 7.

The numerical coefficients C_1, C_2 are given by

$$C_1=\tfrac{3}{4}\pi\nu=2.35,\ 2.96,\ 2.81, \quad (136)$$

$$C_2=\omega\pi^2\nu^2=10.2,\ 14.6,\ 13.7, \quad (137)$$

for the three types of lattice. The coefficient C_3 depends also on S. If we make the very slight approximation of equating the two coefficients $\Gamma_1{}^f$ and $\Gamma_2{}^f$ which are defined for the face-centered lattice by Eqs. (I, 94) and (I, 95), then C_3 is for all three lattice types equal to

$$C_3=QC_1,\quad Q=1+4/3[GS-1]^{-1}+\alpha(3S)^{-1}, \quad (138)$$

with

$$G=2\Gamma^{-1}=10,\ 24,\ 16, \quad (139)$$

$$\alpha=0.52,\ 0.34,\ 0.39. \quad (140)$$

Equation (138) gives, for $S=\frac{1}{2}$,

$$C_3=3.97,\ 4.00,\ 4.08, \quad (141)$$

and for $S=1$,

$$C_3=3.10,\ 3.46,\ 3.43. \quad (142)$$

In the limit as $S\rightarrow\infty$, we have $C_3\rightarrow C_1$.

The formula for the spontaneous magnetization per atom in zero external field is by Eqs. (69) and (131)

$$\begin{aligned}M(T)=(m/S)[S-a_0\theta^{3/2}-a_1\theta^{5/2}-a_2\theta^{7/2}&\\-a_3S^{-1}\theta^4+O(\theta^{9/2})],&\end{aligned} \quad (143)$$

where m is the magnetic moment of each atom and

$$a_0=\zeta(3/2)\qquad=2.612, \quad (144)$$

$$a_1=\zeta(5/2)C_1\qquad=3.15,\ 3.97,\ 3.77, \quad (145)$$

$$a_2=\zeta(7/2)C_2\qquad=11.5,\ 16.4,\ 15.4, \quad (146)$$

$$a_3=2\zeta(3/2)\zeta(5/2)C_3=27.8,\ 28.0,\ 28.6,\ (S=\tfrac{1}{2}), \quad (147)$$

$$=21.7,\ 24.2,\ 24.0,\ (S=1), \quad (148)$$

$$=16.5,\ 20.7,\ 19.7,\ (S=\infty). \quad (149)$$

In the temperature range over which these results might reasonably be applied, say for $0<T<\frac{1}{2}T_c$, the numerical value of $\theta=(T/2\pi T_c)$ does not exceed (1/12). Over this range the a_3 term in Eq. (143) is less than 4% of the a_0 term when $S=\frac{1}{2}$, and less than 2% when $S=1$.

It is therefore unlikely that the a_3 term, representing the effect of interactions between spin waves, could ever be observable in a real ferromagnet. The physical differences between a real ferromagnet and the Heisenberg model will certainly cause deviations from Eq. (143) large enough to hide the a_3 term completely. The practical conclusion of the whole investigation is simply this, that the linear Bloch theory with noninteracting spin waves is good enough for all practical purposes.

ACKNOWLEDGMENTS

We wish to thank Professor Van Kranendonk for communications in advance of publication, and Professor Kittel for raising the question which this paper answers.

APPENDIX I. PROOF OF EQ. (37)

Theorem.—Let $\mathbf{S}_1$ and $\mathbf{S}_2$ be two independent spins each of magnitude S. Then, for any state of the combined system,

$$S^2-\langle \mathbf{S}_1\cdot \mathbf{S}_2\rangle \geq (8S)^{-1}[\langle S_{1z}\rangle-\langle S_{2z}\rangle]^2.$$

Proof.—Any state of the combined system may be written

$$\psi=a\psi_{2S}+b\psi', \quad |a|^2+|b|^2=1,$$

where ψ_{2S} is an eigenstate of the total spin

$$(\mathbf{S}_1+\mathbf{S}_2)^2\psi_{2S}=J(J+1)\psi_{2S}$$

with $J=2S$, and ψ' is a combination of eigenstates with $J\leq 2S-1$. Then

$$\begin{aligned} S^2-\langle \mathbf{S}_1\cdot \mathbf{S}_2\rangle &= S(2S+1)-\tfrac{1}{2}\langle(\mathbf{S}_1+\mathbf{S}_2)^2\rangle \\ &\geq |b|^2[S(2S+1)-S(2S-1)]=2S|b|^2. \end{aligned} \tag{A1}$$

The state ψ_{2S} is symmetric with respect to interchange of the two spins, and therefore

$$(\psi_{2S}^*(S_{1z}-S_{2z})\psi_{2S})=0.$$

Hence

$$\langle S_{1z}\rangle-\langle S_{2z}\rangle=b(\psi^*(S_{1z}-S_{2z})\psi') +ab^*(\psi'^*(S_{1z}-S_{2z})\psi_{2S}).$$

But all eigenvalues of $(S_{1z}-S_{2z})$ are bounded by $2S$ in absolute magnitude, so that

$$|\langle S_{1z}\rangle-\langle S_{2z}\rangle|\leq 2S[|b|+|a|\,|b|]\leq 4S|b|. \tag{A2}$$

Together, Eqs. (A1) and (A2) imply the theorem.

APPENDIX II. SECOND VIRIAL COEFFICIENT OF A PHOTON GAS

In the case of the Maxwell field, the second virial coefficient b_2' is an effect of the scattering of light by light.[22] We may expect an unusual temperature dependence of b_2' because, in the scattering of two low-energy photons with relative momentum k, the largest phase shifts η are proportional to k^4. We define the virial coefficients by the formula analogous to Eq. (64),

$$A=-(2/\pi^2)(kT/\hbar c)^3kT\sum_{n=1}^{\infty}b_ne^{-n\beta L}, \tag{A3}$$

giving the free energy per unit volume at temperature T, for a photon gas with a "chemical potential" L. The quantity L is introduced for mathematical convenience, and is put equal to zero after any necessary differentiations have been performed. The normalization is chosen so that

$$b_1=1, \quad b_2=2^{-4}+b_2'. \tag{A4}$$

The value of b_2' obtained from the photon-photon interaction is then

$$b_2'=(44/15)(\alpha/\pi)^2(kT/mc^2)^4, \tag{A5}$$

where $\alpha=(1/137)$ and mc^2 is the electron rest energy. The lowest order quantum-electrodynamical correction to the Stefan-Boltzmann formula for the energy density ρ in a radiation enclosure at temperature T is given by

$$\rho=(\pi^2/15)(kT/\hbar c)^3kT[1+(7/3)\zeta(4)b_2']. \tag{A6}$$

The temperature dependence of Eq. (A5) is even stronger than that of Eq. (119), mainly because the photon mass is zero while the effective spin-wave mass is finite. Owing to the difference in mass, the volume of phase space accessible to a photon at temperature T is proportional to T^3, while the volume accessible to a spin wave is proportional to $T^{\frac{3}{2}}$. The phase-space factor has the effect of making the spin wave b_2' intermediate in behavior between the b_2' of an atomic gas and that of a photon gas. But in its qualitative features, the interaction between two spin waves is much more similar to the photon-photon interaction than to any normal interatomic potential.

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[22] See J. M. Jauch and F. Rohrlich, *The Theory oj Photons and Electrons* (Addison-Wesley Press, Cambridge, 1955), Chap. 13.