

## Short-Range Magnetic Order in a Modified Weiss Molecular-Field Theory

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The fact that two different expressions for the isothermal susceptibility  $\chi_T$  can be obtained within the framework of the Weiss molecular-field theory of ferromagnetism (WMFT) is discussed. We conclude that it is inconsistent within the WMFT to assume no spin correlation in treating two-spin correlation functions. The requirement that the two methods for computing  $\chi_T$  give identical expressions provides a measure of the spin correlations. A second consistency condition is also imposed. These, together with the Weiss theory for single-spin averages, do not completely determine a modified theory, except at high temperature, where the resulting expressions for short-range order and specific heat are asymptotically correct. No further conditions or constraints have been uncovered, so that an *ad hoc* assumption is required to complete the theory for all temperatures and magnetic fields. Several simple assumptions give respectable short-range order and specific-heat curves. The theory is essentially a Weiss theory, modified so as to be consistent when forming two-spin averages.

### 1. INTRODUCTION AND DISCUSSION

OF all the effective-field theories of magnetism, the Weiss molecular-field theory (WMFT) is the most widely applied because of its great simplicity. Smart, in his recent book,<sup>1</sup> gives a careful exposition of many of its uses. It is discussed briefly in most texts on solid-state physics. Brout<sup>2</sup> and Mattis<sup>3</sup> have given clear discussions of it. Ter Haar<sup>4</sup> considers it in the language of the related Bragg-Williams order-disorder theory.

The WMFT assumes that the interactions of a given spin with its neighbors may be replaced by an effective magnetic field—the Weiss molecular field—and that there are no correlations between the spins. For describing quantities which are expressed by single-particle operators, such as the magnetization, the WMFT is qualitatively correct: It predicts spontaneous magnetization, and it gives the famous Curie-Weiss law, which is quantitatively accurate at sufficiently high temperatures. However, for describing quantities expressed by two-particle operators, such as the exchange energy, heat capacity, or short-range order, it is completely incorrect in the paramagnetic region at zero applied field. It also has other gross defects which will be discussed in this paper. These are a direct consequence of the assumption of no correlation between the spins.

We show here that two different expressions for the isothermal susceptibility  $\chi_T$  can be obtained within the framework of the WMFT. In the one method it is necessary to evaluate two-spin correlation functions and the result is clearly incorrect. Two-spin correlation functions do not arise in the other method, whose result is the Curie-Weiss law. We interpret this discrepancy to mean that the use of the assumption of no

spin correlation is inconsistent when evaluating two-spin correlation functions in the WMFT. A two-particle distribution function is necessary for such.

The cluster-expansion theories<sup>5-13</sup> provide just such two-particle, and higher, distribution functions. Not only correlation functions, but also the magnetization, a one-spin quantity, may be evaluated with these multiparticle distribution functions; the result for the magnetization is more accurate than the WMFT result in most respects, at the expense of additional labor, of course.

Our purpose in this paper is to discuss the mentioned inconsistent feature of the WMFT, and to show that the Weiss theory can be modified in a natural way, so as to allow a consistent treatment of two-spin correlation functions. The modified theory is required to be identical to the Weiss theory in its description of the magnetization. It is not meant to compete with the cluster-expansion theories in accuracy; rather, it is offered as a simple and consistent method by which the WMFT should be used.

The demonstration that the WMFT can give two different results for  $\chi_T$  can be developed very simply in a special case, and we shall do this now. With a canonical distribution, the total average magnetic moment of a system of identical spins is given by

$$\langle M_z \rangle = \sum_{i=1}^N \frac{\text{Tr}[M_z^i \exp(-\beta\mathcal{H})]}{\text{Tr}[\exp(-\beta\mathcal{H})]}, \quad (1)$$

where  $\beta = (kT)^{-1}$ , and  $\mathcal{H}$  is the Hamiltonian, which

<sup>1</sup> J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Philadelphia, 1966).

<sup>2</sup> R. Brout, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA.

<sup>3</sup> D. C. Mattis, *The Theory of Magnetism* (Harper and Row, New York, 1965), p. 227.

<sup>4</sup> D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart and Co., New York, 1954), Chap. 12.

<sup>5</sup> T. Oguchi, *Progr. Theoret. Phys. (Kyoto)* **13**, 148 (1955).

<sup>6</sup> R. Peierls, *Proc. Cambridge Phil. Soc.* **32**, 477 (1936).

<sup>7</sup> P. R. Weiss, *Phys. Rev.* **74**, 1493 (1948).

<sup>8</sup> P. W. Kasteleijn and J. Van Kranendonk, *Physica* **22**, 317 (1956).

<sup>9</sup> R. Kikuchi, *Ann. Phys. (N.Y.)* **4**, 1 (1958).

<sup>10</sup> B. Strieb, H. B. Callen, and G. Horwitz, *Phys. Rev.* **130**, 1798 (1963).

<sup>11</sup> H. B. Callen and E. Callen, *Phys. Rev.* **136**, A1675 (1964).

<sup>12</sup> T. Fujishiro, F. Takano, and T. Oguchi, *J. Phys. Soc. Japan* **19**, 1666 (1964).

<sup>13</sup> T. Morita and T. Tanaka, *Phys. Rev.* **145**, 288 (1966).

contains a Zeeman term for an applied field  $H_0$  in the  $z$  direction and an isotropic exchange interaction. The differential isothermal susceptibility  $\chi_T$  is defined as the derivative of  $\langle M_z \rangle$  with respect to  $H_0$  at constant  $T$ . One may calculate this in either of two ways—by evaluating  $\langle M_z \rangle$  first, then taking the derivative; or by taking the derivative of Eq. (1) first, formally and exactly, then evaluating the result. In the WMFT, both methods can be carried out exactly, that is, without using any approximations in addition to those which form the basis of the theory.

By evaluating  $\langle M_z \rangle$  first, in the WMFT, then finding  $\chi_T$ , one readily obtains at  $H_0=0$  and  $T>\theta$  the well-known Curie-Weiss law

$$\chi_T = C/(T-\theta), \quad (2)$$

where  $C$  and  $\theta$  are the Curie constant and paramagnetic Curie temperature, respectively, defined in Sec. 2. Alternatively, by taking the derivative of Eq. (1) first, one obtains ( $\Omega$  is the volume)

$$\begin{aligned} \chi_T &= (\beta/\Omega) [\langle M_z^2 \rangle - \langle M_z \rangle^2] \\ &= (\beta/\Omega) [N \langle (M_z^i)^2 \rangle + \sum_{i \neq j} \langle M_z^i M_z^j \rangle - N^2 \langle M_z^i \rangle^2]. \end{aligned} \quad (3)$$

(If  $M_z$  did not commute with the Hamiltonian, a more complicated expression would result.<sup>14</sup>) Equation (3) is exact and is a standard statistical-mechanical formula. According to the WMFT, the different spins are uncorrelated:

$$\langle M_z^i M_z^j \rangle = \langle M_z^i \rangle \langle M_z^j \rangle \quad (i \neq j).$$

Consider again only the zero-field case in the paramagnetic region. Then the second and third terms on the right in Eq. (3) vanish. Further, for spin  $\frac{1}{2}$ ,  $\langle (S_z^i)^2 \rangle = \frac{1}{4}$  (in any theory). The result is

$$\chi_T = C/T, \quad (4)$$

which is clearly incorrect, containing no information whatever about interparticle interactions. Note that this result is obtained without use of the molecular field, and results from any theory which uses an assumption of no correlation and which correctly gives  $\langle M_z^i \rangle = 0$  at  $H_0=0$  in the paramagnetic region. Thus our complaint, that the common use of the WMFT is inconsistent in this respect, applies as well to any theory of magnetism which assumes no correlation. The argument can be extended to the truncation of correlation at higher orders also.<sup>15</sup>

<sup>14</sup> R. L. Peterson, Rev. Mod. Phys. **39**, 69 (1967).

<sup>15</sup> For example, in the Oguchi two-spin theory (Ref. 5) with exchange connecting only nearest neighbors, the expression for  $\chi_T$  based upon Eq. (3), assuming that only nearest neighbors are correlated, does not agree with the conventional Oguchi result. In this case, the disparity between the two results is not so drastic as in the WMFT, since the result based upon Eq. (3) contains the exchange interaction, and in fact is not grossly incorrect.

This inconsistency in the computation of  $\chi_T$ , which does not seem to have been discussed previously in the literature, is of course not the only gross inadequacy of the WMFT, and one must seek to understand its relation to the others. In particular, it is well known that one cannot obtain the WMFT expression for the magnetization by minimizing the free energy when it is written in the form

$$F = -NkT \ln \text{Tr} \exp(-\beta \mathcal{H}_i),$$

where  $\mathcal{H}_i$  is the Weiss Hamiltonian for spin  $i$ .<sup>16</sup> The difficulty here involves the correct use of the self-energy term in a theory without correlation. By using the form  $F = \langle \mathcal{H}_i \rangle - TS'$ , where the entropy  $S'$  is written as  $-Nk \text{Tr}(\rho_i \ln \rho_i)$ , and  $\rho_i$  is the canonical density matrix with the Weiss Hamiltonian for a single spin, Callen and Callen<sup>17</sup> have shown that the usual Weiss expression for the magnetization is obtained. Brout<sup>2</sup> discusses the free-energy method whereby one writes the entropy simply as  $k \ln W$  and enumerates the degeneracy of states  $W$  corresponding to a given magnetization. This also gives the Weiss expression. Hence the free-energy minimization principle can successfully obtain the Weiss theory without correlation.

The susceptibility disparity does not seem closely related to the free-energy problem. It does not contain a self-energy term. In fact, the application of the WMFT rules to the exact Eq. (3) is so elementary that no manipulative ambiguities can arise, as can happen in the taking of derivatives in the WMFT. If it were not for this fact, we would be tempted to dismiss this problem on the grounds that it represents just another quirk in the WMFT, and that there are better theories anyway.

However, we can see no way of avoiding or modifying the results of Eq. (3) within the WMFT. We believe that a real inconsistency is involved, which must be considered. Specifically, because various quantities (for example, isothermal susceptibility and heat capacity) can be expressed in alternative ways which involve correlation functions of different orders, certain consistency conditions are imposed. A set of rules regarding the use of a one-particle distribution function will provide through these conditions certain information about two-particle and higher-order distribution functions.

The usual method of classifying and applying the effective-field theories is as follows: The first level of approximation consists in performing all averages with a one-particle distribution function (the WMFT); in the next level all averages are performed with a two-particle distribution function, and so on. Such usage

<sup>16</sup> This difficulty is not unique to the WMFT (cf. Ref. 15). If one assumes the spin-pair of the Oguchi theory to be in a molecular field and uncorrelated with its neighbors, a similar argument requires that  $\langle S_z^i \rangle = 0$ .

<sup>17</sup> E. R. Callen and H. B. Callen, J. Phys. Chem. Solids **16**, 310 (1960), Appendix E.

may be characterized as being uniform, although not necessarily consistent, as we have just discussed.

We shall here make a nonuniform use of the distribution function. Wanting to retain an essentially Weiss theory for reasons of simplicity, we adopt the Weiss one-particle distribution function for treating one-particle quantities (i.e., the magnetization). For treating two-spin correlations, we adopt a two-particle distribution function, whose form is only implied, having the property that the two mentioned methods for evaluating  $\chi_T$  give identical results. An outcome of this is that the short-range order and heat capacity do not vanish in the paramagnetic region at zero field, and explicit expressions can be obtained for them.

This procedure may be compared with the two-particle distribution theories, such as that of Kasteleijn and van Kranendonk.<sup>8</sup> There, an explicit two-particle distribution function is used, and the magnetization computed with it is made to be consistent with a one-particle distribution calculation. We mention also the work of Elliott and Marshall,<sup>18</sup> who extended the Bethe-Peierls-Weiss theory<sup>1,7</sup> to critical scattering, and invoke Eq. (3) as a consistency condition.

In Sec. 2 we review some of the defects of WMFT, emphasizing the role played by the assumption of no spin correlation. The consistency conditions are introduced and discussed in Sec. 3. Together with the Weiss one-particle distribution function, they still do not completely determine the theory except at high temperature, where the theory becomes exact. We have not uncovered any further conditions or constraints on the two-spin distribution function, and so have considered various *ad hoc* assumptions to complete the theory for all temperatures and magnetic fields. Several give respectable short-range order and specific-heat curves.

This paper is given in the language of ferromagnetism but applies to antiferromagnetic and ferrimagnetic substances as well. The arguments do not depend essentially upon the number of sublattices or upon the signs of the exchange interactions.

## 2. WMFT AND SOME OF ITS DEFECTS

In this section, we develop briefly those parts of the WMFT relevant to our discussion, and discuss several of its gross defects.

The Hamiltonian of the system consists of the Zeeman interaction in an applied field  $H_0$  directed along the positive  $z$  axis, plus an isotropic exchange interaction. There are  $N$  spins, where  $N$  is sufficiently large that surface effects can be neglected. Thus

$$\mathcal{H} = g\mu_B H_0 \sum_{i=1}^N S_z^i - 2 \sum J_{ij} \mathbf{S}^i \cdot \mathbf{S}^j, \quad (5)$$

where  $g$  is the  $g$  factor,  $\mu_B$  is the Bohr magneton (used here as positive),  $J_{ij}$  is the exchange coupling constant

between spins  $i$  and  $j$ , and  $\mathbf{S}^i$  is the spin operator for particle  $i$ . The second summation in Eq. (5) is over all pairs. In the WMFT, one constructs a Hamiltonian for spin  $i$  which is uncoupled from the Hamiltonian of the remaining system:

$$\mathcal{H}_i = g\mu_B H_0 S_z^i - 2\mathbf{S}^i \cdot \sum_j J_{ij} \langle \mathbf{S}^j \rangle \equiv kT h S_z^i. \quad (6)$$

The second part of Eq. (6) defines the quantity  $h$ . The angular brackets represent the thermal average, and  $\beta = (kT)^{-1}$ .  $\langle S_z^j \rangle$  is independent of  $j$  in the ferromagnetic case. With the Hamiltonian of Eq. (6), one obtains

$$\begin{aligned} -\langle M_z \rangle / N g \mu_B &= \langle S_z^i \rangle \\ &= \text{Tr}[S_z^i \exp(-h S_z^i)] / \text{Tr}[\exp(-h S_z^i)] \\ &= -S B_s(h). \end{aligned} \quad (7)$$

In Eq. (7), the trace is over the states of spin  $i$ , and  $B_s(h)$  is the Brillouin function:

$$B_s(h) = (2S+1)/2S \coth \frac{1}{2} h (2S+1) - (2S)^{-1} \coth \frac{1}{2} h. \quad (8)$$

The quantity  $h$  defined in Eq. (6) may be written

$$h = \beta g \mu_B H_0 + (\theta/T) [3/(S+1)] B_s(h), \quad (9)$$

where the paramagnetic Curie temperature  $\theta$  is defined by

$$\theta = 2S(S+1) \sum_j (J_{ij}/3k). \quad (10)$$

For  $H_0=0$  and  $T > \theta$ , the only solution to Eq. (9) is  $h=0$ , giving  $\langle S_z^i \rangle = 0$ , the correct zero-field result in the paramagnetic region.

The short-range order parameter is commonly defined by

$$\tau \equiv \langle \mathbf{S}^i \cdot \mathbf{S}^j \rangle / S^2 \quad (i, j \text{ nearest neighbors}). \quad (11)$$

Hence the assumption of no spin correlation gives the well-known incorrect result that  $\tau=0$  for  $H_0=0$  in the paramagnetic region. This result is clearly independent of the use of a molecular field. Similarly, for  $H_0=0$  and  $T > \theta$ ,

$$\langle \mathcal{H} \rangle = \langle \mathcal{H}_{\text{ex}} \rangle = -2 \sum J_{ij} \langle \mathbf{S}^i \cdot \mathbf{S}^j \rangle = 0,$$

and, consequently, the heat capacity

$$C_{H_0} = -k\beta^2 (\partial/\partial\beta) \langle \mathcal{H} \rangle |_{H_0} \quad (12)$$

also incorrectly vanishes for  $H_0=0$  and  $T > \theta$ .

The differential isothermal susceptibility is

$$\chi_T \equiv \Omega^{-1} (\partial \langle M_z \rangle / \partial H_0) |_T. \quad (13)$$

From Eq. (9), one has

$$\partial h / \partial H_0 |_T = g\mu_B / k (T - \theta F_s) \quad (14)$$

and

$$\partial h / \partial \beta |_{H_0} = kT^2 h / (T - \theta F_s), \quad (15)$$

<sup>18</sup> R. J. Elliott and W. Marshall, Rev. Mod. Phys. **30**, 75 (1958).

where

$$F_s = 3/(S+1)(d/dh)B_s(h). \quad (16)$$

The quantity  $F_s$  is unity at  $H_0=0$  and  $T>\theta$ , and approaches zero more rapidly than  $T$  for  $T<\theta$ . With the use of Eqs. (7) and (13)–(16), the differential isothermal susceptibility becomes

$$\chi_T = CF_s/(T-\theta F_s), \quad (17)$$

where  $C$  is the Curie constant equal to

$$Ng^2\mu_B^2 S(S+1)/3k\Omega.$$

Equation (17) holds for all  $T$  and  $H_0$  and is the accepted result of the WMFT.

A defect of the WMFT which is not widely known is the fact that the isentropic susceptibility  $\chi_S$  vanishes for all  $H_0$  and  $T$ , as we now show. According to a thermodynamic identity,

$$\chi_S = \chi_T - (T/\Omega C_{H_0})(\partial\langle M_z \rangle/\partial T)^2_{H_0}. \quad (18)$$

In the WMFT, one obtains

$$\partial\langle M_z \rangle/\partial T|_{H_0} = -Ng\mu_B S(S+1)hF_s/3(T-\theta F_s).$$

Also, from Eqs. (5) and (12),

$$C_{H_0} = NkTS(S+1)F_s h^2/3(T-\theta F_s).$$

Hence

$$T/\Omega C_{H_0}(\partial\langle M_z \rangle/\partial T)^2_{H_0} = CF_s/(T-\theta F_s) = \chi_T.$$

By Eq. (18), one obtains  $\chi_S=0$ . That this is incorrect may be seen immediately from Eq. (18) at  $H_0=0$  and  $T>\theta$ . Since  $\langle M_z \rangle=0$  for this case, one should obtain  $\chi_S=\chi_T$ .

Next we turn to the alternate evaluation of  $\chi_T$ , mentioned in Sec. 1 and based on the exact expression (3). The first term on the right in Eq. (3) is a single-particle operator and is evaluated with the use of the molecular-field assumption alone. One finds

$$\langle (M_z^i)^2 \rangle = g^2\mu_B^2 S[SB_s^2(h) + \frac{1}{3}(S+1)F_s]. \quad (19)$$

Using the assumption of no spin correlation for the second term on the right in Eq. (3), and using Eq. (7), one then obtains

$$\chi_T = CF_s/T, \quad (20)$$

where  $F_s$  is given by Eq. (16). Equation (20) agrees neither with Eq. (17) nor with experiment, and demonstrates the inconsistency in the WMFT discussed earlier.

### 3. WEISS THEORY WITH CORRELATION

We turn now to the prescription, mentioned in Sec. 1, for obtaining a measure of the two-particle correlations in a modified Weiss theory. A consistent theory should give the same result for  $\chi_T$  via Eq. (3) as via the use of the more conventional approach described in Eqs. (13)–(17). Thus we set the right-hand sides of Eqs. (3)

and (17) equal to each other, obtaining, with the use of Eqs. (7) and (19),

$$\sum_{j=1}^N \langle S_z^i S_z^j \rangle + \frac{1}{3}[S(S+1)]F_s - (N-1)S^2 B_s^2(h) = \frac{1}{3}S(S+1)[F_s T/(T-\theta F_s)]. \quad (21)$$

Equation (21), in which only the Weiss one-particle distribution function has been used, determines the sum of the  $z$ -component two-spin correlation functions. Writing each correlation function as the sum of its uncorrelated and correlated parts, i.e.,

$$\langle S_{\alpha}^i S_{\alpha}^j \rangle = \langle S_{\alpha}^i \rangle^2 + C_{ij}^{\alpha}, \quad (22)$$

where  $\alpha$  signifies a Cartesian component, we obtain from Eq. (21)

$$\sum_{j=1}^N C_{ij}^z = S(S+1)\theta F_s^2/3(T-\theta F_s). \quad (23)$$

That the correlation sum as given by Eq. (23) is of order unity in terms of  $N$  is not a peculiarity of the Weiss theory. This may be observed by substituting Eq. (22) into the exact Eq. (3).

The consistency condition [Eq. (23)] does not determine the individual two-spin correlations  $C_{ij}^z$ , and it is natural to search for additional conditions. The equilibrium-fluctuation formula for the heat capacity, analogous to Eq. (3), contains three- and four-spin correlations as well as two-spin correlations, and the desired information cannot be obtained from it. The equilibrium-fluctuation expressions for  $\partial\langle \mathcal{H}_{\text{ex}} \rangle/\partial H_0$  and  $\partial\langle M_z \rangle/\partial \beta$  each contain two- and three-spin correlations. However, in the proper linear combination of these quantities, the three-spin correlations vanish, and a second consistency condition on the two-spin correlations obtains. Thus

$$\partial\langle \mathcal{H}_{\text{ex}} \rangle/\partial H_0|_T + \beta(\partial\langle M_z \rangle/\partial \beta)|_{H_0} = H_0\beta[\langle M_z^2 \rangle - \langle M_z \rangle^2] = H_0\Omega\chi_T. \quad (24)$$

Here Eq. (3) has been used, but no approximations are involved. Using Eq. (22) and the Weiss result for the magnetization, one obtains from Eq. (24)

$$\sum_i J_{ij}(\partial/\partial H_0)[C_{ij}^x + C_{ij}^y + C_{ij}^z] = 0. \quad (25)$$

If Eq. (25) is to be true for exchange couplings of arbitrary size, the second consistency condition is

$$(\partial/\partial H_0)(C_{ij}^x + C_{ij}^y + C_{ij}^z) = 0. \quad (26)$$

Until now, the discussion has been the same for both Ising and isotropic Heisenberg interactions, since the WMFT ignores the transverse components of the Heisenberg interaction. For the Ising interaction,  $C_{ij}^x$  and  $C_{ij}^y$  are absent in Eq. (26), and so  $C_{ij}^z$  is independent of field for all temperature. In the Heisenberg model, no such definite statement can be made.

However, it is known<sup>18</sup> that the transverse and longitudinal correlations are not greatly different at zero field in the ordered state, and of course they are identical at zero field in the paramagnetic region. To the extent that one can take the components to be equal, one can say, by Eq. (26), that they are also field-independent.

However, the principal theoretical interest lies in the zero-field case, and for this the consistency condition (26) is of no use. We have not discovered any further conditions. In lieu of further developments along this line, one is forced to introduce an *ad hoc* assumption about the correlations, in order that the modified Weiss theory be complete. However, one can still obtain explicit high-temperature formulas from the preceding analysis in the following way.

Let  $z_n$ ,  $J_n$ , and  $C_n^z$  be, respectively, the number of  $n$ th neighbors of a given spin, the exchange coupling between  $n$ th neighbors, and the  $z$ -component pair correlation between  $n$ th neighbors. Write

$$\sum_{j=1}^N C_{ij}^z \equiv A(T, H_0) C_1^z = S(S+1)\theta F_s^2/3(T-\theta F_s). \quad (27)$$

Equation (27) defines the function  $A(T, H_0)$ , which is a measure of the correlation range, and may be written

$$A(T, H_0) = z_1 + z_2 C_2^z/C_1^z + \cdots + z_n C_n^z/C_1^z + \cdots \quad (28)$$

The asymptotic value  $A_\infty$  of  $A(T, H_0)$  as  $T \rightarrow \infty$  at  $H_0 = 0$  can be determined without recourse to the present theory. That is, using the high-temperature expansion method, one has at  $H_0 = 0$  and high temperature,

$$\begin{aligned} C_n^z &= \langle S_z^i S_z^j \rangle_n \\ &= \frac{\text{Tr}(S_z^i S_z^j)_n}{\text{Tr}1} - \beta \frac{\text{Tr}(S_z^i S_z^j) \mathfrak{C}_{\text{ex}}}{\text{Tr}1} + O(\beta^2) \\ &= 2\beta S^2(S+1)^2 J_n/9 + O(\beta^2). \end{aligned} \quad (29)$$

Substitution of Eq. (29) into (27) gives

$$A_\infty = z_1 + z_2 J_2/J_1 + \cdots + z_n J_n/J_1 + \cdots \quad (30)$$

The second part of Eq. (27) also leads to Eq. (30) with the aid of the high-temperature expansion, and confirms the general correctness of the modified Weiss theory at high temperature. The high-temperature

expressions for the short-range order and heat capacity obtained with the use of Eq. (27) agree with the exact high-temperature expressions.

Since  $C_1^z$  is bounded, the singular character of Eq. (27) must occur in  $A(T, H_0)$ . If we set

$$A(T, H_0) = [A_\infty T/(T-\theta F_s)] a(T, H_0), \quad (31)$$

then  $a(T, H_0)$  goes to unity as  $T \rightarrow \infty$  at  $H_0 = 0$ . The work of Elliott and Marshall<sup>18</sup> suggests that  $C_n^z/C_1^z$  vanishes as  $T \rightarrow 0$  at  $H_0 = 0$ , so that  $a(T, H_0)$  probably becomes unity in this limit also. The expression for  $C_1^z$  in terms of  $a(T, H_0)$  is

$$C_1^z = S(S+1)\theta F_s^2/3A_\infty T a(T, H_0). \quad (32)$$

The introduction of an *ad hoc* assumption to complete the modified Weiss theory now amounts to making a statement about  $a(T, H_0)$ . In the Ising model, since  $C_1^z$  is there independent of  $H_0$ , the quantity  $F_s^2/a$  must be field-independent, and we expect that this would be approximately so in the Heisenberg model also.

It is not difficult to write functions  $a(T, 0)$ , approaching unity for both  $T \rightarrow \infty$  and  $T \rightarrow 0$ , which give qualitatively satisfactory short-range order and heat-capacity curves. For example, functions of the type

$$1 + nF_s/(T/\theta + m), \quad 1 + nF_s^2/(T/\theta + m),$$

and

$$1 + nF_s^2/(T^2/\theta^2 + m),$$

where the zero-field form of  $F_s$  is used, and  $n$  and  $m$  are suitably chosen small numbers, give respectable results. For  $T < \theta$ , the specific-heat curves lie just below the WMFT curve and are  $z_n$ -dependent (the WMFT curves are not). At  $T > \theta$ , a specific-heat tail occurs, going as  $T^{-2}$  at large  $T$ .

Finally, we remark that the isentropic susceptibility difficulty mentioned in Sec. 2 does not occur in the modified theory. That is, at  $H_0 = 0$  and  $T > \theta$ ,  $\chi_s = \chi_r$  as it should.

To sum up, a modified Weiss theory with correlation can be constructed in a natural way. Unfortunately, the consistency conditions used are not sufficient to determine the theory completely except at high temperature, and unless other conditions can be found or constructed, an *ad hoc* assumption about the correlations is necessary. Several such simple assumptions give "respectable" results, but there is little reason to select one of these over another.