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## Modified cluster-field method for statistics of ordering systems

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**Abstract.** A relatively simple cluster approximation for the investigation of the phase transition thermodynamics in order–disorder systems is proposed. The approximation is demonstrated on the square and simple-cubic Ising lattices with nearest-neighbour ferromagnetic coupling. The accuracy of the approximation is shown to be no worse than that of the well known cluster-variation method (CVM). At the same time the modified cluster-field method has fewer variational parameters and is easier to use than the CVM, allowing use of larger clusters for better accuracy.

### 1. Introduction

Phase transitions related to ordering of ions, atomic groups or spins in the double-well potential are successfully described on the basis of lattice-gas or Ising models. Since a number of suitable models are complicated and an exact treatment cannot be performed, the thermodynamic properties of the phase transitions are investigated by means of analytical approximations or numerical simulation.

Numerical simulation (Monte Carlo method) allows one to obtain values of thermodynamic properties with high accuracy. However, the Monte Carlo method is computer time-consuming and it requires complicated data analysis. Since the model Hamiltonian of a complicated system often includes phenomenological parameters, which are not initially known, one has to evaluate these parameters by fitting theoretical results to experimental data. This procedure demands repeated calculation of thermodynamic parameters. Therefore, the above-mentioned shortcomings of numerical simulation become rather serious. Applications of the renormalisation-group method to order–disorder phase transitions raise the same problems.

An alternative approach is offered by analytical approximations, based on the variational principle of statistical mechanics. These methods are relatively simple though they are not as accurate as the numerical ones. The earliest, simplest and most widely used are the mean-field approximations. Later, various cluster approximations were developed as an extension of the mean-field approximation.

The choice of analytical approximation depends mainly on the magnitude of short-range correlations of spins or ordering particles. The value of  $f = \exp(\beta_c |J|) - 1$  is a quantitative characteristic of these correlations. Here  $\beta_c = 1/T_c$  is the inverse transition

temperature and  $J$  is the coupling constant. Over the range  $f \ll 1$ , the mean-field approximation is quite acceptable; but, for  $f > 1$ , the short-range correlations are usually taken into account by means of cluster methods (see e.g. Domb 1960, Ziman 1979).

Among the available cluster approximations, the cluster-variation method (CVM) introduced by Kikuchi (1951) is the most accurate method. This method in the form developed by Morita (1957) was applied for the calculation of thermodynamic properties of real ordering systems (see e.g. Sanchez *et al* 1982). Recently the CVM was used for the description of the state diagram of the high- $T_c$  superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Wille *et al* 1988).

The accuracy of the cluster methods depends on the size of the largest (basic) cluster involved. However, one cannot initially determine the accuracy of the method with the particular basic cluster. Therefore, the cluster approximation with a certain basic cluster has to be initially verified on a well investigated model, e.g. the simplest Ising ferromagnet (Kikuchi 1951, Aggarwal and Tanaka 1977, Sanchez and de Fontaine 1978), and then it can be applied to the actual problem.

It is known that the accuracy of the CVM usually increases on enlarging the basic cluster. Consequently, the number of variational parameters also increases and the free energy minimisation problem becomes rather complicated. However, large basic clusters often are necessary in order to include all interactions in the cluster. In this case a simplified cluster approximation—the cluster-field method (CFM)—may be used (Vaks *et al* 1988). The CFM allows one to reduce the number of variational parameters compared with the CVM. The accuracy of the CFM is lower than that of the CVM. Nevertheless the CFM and its analogues were used for the calculations of thermodynamic properties and state diagrams of KDP-type ferroelectrics (Blinic and Svetina 1966), ices (Schneider and Tornau 1985), solid orthohydrogen (Lee and Raich 1972), ammonium halogenides (Vaks and Schneider 1976) and squaric acid ( $\text{C}_4\text{H}_2\text{O}_4$ ) (Matsushita and Matsubara 1982).

In this paper a modified cluster-field method (MCFM) is presented. The MCFM is a further development of the CFM, though it can be considered as a version of the CVM. The method offers a simplification of calculations compared with the CVM without a loss of accuracy.

In § 2 the basic principles of the MCFM are formulated. In § 3 the application of the MCFM to the two-dimensional Ising ferromagnet is demonstrated. In § 4 the comparison of the MCFM with the CVM and the CFM is given. Finally, § 5 is devoted to the description of the MCFM properties in the case of large basic clusters.

## 2. Calculation of thermodynamic parameters

We shall describe the MCFM for the Ising model, when the state of the lattice site is characterised by the spin  $\sigma = \pm 1$  and the Hamiltonian of the system is

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j - h \sum_i \sigma_i \quad (1)$$

where  $J_{ij}$  is the pair coupling constant between sites  $i$  and  $j$ , and  $h$  is an external magnetic field. Then the equilibrium density matrix according to the canonical distribution is described by

$$\rho = e^{\beta(F-H)} \quad (2)$$

where  $F$  is the free energy of the system, which has the form

$$F = -T \ln \text{Sp } e^{-\beta H} \quad (3)$$

and is obtained from normalisation condition  $\text{Sp } \rho = 1$ .  $\text{Sp}$  means summation over all

configurations of the system. Since the number of sites  $N \rightarrow \infty$ , the summation in (3) cannot be carried out directly, except in some special cases. Therefore, the equilibrium free energy can be obtained using approximate methods. A lot of them are based on the exact variational principle of statistical mechanics in which the equilibrium free energy is the minimum of the functional

$$F = \text{Sp } \rho_t (H + T \ln \rho_t) \quad (4)$$

with respect to a trial  $N$ -site density matrix under the normalisation constraint

$$\text{Sp } \rho_t = 1. \quad (5)$$

In (4) and (5),  $\rho_t$  must be expressed in terms of variational parameters. Then (4) must be minimised with respect to those parameters. However, the number of variational parameters is  $2^N - 1$  in the general case, so it is too large for practical use, though it can be reduced according to symmetry considerations. The approximation consists of two stages:

(i) The  $N$ -site density matrix  $\rho_t$  is replaced in (4) and (5) by reduced trial density matrices  $\rho_t(K)$ , where  $K$  denotes a set of lattice sites (cluster).

(ii) The minimisation of (4) is carried out after  $\rho_t(K)$  is expressed in terms of a limited number of variational parameters.

The first problem can be solved by the cluster-cumulant expansion of the free energy functional (4) (Morita 1957, Kubo 1962), and the second problem deals with the structure of the reduced trial density matrix.

### 2.1. The cluster-cumulant expansion

We shall denote a cluster consisting of sites  $(i_1, i_2, \dots, i_l)$  by  $L$ . Here  $l$  is the number of sites in the cluster  $L$ . When all sites of the cluster  $L$  are also sites of another cluster  $K$  with  $k > l$ ,  $L$  is called the subcluster of  $K$  ( $L \in K$ ).

The functional (4) can be expressed as the cluster-cumulant expansion

$$F = \sum_L \tilde{F}(L) = \sum_L \text{Sp } \rho_t [\tilde{H}(L) + T \ln \tilde{\rho}_t(L)] \quad (6)$$

where the sum runs over all clusters of the whole  $N$ -site lattice  $\{N\}$ . The cumulants  $\tilde{H}(L)$  and  $\ln \tilde{\rho}_t(L)$  are determined by the equations

$$H(K) = \sum_{L \in K} \tilde{H}(L) \quad (7)$$

$$\ln \rho_t(K) = \sum_{L \in K} \ln \tilde{\rho}_t(L) \quad (8)$$

for every cluster  $K$ , and the summation is carried out over all subclusters of  $K$  including  $L = K$ . The reduced density matrices are defined as

$$\rho_t(K) = \text{Sp}_{i \notin K} \rho_t \quad (9)$$

where  $\text{Sp}_{i \notin K}$  means summation over configurations of all sites except those included in cluster  $K$ . Owing to the symmetry of the lattice many of the clusters included in (6) are

equivalent. Therefore, expression (6) can be replaced by the expansion over non-equivalent clusters only,

$$F/N = \sum_L \rho_t a_L [\tilde{H}(L) + T \ln \tilde{\rho}_t(L)] \quad (10)$$

where  $a_L$  is the number of equivalent clusters  $L$  per spin ( $L$  in this case denotes the type of equivalent cluster). In the same way equations (7) and (8) can be expressed as

$$H(K) = \sum_{L \in K} b_L \tilde{H}(L) \quad (11)$$

$$\ln \rho_t(K) = \sum_{L \in K} b_L \ln \tilde{\rho}_t(L) \quad (12)$$

with  $b_L$  denoting the number of equivalent  $L$  clusters in cluster  $K$ .

If only pair interactions are included in the Hamiltonian (1), the cumulants  $\tilde{H}(L)$  equal zero for the clusters  $L$  consisting of more than two sites.

In the approximation, expression (10) is truncated assuming  $\ln \tilde{\rho}_t(L)$  to be zero for the cluster  $L$  larger than a certain cluster (basic cluster). This assumption is based on the fact that the cumulants  $\ln \tilde{\rho}_t(L)$  are exactly equal to zero if  $L$  contains statistically independent parts (Kubo 1962). In sufficiently large clusters, the most remote sites correlate weakly (at least not in the vicinity of the critical point). Hence  $\ln \tilde{\rho}_t(L)$  must be rather small. In the case of non-interacting sites  $\ln \tilde{\rho}_t(L)$  are not equal to zero only for single-site clusters. Then according to (8) the  $N$ -site density matrix has the form

$$\rho_t(1, 2, \dots, N) = \prod_{i=1}^N \rho_t(i). \quad (13)$$

The basic cluster  $B$  is usually chosen large enough to contain all the non-zero cumulants  $\tilde{H}(L)$ . Then the expansion of  $H$  in (10) is not truncated.

Taking (9) into account, the functional (10) can be rewritten as

$$F/N = \sum_{L \in B} \text{Sp } \rho_t(L) a_L [\tilde{H}(L) + T \ln \tilde{\rho}_t(L)]. \quad (14)$$

The equations (11) and (12) for the basic cluster and all its subclusters represent systems of linear equations from which  $\tilde{H}$  and  $\ln \tilde{\rho}$  can be expressed in terms of  $H$  and  $\ln \rho$ . Replacing the cumulants in (14) by the expressions obtained from these systems, we arrive at the functional

$$F/N = (1/N) \text{Sp } \rho_t(B) H + T \sum_{L \in B} \lambda_L \text{Sp } \rho_t(L) \ln \rho_t(L) \quad (15)$$

where  $\lambda_K$  are integer coefficients. Some of the  $\lambda_K$  may be equal to zero, i.e. not all subclusters of the basic cluster must contribute to (15). Reduced trial density matrices  $\rho_t(L)$  of all clusters involved in (15) are parametrised and the functional (15) is minimised under the normalisation constraints (5) and the self-consistency constraints

$$\rho_t(L) = \text{Sp}_{i \notin L} \rho_t(K) \quad (16)$$

following from the definition of the reduced density matrix (9).

2.2. Structure of the reduced trial density matrix

In the MCFM the reduced trial density matrix  $\rho_i(L)$  has the form

$$\rho_i(K) = e^{\beta(F_K - H_K)} \tag{17}$$

where  $F_K$  is the cluster free energy, obtained from the normalisation condition for (17):

$$F_K = -T \ln \text{Sp } e^{-\beta H_K}. \tag{18}$$

Here  $H_K$  is the cluster Hamiltonian, which is assumed to be of the form

$$H_K = \sum_{L \in K} \tilde{H}(L) + \sum_{i \in K} \varphi_K^i \sigma_i + \sum_{(ij) \in K} \psi_K^{(ij)} \sigma_i \sigma_j + \dots \tag{19}$$

where the effective fields  $\varphi$  and the effective coupling parameters  $\psi$  are introduced in order to ensure the self-consistency conditions (16). According to these conditions, the moments  $\langle \sigma_i \rangle_K, \langle \sigma_i \sigma_j \rangle_K$  etc should be equal averaged with the density matrix of any cluster  $K$  containing corresponding sites ( $i$ ), pairs ( $ij$ ), etc. Here  $\langle \dots \rangle_K$  denotes averaging with density matrix  $\rho(K)$ . It should be noted that parameters  $\psi$  are introduced only for the spin products  $\sigma_{i_1} \sigma_{i_2} \dots \sigma_{i_l}$  of such subclusters  $L$ , which are contained in at least two clusters involved in the approximation, since only in this case can the self-consistency conditions be formulated. However, application of the MCFM to concrete models has shown that it is sufficient to introduce  $\psi$ s for spin pairs only, if only pair interactions are included in the Hamiltonian (1). Though in this case the self-consistency conditions are not always fulfilled completely, it has little influence on the accuracy of the MCFM (a small fraction of a per cent). Inserting the expression for the reduced trial density matrix (17) together with (19) into the functional (15), the following expression is obtained:

$$F/N = \sum_{K \in B} \lambda_K F_K + (1/N) \langle H \rangle_B - \sum_{K \in B} \lambda_K \langle H_K \rangle_K. \tag{20}$$

Note that according to (1) and (19) the average energies  $\langle H \rangle$  and  $\langle H_K \rangle$  are expressed as linear combinations of the moments  $\langle \sigma_i \rangle, \langle \sigma_i \sigma_j \rangle$ , etc. Differentiating (20) with respect to parameters  $\varphi$  and  $\psi$ , equating derivatives to zero and taking into account the self-consistency conditions (16), the stationarity conditions for the functional (20) are obtained. They can be conveniently written as

$$\langle H \rangle = \sum_{K \in B} \lambda_K \langle H_K \rangle \tag{21}$$

where it is assumed that equation (21) is valid for every moment  $\langle \sigma_i \rangle, \langle \sigma_i \sigma_j \rangle$ , etc., independently. Then equation (21) represents the system of equations of the type

$$\sum_{K \in B} \lambda_K \sum_{i \in K} \varphi_K^i = 0 \quad \sum_{K \in B} \lambda_K \sum_{(ij) \in K} \psi_K^{(ij)} = 0 \tag{22}$$

etc. Equations (22) together with the self-consistency condition (16) give a complete set of equations from which to obtain equilibrium values of the variational parameters  $\varphi$  and  $\psi$ , and, consequently, the equilibrium density matrix  $\rho(B)$ . In practice, the linear relations (22) allow one to reduce the number of linearly independent variational parameters and then to solve the self-consistency equations with respect to those parameters. According to (20) and (21) the equilibrium free energy has the form

$$F = \sum_{K \in B} \lambda_K F_K. \tag{23}$$

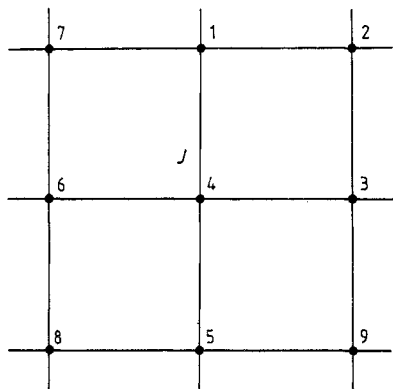


Figure 1. Square Ising lattice with nearest-neighbour coupling constant  $J$  and enumeration of spins used in this paper.

Table 1. The cumulants  $\tilde{F}$  for simplest clusters.

| Cluster         | Cumulant   |
|-----------------|--|
| (1)             | $\tilde{F}_1 = F_1$                              |
| (1, 2)          | $\tilde{F}_2 = F_2 - 2F_1$                       |
| (1, 3)          | $\tilde{F}'_2 = F'_2 - 2F_1$                     |
| (1, 2, 3)       | $\tilde{F}_3 = F_3 - 2F_2 - F'_2 + 3F_1$         |
| (1, 2, 3, 4)    | $\tilde{F}_4 = F_4 - 4F_3 + 4F_2 + 2F'_2 - 4F_1$ |
| (1, 3, 4, 5, 6) | $\tilde{F}_5 = F_5 - 4F_3 + 4F_2 - F_1$          |

### 3. Application to the square Ising lattice

Let us illustrate the MCFM on the square Ising ferromagnet (the enumeration of sites is given in figure 1), since the critical temperature of this model is exactly known.

The cluster-cumulant expansion for the free energy per spin of the square lattice is

$$F = \tilde{F}_1 + 2\tilde{F}_2 + 2\tilde{F}'_2 + 4\tilde{F}_3 + \tilde{F}_4 + \tilde{F}_5 + \dots \tag{24}$$

the  $\tilde{F}$ s corresponding to the clusters listed in table 1. The cumulant  $\tilde{F}'_2$  corresponds to the pair of non-interacting (diagonal) spins. In  $\tilde{F}_5$ , several cumulants are included for simplicity. The coefficients of the  $\tilde{F}_K$  terms in (24) are equal to the number of corresponding clusters per spin and are obtained from geometrical considerations. The expressions of the  $\tilde{F}$ s in terms of the  $F$ s are also listed in table 1. In the approximation, expression (24) is truncated and the cumulants  $\tilde{F}$  are substituted by  $F$ s according to table 1. Several expressions of  $F$  for various basic clusters are as follows:

$$(2 + 1)\text{-clusters (pair)} \quad F = 2F_2 - 3F_1 \tag{25}$$

$$(3 + 2 + 1)\text{-clusters (triangle)} \quad F = 4F_3 - 6F_2 - 2F'_2 + 5F_1 \tag{26}$$

$$(4 + 2 + 1)\text{-clusters (square)} \quad F = F_4 - 2F_2 + F_1 \tag{27}$$

$$(5 + 4 + 3 + 2)\text{-clusters} \quad F = F_5 + F_4 - 4F_3 + 2F_2. \tag{28}$$

Note that in the last approximation two basic clusters—5-cluster and 4-cluster—are involved, since no one of these clusters is the subcluster of another.

**Table 2.** The transition temperatures  $t_c = T_c/zJ$  and entropies  $S_c$  of the Ising model in various approximations.

| Approximation            | Square lattice, $z = 4$ |        | Simple cubic lattice, $z = 6$ |       |
|--------------------------|-------------------------|--------|-------------------------------|-------|
|                          | $t_c$                   | $S_c$  | $t_c$                         | $S_c$ |
| Mean-field (Weiss)       | 1                       | 0.693  | 1                             | 0.693 |
| Cluster-field            |                         |        |                               |       |
| (2 + 1) clusters         | 0.721                   | 0.580  | 0.822                         | 0.633 |
| (4 + 1) clusters         | 0.693                   | 0.552  | 0.815                         | 0.628 |
| (4 + 2) clusters         | 0.676                   | 0.534  | 0.811                         | 0.625 |
| (8 + 4) clusters         | —                       | —      | 0.797                         | 0.614 |
| (9 + 4) clusters         | 0.654                   | 0.500  | —                             | —     |
| (4 + 2 + 1) clusters     | 0.656                   | 0.513  | 0.794                         | 0.613 |
| (8 + 4 + 2 + 1) clusters | —                       | —      | 0.784                         | 0.604 |
| (9 + 6 + 4) clusters     | 0.624                   | 0.442  | —                             | —     |
| Modified cluster-field   |                         |        |                               |       |
| (4 + 2 + 1) clusters     | 0.606                   | 0.428  | 0.768                         | 0.587 |
| (5 + 4 + 3 + 2) clusters | 0.596                   | 0.405  | —                             | —     |
| (8 + 4 + 2 + 1) clusters | —                       | —      | 0.7631                        | 0.580 |
| (9 + 6 + 4) clusters     | 0.5856                  | 0.3774 | —                             | —     |
| Exact                    | 0.567                   | 0.306  | 0.752                         | 0.541 |

We shall describe explicitly the square approximation. Three clusters make contributions to the free energy expression (27). Therefore the reduced trial density matrices have to be introduced for the square (4-cluster), the pair (2-cluster) and the single spin (1-cluster). The cluster Hamiltonians are

$$H_4 = -(J + \psi_4)(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_4 + \sigma_1\sigma_4) - \varphi_4 \sum_{i=1}^4 \sigma_i \tag{29}$$

$$H_2 = -(J + \psi_2)\sigma_1\sigma_2 - \varphi_2(\sigma_1 + \sigma_2) \tag{30}$$

$$H_1 = -\varphi_1\sigma_1. \tag{31}$$

In order to calculate the five unknown parameters  $\varphi_1, \varphi_2, \varphi_4, \psi_2$  and  $\psi_4$ , the self-consistency conditions are to be solved. They correspond to equalities between average spins  $\langle\sigma_i\rangle$  and nearest-neighbour pair correlation functions  $\langle\sigma_i\sigma_j\rangle$  calculated with the density matrices  $\rho_K = e^{\beta(F_K - H_K)}$  of various clusters:

$$\text{Sp } \sigma_1\rho_1 = \text{Sp } \sigma_1\rho_2 = \text{Sp } \sigma_1\rho_4 \tag{32a}$$

$$\text{Sp } \sigma_1\sigma_2\rho_2 = \text{Sp } \sigma_1\sigma_2\rho_4. \tag{32b}$$

Another two equations follow from the condition (21), which has the form

$$\langle H \rangle / N = \langle H_4 \rangle - 2\langle H_2 \rangle + \langle H_1 \rangle. \tag{33}$$

For the square Ising lattice in zero magnetic field  $\langle H \rangle / N = -2J\langle\sigma_1\sigma_2\rangle$ . From (33) we obtain

$$4\varphi_4 - 4\varphi_2 + \varphi_1 = 0 \tag{34a}$$

$$4\psi_4 - 2\psi_2 = 0. \tag{34b}$$



Relations (34) allow one to reduce the number of linearly independent variational parameters to three. These parameters are obtained from (32). In the paramagnetic (disordered) phase  $\langle \sigma_i \rangle = 0$ , and hence  $\varphi_4 = \varphi_2 = \varphi_1 = 0$ . Then (32a) turns out to be an identity and from (32b) we obtain

$$e^{4\beta\psi_4} = \frac{1}{K^2} \left( \frac{K^{-2} - 3}{K^2 - 3} \right) \quad (35)$$

where  $K = e^{\beta J}$  and  $\psi_4 = \psi_2/2$  according to (34b). The critical temperature  $T_c$  is obtained from the condition  $(\partial^2 F / \partial \langle \sigma \rangle^2) = 0$ , which is identical to

$$(4\delta\varphi_4 / \partial \langle \sigma \rangle - 4\delta\varphi_2 / \partial \langle \sigma \rangle + \delta\varphi_1 / \partial \langle \sigma \rangle)_{\langle \sigma \rangle = 0} = 0. \quad (36)$$

The derivatives of (36) can be obtained by differentiating the expressions  $\langle \sigma \rangle = \text{Sp } \sigma_1 \rho_K$  with  $K = 1, 2, 4$ . Then the equation for the critical temperature has the form

$$2K_c^4 - 5K_c^2 + 1 = 0 \quad (37)$$

where  $K_c = e^{J/T_c}$ . The solution of (37) gives the following value for the transition temperature

$$\frac{T_c}{4J} = \frac{1}{2 \ln[(5 + \sqrt{17})/4]} = 0.6064. \quad (38)$$

The transition entropy per spin is obtained from (27) according to the thermodynamic relation  $F = E - TS$  and is equal to

$$S_c = -2\beta_c J \langle \sigma_1 \sigma_2 \rangle_{T=T_c} - \beta_c (F_4 - 2F_2 + F_1)_{T=T_c} = 0.4283. \quad (39)$$

We have made analogous MCFM calculations in the  $(5 + 4 + 3 + 2)$ -cluster approximation for the square Ising lattice and in the  $(4 + 2 + 1)$  and  $(8 + 4 + 2 + 1)$  approximations for the simple cubic lattice ( $z = 6$ ) with cube as the 8-cluster. The results are listed in table 2.

#### 4. Comparison with other cluster approximations

The CVM uses the same scheme of cluster-cumulant expansion, but has a different structure of reduced trial density matrices. In the most widely used version of the CVM (Aggarwal and Tanaka 1977, Sanchez and de Fontaine 1978) the reduced trial density matrices are expressed via various moments  $\langle \sigma_i \rangle$ ,  $\langle \sigma_i \sigma_j \rangle$ , etc., in order for the normalisation and self-consistency conditions to be automatically fulfilled. Therefore, when the reduced trial density matrices are substituted in the free energy functional, it is then minimised with respect to those moments. In this way, average spins and various correlation functions are obtained directly. However, there are more variational parameters in the CVM than in the MCFM, at least for the Ising ferromagnet. For example, to describe the ferromagnetic phase of the square Ising lattice in the square approximation five linearly independent parameters should be introduced in the CVM and only three in the MCFM. In the cubic approximation of the simple cubic lattice the corresponding numbers are respectively 21 and six. Nevertheless, the MCFM has the same accuracy as the CVM. In the square approximations both methods give identical critical temperatures; in the cubic approximation  $T_c$  of the MCFM is lower by 0.05% than that of the CVM. Besides that, at low temperatures the problem of the free energy minimisation

in the CVM appears to be more complicated than the solution of the self-consistency equations in the MCFM.

Recently, a method was proposed to reduce the number of variational parameters of the CVM (Schlijper and Westerhof 1987). In this method the reduced trial density matrix of the largest cluster is expressed approximately in terms of the reduced density matrices of smaller clusters. Since the density matrices of smaller clusters have fewer parameters, the variational basis of the free energy is reduced and the minimisation procedure is simplified. However, the accuracy of this method is lower compared to the original CVM.

The CFM (see e.g. Vaks and Zinenko 1986) is an extension of the constant-coupling method (Kasteleijn and van Kranendonk 1956) to the arbitrary size of the basic cluster. The structure of the reduced density matrices in the CFM is the same as in the MCFM. However, only effective fields  $\varphi$  are introduced in the CFM cluster Hamiltonians. These fields are assumed to be proportional to the number of bonds connecting the cluster spin with its neighbours outside the cluster. The values of effective fields are obtained by equating the average spins  $\langle\sigma\rangle$  calculated with density matrices of all clusters of the approximation. They can be obtained also from the free energy minimum condition. Usually two clusters are involved in the CFM. Then the free energy  $F$  is not written in accordance with the cluster-cumulant expansion, but from the requirement of the proper number of sites and pairs of interacting spins to be included in the free energy. If more than two clusters are involved in the CFM, the self-consistency condition and the free energy minimum condition may not be equivalent, making the CFM ambiguous. The accuracy of the CFM is much lower than that of the CVM or MCFM. Some results of  $T_c$  calculations for the Ising model in the CFM are listed in table 2 as ' $(m+n)$  clusters'. Besides we applied the cluster-cumulant expansion to the CFM formally taking the effective coupling parameters  $\psi$  of the MCFM to be equal to zero. As can be seen from table 2 (the last three approximations of the CFM) this procedure, though inconsistent, offers a considerable improvement over the CFM with the same basic cluster. Note that for 'pair' as a basic cluster ( $(2+1)$ -cluster approximation) all the methods—the CVM, CFM and MCFM—give the same result identical to that of the Bethe approximation.

## 5. Large clusters in the modified cluster-field method

The MCFM shows a peculiarity when clusters with the dimensions of several lattice periods are used. Let us examine the approximation with a nine-site basic cluster. The free energy is described as

$$F/N = F_g - 2F_6 + F_4 \quad (40)$$

where the 9-cluster consists of four squares (sites 1–9 in figure 1), the 6-cluster of two squares (sites 1, 2, 3, 4, 6, 7) and the 4-cluster of one square (sites 1–4). In the four nearest coordination spheres the main cluster has seven types of non-equivalent spin pairs for which the self-consistency conditions can be written. The seven parameters  $\psi$  should be introduced. The 6-cluster has six parameters and the 4-cluster has two. The critical temperature and entropy in this approximation are given in table 2. In table 3, the  $\psi$ s are listed together with the corresponding spin pairs and the values of  $\psi_i/T_c$ . One can see that the values of  $\psi$  of the edge spin pairs (i.e.  $\psi_1, \psi_5, \psi_9, \psi_{10}, \psi_{12}, \psi_{14}$ ) are considerably higher than those of the inner spin pairs. This is obviously due to a decrease

**Table 3.** The effective coupling parameters in (9 + 6 + 4)-clusters approximation at the transition temperature.

|           | Parameter   | Spin pairs   | Coordination sphere | $\psi_i/T_c$ | $\psi_i/\psi_{\max}$ |
|-----------|-------------|--|---------------------|--------------|----------------------|
| 9-cluster | $\psi_1$    | (1-2), (2-3), (3-9), (5-9), (5-8), (6-8), (6-7), (1-7) | 1                   | 0.0951       | 0.713                |
|           | $\psi_2$    | (1-4), (3-4), (4-5), (4-6)                             | 1                   | -0.00124     | -0.00928             |
|           | $\psi_3$    | (2-4), (7-4), (4-9), (4-8)                             | 2                   | 0.00263      | 0.0197               |
|           | $\psi_4$    | (1-3), (3-5), (5-6), (1-6)                             | 2                   | 0.0119       | 0.0890               |
|           | $\psi_5$    | (2-7), (2-9), (8-9), (7-8)                             | 3                   | 0.0742       | 0.556                |
|           | $\psi_6$    | (1-5), (3-6)   | 3                   | 0.00227      | 0.0170               |
|           | $\psi_7$    | (2-6), (3-7), (1-9), (2-5), (3-8), (6-9), (1-8), (5-7) | 4                   | 0.00930      | 0.0698               |
| 6-cluster | $\psi_8$    | (1-4)  | 1                   | 0.00214      | 0.0161               |
|           | $\psi_9$    | (7-6), (2-3)   | 1                   | 0.130        | 0.974                |
|           | $\psi_{10}$ | (1-7), (1-2), (3-4), (4-6)                             | 1                   | 0.0956       | 0.717                |
|           | $\psi_{11}$ | (1-3), (2-4), (4-7), (1-6)                             | 2                   | 0.0177       | 0.132                |
|           | $\psi_{12}$ | (2-7), (3-6)   | 3                   | 0.0753       | 0.565                |
|           | $\psi_{13}$ | (2-6), (3-7)   | 4                   | 0.0186       | 0.139                |
| 4-cluster | $\psi_{14}$ | (1-2), (2-3), (3-4), (1-4)                             | 1                   | 0.133 (max)  | 1                    |
|           | $\psi_{15}$ | (2-4), (1-3)   | 3                   | 0.0417       | 0.313                |

in the influence of the cluster edge on the inner correlations as the cluster size increases. Indeed, in the limit of an infinite cluster the density matrix becomes exact without any effective parameters.

Since in the (9 + 6 + 4)-cluster approximation, only several nearest- and third-neighbour spin pairs are edge spin pairs, one might suspect that omission of the second- and fourth-neighbour  $\psi$ s would not strongly decrease the accuracy but at the same time would considerably simplify the solution. Actually, in the latter case the results are even somewhat better:  $T_c/4J = 0.5853$ ,  $S_c = 0.3770$ . We hope that this assumption is valid for other applications of the MCFM.

## 6. Conclusions

The modified cluster-field method proposed in this paper is an analytical approximation for the order-disorder problem. The method was developed as an improvement of the cluster-field method. We suppose the MCFM to be simpler and easier to use than the CVM. The MCFM allows one to use larger basic clusters, so as to achieve a better accuracy and to carry out calculations at lower temperatures. The MCFM is useful for the calculation of properties of physically adequate and thus complicated models (Ising or lattice gas) with a large number of coupling constants, especially when repeated calculations are needed. The method is a compromise between simple and non-accurate mean-field approximations and precise but complicated and time-consuming Monte Carlo or renormalisation-group methods. Though the MCFM, as a classical theory, gives classical critical indices, the accuracy of  $T_c$  determination is rather good—3–7% for the two-dimensional and about 2% for the three-dimensional lattices.

In the present paper in order to evaluate the accuracy of the MCFM we have applied the method to the well known and exactly solvable Ising model with nearest-neighbour coupling (the Ising model, as a rule, is used for the demonstration and comparison of various approximations). In practice, various analytical methods are valuable only for the investigation of more complicated models, which (for certain reasons) cannot be investigated with more precise methods.

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