

Cluster Expansion for the Heisenberg Ferromagnet*

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A cluster series is derived for the Heisenberg ferromagnet. The theory is evaluated in zero order, for two-spin clusters, and for three-spin renormalized clusters. The zero-order result is the Weiss molecular field approximation, and the two-spin cluster is identical to the constant coupling approximation. The three-spin cluster result does not coincide with any existing phenomenological cluster approximation. The origin and nature of the inconsistencies in the phenomenological cluster methods (Oguchi, Bethe-Peierls-Weiss, etc.) is discussed.

I. INTRODUCTION

THE statistical mechanics of a simple Heisenberg ferromagnet has been rigorously analyzed by Dyson¹ in terms of a series expansion in powers of T (the spin-wave solution), valid at low temperatures, and by Opechowski,² and Brown and Luttinger,^{3,4} in terms of a series expansion in $1/T$, valid at high temperatures. Each of these solutions is valid only far from the transition temperature and, therefore, various approximations have been proposed to study the behavior at intermediate temperatures. Most of these are of the small cluster type. Our purpose here is to study the nature of the small cluster approximations and, as a standard of comparison, to derive a cluster series from a direct expansion of the partition function. The two-spin and three-spin cluster results are explicitly evaluated, giving Curie temperatures for representative lattices with nearest neighbor exchange and spin $\frac{1}{2}$. These results differ from the common cluster results, such as those obtained by the Oguchi⁵ and Bethe-Peierls-Weiss^{6,7} (BPW) methods, both of which contain internal inconsistencies. The nature of those inconsistencies will be discussed.

The zero-order result of the theory is the Weiss molecular field approximation, and the two-spin cluster result is identical to the constant coupling approximation of Kasteleijn and Van Kranendonk.⁸ The three-spin cluster results make significant changes in the Curie temperatures (relative to the two-spin cluster results).

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¹ F. J. Dyson, Phys. Rev. **102**, 1217, 1230 (1956).

² W. Opechowski, Physica **4**, 181 (1937); **6**, 1112 (1938).

³ H. A. Brown and J. M. Luttinger, Phys. Rev. **100**, 685 (1955).

⁴ H. A. Brown, Phys. Rev. **104**, 624 (1956).

⁵ T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955).

⁶ R. Peierls, Proc. Cambridge Phil. Soc. **32**, 477 (1936).

⁷ P. R. Weiss, Phys. Rev. **74**, 1493 (1948).

⁸ P. W. Kasteleijn and J. van Kranendonk, Physica **22**, 317 (1956).

Expansion in spin-deviation operators implicitly renormalizes the clusters, summing into the clusters certain classes of diagrams actually lying outside the clusters. In particular the zero-order approximation implicitly sums all tree diagrams,⁹ corresponding to the high-density limit. Because of this renormalization the cluster expansion, which is nominally a low-density expansion, contains at least some elements of a high-density approximation as well.

We hasten to stress that our purpose is to analyze existing cluster approximations, deriving a rigorous cluster series in the process; we do not claim that the leading terms of this series are a satisfactory approximation for dense ferromagnets. In fact, in dense ferromagnets the long loop diagrams almost certainly dominate the ladder diagrams of the cluster methods at temperatures below the Curie temperature.⁹ In sufficiently dilute ferromagnets, on the other hand, small clusters dominate at all temperatures.

II. CONVENTIONAL CLUSTER APPROXIMATIONS

To establish a basis of discussion we briefly summarize several representative cluster approximations, selecting, in particular, the Weiss molecular field approximation (a single-spin cluster), the Oguchi first approximation (a two-spin cluster), the Oguchi second approximation (a three-spin cluster), and the Bethe-Peierls-Weiss approximation (a cluster consisting of a spin and all of its nearest neighbors).

The given problem is described by the Heisenberg Hamiltonian

$$\mathcal{H} = -g\mu_0 H \sum_i S_{iz} - 2 \sum_{(i,j)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where g is the Landé factor, μ_0 the Bohr magneton, and H is the magnetic field, which is assumed to be in the negative z direction. The first summation is over all lattice sites i , and the second over all pairs of sites (i,j) . The exchange integral J_{ij} is assumed to be a function of the distance between the sites i and j (not restricted to nearest neighbors), but of such a sign and magnitude

⁹ G. Horwitz and H. B. Callen, Phys. Rev. **124**, 1757 (1961).

that the ground state of the system is one in which the average value of S_{iz} , $\langle S_{iz} \rangle$, is equal to $+S$ for all i . S is the magnitude of the spin on each site.

In principle, the solution is provided by the density operator

$$\rho = \exp(-\beta\mathcal{H}) / \text{tr} \exp(-\beta\mathcal{H}), \quad (2)$$

which determines the magnetization, or the average value of S_z , by

$$\langle S_z \rangle = \text{tr} S_{iz} \rho. \quad (3)$$

The conventional cluster methods generally proceed by selecting some small cluster of spins and by replacing the spin operators for all other spins in the Hamiltonian (1) by

$$S_x = S_y = 0, \quad S_{iz} = \langle S_z \rangle. \quad (4)$$

The Hamiltonian, and thence ρ , thereby depends on $\langle S_z \rangle$ and Eq. (3) becomes an implicit or "self-consistent" equation for $\langle S_z \rangle$.

The Weiss approximation¹⁰ selects a cluster consisting of a single spin, so that the cluster Hamiltonian becomes

$$\mathcal{H}_{cl}^{(1)} = -[g\mu_0 H + 2J_0 \langle S_z \rangle] S_{iz}, \quad (5)$$

where

$$J_0 = \sum_j J_{ij}, \quad (6)$$

and where terms not involving the i th spin, being merely constants, are omitted. As the trace in Eq. (3) now involves only the summation over $(2S+1)$ states, evaluation is simple, yielding the familiar equation

$$\langle S_z \rangle = SB_S(\beta S(g\mu_0 H + 2J_0 \langle S_z \rangle)), \quad (7)$$

where $B_S(x)$ is the Brillouin function

$$B_S(x) = \frac{1}{2S} \left[(2S+1) \coth\left(\frac{2S+1}{2S}x\right) - \coth\left(\frac{x}{2S}\right) \right]. \quad (8)$$

The Oguchi first approximation selects a cluster of two nearest neighbor spins. The cluster Hamiltonian then becomes

$$\mathcal{H}_{cl}^{(2)} = -2J \mathbf{S}_1 \cdot \mathbf{S}_2 - g\mu_0 \left(H + \frac{2(J_0 - J)}{g\mu_0} \langle S_z \rangle \right) (S_{1z} + S_{2z}), \quad (9)$$

where J is the value of the exchange integral for nearest neighbor spins and J_0 is defined in Eq. (6). In the special, but commonly considered, case in which J_{ij} is zero except for i and j nearest neighbors, the quantity $(J_0 - J)$ becomes $J(z-1)$ where z is the number of nearest neighbors. Again the trace in Eq. (3) can be evaluated easily, giving for spin $\frac{1}{2}$

$$\langle S_z \rangle = \frac{1}{2} \langle S_{1z} + S_{2z} \rangle = \frac{1}{2} \left(\frac{\sinh(\beta g\mu_0 H_{\text{eff}})}{e^{-\beta J} \cosh(\beta J) + \cosh(\beta g\mu_0 H_{\text{eff}})} \right), \quad (10)$$

where H_{eff} is the expression in large parentheses in Eq. (9). The Curie temperatures evaluated by solution of Eq. (10) are listed in Table I.

An unfortunate aspect of this theory is the fact that it predicts a Curie temperature for all lattices (as does the molecular field theory), whereas one-dimensional lattices with nearest neighbor interactions, for instance, cannot be ferromagnetic.

The Oguchi second approximation selects a cluster of three spins. For simplicity we restrict the description to the case of nearest neighbor exchange only. The cluster is selected so that spins 1 and 3 are nearest neighbors of spin 2 but not of each other. Then the cluster Hamiltonian is

$$\mathcal{H}_{cl}^{(3)} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3) - 2J(z-1)\langle S_z \rangle(S_{1z} + S_{3z}) - 2J(z-2)\langle S_z \rangle S_{2z} - g\mu_0 H(S_{1z} + S_{2z} + S_{3z}). \quad (11)$$

The trace in Eq. (3) can be evaluated for spin $\frac{1}{2}$ giving

$$\langle S_z \rangle = \frac{1}{3} \text{tr}(S_{1z} + S_{2z} + S_{3z}) \times \exp(-\beta\mathcal{H}_{cl}^{(3)}) / \text{tr} \exp(-\beta\mathcal{H}_{cl}^{(3)}), \quad (12)$$

where

$$\begin{aligned} & \text{tr}(S_{1z} + S_{2z} + S_{3z}) \exp(-\beta\mathcal{H}_{cl}^{(3)}) \\ &= 3e^{\beta J} \sinh[\beta J(3z-4)\langle S_z \rangle] + \sinh[\beta J(z-2)\langle S_z \rangle] \\ & \quad + e^{-\frac{1}{2}\beta J[1-2(z-1)\langle S_z \rangle]} \cosh\left[\frac{1}{2}\beta J(\langle S_z \rangle^2 - 4\langle S_z \rangle + 9)^{1/2}\right] \\ & \quad - e^{-\frac{1}{2}\beta J[1+2(z-1)\langle S_z \rangle]} \cosh\left[\frac{1}{2}\beta J(\langle S_z \rangle^2 + 4\langle S_z \rangle + 9)^{1/2}\right], \end{aligned} \quad (13)$$

TABLE I. Values of $2kT_c/zJ$ for various lattices. hl is the hexagonal layer lattice ($z=6$); sc, simple cubic; bcc, body-centered cubic; fcc, face-centered cubic.

	Linear chain	Square	hl	sc	bcc	fcc
Weiss molecular field	1	1	1	1	1	1
Oguchi two-spin cluster	0.625	0.845	0.933	0.933	0.930	0.955
Oguchi three-spin cluster	0.518	0.865	0.937	0.937	0.965	...
Bethe-Peierls-Weiss	none	none	...	0.617	0.725	...
Kramers-Opechowski	...	0.55	0.58	0.61	0.70	...
Our 2-spin cluster (constant coupling)	none	none	0.607	0.607	0.721	0.822
Our 3-spin cluster	none	0.572	0.532	0.694	0.762	0.775

¹⁰ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

and

$$\begin{aligned} \text{tr exp}(-\beta\mathcal{H}_{cl}^{(3)}) \\ = 2e^{\beta J} \cosh[\beta J(3z-4)\langle S_z \rangle] + 2 \cosh[\beta J(z-2)\langle S_z \rangle] \\ + 2e^{-\frac{1}{2}\beta J[1-2(z-1)\langle S_z \rangle]} \cosh[\frac{1}{2}\beta J(\langle S_z \rangle^2 - 4\langle S_z \rangle + 9)^{1/2}] \\ + 2e^{-\frac{1}{2}\beta J[1+2(z-1)\langle S_z \rangle]} \cosh[\frac{1}{2}\beta J(\langle S_z \rangle^2 + 4\langle S_z \rangle + 9)^{1/2}]. \end{aligned} \quad (14)$$

The Curie points evaluated by solving Eq. (12) are given in Table I.

The cluster selected in the Bethe-Peierls-Weiss approximation consists of a central spin \mathbf{S}_0 and all of its nearest neighbors. The cluster Hamiltonian is of the form

$$\mathcal{H}_{cl}^{\text{BPW}} = -2J\mathbf{S}_0 \cdot \sum_{i=1}^z \mathbf{S}_i - g\mu_0 H S_{0z} - g\mu_0 H_1 \sum_{i=1}^z S_{iz}, \quad (15)$$

where H_1 is the effective field acting on an ion in the first shell by virtue of its exchange interaction with ions outside this shell. For simplicity of exposition we have assumed, as we did implicitly in the Oguchi second approximation, that the lattice is such that triangular configurations of nearest neighbors do not exist. Rather than evaluating H_1 by replacing the spin operator of external ions by $\langle S_z \rangle$, as done in the cluster methods described above, the BPW method evaluates H_1 by requiring that

$$\langle S_{iz} \rangle = \langle S_{0z} \rangle. \quad (16)$$

That is, the spin average of an ion in the first shell, $\langle S_{iz} \rangle$, is required to be equal to that of the central ion. The Curie temperatures found by this method are listed in Table I.

The BPW theory has the catastrophic property¹¹ that the system ceases to be ferromagnetic below a certain temperature (the "anti-Curie" temperature), thereby violating the third law of thermodynamics.

III. THE CONSISTENCY CRITERION OF KASTELEIJN AND VAN KRANENDONK

Although cluster methods generally assume a value of $\langle S_z \rangle$ and evaluate it self-consistently, or apply a similar "self-consistency condition" such as Eq. (16), this is certainly no guarantee of the complete consistency of the resultant theory. In fact, the strange and impossible behavior predicted at low temperatures points to the fact that the theories are internally inconsistent. The nature of this defect in the theories has been analyzed by Kasteleijn and van Kranendonk.⁸ They point out that the thermodynamics of the system is completely determined by the two-particle density matrix ρ_{ij} , which is the projection of the full density matrix ρ on the two-particle subspace. If ρ_{ij} is written in the form

$$\rho_{ij} = \exp(-\beta\tilde{\mathcal{H}}_{ij}) / \text{tr exp}(-\beta\tilde{\mathcal{H}}_{ij}), \quad (17)$$

then $\tilde{\mathcal{H}}_{ij}$ is related to the full Hamiltonian in a very complex fashion. It is, of course, this operator $\tilde{\mathcal{H}}_{ij}$ which the cluster methods attempt to compute by replacing some of the spin operators in the Hamiltonian by their average values. In the case of spin $\frac{1}{2}$, Kasteleijn and van Kranendonk observe that \mathcal{H}_{ij} must be of the form

$$\tilde{\mathcal{H}}_{ij} = -2A_1 \mathbf{S}_i \cdot \mathbf{S}_j - 2A_2 S_{iz} S_{jz} - g\mu_0 A_3 (S_{iz} + S_{jz}), \quad (18)$$

where A_1 , A_2 , and A_3 can be functions of the temperature and of the externally applied field. Furthermore, the three functions are subject to a consistency condition derived by requiring that $\langle S_z \rangle$ be the same when computed in either of two ways; first, by computing $\langle S_z \rangle = \frac{1}{2} \text{tr}(S_{iz} + S_{jz})\rho_{ij}$; and second, by differentiating the free energy with respect to the field (the free energy being obtained from the average value of the energy, which, in turn, is obtained by averaging the Hamiltonian over the two-particle distribution ρ_{ij}). In the "constant coupling approximation" Kasteleijn and van Kranendonk attempt to guess a consistent set of values of A_1 , A_2 , and A_3 ; for nearest neighbor interaction they select $A_1 = J$ and $A_2 = 0$ and compute A_3 from the consistency condition, finding

$$zA_3 = H + \frac{z-1}{g\mu_0\beta} \ln\left(\frac{1+2\langle S_z \rangle}{1-2\langle S_z \rangle}\right). \quad (19)$$

However, we are not concerned with the constant coupling approximation at this point, but rather with the implications for the cluster methods of Kasteleijn and van Kranendonk's relation among A_1 , A_2 , and A_3 . The Weiss approximation corresponds to

$$A_1 = A_2 = 0, \quad A_3 = H + 2Jz\langle S_z \rangle / g\mu_0, \quad (20)$$

as is easily seen by comparison of Eqs. (18) and (5); these values do, indeed, satisfy the Kasteleijn and van Kranendonk condition. The Oguchi first approximation corresponds to the same values of A_1 and A_2 as chosen by Kasteleijn and van Kranendonk in their constant coupling approximation, but A_3 is given by the inconsistent value

$$A_3 = H + [2J(z-1)/g\mu_0]\langle S_z \rangle, \quad (21)$$

rather than by Eq. (19). Similarly, the Oguchi second approximation and the Bethe-Peierls-Weiss approximation give density operators which are inconsistent in the sense of Kasteleijn and van Kranendonk's condition. Only the Weiss single spin cluster provides an acceptable approximation to the density operator. It is, therefore, of some interest to derive a cluster series which gives a self-consistent density operator for every order of cluster, and which follows in a logical and direct way from basic principles, without *ad hoc* assumptions.

¹¹ P. W. Anderson, Phys. Rev. **80**, 922 (1950).

IV. HAMILTONIAN

We divide the Hamiltonian (1) into an unperturbed part and a perturbation term by introducing an expansion parameter

$$\sigma_i = \bar{S} - S_{iz}. \quad (22)$$

\bar{S} is a parameter whose best value will be determined by minimizing the free energy F . In contrast to a previous theory⁹ involving a similar parameter, \bar{S} will not turn out to be equal to $\langle S_z \rangle$ so that σ_i is not simply the deviation of the spin from its average value; we shall, of course, return to this question of interpretation subsequently. We note, however, that choosing \bar{S} to minimize the free energy will allow it to somehow embody the behavior of ions outside of the cluster, and we shall find that \bar{S} plays the role of an internal field acting on the spins of the cluster.

The Hamiltonian becomes

$$\mathcal{H} = E_0 + L \sum_i \sigma_i - 2 \sum_{(i,j)} J_{ij} [\sigma_i \sigma_j + \mathbf{S}_i \cdot \mathbf{S}_j - S_{iz} S_{jz}], \quad (23)$$

where

$$E_0 = -g\mu_0 H N \bar{S} - N J_0 \bar{S}, \quad (24)$$

$$L = g\mu_0 H + 2J_0 \bar{S}, \quad (25)$$

and N is the total number of lattice sites. We choose as the unperturbed Hamiltonian those terms which are linear in the spin deviations, defining

$$\mathcal{H}_0 = \mathcal{H}_0 + V, \quad (26)$$

where

$$\mathcal{H}_0 = E_0 + L \sum_i \sigma_i, \quad (27)$$

and

$$V = -2 \sum_{(ij)} J_{ij} [\sigma_i \sigma_j + \mathbf{S}_i \cdot \mathbf{S}_j - S_{iz} S_{jz}]. \quad (28)$$

This choice of the perturbation is reasonable, as the spin deviations are presumably small, whereas $\mathbf{S}_i \cdot \mathbf{S}_j - S_{iz} S_{jz} = S_{ix} S_{jx} + S_{iy} S_{jy}$ and the transverse components of the spin fluctuate around zero.

We now define the unperturbed free energy F_0 ,

$$-\beta F_0 = \ln \text{tr} \exp(-\beta \mathcal{H}_0), \quad (29)$$

and the correction term

$$-\beta F' = -\beta F + \beta F_0 = \ln \text{tr} \exp(-\beta \mathcal{H}) - \ln \text{tr} \exp(-\beta \mathcal{H}_0). \quad (30)$$

The unperturbed portion of the free energy is easily evaluated and gives

$$-\beta F_0 = -\beta N J_0 \bar{S}^2 + N \ln \Phi, \quad (31)$$

where

$$\Phi = \text{tr} e^{\beta L S_{iz}}. \quad (32)$$

Since H_0 and V commute, we get

$$-\beta F' = \ln \left[\frac{\text{tr} \exp(-\beta \mathcal{H}_0) \exp(-\beta V)}{\text{tr} \exp(-\beta H_0)} \right] = \ln \text{tr} \rho_0 e^{-\beta V} = \ln \langle e^{-\beta V} \rangle. \quad (33)$$

Here

$$\rho_0 = \exp(-\beta \mathcal{H}_0) / \text{tr} \exp(-\beta \mathcal{H}_0) \quad (34)$$

and the average is defined with respect to this unperturbed density matrix, i.e.,

$$\langle A \rangle = \text{tr} \rho_0 A. \quad (35)$$

V. ZERO-ORDER APPROXIMATION: THE MOLECULAR FIELD

Before expanding the perturbation F' in a cluster series, we evaluate the zero-order or unperturbed free energy F_0 , as given in Eq. (31). The proper value of \bar{S} is found by minimizing F_0 , which yields directly

$$\bar{S} = \frac{\partial}{\partial (\beta L)} \ln \Phi = S B_S(\beta S(g\mu_0 H + 2J_0 \bar{S})), \quad (36)$$

where B_S is the Brillouin function defined in Eq. (8). To evaluate M_0 , the magnetization, we use the relation

$$M = -\partial F / \partial H, \quad (37)$$

which gives

$$M_0 = N g \mu_0 \frac{\partial}{\partial (\beta L)} \ln \Phi = N g \mu_0 \bar{S}, \quad (38)$$

the second equality following from Eq. (36). Thus, \bar{S} is identified as the average value of S_z , or $\langle S_z \rangle$. This relation, together with Eq. (36), identifies the zero-order approximation of the theory as identical to the Weiss molecular field approximation. In reference 9 it has been shown that the Weiss result corresponds to the summation of all Cayley trees (all diagrams having no closed loops) and that this summation is carried out implicitly by the evaluation of \bar{S} .

 VI. CLUSTER EXPANSION OF F'

Having identified the zero-order free energy in terms of the Weiss theory, we proceed to expand $-\beta F'$ in a cluster series. This is done by expanding it first in clusters of linkages (or spin pairs), after which it is quite easy to regroup the terms of this series so that they refer to clusters of spins.

From Eq. (33) we note that $-\beta F'$ can be written in the form

$$-\beta F' = \ln \langle \exp(\sum_{\alpha} Q_{\alpha}) \rangle, \quad (39)$$

where the index α numbers the pairs (ij) or "links" in the crystal. Thus, α takes $N(N-1)/2$ values, where N is the number of ions. The expansion of $-\beta F'$ as a sum of contributions from each distinct cluster or set of linkages $\{\alpha\}$ in the crystal can be written

$$-\beta F' = \sum_{\{\alpha\}} [-\beta F_{\{\alpha\}}], \quad (40)$$

where the contribution from the cluster $\{\alpha\}$ is given by

$$-\beta F_{\{\alpha\}} = \sum_{\{\alpha'\}} (-1)^{|\alpha| - |\alpha'|} \ln \langle \exp(\sum_{\alpha'} Q_{\alpha'}) \rangle. \quad (41)$$

The sets of links $\{\alpha'\}$ over which the summation is to be carried constitute all subsets of the set $\{\alpha\}$. The symbol $[\alpha]$ denotes the number of links in the set $\{\alpha\}$, and similarly for $[\alpha']$. Finally, the summation over α' in the exponential clearly goes over all links in the set $\{\alpha'\}$.

The cluster expansion of Eqs. (40) and (41) has been given by Horwitz and Callen¹² and by Kubo.¹³ The proof of Horwitz and Callen is based on a direct diagrammatic expansion of $-\beta F'$, and a resummation into the cluster series; this proof is indicated in Appendix I. An alternative simple proof is given below.

We carry out the proof in two steps. We first show that $-\beta F'$ is given by the series claimed, without regard to the significance of the terms $-\beta F_{\{\alpha\}}$. We then show that $-\beta F_{\{\alpha\}}$ does represent the contribution of the cluster $\{\alpha\}$. To carry out the first step we substitute Eq. (41) in the right-hand member of Eq. (40)

$$\sum_{\{\alpha\}} [-\beta F_{\{\alpha\}}] = \sum_{\{\alpha\}} \sum_{\{\alpha'\}} (-1)^{[\alpha]-[\alpha']} \ln \langle \exp(\sum_{\alpha'} Q_{\alpha'}) \rangle. \quad (42)$$

We now group together all those sets $\{\alpha\}$ for which the number of links has some particular value l . We indicate the number of links of a set $\{\alpha\}$ by the subscript l : $\{\alpha\}_l$. Then the sum over sets $\{\alpha\}$ can be done in two stages, first summing over all sets $\{\alpha\}_l$ of a given l and then summing over all l [from $l=1$ to $L \equiv N(N-1)/2$]. Thus,

$$\sum_{\{\alpha\}} [-\beta F_{\{\alpha\}}] = \sum_{l=0}^L (-1)^l \sum_{\{\alpha\}_l} \sum_{m=0}^l (-1)^m \times \sum_{\{\alpha'\}_m} \ln \langle \exp(\sum_{\alpha'} Q_{\alpha'}) \rangle. \quad (43)$$

The double sum $\sum_{l=0}^L \sum_{m=0}^l ()$ is equivalent to $\sum_{m=0}^L \sum_{l=m}^L ()$, and replacing the summation index l by $l' = L - l$ this, in turn, becomes equal to $\sum_{m=0}^L \sum_{l'=0}^{L-m} ()$. Correspondingly,

$$\sum_{\{\alpha\}} [-\beta F_{\{\alpha\}}] = \sum_{m=0}^L (-1)^m \sum_{\{\alpha\}_m} \ln \langle \exp(\sum_{\alpha} Q_{\alpha}) \rangle \sum_{l=0}^{L-m} \sum_{\{\alpha'\}_l} (-1)^l. \quad (44)$$

The summation $\sum_{\{\alpha'\}_l}$ is the number of ways of choosing l objects out of L , or $\binom{L}{l}$. The summation $\sum_{l=0}^{L-m} (-1)^l \binom{L}{l}$ is the binomial expansion of $(1-x)^{L-m}$, with $x=1$; that is, it is equal to zero except for $m=L$,

in which case it is unity. Thus

$$\sum_{\{\alpha\}} [-\beta F_{\{\alpha\}}] = \sum_{m=0}^L \sum_{\{\alpha\}_m} \ln \langle \exp(\sum_{\alpha} Q_{\alpha}) \rangle \delta_{mL} = \ln \langle \exp(\sum_{\alpha} Q_{\alpha}) \rangle. \quad (45)$$

As the right-hand member is $-\beta F'$ we have demonstrated the validity of Eq. (40).

We now demonstrate that $-\beta F_{\{\alpha\}}$ has the significance of the "pure" contribution of the cluster $\{\alpha\}$. That is, it not only contains all terms from the set $\{\alpha\}$, but it contains no terms which arise solely from some smaller cluster embedded in $\{\alpha\}$. In fact, the role of the subtracted terms in Eq. (41) is just to remove all these contributions of smaller clusters $\{\alpha'\}$ from $-\beta F_{\{\alpha\}}$, leaving only the pure $\{\alpha\}$ contribution. To show that $-\beta F_{\{\alpha\}}$ contains no contribution from any subset $\{\alpha'\}$ smaller than $\{\alpha\}$ we merely demonstrate that if any single bond Q_{γ} in $\{\alpha\}$ vanishes then the entire contribution $-\beta F_{\{\alpha\}}$ vanishes with it. Dividing $-\beta F_{\{\alpha\}}$ into two parts, one of which has all terms containing Q_{γ} and the other of which has all terms not containing Q_{γ} , gives

$$-\beta F_{\{\alpha\}} = \sum_{\{\alpha\} \ni \gamma} (-1)^{[\alpha]-[\alpha']} \ln \langle \exp(Q_{\gamma} + \sum_{\alpha'} Q_{\alpha'}) \rangle + \sum_{\{\alpha\} \not\ni \gamma} (-1)^{[\alpha]-[\alpha']} \ln \langle \exp(\sum_{\alpha'} Q_{\alpha'}) \rangle, \quad (46)$$

where the prime on the summation in the exponent indicates that γ is not included in the summation. Letting $Q_{\gamma} \rightarrow 0$ we see that the two summations are the same except for an additional minus sign in the first, since $[\alpha']$ in the first summation exceeds $[\alpha]$ in the second summation by unity. Consequently, $-\beta F_{\{\alpha\}}$ is the contribution of the pure cluster $\{\alpha\}$; from the diagrammatic viewpoint it contains no diagram in which any link in $\{\alpha\}$ is unoccupied.

Whereas the cluster series (40) has not been made to depend on the specific form of the average in Eq. (39), we now demonstrate that under certain specific forms of averaging the series (40) is restricted to linked or connected clusters only. In particular, if the density operator defining the average is factorizable into operators for individual links, or for individual vertices (spins), only linked clusters appear. This is obvious, for any unconnected cluster gives two additive and independent contributions to $-\beta F_{\{\alpha\}}$. But since the total contribution must vanish if any one bond in the cluster Q_{γ} vanishes, each contribution separately must vanish.

Having now established the linked cluster series for clusters of links we can easily rearrange this into a cluster series for clusters of spins. For consider a cluster of spins $\{\delta\}$. Let $\{\alpha\}_{\delta}$ designate a set of links which can be drawn among the spins of $\{\delta\}$, in such a way that there exists some path from each spin to every other spin in $\{\delta\}$. Thus, if $\{\delta\}$ is a set of three spins,

¹² G. Horwitz and H. B. Callen, Bull. Am. Phys. Soc. 7, 218 (1962).

¹³ R. Kubo, J. Phys. Soc. Japan 17, 1100 (1962).

there are four sets of links $\{\alpha\}_\delta$. One set consists of three links, in triangular configuration. The other three sets each contain two links with a common vertex. Then the cluster series for sets of spins is clearly

$$-\beta F' = \sum_{\{\delta\}} [\sum_{\{\alpha\}_\delta} (-\beta F_{\{\alpha\}_\delta})] = \sum_{\{\delta\}} [-\beta F_{\{\delta\}}]. \quad (47)$$

VII. FIRST APPROXIMATION: CONSTANT COUPLING

Successive approximations are made by taking progressively larger linked clusters. The first approximation consists of a pair of spins. We show that the result of this approximation is identical to Kasteleijn and von Kranendonk's constant coupling approximation. The contribution to the free energy from all pairs is

$$-\beta F_{(2)}' = \sum_{\langle i,j \rangle} \ln(\exp(2\beta J_{ij} \hat{Q}_{ij})), \quad (48)$$

where

$$\hat{Q}_{ij} = \mathbf{S}_i \cdot \mathbf{S}_j - \bar{S}(S_{iz} + S_{jz}) + \bar{S}^2. \quad (49)$$

For definiteness we consider the case of nearest neighbor exchange only. There are then $\frac{1}{2}Nz$ pairs, and

$$\begin{aligned} -\beta F_{(2)}' &= \frac{1}{2}Nz \ln(\exp(2\beta JQ)) \\ &= \frac{1}{2}Nz \ln \text{tr} \exp(2\beta JQ) \exp(-\beta \mathcal{H}_0) \\ &\quad - \frac{1}{2}Nz \ln \text{tr} \exp(-\beta \mathcal{H}_0) \\ &= \frac{1}{2}Nz \ln [\sum_i \exp(-\beta \nu_i)] \\ &\quad + Nz\beta J \bar{S}^2 - Nz \ln \Phi, \end{aligned} \quad (50)$$

where it will be recalled that Φ is defined in Eq. (32) and where the ν_i are the eigenvalues of

$$\mathcal{H}_{(2)} = -2J\mathbf{S}_i \cdot \mathbf{S}_j - [g\mu_0 H + 2J(z-1)\bar{S}](S_{iz} + S_{jz}). \quad (51)$$

For the case of spin $\frac{1}{2}$ these eigenvalues ν_i are listed in Table IV where the subscripts (1,2,3) refer to the triplet state, while (4) refers to the singlet state of the two spins in the cluster.

The two-spin cluster approximation to the free energy is thus

$$\begin{aligned} -\beta F_{(2)} &= -\beta(F_0 + F_{(2)}') \\ &= N(1-z) \ln \Phi + \frac{1}{2}Nz \ln [\sum_i e^{-\beta \nu_i}]. \end{aligned} \quad (52)$$

Minimizing $F_{(2)}$ with respect to \bar{S} we find that \bar{S} is determined by the solution of the equation

$$\frac{\text{tr} S_{1z} e^{-\beta L \sigma_1}}{\text{tr} e^{-\beta L \sigma_1}} = \text{tr} \frac{1}{2}(S_{1z} + S_{2z}) \rho_{(2)}, \quad (53)$$

where

$$\rho_{(2)} = \exp(-\beta \mathcal{H}_{(2)}) / \text{tr} \exp(-\beta \mathcal{H}_{(2)}). \quad (54)$$

When written out explicitly this condition is

$$\frac{\tanh[\frac{1}{2}\beta(g\mu_0 H + 2Jz\bar{S})]}{e^{\beta J} \sinh\{\beta[g\mu_0 H + 2J(z-1)\bar{S}]\} + \cosh\beta J + e^{\beta J} \cosh\{\beta[g\mu_0 H + 2J(z-1)\bar{S}]\}} = 0. \quad (55)$$

In the form of Eq. (53) the condition is subject to a physical interpretation; \bar{S} is determined in such a way

that the average value of S_z is the same when computed from either the one-particle density operator or from the two-particle density operator. Or, stated equivalently, the choice of \bar{S} is such as to insure that the projection of the two-particle density operator onto the space of one particle is equivalent to the one-particle density operator; the equivalence referred to is that each of the resultant one-particle density operators must yield the same average value of S_z .

The magnetization is computed by differentiating $F_{(2)}$ with respect to H . Invoking Eq. (55) we, thereby, find

$$M_1/Ng\mu_0 = \langle S_z \rangle = \frac{1}{2} \tanh[\frac{1}{2}\beta(g\mu_0 H + 2Jz\bar{S})]. \quad (56)$$

This result is precisely of the same form as that found for a single-spin cluster (the Weiss result) for spin $\frac{1}{2}$, except that \bar{S} replaces $\langle S_z \rangle$ in the right-hand member. Thus, \bar{S} determines an effective internal field acting on the spins of the cluster.

At this point we observe that we have, in fact, derived the constant coupling approximation. For the cluster Hamiltonian $\mathcal{H}_{(2)}$ [Eq. (51)] which determines the two-particle density operator [Eq. (54)] is of the form of Eq. (18) with

$$A_1 = J, \quad A_2 = 0, \quad \text{and} \quad A_3 = H + \frac{2J(z-1)}{g\mu_0} \bar{S}, \quad (57)$$

which, incidentally, again demonstrates the role of \bar{S} as determining an effective internal field. Solving Eq. (56) for \bar{S} we find

$$\bar{S} = -\frac{g\mu_0 H}{2Jz} + \frac{1}{2\beta Jz} \ln \left(\frac{1+2\langle S_z \rangle}{1-2\langle S_z \rangle} \right). \quad (58)$$

Substitution of this value into Eq. (57) for \bar{S} , and comparison with Eq. (19), then demonstrates that the two-particle density operator is identical to that of the constant coupling approximation.

In contrast, we recall that the values of A_1 , A_2 , and A_3 which are predicted by the Oguchi two-spin cluster approximation [Eq. (20)] are similar to those of Eq. (57), except that \bar{S} is replaced by $\langle S_z \rangle$.

The Curie temperature is easily found⁸ to be

$$kT_c = 2J \left[\ln \left(\frac{z}{z-4} \right) \right]^{-1}, \quad (59)$$

and values are tabulated in Table I. It is to be noted that the condition that a lattice be ferromagnetic is that the number of nearest neighbors must exceed four—an improvement on the Oguchi two-spin cluster prediction that all lattices are ferromagnetic.

VIII. THREE-SPIN CLUSTERS

The next approximation represents clusters consisting of three spins. The two types of pure diagram, or clusters of links, which are associated with clusters of three spins, are triangles and a joined pair of links.

TABLE II. The contributions of various site configurations to the free energy for the case of nearest neighbor interactions. Sites (i, j, k) connected by links are nearest neighbors; those unconnected are not nearest neighbors. z_1 is the number of common nearest neighbors that two sites have when they themselves are nearest neighbors.

Type of diagram	Number of diagrams	Contribution to free energy
(1) i, j, k , each a n.n. of one another	$Nz_1/3!$	$\ln\langle e^{2\beta J(Q_{12}+Q_{23}+Q_{31})} \rangle - 3 \ln\langle e^{2\beta JQ} \rangle$
(2) i, k n.n. of j but not of each other	$(Nz/2)(z-z_1-1)$	$\ln\langle e^{2\beta J(Q_{12}+Q_{23})} \rangle - 2 \ln\langle e^{2\beta JQ} \rangle$
(3) i, j n.n. of each other but k not a n.n. of either	0	0
(4) i, j, k not n.n.	0	0

From Eqs. (40) and (41) the contribution of the pure triangles to $-\beta F'$ is

$$\sum_{(ijk)} [\ln\langle e^{2\beta(J_{ij}Q_{ij}+J_{jk}Q_{jk}+J_{ki}Q_{ki})} \rangle - \ln\langle e^{2\beta(J_{ij}Q_{ij}+J_{jk}Q_{jk})} \rangle - \ln\langle e^{2\beta(J_{jk}Q_{jk}+J_{ki}Q_{ki})} \rangle - \ln\langle e^{2\beta(J_{ki}Q_{ki}+J_{ij}Q_{ij})} \rangle + \ln\langle e^{2\beta J_{ij}Q_{ij}} \rangle + \ln\langle e^{2\beta J_{jk}Q_{jk}} \rangle + \ln\langle e^{2\beta J_{ki}Q_{ki}} \rangle], \quad (60)$$

where the summation is over all lattice triplets. The contribution of the pure V -linked diagrams to $-\beta F'$ is

$$\sum_{(ijk)} [\ln\langle e^{2\beta(J_{ij}Q_{ij}+J_{jk}Q_{jk})} \rangle + \ln\langle e^{2\beta(J_{jk}Q_{jk}+J_{ki}Q_{ki})} \rangle + \ln\langle e^{2\beta(J_{ki}Q_{ki}+J_{ij}Q_{ij})} \rangle - 2 \ln\langle e^{2\beta J_{ij}Q_{ij}} \rangle - 2 \ln\langle e^{2\beta J_{jk}Q_{jk}} \rangle - 2 \ln\langle e^{2\beta J_{ki}Q_{ki}} \rangle]. \quad (61)$$

The total contribution of all pure three-vertex diagrams is, therefore,

$$-\beta F_{(3)}' = \sum_{(ijk)} [\ln\langle e^{2\beta(J_{ij}Q_{ij}+J_{jk}Q_{jk}+J_{ki}Q_{ki})} \rangle - \ln\langle e^{2\beta J_{ij}Q_{ij}} \rangle - \ln\langle e^{2\beta J_{jk}Q_{jk}} \rangle - \ln\langle e^{2\beta J_{ki}Q_{ki}} \rangle]. \quad (62)$$

Assuming nearest neighbor interactions only we find that four types of triplets exist in the lattice. These are listed in Table II along with the frequency of occurrence of each type and the contribution to the free energy of a single diagram of this type. The last two types give no contribution to the free energy so that their weights are not listed. z_1 is the number of common nearest neighbors that two sites have when they themselves

are nearest neighbors. Adding all three-vertex diagrams gives

$$-\beta F_{(3)}' = \frac{Nz_1}{3!} \ln\langle e^{2\beta J(Q_{12}+Q_{23}+Q_{31})} \rangle + \frac{1}{2} Nz(z-z_1-1) \ln\langle e^{2\beta J(Q_{12}+Q_{23})} \rangle + \frac{1}{2} Nz(z_1-2z+2) \ln\langle e^{2\beta JQ} \rangle. \quad (63)$$

Adding this to the zero-order and two-vertex free energy, $-\beta F_0 + (Nz/2) \ln\langle e^{2\beta JQ} \rangle$, gives our three-vertex approximation for the free energy

$$-\beta F_{(3)} = -\beta NJz\bar{S}^2 + N \ln\Phi + \frac{1}{2} Nz(z_1-2z+3) \ln\langle e^{2\beta JQ} \rangle + \frac{1}{2} Nz(z-z_1-1) \ln\langle e^{2\beta J(Q_{12}+Q_{23})} \rangle + \frac{Nz_1}{3!} \ln\langle e^{2\beta J(Q_{12}+Q_{23}+Q_{31})} \rangle \quad (64)$$

$$= Nc_0 \ln\Phi + Nz_{C_1} \ln[\sum_i e^{-\beta\nu_i}] + Nz_{C_2} \ln[\sum_i e^{-\beta\lambda_i}] + Nz_{C_3} \ln[\sum_i e^{-\beta\mu_i}]. \quad (65)$$

The coefficients c_i are listed in Table III, with their values for various lattices. The ν_i are the eigenvalues of $H_{(2)}$ [Eq. (51)]. The μ_i are the eigenvalues of

$$\mathcal{H}_{(3)}^{(1)} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_1) - [g\mu_0 H + 2J(z-2)\bar{S}](S_{1z} + S_{2z} + S_{3z}), \quad (66)$$

and the λ_i are eigenvalues of

$$\mathcal{H}_{(3)}^{(2)} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3) - [g\mu_0 H + 2J(z-1)\bar{S}](S_{1z} + S_{3z}) - [g\mu_0 H + 2J(z-2)\bar{S}]S_{2z}. \quad (67)$$

The μ_i arise from the first type of triplet (triangles of nearest neighbors); the λ_i from the second type (V 's of nearest neighbors). The eigenstates of $\mathcal{H}_{(3)}^{(1)}$ for spin $\frac{1}{2}$ are well known¹⁴; four states (1 to 4) of $S_{\text{tot}} = \frac{3}{2}$ and four states (5 to 8) of $S_{\text{tot}} = \frac{1}{2}$. Four eigenstates of $\mathcal{H}_{(3)}^{(2)}$ for spin $\frac{1}{2}$ can easily be guessed,

$$\begin{aligned} |1\rangle &= \alpha_1 \alpha_2 \alpha_3; & |4\rangle &= 2^{-1/2}(\alpha_1 \alpha_2 \beta_3 - \beta_1 \alpha_2 \alpha_3); \\ |8\rangle &= \beta_1 \beta_2 \beta_3; & |5\rangle &= 2^{-1/2}(\alpha_1 \beta_2 \beta_3 - \beta_1 \beta_2 \alpha_3). \end{aligned} \quad (68)$$

Their eigenvalues are easily found; the four others can be found by diagonalizing the two-by-two matrices

TABLE III. The coefficients c_i [of Eq. (65)] for various lattices.

		Linear chain	Square	hl	sc	bcc	fcc
c_0	$\frac{1}{2}(z-1)(z-2)$	0	3	10	10	21	55
c_1	$\frac{1}{2}(z_1-2z+3)$	$-\frac{1}{2}$	$-5/2$	$-7/2$	$-9/2$	$-13/2$	$-17/2$
c_2	$\frac{1}{2}(z-z_1-1)$	$\frac{1}{2}$	$3/2$	$3/2$	$5/2$	$7/2$	$7/2$
c_3	$z_1/6$	0	0	$1/3$	0	0	$2/3$

¹⁴ F. Mandl, *Quantum Mechanics* (Butterworths Scientific Publications Ltd., London, 1957).

TABLE IV. Eigenvalues of effective cluster Hamiltonians. The ν_i are eigenvalues of $\mathcal{H}_{(2)}$ [Eq. (51)]; μ_i are eigenvalues of $\mathcal{H}_{(3)}^{(1)}$ [Eq. (66)]; λ_i are eigenvalues of $\mathcal{H}_{(3)}^{(2)}$ [Eq. (67)].

$\mu_1 = -\frac{3}{2}g\mu_0H - \frac{3}{2}J - 3J\bar{S}(z-2)$	$\nu_1 = -g\mu_0H - \frac{1}{2}J - 2J\bar{S}(z-1)$
$\mu_2 = -\frac{1}{2}g\mu_0H - \frac{3}{2}J - J\bar{S}(z-2)$	$\nu_2 = \frac{1}{2}J$
$\mu_3 = \frac{1}{2}g\mu_0H - \frac{3}{2}J + J\bar{S}(z-2)$	$\nu_3 = g\mu_0H - \frac{1}{2}J + 2J\bar{S}(z-1)$
$\mu_4 = \frac{3}{2}g\mu_0H - \frac{3}{2}J + 3J\bar{S}(z-2)$	$\nu_4 = \frac{3}{2}J$
$\mu_5, \mu_7 = -\frac{1}{2}g\mu_0H + \frac{3}{2}J - J\bar{S}(z-2)$	
$\mu_6, \mu_8 = \frac{1}{2}g\mu_0H + \frac{3}{2}J + J\bar{S}(z-2)$	
$\lambda_1 = -\frac{3}{2}g\mu_0H - J - J\bar{S}(3z-4)$	
$\lambda_2 = -\frac{1}{2}g\mu_0H + \frac{1}{2}J - J\bar{S}(z-1) - \frac{1}{2}J\Gamma_0^a$	
$\lambda_3 = -\frac{1}{2}g\mu_0H + \frac{1}{2}J - J\bar{S}(z-1) + \frac{1}{2}J\Gamma_0$	
$\lambda_4 = -\frac{3}{2}g\mu_0H - J\bar{S}(z-2)$	
$\lambda_5 = \frac{1}{2}g\mu_0H + J\bar{S}(z-2)$	
$\lambda_6 = \frac{1}{2}g\mu_0H + \frac{1}{2}J + J\bar{S}(z-1) + \frac{1}{2}J\Gamma_1^b$	
$\lambda_7 = \frac{1}{2}g\mu_0H + \frac{1}{2}J + J\bar{S}(z-1) - \frac{1}{2}J\Gamma_1$	
$\lambda_8 = \frac{3}{2}g\mu_0H - J + J\bar{S}(3z-4)$	

$$^a \Gamma_0 = [4\bar{S}^2 - 4\bar{S} + 9]^{1/2}.$$

$$^b \Gamma_1 = [4\bar{S}^2 + 4\bar{S} + 9]^{1/2}.$$

formed by taking $\mathcal{H}_{(3)}^{(2)}$ between pairs of the basis states

$$\begin{aligned} |2\rangle &= 2^{-1/2}(\alpha_1\alpha_2\beta_3 + \beta_1\alpha_2\alpha_3), \\ |3\rangle &= \alpha_1\beta_2\alpha_3, \\ |6\rangle &= \beta_1\alpha_2\beta_3, \\ |7\rangle &= 2^{-1/2}(\alpha_1\beta_2\beta_3 + \beta_1\beta_2\alpha_3). \end{aligned} \quad (69)$$

The eigenvalues μ_i and λ_i thus found are listed in Table IV.

Again \bar{S} is determined by setting $\partial F_{(3)}/\partial \bar{S} = 0$. This gives the following expression for \bar{S} as a function of temperature and field:

$$\begin{aligned} Jc_0 \tanh\left(\frac{1}{2}\beta g\mu_0H + \beta Jz\bar{S}\right) - c_1 \frac{d}{d\bar{S}} \ln \sum_i e^{-\beta\nu_i} \\ - c_2 \frac{d}{d\bar{S}} \ln \sum_i e^{-\beta\lambda_i} - c_3 \frac{d}{d\bar{S}} \ln \sum_i e^{-\beta\mu_i} = 0, \end{aligned} \quad (70)$$

where

$$\sum_i e^{-\beta\nu_i} = 2e^{\beta J/2} \cosh[\beta g\mu_0H + 2\beta J\bar{S}(z-1)] + 2e^{-\beta J/2} \cosh\beta J, \quad (71)$$

$$\begin{aligned} \sum_i e^{-\beta\lambda_i} &= 2e^{\beta J} \cosh\left[\frac{3}{2}\beta g\mu_0H + \beta J\bar{S}(3z-4)\right] \\ &+ 2 \cosh\left[\frac{1}{2}\beta g\mu_0H + \beta J\bar{S}(z-2)\right] \\ &+ 2 \exp\left[\frac{1}{2}\beta g\mu_0H - \frac{1}{2}\beta J\bar{S}(z-1)\right] \\ &\times \cosh\left[\frac{1}{2}\beta J(4\bar{S}^2 - 4\bar{S} + 9)^{1/2}\right] \\ &+ 2 \exp\left[-\frac{1}{2}\beta g\mu_0H - \frac{1}{2}\beta J - \beta J\bar{S}(z-1)\right] \\ &\times \cosh\left[\frac{1}{2}\beta J(4\bar{S}^2 + 4\bar{S} + 9)^{1/2}\right], \end{aligned} \quad (72)$$

$$\begin{aligned} \sum_i e^{-\beta\mu_i} &= 2e^{\beta J/2} \cosh\left[\frac{3}{2}\beta g\mu_0H + 3\beta J\bar{S}(z-2)\right] \\ &+ 2(e^{2\beta J/2} + 2e^{-3\beta J/2}) \\ &\times \cosh\left[\frac{1}{2}\beta g\mu_0H + \beta J\bar{S}(z-2)\right]. \end{aligned} \quad (73)$$

The magnetization is found by differentiation of $F_{(3)}$ with respect to H , whence,

$$\begin{aligned} M &= \frac{1}{2}N g\mu_0 c_0 \tanh\left(\frac{1}{2}\beta g\mu_0H + \beta Jz\bar{S}\right) \\ &- N z c_1 \frac{d}{dH} \ln \sum_i e^{-\beta\nu_i} - N z c_2 \frac{d}{dH} \ln \sum_i e^{-\beta\lambda_i} \\ &- N z c_3 \frac{d}{dH} \ln \sum_i e^{-\beta\mu_i}. \end{aligned} \quad (74)$$

The Curie temperature is defined as the temperature at which, for zero applied field, the susceptibility diverges

$$\chi^{-1} = 0. \quad (75)$$

The susceptibility χ is given by

$$\chi = \frac{1}{N} \frac{dM}{dH} = \frac{1}{N} \left[\frac{\partial M}{\partial H} + \frac{\partial M}{\partial \bar{S}} \frac{\partial \bar{S}}{\partial H} \right]. \quad (76)$$

Now we note that for zero external field $\bar{S} = 0$ is a solution of Eq. (70), and correspondingly $M = 0$. Thus, in evaluating the right-hand member of (76) at T_c we put $\bar{S} = 0$. Examination of the derivatives $(\partial M/\partial H)_{H=\bar{S}=0}$ and $(\partial M/\partial \bar{S})_{H=\bar{S}=0}$ shows that they are always bounded. Hence, the divergence of χ must result from the divergence of the derivative $(\partial \bar{S}/\partial H)_{H=\bar{S}=0}$. In order to investigate this derivative we note that Eq. (70) which determines \bar{S} is of the form

$$g(\beta, H, \bar{S}) = 0. \quad (77)$$

Taking the total derivative with respect to H we get

$$\frac{dg}{dH} = \frac{\partial g}{\partial H} + \frac{\partial g}{\partial \bar{S}} \frac{\partial \bar{S}}{\partial H} = 0. \quad (78)$$

TABLE V. The coefficients $a_i^{(j)}$ [of Eq. (88)] for various lattices.

		Linear chain	Square	hl	sc	bcc	fcc
a_0	$\frac{1}{4}z(z-1)(z-2)$	0	6	30	30	84	330
a_1	$2(z-1)^2(z_1-2z+3)$	-2	-90	-350	-450	-1274	-4114
$a_2^{(0)}$	$\frac{1}{4}(z-\frac{2}{3})^2(z-z_1-1)$	4/9	25/3	64/3	320/9	847/9	2026/9
$a_2^{(2)}$	$\frac{1}{4}(z-2)^2(z-z_1-1)$	0	3	12	20	63	175
$a_2^{(3)}$	$\frac{5}{2}(z-\frac{4}{3})^2(z-z_1-1)$	10/9	160/3	490/3	2450/9	7000/9	17920/9
$a_2^{(4)}$	$(4/27)(z-z_1-1)$	4/27	4/9	4/9	20/27	28/27	28/27
a_3	$(1/12)z_1(z-2)^2$	0	0	8/3	0	0	100/3

Solving for $\partial\bar{S}/\partial H$ we find that the pole of the susceptibility occurs at the root of $\partial g/\partial\bar{S}$. Therefore, the equation for the Curie temperature is

$$(\partial g/\partial\bar{S})_{\beta=\beta_c, H=\bar{S}=0}=0. \quad (79)$$

Performing the indicated operations and setting $y=e^{\beta_c J}$ gives the following equation for the Curie temperature:

$$a_0 + a_1 \left[\frac{y^2}{1+3y^2} \right] + [2y^3 + y^2 + 1]^{-1} \times \left[a_2^{(0)} + a_2^{(2)}y^2 + a_2^{(3)}y^3 + a_2^{(4)} \frac{(y^3-1)}{\ln y} \right] + a_3 \left[\frac{1+5y^3}{1+y^3} \right] = 0, \quad (80)$$

where the coefficients $a_i^{(j)}$ are given in Table V for six representative lattices: linear chain, square layer, hexagonal layer, simple cubic, body-centered cubic, and face-centered cubic. Equation (80) has been solved numerically for the Curie point, and the values of T_c are listed in Table I. Only one critical temperature is found for each lattice so that there are no anti-Curie temperatures such as those found in the Bethe-Peierls-Weiss approximation.

For the face-centered cubic lattice the Curie temperature predicted by successive approximations (zero-order, two-spin, and three-spin clusters) decreases monotonically, but the predicted Curie temperatures for both the simple cubic and body-centered cubic lattices oscillate. As indicated in the introduction, successive cluster approximations should not be expected to converge rapidly for the dense ferromagnet, and in fact they do not appear to do so.

The high-temperature susceptibility can be expressed in the form

$$\chi = \frac{1}{4}\beta(g\mu_0)^2 \sum_0^\infty A_n(\beta J)^n. \quad (81)$$

The coefficients A_n are listed in Table VI, up to $n=4$, for sc, bcc, and fcc lattices. The exact values, and the values predicted by other approximation methods, are also given. Our results for three-spin clusters are exact

to order β^4 , whereas the constant coupling results are exact only to order β^3 . However, the two-spin cluster results are correct for β^4 for those lattices which have no triangular configurations of nearest neighbors. It is also of interest to note that for the fcc lattice the three-spin cluster results are an improvement over the two-spin cluster results for the coefficient of β^5 , but that the accuracy becomes slightly worse for sc and bcc lattices.

Finally, the zero-temperature behavior of the magnetization is of interest. As in the constant coupling approximation, the magnetization curve undergoes a small but definite increase as the temperature decreases through the region $kT \simeq g\mu_0 H$. Consequently, the limiting $T=0$ value depends upon the relative order in which T and H approach zero. If T goes to zero more rapidly than H , then

$$M_{T=0} = \frac{1}{2} N g \mu_0 (c_0 + 2zc_1 + 3zc_2 + 3zc_3). \quad (82)$$

As can be corroborated by reference to Table III, the bracketed quantity is identically equal to unity for all lattices, so that the magnetization reaches its absolute saturation value at $T=0$. If H goes to zero more rapidly than T , however, the limiting magnetization is slightly less than the absolute saturation value.

TABLE VI. Coefficients in the high-temperature expansion of the susceptibility $\chi = \frac{1}{4}\beta(g\mu_0)^2 \sum A_n(\beta J)^n$.

	A_0	A_1	A_2	A_3	A_4
sc: MF ^a	1	3	9	27	81
exact	1	3	6	11	20.63
2-spin	1	3	6	11	20
3-spin	1	3	6	11	23.13
bcc: MF	1	4	16	64	256
exact	1	4	12	34.67	95.83
2-spin	1	4	12	34.67	100
3-spin	1	4	12	34.67	105.83
fcc: MF	1	6	36	216	1296
exact	1	6	30	138	608.25
2-spin	1	6	30	148	730
3-spin	1	6	30	138	638.75

^a Molecular field.

APPENDIX

In this Appendix we briefly indicate the direct diagrammatic derivation of the cluster expansion [Eq. (41)], as given by Horwitz and Callen.¹²

The perturbative free energy $-\beta F'$ is [Eq. (33)]

$$-\beta F' = \ln \langle \exp(-\beta \sum_{(ij)} \mathcal{I} C_{ij}) \rangle \\ = \ln \text{tr} \rho_0 \exp(-\beta \sum_{(ij)} \mathcal{I} C_{ij}). \quad (\text{A1})$$

It is convenient to rewrite this in the form

$$-\beta F' = \lim_{\{\gamma\} \rightarrow 0} \exp(-\beta \sum_{(ij)} D_{ij}) \ln \text{tr} \rho_\gamma, \quad (\text{A2})$$

where

$$\rho_\gamma \equiv \rho_0 \exp(-\sum_{(ij)} \gamma_{ij} \mathcal{I} C_{ij}), \quad (\text{A3})$$

and

$$D_{ij} = \partial / \partial \gamma_{ij}. \quad (\text{A4})$$

The identity (A2) is evident when we recall that $e^{-\beta D_{ij}}$ is the operator which replaces γ_{ij} by β . Expansion of the operator $\exp(-\beta \sum_{(ij)} D_{ij})$ in a power series leads to powers of $(\sum_{(ij)} D_{ij})$, which can be expanded in turn by the multinomial expansion

$$\left(\sum_{(ij)} D_{ij} \right)^n = n! \sum_{\{P_{ij}\}} \prod_{(ij)} \frac{1}{P_{ij}!} D_{ij}^{P_{ij}}, \quad (\text{A5})$$

where the summation is over all sets of non-negative integers P_{ij} satisfying $\sum_{(ij)} P_{ij} = n$. Inserting the

sultant series in (A2) gives

$$-\beta F' = \lim_{\{\gamma\} \rightarrow 0} \sum_{\{P_{ij}\}} \prod_{(ij)} \frac{1}{P_{ij}!} (-\beta D_{ij})^{P_{ij}} \ln \text{tr} \rho_\gamma, \quad (\text{A6})$$

where the summation is now over all sets of non-negative integers P_{ij} ; the restriction on the sum of the P_{ij} implicit in (A5) has disappeared in (A6) by virtue of summing over n .

The expansion (A6) can be represented diagrammatically. To do so for a particular term we simply draw P_{ij} bonds between vertices i and j for each integer P_{ij} in the set $\{P_{ij}\}$ corresponding to that term.

The diagrams can be arranged to pertain to clusters. Thus, the sum of all two-spin cluster diagrams clearly is

$$-\beta F'_{(2)} = \lim_{\{\gamma\} \rightarrow 0} \sum_{(ij)} \sum_{P_{ij}=0}^{\infty} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \ln \text{tr} \rho_\gamma \\ = \lim_{\{\gamma\} \rightarrow 0} \sum_{(ij)} \exp(-\beta D_{ij}) \ln \text{tr} \rho_\gamma \\ = \sum_{(ij)} \ln \text{tr} \rho_0 \exp(-\beta \mathcal{I} C_{ij}) \\ = \sum_{(ij)} \ln \langle \exp(-\beta \mathcal{I} C_{ij}) \rangle. \quad (\text{A7})$$

The sum of all diagrams on three-spin clusters containing at least one bond on each link (i.e., pure triangles) is

$$\lim_{\{\gamma\} \rightarrow 0} \sum_{(ijk)} \sum_{P_{ij}, P_{jk}, P_{ki}=1}^{\infty} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \ln \text{tr} \rho_\gamma \\ = \lim_{\{\gamma\} \rightarrow 0} \sum_{(ijk)} \left[\sum_{P_{ij}, P_{jk}, P_{ki}=0}^{\infty} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \ln \text{tr} \rho_\gamma - \sum_{P_{ij}, P_{jk}=0}^{\infty} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \ln \text{tr} \rho_\gamma \right. \\ \left. - \sum_{P_{jk}, P_{ki}=0}^{\infty} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \ln \text{tr} \rho_\gamma - \sum_{P_{ki}, P_{ij}=0}^{\infty} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \ln \text{tr} \rho_\gamma + \sum_{P_{ij}=0}^{\infty} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \ln \text{tr} \rho_\gamma \right. \\ \left. + \sum_{P_{jk}=0}^{\infty} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \ln \text{tr} \rho_\gamma + \sum_{P_{ki}=0}^{\infty} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \ln \text{tr} \rho_\gamma \right] \quad (\text{A8}) \\ = \sum_{(ijk)} [\ln \langle \exp[-\beta(\mathcal{I} C_{ij} + \mathcal{I} C_{jk} + \mathcal{I} C_{ki})] \rangle - \ln \langle \exp[-\beta(\mathcal{I} C_{ij} + \mathcal{I} C_{jk})] \rangle - \ln \langle \exp[-\beta(\mathcal{I} C_{jk} + \mathcal{I} C_{ki})] \rangle \\ - \ln \langle \exp[-\beta(\mathcal{I} C_{ki} + \mathcal{I} C_{ij})] \rangle + \ln \langle \exp(-\beta \mathcal{I} C_{ij}) \rangle + \ln \langle \exp(-\beta \mathcal{I} C_{jk}) \rangle + \ln \langle \exp(-\beta \mathcal{I} C_{ki}) \rangle]. \quad (\text{A9})$$

This is the result given in the text for pure triangles and has the form of a basic term plus others which subtract off "imbedded" clusters.

By adding and subtracting appropriate terms to reduce summations of P_{ij} 's from 1 to ∞ to 0 to ∞ , as done in Eq. (A8), pure diagrams are written as sums and differences of impure diagrams, as in Eq. (A9).

The V -linked diagrams on three spins are easily written in the appropriate form

$$\sum_{(ijk)} \left[\sum_{P_{ij}, P_{jk}=1}^{\infty} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \ln \text{tr} \rho_\gamma + \sum_{P_{jk}, P_{ki}=1}^{\infty} \frac{(-\beta D_{jk})^{P_{jk}}}{P_{jk}!} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \ln \text{tr} \rho_\gamma \right. \\ \left. + \sum_{P_{ki}, P_{ij}=1}^{\infty} \frac{(-\beta D_{ki})^{P_{ki}}}{P_{ki}!} \frac{(-\beta D_{ij})^{P_{ij}}}{P_{ij}!} \ln \text{tr} \rho_\gamma \right] \\ = \sum_{(ijk)} [\ln \langle \exp[-\beta(\mathcal{I} C_{ij} + \mathcal{I} C_{jk})] \rangle + \ln \langle \exp[-\beta(\mathcal{I} C_{jk} + \mathcal{I} C_{ki})] \rangle \\ + \ln \langle \exp[-\beta(\mathcal{I} C_{ki} + \mathcal{I} C_{ij})] \rangle - 2 \ln \langle \exp(-\beta \mathcal{I} C_{ij}) \rangle - 2 \ln \langle \exp(-\beta \mathcal{I} C_{jk}) \rangle - 2 \ln \langle \exp(-\beta \mathcal{I} C_{ki}) \rangle]. \quad (\text{A10})$$

Extension of the relationship to larger clusters is obvious, demonstrating the expansion (41).

It is easily seen that any term in (A6) corresponding to a choice of integers $\{P_{ij}\}$ vanishes if the nonzero integers P_{ij} can be divided into two sets with no indices in common. That is, all "unlinked diagrams" vanish. This follows from the fact that, in generating the term by operating with the D 's we can first apply all the D_{kl} in one set. When we then apply a D_{ij} from the second (nonoverlapping) set, the quantity immediately vanishes. To see this we let $\langle\phi\rangle$ be one of the averages generated by the D_{kl} of the first set so that ϕ involves

only the \mathcal{C}_{kl} in this set. We can let all the γ_{ki} which join the two sets vanish, and ρ_γ factors into $\rho_1\rho_2$ where ρ_1 involves the spins of the first set and ρ_2 involves the spins of the second set. Then

$$\langle\phi\rangle = \text{tr}\phi\rho_1\rho_2/\text{tr}\rho_1\rho_2 = (\text{tr}\phi\rho_1)(\text{tr}\rho_2)/(\text{tr}\rho_1)(\text{tr}\rho_2) \\ = \text{tr}(\phi\rho_1)/\text{tr}\rho_1, \quad (\text{A11})$$

and this quantity is independent of the indices of the second set. Hence, if D_{ij} belongs in the second set, $D_{ij}\langle\phi\rangle=0$, proving that all such unlinked diagrams vanish.

Critical Fields of Thin Superconducting Films. II. Mean Free Path Effects in Indium-Tin Alloy Films

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In a previous paper, a theoretical model was presented from which the critical magnetic fields of thin superconducting films could be calculated. The model was worked out for the nonlocal model of Pippard, but only thickness effects were discussed in detail and compared to experimental data on pure indium films. In this paper, mean free path effects as well as thickness effects are discussed, and the results are found to be in good agreement with critical field measurements on thin alloy films of indium containing 0–4.6 at. % tin, if one assumes that $\xi_0\lambda_L^2$ is equal to 1.62×10^9 (\AA)³ at $0.9T_c$, ξ_0 is equal to 2600 \AA , and ρl is approximately 2.0×10^{-11} $\Omega\text{-cm}^2$. For these values of ξ_0 and ρl , the coherence length, ξ , has been calculated for each film from measurements of resistivity and thickness, and is found to vary from 2600 \AA at 0 at. % Sn to 1000 \AA at 4.6 at. % Sn. Also, the question of whether size effects in thin films are equivalent to mean free path effects is discussed in detail. It is concluded that size effects are not equivalent to mean free path effects, or more precisely, boundary scattering is not equivalent to scattering by randomly distributed defects. In fact, it is demonstrated that whereas the London or "local" limit obtains in the presence of high concentrations of randomly distributed defects, the Pippard or "nonlocal" limit obtains in very thin films, where boundary scattering predominates.

1. INTRODUCTION

IN a previous paper,¹ hereafter referred to as I, a theoretical model was presented which relates the critical magnetic fields of thin superconducting films to the kernel of the current-vector-potential relationship for any theory of superconductivity. The model was worked out for the nonlocal theory of Pippard,² but only thickness effects were discussed in detail and compared to experimental data. In this paper, mean free path effects, as well as thickness effects, will be discussed and compared to critical field data obtained for indium-tin alloy films. The theoretical discussion will be limited to the nonlocal theory of Pippard with specular boundary conditions. Because of the similarity between the kernels of the Pippard and BCS³ theories, it is expected that the results are substantially the same that would be obtained from the BCS kernel. In addition, the ques-

tion of whether size effects in thin films are equivalent to mean free path effects is discussed in detail.

2. THEORETICAL

For the case of the Pippard kernel with specular boundary conditions, an expression for the critical field is derived in I which is of the form

$$h_c/H_c = g(\xi_0\lambda_L^2/a^3, \xi/a), \quad (1)$$

where h_c is the critical field of the film, H_c is the bulk critical field, ξ is the coherence distance, ξ_0 is the coherence distance in pure material, λ_L is the London penetration depth, a is the half-thickness of the film, and g is a function which can be numerically evaluated. The evaluation is carried out most conveniently in two steps. First, the film susceptibility is calculated from the results of Schrieffer,⁴

$$\left(\frac{\kappa}{\kappa_0}\right)_{\text{spec}} = 1 - \frac{2}{a^2} \sum_{n=0}^{\infty} [k_n^2 + K(k_n)]^{-1}, \quad (2)$$

⁴ J. R. Schrieffer, Phys. Rev. **106**, 47 (1957).

¹ A. M. Toxen, Phys. Rev. **127**, 382 (1962).

² A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

³ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).