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## LETTER TO THE EDITOR

**Quadratic short-range order corrections to the mean-field free energy**

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**Abstract.** A method for calculating the short-range order part of the free energy of order-disorder systems is proposed. The method is based on the application of the cumulant expansion to the exact configurational entropy. Second-order correlation corrections to the mean-field approximation for the free energy are calculated for arbitrary thermodynamic phases and types of interaction. The resulting quadratic approximation for the correlation entropy leads to substantially better values of transition temperatures for the nearest-neighbour cubic Ising ferromagnets.

In a recent paper [1] we developed a method of deriving very simple polynomial approximations for the variational configurational entropy in which the well-known and reliable cluster variation method (CVM) of Kikuchi [2] was used as a starting point. It was observed that in the absolute majority of the CVM approximations the number of variational parameters in the entropy is substantially greater than in the internal energy. As a result, the minimization of the free energy with respect to those variables which are not present in the internal energy reduces to the maximization of the entropy. The corresponding equations simply relate different variational parameters, since the configurational entropy contains no information about the character and strength of interactions in the system. Most of the variables in the CVM free energy are therefore redundant and can in principle be eliminated by solving these equations. However, the equations are non-linear and apparently cannot be solved exactly; even if this was possible, the resulting expression for the entropy would be far too complicated. To overcome this difficulty, it was proposed to expand all the redundant parameters in powers of cumulants of those pair and higher-order averages which enter the expression for the internal energy; such cumulants are usually sufficiently small. In this case the initial equations reduce to those for the corresponding expansion coefficients, and the latter can be easily solved. The final approximation for the entropy is a polynomial of some order in the cumulants of only those averages which are present in the internal energy. The proposed method can be regarded as a simplification of the CVM.

The described approach, however, combines two very different approximations, since its aim is to find an approximate analytical solution of the already approximate CVM equations (which are usually treated only numerically). In the present letter we show that it is possible to apply the same idea of the cumulant expansion directly to the exact configurational entropy, thus avoiding using the CVM for constructing the initial approximation. The general formalism is presented and the first non-zero (quadratic)

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corrections due to short-range order (SRO) to the mean-field approximation (MFA) for the free energy are calculated. Considerably more complicated calculation of higher-order terms is left for a discussion elsewhere [3]. It is shown that the obtained quadratic approximation for the correlation entropy significantly improves, in comparison with the MFA, calculated transition temperatures for the nearest-neighbour (NN) cubic Ising ferromagnets.

The formally exact expression for the configurational entropy has the form

$$S = -k_B \sum_{i_1 \dots i_N} P_{1\dots N}^{i_1 \dots i_N} \ln P_{1\dots N}^{i_1 \dots i_N}. \quad (1)$$

Here  $k_B$  is the Boltzmann constant, the  $N$ -site probability

$$P_{1\dots N}^{i_1 \dots i_N} = \langle p_1^{i_1} \dots p_N^{i_N} \rangle \quad (2)$$

is the statistical average of the product of  $N$  occupation numbers, and  $N$  is the number of lattice sites in the system. The occupation number  $p_n^i$  for a particular spin orientation (up or down) is equal to 1 or 0 depending on whether the spin at the lattice site  $n$  has this orientation or not. It is convenient for our purposes to define the orientation index  $i$  as taking on values  $\pm 1$ . Equation (1) is a slightly more detailed version of the familiar result [4]

$$S = -k_B \text{Tr} \rho \ln \rho \quad (3)$$

where  $\rho$  is the density matrix and Tr denotes the trace of a matrix.

The cumulant average [5] of a product of  $l$  variables is the  $l$ th-order residue when all combinations of cumulant averages of lower order are subtracted from the actual average of the product. The cumulant averages of the occupation numbers are thus defined by the relations

$$\begin{aligned} \langle p_{n_1}^{j_1} \rangle &= \langle p_{n_1}^{j_1} \rangle_c \\ \langle p_{n_1}^{j_1} p_{n_2}^{j_2} \rangle &= \langle p_{n_1}^{j_1} \rangle_c \langle p_{n_2}^{j_2} \rangle_c + \langle p_{n_1}^{j_1} p_{n_2}^{j_2} \rangle_c \\ \langle p_{n_1}^{j_1} p_{n_2}^{j_2} p_{n_3}^{j_3} \rangle &= \langle p_{n_1}^{j_1} \rangle_c \langle p_{n_2}^{j_2} \rangle_c \langle p_{n_3}^{j_3} \rangle_c + \langle p_{n_1}^{j_1} p_{n_2}^{j_2} \rangle_c \langle p_{n_3}^{j_3} \rangle_c + \langle p_{n_1}^{j_1} p_{n_3}^{j_3} \rangle_c \langle p_{n_2}^{j_2} \rangle_c \\ &\quad + \langle p_{n_2}^{j_2} p_{n_3}^{j_3} \rangle_c \langle p_{n_1}^{j_1} \rangle_c + \langle p_{n_1}^{j_1} p_{n_2}^{j_2} p_{n_3}^{j_3} \rangle_c \end{aligned} \quad (4)$$

etc, where the subscript  $c$  denotes a cumulant average. Correspondingly, the  $N$ -site probability (2) is written as

$$\begin{aligned} P_{1\dots N}^{i_1 \dots i_N} &= \langle p_1^{i_1} \rangle_c \dots \langle p_N^{i_N} \rangle_c + \left[ \langle p_1^{i_1} p_2^{i_2} \rangle_c \langle p_3^{i_3} \rangle_c \dots \langle p_N^{i_N} \rangle_c + \dots \right. \\ &\quad \left. + \langle p_1^{i_1} \rangle_c \dots \langle p_{N-2}^{i_{N-2}} \rangle_c \langle p_{N-1}^{i_{N-1}} p_N^{i_N} \rangle_c \right] \\ &\quad + \left[ \langle p_1^{i_1} p_2^{i_2} p_3^{i_3} \rangle_c \langle p_4^{i_4} \rangle_c \dots \langle p_N^{i_N} \rangle_c + \dots \right. \\ &\quad \left. + \langle p_1^{i_1} \rangle_c \dots \langle p_{N-3}^{i_{N-3}} \rangle_c \langle p_{N-2}^{i_{N-2}} p_{N-1}^{i_{N-1}} p_N^{i_N} \rangle_c \right] + \dots \\ &\quad + \left[ \langle p_1^{i_1} p_2^{i_2} \rangle_c \langle p_3^{i_3} p_4^{i_4} \rangle_c \langle p_5^{i_5} \rangle_c \dots \langle p_N^{i_N} \rangle_c + \dots \right. \\ &\quad \left. + \langle p_1^{i_1} \rangle_c \dots \langle p_{N-4}^{i_{N-4}} \rangle_c \langle p_{N-3}^{i_{N-3}} p_{N-2}^{i_{N-2}} \rangle_c \langle p_{N-1}^{i_{N-1}} p_N^{i_N} \rangle_c \right] + \dots \\ &\quad + \langle p_1^{i_1} \rangle_c \dots \langle p_N^{i_N} \rangle_c. \end{aligned} \quad (5)$$

Introducing notations

$$P_{n_1 \dots n_q}^{j_1 \dots j_q} = \langle p_{n_1}^{j_1} \dots p_{n_q}^{j_q} \rangle \quad C_{n_1 \dots n_q}^{j_1 \dots j_q} = \langle p_{n_1}^{j_1} \dots p_{n_q}^{j_q} \rangle_c \quad (6)$$

and noticing that  $P_n^j = C_n^j$  as given by the first of equations (4), we rewrite the rest of equations (4) and equation (5) as follows,

$$\begin{aligned}
 P_{n_1 n_2}^{j_1 j_2} &= P_{n_1}^{j_1} P_{n_2}^{j_2} + C_{n_1 n_2}^{j_1 j_2} \\
 P_{n_1 n_2 n_3}^{j_1 j_2 j_3} &= P_{n_1}^{j_1} P_{n_2}^{j_2} P_{n_3}^{j_3} + C_{n_1 n_2}^{j_1 j_2} P_{n_3}^{j_3} + C_{n_1 n_3}^{j_1 j_3} P_{n_2}^{j_2} + C_{n_2 n_3}^{j_2 j_3} P_{n_1}^{j_1} + C_{n_1 n_2 n_3}^{j_1 j_2 j_3} \\
 &\dots \\
 P_{1 \dots N}^{i_1 \dots i_N} &= P_1^{i_1} \dots P_N^{i_N} + \left( C_{12}^{i_1 i_2} P_3^{i_3} \dots P_N^{i_N} + \dots + P_1^{i_1} \dots P_{N-2}^{i_{N-2}} C_{N-1, N}^{i_{N-1} i_N} \right) \\
 &\quad + \left( C_{123}^{i_1 i_2 i_3} P_4^{i_4} \dots P_N^{i_N} + \dots + P_1^{i_1} \dots P_{N-3}^{i_{N-3}} C_{N-2, N-1, N}^{i_{N-2} i_{N-1} i_N} \right) + \dots \\
 &\quad + \left( C_{12}^{i_1 i_2} C_{34}^{i_3 i_4} P_5^{i_5} \dots P_N^{i_N} + \dots + P_1^{i_1} \dots P_{N-4}^{i_{N-4}} C_{N-3, N-2}^{i_{N-3} i_{N-2}} C_{N-1, N}^{i_{N-1} i_N} \right) \\
 &\quad + \dots + C_{1 \dots N}^{i_1 \dots i_N}.
 \end{aligned} \tag{7}$$

Finally, defining new quantities

$$Q_{n_1 \dots n_q}^{j_1 \dots j_q} = \frac{C_{n_1 \dots n_q}^{j_1 \dots j_q}}{P_{n_1}^{j_1} \dots P_{n_q}^{j_q}} \tag{8}$$

we represent equations (7) in the form

$$\begin{aligned}
 P_{n_1 n_2}^{j_1 j_2} &= P_{n_1}^{j_1} P_{n_2}^{j_2} (1 + Q_{n_1 n_2}^{j_1 j_2}) \\
 P_{n_1 n_2 n_3}^{j_1 j_2 j_3} &= P_{n_1}^{j_1} P_{n_2}^{j_2} P_{n_3}^{j_3} (1 + Q_{n_1 n_2}^{j_1 j_2} + Q_{n_1 n_3}^{j_1 j_3} + Q_{n_2 n_3}^{j_2 j_3} + Q_{n_1 n_2 n_3}^{j_1 j_2 j_3}) \\
 &\dots \\
 P_{1 \dots N}^{i_1 \dots i_N} &= P_1^{i_1} \dots P_N^{i_N} (1 + X_{1 \dots N}^{i_1 \dots i_N})
 \end{aligned} \tag{9}$$

where in the last equation

$$\begin{aligned}
 X_{1 \dots N}^{i_1 \dots i_N} &= \sum_{q \geq 2} \sum_{\langle n_1 \dots n_q \rangle} Q_{n_1 \dots n_q}^{i_1 \dots i_q} \\
 &\quad + \sum_{q \geq 2} \sum_{p \geq 2} \sum_{\langle n_1 \dots n_q \rangle} \sum_{\langle n_{q+1} \dots n_{q+p} \rangle} Q_{n_1 \dots n_q}^{i_1 \dots i_q} Q_{n_{q+1} \dots n_{q+p}}^{i_{q+1} \dots i_{q+p}} + O(C^3).
 \end{aligned} \tag{10}$$

Here notation  $\langle n_1 \dots n_q \rangle$  corresponds to summation over clusters consisting of lattice sites  $n_1, \dots, n_q$ , the sites  $n_1, \dots, n_q, n_{q+1}, \dots, n_{q+p}$  in the second term are all different, and the last term denotes all contributions containing products of three or more cumulants  $C_{n_1 \dots n_q}^{j_1 \dots j_q}$ . Insertion of the result for the  $N$ -site probability (the last of equations (9)) into equation (1) leads to the natural separation of the long-range order (MFA) and SRO (correlation) contributions to the configurational entropy,

$$S = S_0 + S_1 \tag{11a}$$

$$S_0 = -k_B \sum_{in} P_n^i \ln P_n^i \tag{11b}$$

$$S_1 = -k_B \sum_{i_1 \dots i_N} P_1^{i_1} \dots P_N^{i_N} (1 + X_{1 \dots N}^{i_1 \dots i_N}) \ln (1 + X_{1 \dots N}^{i_1 \dots i_N}). \tag{11c}$$

We now expand the correlation entropy  $S_1$  in powers of  $X_{1 \dots N}^{i_1 \dots i_N}$ . It can be shown that the linear term vanishes [3]; e.g., for the first term in equation (10) this follows simply from the

fact that the entropy is maximal in the absence of correlations. Substitution of equation (10) into equation (11c) then gives

$$S_1 = -\frac{1}{2}k_B \sum_{i_1 \dots i_N} P_1^{i_1} \dots P_N^{i_N} \sum_{q \geq 2} \sum_{p \geq 2} \sum_{\langle n_1 \dots n_q \rangle} \sum_{\langle m_1 \dots m_p \rangle} Q_{n_1 \dots n_q}^{j_1 \dots j_q} Q_{m_1 \dots m_p}^{k_1 \dots k_p} + O(C^3). \quad (12)$$

The next step is to use the relation

$$C_{n_1 \dots n_q}^{j_1 \dots j_q} = 2^{-q} j_1 \dots j_q C_{n_1 \dots n_q} \quad (13)$$

where  $C_{n_1 \dots n_q}$  is the cumulant average of the product of the corresponding spin variables  $s_n$  which are linearly related to the occupation numbers and acquire values  $+1$  for spin up and  $-1$  for spin down,

$$C_{n_1 \dots n_q} = \langle s_{n_1} \dots s_{n_q} \rangle_c. \quad (14)$$

The proof of equation (13) is not given here to save space [3], but its validity can be directly checked, at least for low-order cumulants. Inserting equation (13) into equation (8), and then inserting the result into equation (12), we obtain

$$S_1 = -k_B \sum_{q \geq 2} \sum_{p \geq 2} 2^{-(q+p+1)} \sum_{\langle n_1 \dots n_q \rangle} \sum_{\langle m_1 \dots m_p \rangle} \left( \sum_{i_1 \dots i_N} \frac{j_1 \dots j_q k_1 \dots k_p P_1^{i_1} \dots P_N^{i_N}}{P_{n_1}^{j_1} \dots P_{n_q}^{j_q} P_{m_1}^{k_1} \dots P_{m_p}^{k_p}} \right) \times C_{n_1 \dots n_q} C_{m_1 \dots m_p} + O(C^3). \quad (15)$$

The expression in the round brackets in equation (15) factorizes into the product of sums over orientations of individual spins. The result of each such summation depends on whether the corresponding lattice site belongs to both sets  $n_1, \dots, n_q$  and  $m_1, \dots, m_p$ , to only one of them, or to neither, and is

$$\sum_j j^2 (P_n^j)^{-1} = (+1)^2 (P_n^+)^{-1} + (-1)^2 (P_n^-)^{-1} = (P_n^+ P_n^-)^{-1} \quad (16a)$$

$$\sum_j j = (+1) + (-1) = 0 \quad (16b)$$

$$\sum_j P_n^j = P_n^+ + P_n^- = 1 \quad (16c)$$

for these three cases, respectively (in the second case the probabilities in the numerator and denominator cancel each other). Equation (16b) shows that the only surviving terms in equation (15) are those in which the sets  $n_1, \dots, n_q$  and  $m_1, \dots, m_p$  represent the same lattice cluster. Substituting equations (16a)–(16c) into equation (15) and neglecting products of three or more cumulants  $C_{n_1 \dots n_q}$ , we finally obtain the expression for the correlation entropy in the second-order approximation,

$$S_1 = -k_B \sum_{q \geq 2} 2^{-(2q+1)} \sum_{\langle n_1 \dots n_q \rangle} \left( P_{n_1}^+ P_{n_1}^- \dots P_{n_q}^+ P_{n_q}^- \right)^{-1} C_{n_1 \dots n_q}^2. \quad (17)$$

In this order the correlation entropy is thus a linear combination of squares of the cumulants, i.e., contains no cross-terms. The minimization of the free energy then leads to vanishing of all those cumulants which are not present in the internal energy.

Equation (17) for the correlation entropy has been obtained without any assumptions about the nature of a thermodynamic phase or interactions in the system. We now list several frequently encountered situations in which the result for the free energy has particularly simple form.

(i) In the absence of sublattices, when all lattice sites are equivalent (such as in the case of disordered or ferromagnetically ordered material), the point probabilities  $P_n^i$  do not depend on the site index  $n$ ,

$$P_n^+ = \frac{1+m}{2} \quad P_n^- = \frac{1-m}{2} \quad (18)$$

where  $m = \langle s_n \rangle$  is the site magnetization. Equations (11b) and (17) therefore become

$$S_0 = -Nk_B \left( \frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right) \quad (19a)$$

$$S_1 = -\frac{1}{2}k_B \sum_{q \geq 2} (1-m^2)^{-q} \sum_{\langle n_1 \dots n_q \rangle} C_{n_1 \dots n_q}^2. \quad (19b)$$

(ii) If pairwise interactions are assumed in the case (i), then the only terms it is necessary to retain in equation (19b) are those with  $q = 2$ . All other, higher-order cumulants vanish at equilibrium, since the internal energy is independent of corresponding averages. As a result,

$$S_1 = -\frac{1}{2}k_B (1-m^2)^{-2} \sum_{\langle nm \rangle} C_{nm}^2. \quad (20)$$

At this stage it is convenient to use pair SRO parameters  $\alpha_{nm}$  instead of pair cumulants  $C_{nm}$ ; the relation between them is [6]

$$C_{nm} = (1-m^2) \alpha_{nm}. \quad (21)$$

In terms of the SRO parameters, equation (20) has the form

$$S_1 = -\frac{1}{2}k_B \sum_{\langle nm \rangle} \alpha_{nm}^2 = -\frac{1}{4}Nk_B \sum_l Z_l \alpha_l^2 \quad (22)$$

where in the second equation  $Z_l$  and  $\alpha_l$  are the coordination number and SRO parameter for the coordination shell  $l$ , and the summation is performed over all coordination shells.

(iii) When only the NN spins interact in the case (ii), it is sufficient to take into account in the second of equations (22) only the term corresponding to the first coordination shell. The rest of the SRO parameters vanish at equilibrium for the same reason as before. The correlation entropy in this case is simply

$$S_1 = -\frac{1}{4}Nk_B Z \alpha^2. \quad (23)$$

Here we have dropped the subscripts in the NN coordination number and in the NN SRO parameter. For the FCC lattice ( $Z = 12$ ) this result coincides with that obtained in [1] within the tetrahedron CVM approximation. This means that the tetrahedron version of the CVM reproduces correctly the exact expansion for the configurational entropy up to at least second order in  $\alpha$ .

Finally, to test the obtained approximation for the free energy, we consider thermodynamics of the NN Ising ferromagnet, an example which corresponds to the simplest case (iii). The Hamiltonian of the Ising model is written as

$$H = -\sum_{\langle nm \rangle} J_{nm} s_n s_m - h \sum_n s_n. \quad (24)$$

Here  $J_{nm}$  is the exchange integral equal to  $J > 0$  for NN sites and to zero otherwise, and  $h$  is the magnetic field. The internal energy, being the statistical average of the Hamiltonian, is therefore

$$E = -\frac{1}{2}NZJ [m^2 + (1-m^2)\alpha] - Nhm \quad (25)$$

where the first two of equations (4) for the spin variables and equation (21) were used. Combining equations (19a), (23) and (25), we get for the free energy  $F = E - TS$  ( $T$  is the absolute temperature)

$$F = N \left[ \left( -\frac{1}{2} Z J m^2 - h m \right) - \frac{1}{2} Z J (1 - m^2) \alpha + k_B T \left( \frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right) + \frac{1}{4} k_B T Z \alpha^2 \right]. \quad (26)$$

The four terms in equation (26), left to right, are the MFA internal energy, correlation internal energy, MFA entropy and correlation entropy, respectively. The variational free energy is now a function of two minimization parameters  $m$  and  $\alpha$ , whose equilibrium values are determined by the conditions

$$\frac{\partial F}{\partial m} = 0 \quad \frac{\partial F}{\partial \alpha} = 0. \quad (27)$$

They lead to the following equations for  $m$  and  $\alpha$ ,

$$m = \tanh \left[ \frac{m(1-\alpha) + \mu}{t} \right] \quad \alpha = \frac{(1-m^2)}{Zt} \quad (28)$$

where  $t = k_B T / ZJ$  and  $\mu = h / ZJ$  are the dimensionless temperature and magnetic field. Note that the first of equations (28) differs from its well-known MFA counterpart by the factor  $1 - \alpha$ . The temperature of the second-order transition is the solution of the equation

$$\left( \frac{\partial^2 F}{\partial m^2} \right)_{m=0} = 0. \quad (29)$$

Combining this equation with the second of equations (28) for  $m = 0$ , we obtain the equation for  $t_c$ ,

$$t_c = 1 - (Zt_c)^{-1}. \quad (30)$$

The  $Z$ -independent MFA result  $t_c = 1$  is obtained from this equation in the limit  $Z \rightarrow \infty$ . Equation (30) shows that the derived SRO corrections to the free energy lead to the decrease in  $t_c$  of order  $Z^{-1}$ , as expected [7]. Results of the numerical solution of equation (30) for the three cubic lattices are given in table 1; they are compared with the best-known  $t_c$  values [8]. It is seen that the quadratic approximation for the correlation entropy improves the accuracy of the calculated  $t_c$  from 20–30% in the MFA to 5–10%, and the accuracy increases with decreasing coordination number.

**Table 1.** Normalized temperature  $t_c = k_B T_c / ZJ$  of the second-order phase transition for the NN Ising ferromagnet on the simple cubic (SC), body-centred cubic (BCC), and face-centred cubic (FCC) lattices calculated using equation (30), i.e., within the quadratic approximation (23) for the correlation entropy. The best-known  $t_c$  values (which can be considered as essentially exact), the MFA results and the corresponding ratios are shown for comparison.

Lattice	$Z$	$t_c$	$t_c^{MFA}$	$t_c^{exact}$	$t_c / t_c^{exact}$	$t_c^{MFA} / t_c^{exact}$
SC	6	0.789	1	0.752	1.049	1.330
BCC	8	0.854	1	0.794	1.075	1.259
FCC	12	0.908	1	0.816	1.113	1.225

To conclude, in this letter we have developed a method of calculating the correlation contribution to the free energy of a system which undergoes the order–disorder transition.

The essence of this method is the expansion in powers of cumulant averages as applied to the exact configurational entropy. It has been shown that this approach leads to the construction of simple polynomial approximations for the entropy. First corrections to the MFA free energy (see equation (17) for the correlation entropy) have been calculated without any assumptions about the thermodynamic phase or the character and range of the interactions in the system. Previously, the same idea was utilized by the author [1] to simplify the widely used CVM by eliminating redundant variables in the CVM variational entropy. However, the approach presented here is more consistent, since the smallness of the pair and higher-order cumulants is the only assumption used, while in [1] this assumption was combined with the very different CVM approximation. The advantage of both proposed methods is that the entropy polynomial needs to be derived once and for all for a given Hamiltonian and type of order; after that thermodynamic calculations become extremely easy and can be performed either analytically or using a pocket calculator, at least in relatively simple cases. For the quadratic approximation considered here, this has been shown by the above example of the NN Ising ferromagnet. The SRO corrections lead to considerably better agreement, in comparison with the MFA, of the approximate transition temperatures with the corresponding best-known values. Calculation of the higher-order terms of the cumulant expansion for the configurational entropy is less straightforward, though perfectly possible, and is beyond the scope of the present short letter; this issue will be discussed in a separate publication [3].

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