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The fcc Ising model in the cluster variation approximation

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The cluster-variation method was used to calculate the critical temperature for the fcc Ising ferromagnet in three different cluster approximations. A scheme for determing a set of independent cluster variables is presented, which considerably simplifies the minimization of the free energy. The system of equations arising from such minimization is solved, in the disordered state, by means of a simple iteration technique. The highest level of approximation treated in this work yields a critical temperature which is only 1.5% above the one estimated by the exact high-temperature expansion of the zero-field susceptibility. Furthermore, the high-temperature expansion for the specific heat gives four exact coefficients and the fifth is determined to within 0.4%.

I. INTRODUCTION

The central problem of the cluster variation method (CVM) is that of calculating approximate expressions for the number of configurations Ω of a crystal lattice having definite distribution of clusters (pairs, triads, etc.) of lattice points which may be, in general, occupied by any one of a given set of atomic "species".[1] The equilibrium cluster distribution is then determined by minimizing the free energy

$$F = E - TS = E - k_B T \ln \Omega \quad ,$$

where E, a linear function of the cluster concentrations, is the energy of the configuration in question and where S corresponds, for the equilibrium cluster distribution, to the entropy of the system.

Although it is found that larger clusters yield, in general, successively higher levels of approximations,[2] the degree of difficulty involved in the minimization of the free energy increases sharply with the size of the basic cluster. Due to such difficulties, and despite the fact that the CVM represents a remarkable improvement over other approximate methods such as the molecular-field and quasichemical approximations, only clusters containing a relatively small number of lattice points have been treated thus far.

Kikuchi's heuristic approach consists in writing a number of configurations Ω as a product of combinatorial factors arising from the constraint that the distribution of clusters, which includes the basic configurational cluster and its subclusters, remain unchanged after introducing an additional lattice point to the system.[1] This approach, although particularly graphic and conceptually simple, becomes extremely cumbersome for large cluster sizes.

The CVM was subsequently reformulated by Barker[3] and more recently by Morita.[4] The latter author showed that the CVM is based on the exact variational principle of equilibrium statistical mechanics and furthermore that the entropy can be written as a cumulant expansion in terms of the reduced density matrices. Barker's approach provides perhaps the simplest and most systematic way of calculating the entropy in the CVM approximation for an arbitrary n-point cluster. Such an approach is essentially a generalization of the quasichemical method and it results in a particularly simple expression for the configurational entropy.

The object of this investigation is to extend CVM calculations in the fcc lattice for the spin-$\frac{1}{2}$ Ising ferromagnet to cluster sizes larger than the nearest-neighbor (nn) tetrahedron originally treated by Kikuchi.[1] Specifically, the double-tetrahedron (DT), octahedron-tetrahedron (OT), and double-tetrahedron–octahedron (DTO) approximations will be considered. The entropy for the first of these approximations (DT) was derived by Kikuchi,[5] whereas the second one, i.e., the OT, was recently treated independently by Aggarwal and Tanaka.[6]

Although the nature of the CVM is such that all critical exponents for higher-order transitions are classical, very accurate values for the critical temperature can be obtained with a minimum of computational difficulty. For example, the highest CVM approximation treated presently in fcc lattices, namely, the DTO approximation, yields, as we shall see, a critical temperature which is only 1.5% higher than the one obtained from the exact high-temperature expansion of the zero-field susceptibility.

In Sec. II, the entropy expressions for the OT and DTO approximations will be derived. The problem of characterizing the concentration of the different cluster configurations in terms of a set of independent variables will be the subject of Sec. III. As we shall see, the scheme to be presented in Sec. III will simplify considerably the minimization of the free energy and the calculation of critical temperatures (Sec. IV). Finally, in Sec. V, we derive a simple recursive relation for calculating the high-temperature expansion coefficients for the specific heat.

II. CONFIGURATIONAL ENTROPY

A set of r lattice points defining an arbitrary geometrical figure will be termed an r-point cluster. In cases where sublattices are not required, such as the Ising ferromagnet, two clusters related by the symmetry operations of the lattice (point group plus translations) will be considered to be identical. All distinct r-point clusters will be classified and labeled by the index $t(t=1, \cdots)$. Thus the pair of integers (r,t) refers to a specific r-point cluster in our classification scheme.

In a binary system, the points of a given (r,t) cluster can be occupied by any one of the two "atomic species," thus determining 2^r distinguishable configurations of (r,t). In principle, a particular (r,t) cluster configuration can be specified by a set of r numbers $\{i,j,\ldots,k\}$ where, by convention, $i,j,\ldots,k$ takes values 1 and -1 for each of the two components in the system. However, all configurations $\{i,j,\ldots,k\}$ of (r,t) which are related by the symmetry operations of the (r,t) cluster will have the same probability (concentration in the crystal). Thus we can label the (r,t) cluster configurations by a single index l where, in general, $l=1,\ldots,s$ with $s \leq 2^r$. The configuration l of (r,t) will have associated with it a degeneracy factor $\alpha_l(r,t)$ defined as the number of distinguishable $\{i,j,\ldots,k\}$ configurations which can be generated by the symmetry operations of the (r,t) cluster.

The configurational entropy in the CVM is given by

$$S = Nk_B \sum_{(r,t)} \gamma(r,t) \sum_l \alpha_l(r,t) x_l(r,t) \ln x_l(r,t) \ , \qquad (1)$$

with k_B the Boltzmann constant, N the total number of lattice points and $x_l(r,t)$ the concentration of the (r,t) cluster in the l configuration. If the largest clusters to be considered, henceforth referred to as the basic clusters, contain n points, the coefficients $\gamma(r,t)$ are given by[3]

$$\gamma(n,t) = -N(n,t)/N \qquad (2a)$$

and

$$\gamma(r,t) = -\frac{N(r,t)}{N} - \sum_{q=r+1}^{n} \sum_s M(r,t;q,s)\gamma(q,s)$$

$$(1 \leq r < n) \ , \qquad (2b)$$

where $N(r,t)$ is the total number of (r,t) clusters in the system, N is the total number of lattice points, and $M(r,t;q,s)$ is the number of (r,t) clusters contained in a (q,s) cluster. Although it appears that we are now confronted with the formidable task of calculating $N(r,t)$ and $M(r,t;q,s)$ for all subclusters of the basic clusters (n,t), the structure of Eqs. (2) is such that most of the $\gamma(r,t)$ vanish identically. If the largest subcluster of (n,t), let us say $(n-1,t')$, is such that it is not completely included in the overlapping region of two (n,t) clusters, the latter being related by symmetry operations of the lattice, we have

$$N(n-1,t') = M(n-1,t';n,t)N(n,t)$$

and according to Eqs. (2), the coefficient $\gamma(n-1,t')$ vanishes.

Thus, the largest subclusters of the basic clusters (n,t) for which the coefficients $\gamma(r',t')$ do not vanish are given by all distinct overlapping regions of two adjacent n-point clusters in the lattice. As we shall see in the following examples, when more than one basic cluster is considered, either with the same or different number of lattice points, all possible overlapping regions must be determined. The next subclusters (r'',t'') with nonvanishing $\gamma(r'',t'')$ are likewise given by all possible overlapping regions of adjacent (r',t') subclusters. Repeated application of the above procedure yields a reduced set of clusters for which the solution of Eqs. (2) is trivial.

A. Octahedron-tetrahedron approximation

In the OT approximation, the two basic clusters considered are the first nn regular tetrahedron and the octahedron containing first and second nn (see Fig. 1). In order to calculate the coefficients $\gamma(r,t)$, we need to determine the overlapping region between a pair of adjacent octahedra, tetrahedra, or both. Inspection of Fig. 1 indicates that the subclusters in question are the first nn equilateral triangle (1,2,3)—given by the overlap of the tetrahedron (1,2,3,4) and the octahedron (1,2,3,5,6,7)—and the first nn pair resulting from the overlap of either two adjacent octahedra or tetrahedra. Determination of all possible overlap regions between the equilateral triangle and the first nn pair yields one additional "cluster," namely, the point. Thus the entropy in the OT approximation will contain contributions arising from five different clusters: point, first nn pair, first nn equilateral triangle, first nn regular tetrahedron, and the octahedron. The coefficients $\gamma(r)$ are calculated and shown in Table I, the index t being omitted since no possibility of confusion arises. Thus the entropy is written as

$$S_{\mathrm{OT}} = Nk_B \left[\sum_l x_l(1) \ln x_l(1) + 8 \sum_l \alpha_l(3) x_l(3) \ln x_l(3) - 6 \sum_l \alpha_l(2) x_l(2) \ln x_l(2) - 2 \sum_l \alpha_l(4) \ln x_l(4) - \sum_l \alpha_l(6) x_l(6) \ln x_l(6) \right] .$$

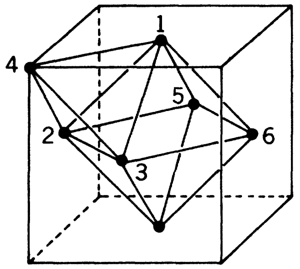


FIG. 1. Basic clusters used in the octahedron-tetrahedron approximation.

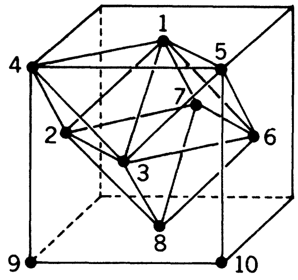
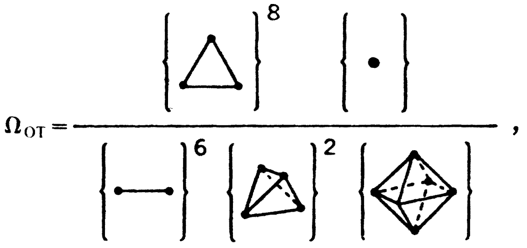


FIG. 2. Basic clusters used in the double-tetrahedron–octahedron approximation.

Using the asymptotic form of the factorial function, we can alternatively write S_{OT}/k_B as the logarithm of the number of configurations Ω_{OT} given by



(3)

where each bracket represents a product of factorials of the form

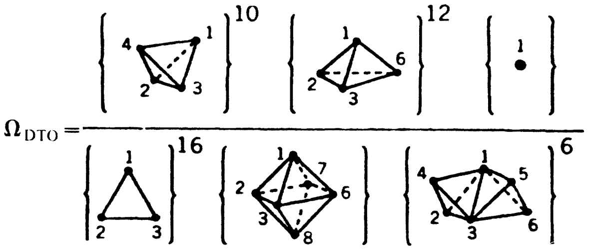
$$\{\ \} = \prod_l [x_l(r,t)N!]^{\alpha_l(r,t)}$$

where $x_l(r,t)$ is the concentration in the l configuration of the (r,t) cluster indicated in the bracket.

B. Double-tetrahedron–octahedron approximation

The basic configurational clusters involved in the DTO approximation are the double tetrahedron (1,2,3,4,5,6) and the octahedron (1,2,3,6,7,8) shown in Fig. 2. The relevant subclusters for the calculation of the entropy are: (i) the regular tetrahedron (1,2,3,4) arising from the overlap of two double tetrahedra, e.g., (1,2,3,4,5,6) and (1,2,3,4,8,9); (ii) the irregular tetrahedron (1,2,3,6) from the overlap of a double tetrahedron and an octahedron; (iii) the equilateral triangle (1,2,3) from the overlapping of both types of tetrahedra; (iv) the triangle (1,2,6) shared by two irregular tetrahedra; (v) the first nn pair; (vi) the second nn pair (2,6); and (vii) the point "cluster."

Table II gives the calculated coefficients $\gamma(r,t)$, from which the number of configurations Ω_{DTO} can be written as



(4)

where each cluster is labeled according to Fig. 1.

C. Higher-order entropies for the fcc and bcc lattices

As recently pointed out by Aggarwal and Tanaka,[6] a remarkable property of the CVM is that of reproducing a given number of the exact temperature expan-

TABLE I. Entropy coefficients for the TO approximations.

r	Cluster (Fig. 1)	$N(r)/N$	$M(6;r)$	$M(4;r)$	$M(3;r)$	$M(2;r)$	$M(1;r)$	$\gamma(r)$
6	(1,2,3,5,6,7)	1	···	···	···	···	···	−1
4	(1,2,3,4)	2	···	···	···	···	···	−2
3	(1,2,3)	8	8	4	···	···	···	8
2	(1,2)	6	12	6	3	···	···	−6
1	(1)	1	6	4	3	2	···	1

TABLE II. Entropy coefficients for the DTO approximation.

r,t	Cluster (Fig. 2)	$N(r,t)/N$	$M(6,1;r,t)$	$M(6,2;r,t)$	$M(4,1;r,t)$	$M(4,2;r,t)$	$M(3,1;r,t)$	$M(3,2;r,t)$	$M(2,1;r,t)$	$M(2,2;r,t)$	$M(1,1;r,t)$	$\gamma(r,t)$
(6,1)	(1,2,3, 6,7,8)	1	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	−1
(6,2)	(1,2,3, 4,5,6)	6	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	−6
(4,1)	(1,2,3, 4)	2	⋯	2	⋯	⋯	⋯	⋯	⋯	⋯	⋯	10
(4,2)	(1,2,3, 6)	12	12	2	⋯	⋯	⋯	⋯	⋯	⋯	⋯	12
(3,1)	(1,2,3)	8	8	8	4	2	⋯	⋯	⋯	⋯	⋯	−16
(3,2)	(1,2,6)	12	12	4	⋯	2	⋯	⋯	⋯	⋯	⋯	0
(2,1)	(1,2)	6	12	11	6	5	3	2	⋯	⋯	⋯	0
(2,2)	(2,6)	3	3	2	⋯	1	⋯	1	⋯	⋯	⋯	0
(1,1)	(1)	1	6	6	4	4	3	3	2	2	⋯	1

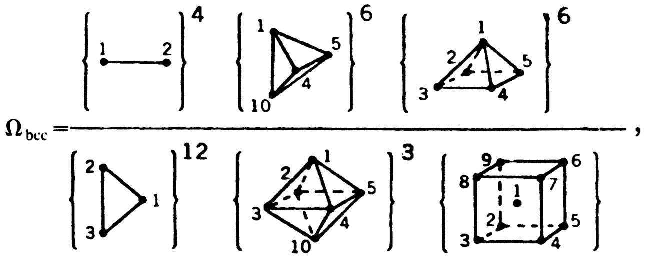
sion coefficients for the specific heat and the reduced susceptibility with a minimum of computational difficulty. In particular, the OT approximation reproduces exactly all the known coefficients (19) for the low-temperature expansion of the specific heat, whereas for the high-temperature expansion, it yields four of the eight known coefficients. Thus, by working with sufficiently large clusters, the CVM may prove to be an important tool for computing, without any additional difficulty, the temperature expansion coefficients in cases where higher-neighbor and many-body interactions are allowed.

An approximation which is expected to improve markedly the accuracy of current CVM calculations in the fcc lattice is that involving the thirteen- and fourteen-point clusters (TF). In the TF approximation, the basic configurational clusters are the fourteen-point fcc unit cell and the thirteen-point cluster formed by an atom surrounded by its twelve first nn. The TF approximation results naturally from that of a 27-point cluster (cube) in the simple cubic lattice in which an additional component (vacancies) is ordered in such a way that the fcc lattice is obtained. This procedure,[7] which allows us to identify those clusters relevant for the calculation of the entropy when combined with Eqs. (2), results in the following expression for the number of configurations $\Omega_{\rm TF}$:

$$\Omega_{\rm TF}=\{T\}^2\{QT\}^6/\{DT\}^6\{13\text{-P}\}\{14\text{-P}\}\ ,$$

where T, DT, and QT stand for the usual product of factorials involving the concentrations of single, double, and quadruple tetrahedra corresponding in Fig. 2 to the clusters (1,2,3,4), (1,2,3,4,5,6), and (1,2,3,4,5,6,9,8,10), respectively, and where 13-P and 14-P refer to the thirteen- and fourteen-point clusters.

An entropy expression for the bcc lattice can be obtained in a similar way by rearranging the vacancies on the 27-point cube of the simple cubic lattice so that the bcc structure is generated. By means of such a procedure, the number of configurations $\Omega_{\rm bcc}$ is found to be



where each cluster has been labeled with reference to Fig. 3.

The minimization of the free energy in the last two approximations (TF and bcc) would require a very involved task of determining a set of independent variables, or, alternatively, the constraint equations

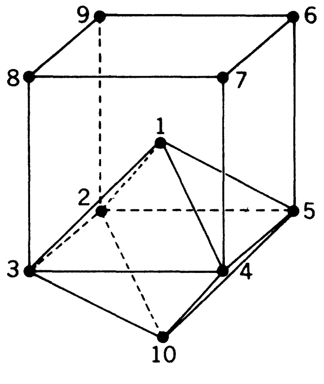


FIG. 3. Basic clusters for the bcc-unit-cell approximation.

among the different cluster configurations. Although the TF and bcc approximations will not be considered further in this paper, the approach for determing a set of independent variables to be presented in Sec. III should facilitate the computations appreciably. The interested reader is referred to the work by Clapp[8] who determined a reduced set of 288 cluster configurations (out of $2^{13}=8192$ distinguishable configurations) and their degeneracies for the thirteen-point cluster in the fcc lattice.

III. CLUSTER ALGEBRA

The final step of the CVM consists in the minimization of the free energy with respect to the configurational variables. A procedure most commonly used is that of minimizing the free energy with respect to the concentration of the largest clusters, subject to the proper constraints. The resulting system of equations can then be solved by means of a simple iteration technique proposed by Kikuchi.[9] Such an approach, although particularly simple for small cluster sizes, becomes extremely cumbersome for large clusters due to the intricacy of the linear constraints existing between different cluster configurations. An alternative approach is that of defining at the onset of the calculations a set of independent variables, of which the most convenient are the r-body correlation functions $\xi(r,t)$. In order to compute the cluster concentrations for a binary system in terms of the correlations functions $\xi(r,t)$, we introduce the operator

$$\Gamma_i(p)=\tfrac{1}{2}[1+i\sigma(p)] \ , \tag{5}$$

where i takes values 1 and -1 for each one of the two components in the system and where $\sigma(p)$ is the spin operator at lattice point p given by

$$\sigma(p)=\begin{cases}+1 & \text{if species } i=1 \text{ at } p \ ,\\ -1 & \text{if species } i=-1 \text{ at } p \ .\end{cases}$$

Thus, $\Gamma_i(p)$ takes value one if species i is at lattice point p and zero otherwise. The concentration of (r,t) clusters in the $l=\{i,j,\ldots,k\}$ configuration can then be written as

$$x_l(r,t)=x_{ij\ldots k}(r,t)$$

$$=\frac{1}{N(r,t)}\sum_{\{p_1\cdots p_r\}_t}\Gamma_i(p_1)\Gamma_j(p_2)\cdots\Gamma_k(p_r) \ , \tag{6}$$

where $N(r,t)$ is the total number of (r,t) clusters in the lattice and where the summation is performed over all lattice points $p_1,p_2,\ldots,p_r$ consistent with the cluster in question. Combining Eqs. (5) and (6), we can write the concentration $x_{i,j,\ldots,k}(r,t)$ as

$$x_{i,j,\ldots,k}(r,t)$$

$$=\frac{1}{2^r}\left[1+\sum_{(r',t')}v_{i,j,\ldots,k}(r,t;r',t')\xi(r',t')\right] \ , \tag{7}$$

where $\xi(r',t')$ is the r'-body correlation function defined by

$$\xi(r',t')=\frac{1}{N(r',t')}\sum_{\{p_1\cdots p_{r'}\}_{t'}}\sigma(p_1)\sigma(p_2)\cdots\sigma(p_{r'})$$

and where $v_{i,j,\ldots,k}(r,t;r',t')$ is, in general, a sum of r'-order products involving the indices $i,j,\ldots,k$ ($i,j,\ldots,k$ take values of ±1). The structure of $v_{i,j,\ldots,k}(r,t;r',t')$, which depends on the symmetry of the cluster in question, can be best illustrated through a specific example. For the first nn equilateral triangle in the fcc lattice, Eq. (6) reads

$$x_{ijk}(3)=\frac{1}{N(3)}\sum_{\{p_1p_2p_3\}}\Gamma_i(p_1)\Gamma_j(p_2)\Gamma_k(p_3)=\frac{1}{2^3}[1+(i+j+k)\xi(1)+(ij+ik+jk)\xi(2)+ijk\xi(3)] \tag{8}$$

and therefore

$$v_{ijk}(3;1)=i+j+k \ , \quad v_{ijk}(3;2)=ij+jk+ki \ ,$$

and

$$v_{ijk}(3;3)=ijk.$$

Thus, in the first nn triangle approximation, the number of independent variables is three [$\xi(1)$, $\xi(2)$, and $\xi(3)$], and the concentration of any one of the 2^3 triangle configurations can be calculated from Eq. (8).

Equation (7), trivial for small clusters, is particularly useful for large cluster sizes since it has a straightforward geometric interpretation. The number of independent variables associated with a given cluster variation (CV) approximation is simply determined by the total number of *distinct* clusters in which the basic cluster can be decomposed, i.e., all subclusters plus the largest cluster itself. To each one of such clusters, a correlation function $\xi(r,t)$ is associated. Furthermore, the coefficients $v_{i,j,\ldots,k}(r,t;r',t')$ for each (r,t) cluster are given by a sum of r'-order products of

TABLE III. Point cluster: (1,1).

n	Cluster (Fig. 2)	(r,t)	$\nu_l(1,1;r,t)$
1	(1)	(1,1)	i

$i,j,\ldots,k$, the number of terms being equal to the number of subclusters (r',t') contained in (r,t).

Talbes III–IX show the subcluster decomposition for those clusters relevant to the entropy expressions Eqs. (3) and (4) derived in Sec. II. The second and third columns show, respectively, the geometry of the cluster and the notation (r,t) adopted. The complete expression for the coefficients $\nu_l(r,t;r',t')$ for an arbitrary $l=\{i,j,\ldots,k\}$ configuration is given in the last column.

In view of the fact that the $\xi(r',t')$ in Eq. (7) are linearly independent, the degeneracy factor $\alpha_l(r,t)$ can be calculated by determining those configurations for which the coefficients $\nu_l(r,t;r',t')$ are equal for *all* values of (r',t'). Table X shows an example of such a calculation for the first nn regular tetrahedron in the fcc lattice.

Before proceeding with the minimization of the free energy, it is convenient to establish some basic properties of the coefficients $\nu_l(r,t;r',t')$. Although the following properties are valid for any arbitrary cluster, the reader is referred to the example of Table X for further clarification. For each configuration $l=\{i,j,\ldots,k\}$ of the (r,t) cluster, there is a complementary one $\bar{l}=\{-i,-j,\ldots,-k\}$ such that

$$\nu_l(r,t;r',t')=(-1)^{r}\,\nu_{\bar{l}}(r,t;r',t') \tag{9}$$

for all subclusters (r',t'). An important property which follows directly from definition of the $\nu_l(r,t;r',t')$ is

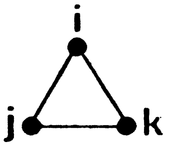
$$\sum_l \alpha_l(r,t)\,\nu_l(r,t;r',t')\,\nu_l(r,t;r'',t'')=0 \tag{10}$$

for $(r',t')\neq(r'',t'')$. Likewise, from the normalization condition

TABLE IV. First nn pair: (2,1).

n	Cluster (Fig. 2)	(r,t)	$\nu_l(2,1;r,t)$
1	(1)	(1,1)	$i+j$
2	(1,2)	(2,1)	ij

TABLE V. First nn equilateral triangle: (3,1).



n	Cluster (Fig. 2)	(r,t)	$\nu_l(3,1;r,t)$
1	(1)	(1,1)	$i+j+k$
2	(1,2)	(2,1)	$ij+ik+jk$
3	(1,2,3)	(3,1)	ijk

$$\sum_l \alpha_l(r,t)\,x_l(r,t)=1 \tag{11}$$

and the fact that the $\xi(r,t)$ are linearly independent, it follows that

$$\sum_l \alpha_l(r,t)\,\nu_l(r,t;r',t')=0. \tag{12}$$

Furthermore, by combining Eqs. (7), (10), and (12), it can be shown that

$$\sum_l \alpha_l(r,t)\,\nu_l^2(r,t;r',t')=2^{r}\nu_1(r,t;r',t') \tag{13}$$

where the configuration $l=1$ corresponds by convention to $i=j=\cdots k=+1$.

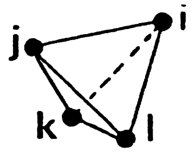
IV. MINIMIZATION OF THE FREE ENERGY

The energy per lattice site for the Ising ferromagnet is given by

$$E/N=-\tfrac{1}{2}zJ\xi(2,1)\ , \tag{14}$$

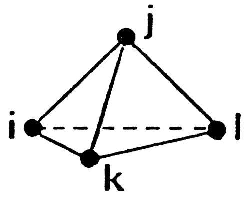
where z, J, and $\xi(2,1)$ are the coordination number,

TABLE VI. First nn regular tetrahedron: (4,1).



n	Cluster (Fig. 2)	(r,t)	$\nu_l(4,1;r,t)$
1	(1)	(1,1)	$i+j+k+l$
2	(1,2)	(2,1)	$ij+ik+il+jk+jl+kl$
3	(1,2,3)	(3,1)	$ijk+ikl+ijl+jkl$
4	(1,2,3,4)	(4,1)	$ijkl$

TABLE VII. Irregular tetrahedron (1,2,3,6 in Fig. 2): (4,2).



n	Cluster (Fig. 2)	(r,t)	$v_l(4,2;r,t)$
1	(1)	(1,1)	$i+j+k+l$
2	(1,2)	(2,1)	$ij+ik+jk+jl+kl$
3	(2,6)	(2,2)	il
4	(1,2,3)	(3,1)	$ijk+jkl$
5	(1,2,6)	(3,2)	$ijl+ikl$
6	(1,2,3,6)	(4,2)	$ijkl$

coupling constant, and pair correlation variable, respectively, for the first nn. The free energy F in an arbitrary CV approximation can be written by combining Eqs. (14) and (1) as

$$\frac{1}{k_BT}\frac{F}{N}=f=-\tfrac{1}{2}z\beta\xi(2,1)$$
$$-\sum_{(r,t)}\gamma(r,t)\sum_l\alpha_l(r,t)x_l(r,t)\ln x_l(r,t) \tag{15}$$

with $\beta=J/k_BT$. From Eqs. (7) and (15), we obtain the following minimization conditions for the free energy:

$$\frac{\partial f}{\partial\xi(r',t')}=-\tfrac{1}{2}z\beta\delta((r',t');(2,1))$$
$$-\sum_{(r,t)}\frac{\gamma(r,t)}{2'}\sum_l\alpha_l(r,t)\,v_l(r,t;r',t')\ln x_l(r,t)$$
$$=0\ , \tag{16}$$

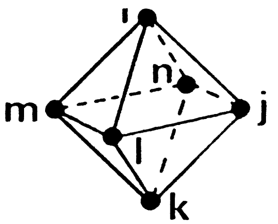
where $\delta((r',t');(2,1))$ takes values one for $(r',t')=(2,1)$ and zero otherwise.

In the disordered state of the Ising ferromagnet, all correlation variables associated with clusters containing an odd number of lattice points vanish. Thus, for odd values of r', Eq. (16) is trivially obeyed since the sum over configurations l vanishes identically [see Eqs. (7) and (9)]. The remaining equations, i.e., those arising from even clusters, were solved by a simple iteration scheme based on the method of the steepest descent. The following recursive relation was used:

$$\hat{\xi}(r,t)=\xi(r,t)-\frac{\partial f}{\partial\xi(r,t)}\Big/\frac{\partial^2 f}{\partial\xi^2(r,t)}\ ,$$

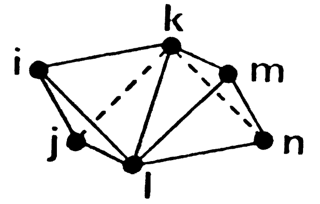
where the iterated value $\hat{\xi}(r,t)$ is calculated using the previous values of $\xi(r,t)$ on the right-hand side. Such an iteration scheme converges in a manner similar to that of the natural-iteration method proposed by Kikuchi,[9] although in general the number of operations involved in each iteration step is generally reduced.

TABLE VIII. Octahedron: (6,1).



n	Cluster (Fig. 2)	(r,t)	$v_l(6,1;r,t)$
1	(1)	(1,1)	$i+j+k+l+m+n$
2	(1,2)	(2,1)	$(n+l)(i+k+j+m)+(m+j)(i+k)$
3	(2,6)	(2,2)	$ik+jm+\mathrm{ln}$
4	(1,2,3)	(3,1)	$(l+n)(j+m)(i+k)$
5	(1,2,6)	(3,2)	$ik(j+l+n+m)+ln(i+j+k+m)+jm(i+k+l+n)$
6	(1,2,3,6)	(4,2)	$ik(jn+jl+lm+nm)+ln(ij+im+mk+jk)+mj(in+il+kl+kn)$
7	(2,3,6,7)	(4,3)	$ilkn+ijkm+jlmn$
8	(1,2,3,6,7)	(5,1)	$jlmn(i+k)+ilkn(m+j)+ijkm(l+n)$
9	(1,2,3,6,7,8)	(6,1)	$ijklmn$

TABLE IX. Double tetrahedron: (6,2).



n	Cluster (Fig. 2)	(r,t)	$v_l(6,2;r,t)$
1	(1)	(1,1)	$i+j+k+l+m+n$
2	(1,2)	(2,1)	$ij+ik+il+jk+jl+kl+km+kn+lm+\ln+mn$
3	(2,6)	(2,2)	$im+jn$
4	(2,5)	(2,3)	$in+jm$
5	(1,2,3)	(3,1)	$ij(k+l)+kl(i+j)+mn(k+l)+kl(n+m)$
6	(1,2,6)	(3,2)	$im(k+l)+jn(k+l)$
7	(2,4,5)	(3,3)	$ji(m+n)+mn(i+j)$
8	(1,2,5)	(3,4)	$in(k+l)+jm(k+l)$
9	(1,2,3,4)	(4,1)	$ijkl+klmn$
10	(1,2,3,6)	(4,2)	$iklm+jkln$
11	(2,4,5,6)	(4,3)	$ijmn$
12	(2,3,4,6)	(4,4)	$ij(ln+kn+km+lm)+mn(ik+il+jk+jl)$
13	(1,2,3,5)	(4,5)	$jklm+ikln$
14	(1,2,3,4,5)	(5,1)	$ijkl(m+n)+klmn(i+j)$
15	(1,2,4,5,6)	(5,2)	$ijkmn+ijlmn$
16	(1,2,3,4,5,6)	(6,2)	$ijklmn$

The critical temperature T is determined by the equation

$$\det(F)_{T_c}=0 \ , \tag{17}$$

where the elements of the symmetric matrix F are second derivatives of the free energy given by

$$\frac{\partial^2 f}{\partial\xi(r,t)\,\partial\xi(r',t')} =-\sum_{(p,s)}\frac{\gamma(p,s)}{2^{2p}}\sum_l \alpha_l(p,s)\,v_l(p,s;r,t)\,\frac{v_l(p,s;r',t')}{x_l(p,s)} \ . \tag{18}$$

From Eqs. (9) and (18), and noting that in the disordered state $x_l(r,t)=x_{\bar{l}}(r,t)$, it follows that the second derivatives are different from zero only when r and r' are both either even or odd. Thus, in the disordered state, F has a block structure and Eq. (17) becomes

$$\det(F_e)_{T_c}\det(F_0)_{T_c}=0 \ ,$$

where the elements of F_e and F_0 are second derivatives of the free energy involving even and odd clusters, respectively. The singularity in the zero-field susceptibility, which determines the critical temperature T_c, occurs when the matrix F_0 becomes singular, i.e., when

$$\det(F_0)_{T_c}=0 \ . \tag{19}$$

TABLE X. Coefficients $v_s(4,1;r,t)$ for the regular tetrahedron.

s	$\{ijkl\}$	$\alpha_s(4,1)$	$v_s(4,1;1,1)$	$v_s(4,1;2,1)$	$v_s(4,1;3,1)$	$v_s(4,1;4,1)$
1	1111	1	4	6	4	1
2	$111\bar{1}$	4	2	0	−2	−1
3	$11\bar{1}\bar{1}$	6	0	−2	0	1
4	$1\bar{1}\bar{1}\bar{1}$	4	−2	0	2	−1
5	$\bar{1}\bar{1}\bar{1}\bar{1}$	1	−4	6	−4	1

Equations (16) and (19) where solved for the DT, OT, and DTO approximations. The entropy expression for the DT approximation, shown in Fig. 4, was derived by Kikuchi[5]; for the OT and DTO approximations, Eqs. (3) and (4) were used.

The total number of independent variables for the DT, OT, and DTO approximations are, respectively, 16 (Table IX), 10 (Tables VI and VIII), and 19 (Tables VIII and IX). However, since in the disordered state all odd correlation functions vanish, the number of equations to be solved above the critical temperature are only 9, 6, and 11 for the DT, OT, and DTO approximations, respectively. Note that the total number of distinguishable configurations of the largest clusters, equal to the number of simultaneous nonlinear equations used in the natural-iteration scheme, are 64 (DT), 80 (OT), and 128 (DTO). Hence the scheme presented here results in a considerable saving of computational labor. Figure 5 shows a plot of the smallest eigenvalue $\lambda_m(T)$ of the matrix F_0 as a function of the reduced temperature k_BT/zJ for the three approximations in question. Note that the smallest eigenvalue $\lambda_m(T)$ is, close to the critical temperature T_c, strictly proportional to $(T-T_c)$. Since the zero-field susceptibility diverges at T_c as λ_m^{-1}, the linearity of λ_m vs T in Fig. 5 illustrates the fact that the CVM predicts a classical critical exponent $\gamma=1$. The critical temperatures obtained by different CVM approximations are compared to Table XI with the value obtained from the high-temperature expansion of the zero-field susceptibility. Note that the DT approximation, although involving a larger cluster than the single tetrahedron approximation, yields a higher critical temperature. In fact, in the DT approximation the octahedron correlations are not taken into account properly. When such correlations are considered, as in the DTO approximation, a considerably improved value of the critical temperature, only 1.5% higher than the high-temperature expansion estimate, is obtained.

TABLE XI. Critical temperature for the fcc Ising ferromagnet.

Approximation	$k_BT_c/12J$
Tetrahedron	0.83544
DT	0.84045
OT	0.83394
DTO	0.82981
High-T expansion(10)	0.81627

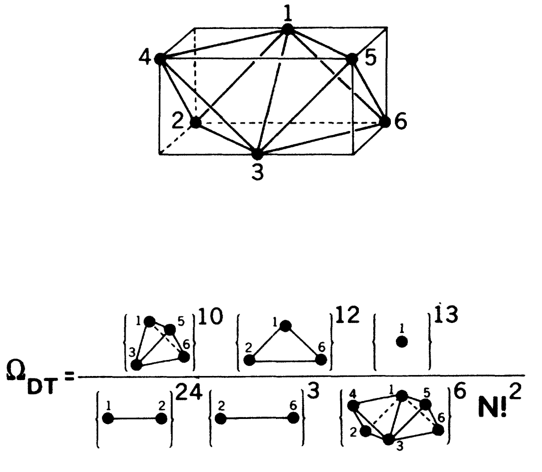


FIG. 4. Form of the number of configurations Ω_{DT} for the double-tetrahedron approximation (Ref. 5).

V. HIGH-TEMPERATURE SPECIFIC HEAT

The specific heat per lattice point $c_v(T)$ for the Ising ferromagnet can be written as

$$\left(\frac{k_BT}{J}\right)^2\frac{c_v(T)}{k_B}=\frac{z}{2}\frac{d\xi(2,1)}{d\beta}\ . \tag{20}$$

The conditions for the minimization of the free energy, Eq. (16), provide us with the relations needed for the calculation of the specific heat. Taking the derivative with respect to the inverse temperature β in Eq. (16), we obtain

$$\sum_{(r',t')}\frac{\partial^2 f}{\partial\xi(r,t)\,\partial\xi(r',t')}\frac{d\xi(r',t')}{d\beta}=\frac{z}{2}\delta((r,t);(2,1))\ .$$

Noting that $d\xi(r',t')/d\beta$ vanishes for r' odd, and that the matrix F whose elements are the second derivatives of the free energy has a block form in the disordered state, we can write

$$\frac{d\xi(2,1)}{d\beta}=-\frac{z}{2}\sum_{(r,t)}\frac{R_c^2(2,1;r,t)}{\lambda_c(r,t)}\ , \tag{21}$$

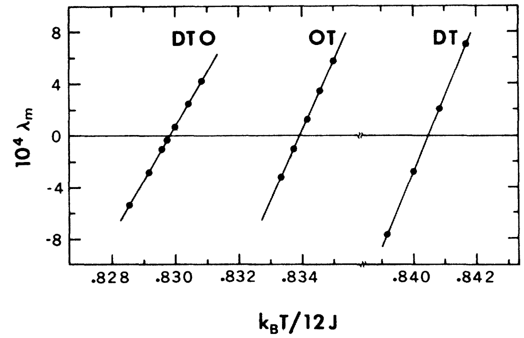


FIG. 5. Smallest eigenvalue λ_m of the matrix F_0 as a function of temperature for the DT, OT, and DTO approximations.

where $R_e(r,t;r',t')$ and $\lambda_e(r,t)$ are, respectively, the eigenvector components and eigenvalues of the matrix F_e defined in Sec. IV.

The high-temperature specific heat, calculated using Eqs. (20) and (21), is shown in Fig. 6 for the DTO approximation. For comparison, the specific heat calculated in the single tetrahedron approximation is also shown in Fig. 6.[1] The calculation of the low-temperature specific heat, which requires the solution of Eq. (16) in the ordered state, will not be performed in this paper. Although the minimization of the free energy in the ordered state does not impose any fundamental difficulties, the number of equations to be solved is roughly twice that of the disordered state, making actual computations more cumbersome.

Of considerable interest is the calculation of the high-temperature expansion coefficients of the specific heat. In the disordered state, c_v is written as

$$\left(\frac{k_B T}{J}\right)^2 \frac{c_v(\omega)}{k_B} = \sum_{n=0}^{\infty} a_n \omega^n \tag{22}$$

with

$$\omega = \tanh\beta$$

and with the coefficients a_n given by

$$a_n = \tfrac{1}{2} z \xi_0^{(n+1)}(2,1) \quad \text{for } n = 0, 1$$

and

$$a_n = \frac{z}{2}\left(\frac{1}{n!}\xi_0^{(n+1)}(2,1) - \frac{1}{(n-2)!}\xi_0^{(n-1)}(2,1)\right)$$

for $n \geqslant 2$,

where $\xi_0^{(n)}(2,1)$ stands for the nth order derivative with respect to ω of the pair correlation function $\xi(2,1)$ evaluated at $\omega = 0$.

A simple recursive equation for calculating the nth order derivative of the correlation functions $\xi(r,t)$ can be obtained from the relation

$$\frac{d^n}{d\omega^n}\left(\frac{\partial f}{\partial \xi(r,t)}\right) = 0 \ , \tag{23}$$

which follows from the minimization conditions given by Eq. (16).

Expanding the logarithm of the concentrations $x_l(r,t)$ in Eq. (16) in powers of the sum on the right-hand side of Eq. (7), and using Eqs. (10) and (13), we obtain, after some straightforward algebra,

$$\xi_0^{(n)}(r',t') = C^{-1}(r',t')\left(-\tfrac{1}{2} z \beta_0^{(n)} \delta((r',t');(2,1)) + \sum_{k=2}^{n} \frac{(-1)^k}{k} \sum_{(r,t)} \frac{\gamma(r,t)}{2^l} \sum_{l} \alpha_l(r,t) v_l(r,t;r',t') [y_l^k(r,t)]_0^{(n)}\right] \tag{24}$$

with

$$C(r',t') = \sum_{(r,t)} \gamma(r,t) v_1(r,t;r',t') \ ,$$

$$\beta_0^{(n)} = \left(\frac{d^n}{d\omega^n}\tanh^{-1}\omega\right)_{\omega=0} = \begin{cases} 0 & n \text{ even} \\ (n-1)! & n \text{ odd} \end{cases} ,$$

and

$$[y_l^k(r,t)]_0^{(n)} = \frac{d^n}{d\omega^n}\left(\sum_{(p,s)} v_l(r,t;p,s)\xi(p,s)\right)^k_{\omega=0} \ . \tag{25}$$

Since $y_l(r,t)$ vanishes at $\omega = 0$, the right-hand side of Eq. (24) will only contain derivatives of the correlation functions $\xi(r,t)$ of order smaller than n. Thus, by means of Eq. (24), the $\xi_0^{(n)}(r,t)$ can be calculated recursively starting from the initial values

$$\xi_0^{(1)}(2,1) = -z/2C(2,1)$$

and

$$\xi_0^{(1)}(r,t) = 0 \quad (r,t) \neq (2,1) \ .$$

Table XII shows the calculated values of the expansion coefficient a_n for the specific heat in the DTO approximation. Four coefficients are reproduced exactly, the fifth one being determined to within 0.4%. Note that the value of the fifth expansion coefficient calculated in the DTO approximation is, as expected, slightly improved with respect to one calculated in the TO approximation.

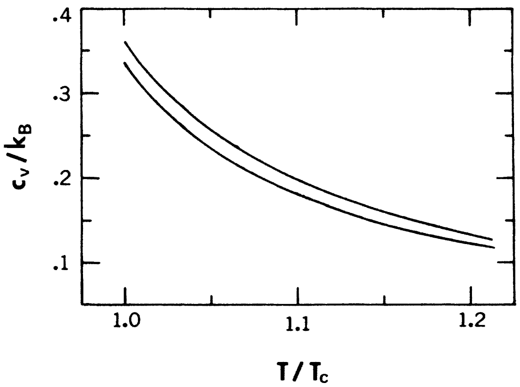


FIG. 6. Specific heat in the disordered state for the DTO (upper curve) and the tetrahedron (Ref. 1) (lower curve) approximations.

VI. CONCLUSIONS

We have calculated the critical temperature T_c and the high-temperature specific heat for the fcc Ising

TABLE XII. Expansion coefficients for specific heat.

n	a_n OT	 DTO	 Exact
0	6	6	6
1	48	48	48
2	390	390	390
3	3216	3216	3216
4	26004	26724	26844

spin-$\frac{1}{2}$ ferromagnet in the cluster variation approximation by using larger clusters (double-tetrahedron–octahedron) than were heretofore considered tractable. The resulting value of T_c was only 1.5% higher than the one determined by an exact high-temperature expansion and the expansion for the high-temperature specific heat gave four coefficients exactly and the fifth one to within 0.4%.

The handling of large clusters was made possible by the development of a "cluster algebra" in Sec. III. The results of Sec. III can be summarized as follows. (i) The number of independent variables for a given CVM approximation is given by the total number of subclusters in which the basic clusters can be decomposed. (ii) The concentration of (r,t) clusters in the configuration $l=\{i,j,\ldots,k\}$ can be written as a linear combination of the correlation functions $\xi(r',t')$ $(r' \leq r)$ associated with all the subclusters of (r,t). The coefficients $v_l(r,t;r',t')$ of such a linear combination are given by a sum of r'-order products of the $i,j,\ldots,k$ indices $(i,j,\ldots,k=\pm 1)$, the number of terms being equal to the number of (r',t') clusters in (r,t). (iii) The degeneracy factor $\alpha_l(r,t)$ for the configuration l of (r,t) can be determined by counting the number of distinguishable configurations $\{i,j,\ldots,k\}$ for which the coefficients $v_{i,j,\ldots,k}(r,t;r',t')$ are equal for all (r',t') (subcluster of (r,t)). The cluster algebra summarized above greatly facilitated the task of minimizing the free energy, since it is then no longer necessary to derive subsidiary constraints which are often very difficult to determine in the case of large clusters.

Although the CVM, being a "classical" theory, fails to yield accurate critical exponents, it yields useful approximate results, provided that large enough clusters are used, with far less computational labor than is commonly required with more precise theoretical methods. More importantly, the CVM as handled here allows the incorporation in the energy expression of second and third nn pair interactions and even many-body interactions with absolutely no additional difficulties. This is a very significant consideration since the stability of various ordered structures found experimentally in fcc and bcc binary alloys can only be demonstrated by appealing to higher-than-first-neighbor pair interactions.[11-13] Hence clusters large enough to contain explicitly second- and third-neighbor distances must be used in the CVM calculations. In fact, the primary objective of the present investigation was that of selecting the most appropriate cluster to be used in calculations of order-disorder binary phase diagrams presently being carried out. The application of the method to the Ising ferromagnet was done for the purpose of testing the various cluster approximation in a case where precise results were well established.

ACKNOWLEDGMENTS

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