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Surface properties of a ferromagnet near the critical temperature: molecular-field approximation†

H H Chen and C S Hsue
Institute of Physics, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

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Abstract. The thermodynamic properties associated with the surface layer of a Heisenberg ferromagnet on the semi-infinite simple cubic lattice are examined systematically in the molecular-field approximation. The surface critical temperature and the critical exponents are determined for various ratios of the surface exchange constant \( J_s = (1 + \Delta)J \) to the bulk exchange constant \( J \). It is found that the surface critical temperature \( T_s \) is higher than the bulk transition temperature \( T_c \) for \( 4\Delta > 1 \). In this case the surface critical exponents are identical with the bulk exponents. On the other hand, for \( 4\Delta < 1 \), it is found that the surface and the bulk phase transitions occur at the same temperature, but with different critical exponents.

1. Introduction

In recent years there have been considerable theoretical studies on the effects of the crystal surfaces on the properties of magnetic materials. Consider a magnetic crystal of \( N \) layers. The free energy per spin of the system can be written as

\[
F_N = F^{(b)} + N^{-1} F^{(s)} + \ldots
\]

where the bulk contribution \( F^{(b)} \) is the free energy per spin of a usual infinite lattice, and \( N^{-1} F^{(s)} \) is the correction due to the presence of surfaces. When the number of layers in the lattice is large and the temperature not too close to the critical temperature, the surface correction to the thermodynamic properties of the system can be neglected. Properties of the surface correction term \( F^{(s)} \) have been studied by many authors (Au-Yang 1973, Binder and Hohenberg 1972, Watson 1972). To understand the behaviour of a crystal lattice of finite extent, it is more important to investigate the thermodynamic properties associated with each individual layer than to study the properties of the surface correction term.

Recently, Au-Yang (1973) has exactly calculated the boundary spontaneous magnetization of a semi-infinite two-dimensional Ising model. For semi-infinite three-dimensional lattices, the spontaneous magnetization and the susceptibility associated with the surface layer have been studied by means of various approximations. Among these studies two results are of particular interest: the existence of surface phase transitions (Mills 1973, Weiner 1973a, b), and the qualitative difference of the surface magnetization

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Magnetic surface phase transitions have not been observed in real systems. The qualitative difference between the surface and the bulk magnetization has been observed experimentally in antiferromagnetic NiO (Palmberg et al 1968, DeWames and Wolfram 1969). It is well known that the bulk magnetization can be measured from neutron diffraction experiments. The surface magnetization, on the other hand, can be measured by means of low-energy electron diffraction (LEED). Neutrons penetrate deeply into a crystal and consequently the intensity of neutron diffraction is proportional to the square of the bulk magnetization. In contrast to neutrons, low-energy electrons penetrate only a few atomic layers, and the LEED intensity is proportional to the square of the surface magnetization. The LEED data on NiO infer that the surface sublattice magnetization of NiO vanishes linearly with temperature as the critical temperature is approached from below. This result is in good agreement with the molecular-field theoretical result (Mills 1971).

In this paper we make a systematic study of the thermodynamic properties associated with the surface layer of a semi-infinite ferromagnet. We assume that the system can be described by the Heisenberg Hamiltonian with exchange interaction between nearest-neighbour spins in a simple cubic lattice. The exchange constant in the surface layer is \( J_s = (1 + \Delta)J \) and the exchange constant elsewhere is \( J \), the value appropriate to the bulk. By using the molecular-field approximation we determine the critical temperature and various critical exponents associated with the surface layer. When \( \Delta = 0 \), the system has been studied by Wolfram and DeWames (1972). For general values of \( \Delta \), Mills (1971, 1973) calculated the surface magnetization in the critical region, and showed that for \( 4\Delta > 1 \) the surface critical temperature \( T^*_s \) is higher than the bulk transition temperature \( T^*_b \). The value of \( T^*_s \), however, has not been determined. In this paper we find that \( T^*_s = T^*_b(4 + 4\Delta + \frac{1}{2}\Delta)/6 \). Here \( T^*_b = 6JS(S + 1)/3k \) with \( S \) the spin value, \( k \) Boltzmann's constant and \( 6 \) the coordination number of the simple cubic lattice. Besides the surface spontaneous magnetization near \( T^*_s \), we calculate in this paper, for any value of \( \Delta \), many more quantities associated with the surface layer: zero-field susceptibility above \( T^*_s \), zero-field susceptibility below and near \( T^*_s \), low-field magnetization at \( T^*_s \), zero-field internal energy and zero-field specific heat. We find that when \( 4\Delta > 1 \) the surface critical exponents are the same as the bulk critical exponents. On the other hand, for \( 4\Delta < 1 \), we find that the surface and the bulk phase transitions occur at the same temperature, but with different critical exponents.

2. Molecular-field approximation

We assume that the semi-infinite simple cubic lattice has a free (100) surface, and occupies the space \( z \geq 0 \). The layer of spins at \( z = la \) ( \( a \) is the lattice spacing) will be referred to as the \( l \)th layer. From the molecular-field approximation, if \( h \) is a uniform external magnetic field applied along the \( z \) axis, the expectation value of the \( z \) component of the magnetic dipole moment of a spin in the \( l \)th layer is given by

\[
m_l = g\mu_B\langle S_{lz} \rangle = g\mu_B S_B [\langle g\mu_B S(h + h_l)/kT \rangle] \tag{2}
\]

where \( g \) is the gyromagnetic ratio, \( \mu_B \) the Bohr magneton and \( S_{lz} \) is the \( z \) component of a spin in the \( l \)th layer. The function

\[
\langle g\mu_B S(h + h_l)/kT \rangle
\]
\[ B_s[y] = \frac{2S + 1}{2S} \coth \left( \frac{2S + 1}{2S} y \right) - \frac{1}{2S} \coth \left( \frac{1}{2Sy} \right) \]
\[ = \frac{S + 1}{3S} \left( y - \frac{S(S + 1) + \frac{1}{4}}{15S^2} y^3 + \ldots \right) \] (3)

is the Brillouin function and
\[ h_i = (m_{i-1} + 4m_i + m_{i+1})J/(g\mu_B)^2 \] (4a)
is the effective field at the position of a spin in the \( l \)th layer due to the four neighbouring spins in the same layer and two spins in the two neighbouring layers. At the surface
\[ h_0 = \left[ 4(1 + \Delta)m_0 + m_1 \right]J/(g\mu_B)^2. \] (4b)

Equation (2) cannot be solved analytically except in some limiting cases. Here we assume that the external magnetic field is very small and that the temperature is either very close to the transition temperature or above the transition temperature. In this case we can use the small argument expansion of the Brillouin function, and (2) reduces to
\[ m_i = \frac{(m_{i-1} + 4m_i + m_{i+1} + h)/6\tau - Xm_i^3 + \ldots}{m_i} \] (5a)
and
\[ m_0 = \left[ 4(1 + \Delta)m_0 + m_1 \right]/6\tau - Xm_0^3 + \ldots. \] (5b)

Here \( \tau = T/T_c \), \( X = [3S(S + 1) + \frac{3}{2}]/[5S^2(S + 1)^2] \) and terms in \( m_i^5, h^5 \) and terms of higher orders are neglected. For convenience, the magnetizations \( m_i \) and the external magnetic field \( h \) are measured in units \( g\mu_B \) and \( J/g\mu_B \), respectively.

3. Zero-field susceptibility at high temperatures

The zero-field susceptibility per ion associated with the \( l \)th layer is defined as \( \chi_i = \lim(h \to 0)\partial m_i/\partial h \). By differentiating equations (5) and letting \( m_i \) approach zero, we obtain the equation
\[ -\chi_{i-1} + (6\tau - 4)\chi_i - \chi_{i+1} = 1 \] (6a)
with the boundary condition
\[ [6\tau - 4(1 + \Delta)]\chi_0 - \chi_1 = 1. \] (6b)

Equation (6a) is a linear difference equation and has the general solution
\[ \chi_i = C[3\tau - 2 - (9\tau^2 - 12\tau + 3)^{1/2}]^l + (6\tau - 6)^{-1}. \] (7)

The constant \( C \) is determined from the boundary condition (6b):
\[ C = (4\Delta - 1)(6\tau - 6)^{-1}[3\tau - 2 - 4\Delta + (9\tau^2 - 12\tau + 3)^{1/2}]^{-1}. \] (8)

For the surface layer
\[ \chi_0 = \frac{(\tau - 1)^{1/2} + (\tau - \frac{1}{4})^{1/2}}{2(\tau - 1)^{1/2}[3\tau - 2 - 4\Delta + (9\tau^2 - 12\tau + 3)^{1/2}].} \] (9)

The factor \( [3\tau - 2 - 4\Delta + (9\tau^2 - 12\tau + 3)^{1/2}] \) vanishes at \( \tau = (4 + 4\Delta + 1/4\Delta)/6 \) for \( 4\Delta > 1 \), but it does not vanish at any real value of \( \tau \) for \( 4\Delta < 1 \). When \( 4\Delta < 1 \), \( \chi_0 \) diverges only at \( \tau = 1 \). The surface transition temperature \( T_c^0 \) and the bulk transition temperature
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\( T_c^b \) are identical. For temperatures above and near the surface critical temperature we define the reduced temperature \( \epsilon = (T - T_c^b)/T_c^b \). For \( 4\Delta < 1 \) and for \( \epsilon = \tau - 1 \ll 1 \), one finds from (9) that

\[ \chi_0 = (1 - 4\Delta)^{-1}(6\epsilon)^{-1/2}. \]

(10)

The surface susceptibility diverges as \( (T - T_c^s)^{-1/2} \), in contrast to the bulk susceptibility which diverges as \( (T - T_c^b)^{-1} \). For \( 4\Delta = 1 \), \( \chi_i = (6\pi - 6)^{-1} \). Each layer has the same susceptibility as that of the bulk. This can be expected in the molecular-field approximation since for each spin in the surface the enhancement of the surface exchange interaction compensates the shortage of one interacting neighbouring spin exactly for \( 4\Delta = 1 \). For \( 4\Delta > 1 \), \( \chi_0 \) diverges either at \( \tau_1 = 1 \) or at \( \tau_2 = (4 + 4\Delta + 1/4\Delta)/6 \). Since \( \tau_2 > \tau_1 \), \( \tau_2 \) is the real critical temperature. For temperatures below \( \tau_2 \) the surface magnetization is nonzero, and (9) is not valid. Therefore, \( \tau_1 = 1 \) is not a critical temperature. This means that if the surface exchange constant increases for more than 25%, the surface transition temperature at which \( \chi_0 \) diverges will be higher than the bulk transition temperature. When the temperature is quite close to \( T_c^s \), \( \epsilon = \tau - (4 + 4\Delta + 1/4\Delta)/6 \ll 1 \). One finds from (9) that the surface susceptibility diverges as \( \epsilon^{-1} \). That is,

\[ \chi_0 = (1 + 1/4\Delta)(6\epsilon)^{-1}. \]

(11)

The critical exponent associated with the surface susceptibility is identical with that of the bulk.

When \( \Delta \to \infty \), the semi-infinite simple cubic lattice reduces to an infinitely extended plane square lattice with exchange constant \( \Delta J \). It is well known from the molecular-field theory that the susceptibility diverges as \( (T - T_c)^{-1} \) at \( T_c = 4AJS(S + 1)/3k \).

4. Spontaneous magnetization near the critical temperature

At small fields and for temperatures just below \( T_c^s \) we can neglect \( h \) and \( m \) in (5). For \( 4\Delta < 1 \), \( T_c^s = T_c^b \), equations (5) give

\[ m_i/m_0 = 1 + (1 - (4\Delta)^i). \]

(12)

while, for \( 4\Delta > 1 \), \( T_c^s = (4 + 4\Delta + 1/4\Delta)T_c^b/6 \), they give

\[ m_i/m_0 = (4\Delta)^i. \]

(13)

Equations (12) and (13) are valid only for \( T = (T_c^s)^- \), and \( h = 0^- \). To study the thermal variation of the layer magnetization below \( T_c^s \), the cubic terms \( m^3 \) have to be retained. For \( 4\Delta < 1 \), or \( 4\Delta \geq 1 \), we see from (12) and (13) that the magnetization varies smoothly in space. We can regard the magnetization as a continuous function \( m(z) \) and rewrite equations (5) as

\[ m(z) = [6m(z) + a^2m''(z) + h]/6\tau - Xm^3(z) \]

(14a)

with the boundary condition

\[ m(0) = [(5 + 4\Delta)m(0) + am'(0) + h]/6\tau - Xm^3(0). \]

(14b)

Here \( m'(z) \) and \( m''(z) \) denote the first and the second derivatives of \( m(z) \), respectively.

For temperatures below \( T_c^s \) we define the reduced temperature \( \epsilon = (T_c^s - T)/T_c^b \). At zero field and for \( 4\Delta < 1 \) and \( \tau = 1 - \epsilon \), equations (14) reduce to
\[-6\epsilon m(z) = a^2 m'(z) - 6X m^3(z),\]  

(15a)

with the boundary condition

\[(1 - 4\Delta)m(0) = am'(0).\]  

(15b)

In equations (15) only the leading terms are retained. In the bulk \(m'(\infty) = m''(\infty) = 0\). Equation (15a) then gives the well known bulk result

\[m(\infty) = (\epsilon/X)^{1/2}.\]  

(16)

If we multiply (15a) by \(m(z)\) and integrate, we obtain

\[-6\epsilon m^2(z) = [am'(z)]^2 - 3X m^4(z) + C.\]  

(17)

The integration constant \(C\) can be determined from the boundary conditions \(m'(\infty) = 0\) and \(m(\infty) = (\epsilon/X)^{1/2}\), and is equal to \(-3\epsilon^2/X\). Equation (17) then reduces to

\[am'(z) = (3X)^{1/2}[\epsilon/X - m^2(z)].\]  

(18)

Here we have used the fact that for \(4\Delta < 1\), \(am'(z) \geq 0\) and \(m(z) \leq m(\infty)\). Equations (15b) and (18) immediately yield

\[m(0) = (3/X)^{1/2}e/(1 - 4\Delta).\]  

(19)

The magnetization of the surface layer varies linearly in \((T_c - T)\). This is qualitatively different from the bulk result. Equation (19) has been obtained by Mills (1971) by an approach which will be used in §6 for calculating the susceptibility below \(T_c\). Equations (15) in fact can be solved exactly, and the solution is given by

\[m(z) = (\epsilon/X)^{1/2} \tanh[(3\epsilon)^{1/2}z/a + C]\]  

(20)

where the constant \(C\) is easily determined from (15b).

When \(4\Delta > 1\) the magnetization does not vary smoothly in space. Equation (14a) is no longer a good approximation. When \(h = 0\) and \(\tau = \tau_c - \epsilon = (4 + 4\Delta + 1/4\Delta)/6 - \epsilon\), equations (5) reduce to

\[m_{l+1} - (4\Delta + 1/4\Delta - 6\epsilon) m_l + m_{l+1} - 6\epsilon X m_l^3 = 0\]  

(21a)

and

\[m_1 - (1/4\Delta - 6\epsilon) m_0 - 6\epsilon X m_0^3 = 0.\]  

(21b)

From (13) we can assume that

\[m_l = m_0[(4\Delta)^{-l} + A_l \epsilon^p + \ldots]\]  

(22)

where \(A_0 = 0\) and \(A_i\) and \(p\) are constants to be determined. Substituting (22) into (21a) and keeping only the leading terms, we obtain

\[A_{l+1} - (4\Delta + 1/4\Delta) A_l + A_{l+1} + 6\epsilon(4\Delta)^{-l} - 6\epsilon X m_0^3(4\Delta)^{-3l} = 0.\]  

(23)

The above equation should be satisfied in the leading power of \(\epsilon\) for all values of \(l\). We find then \(p = 1\) and \(m_0^2\) is of order \(\epsilon\). Assuming \(m_0^2 = B \epsilon\). Equation (23) reduces to a linear difference equation in \(A_l\), with the parameter \(B\) to be determined. Or,

\[A_{l+1} - (4\Delta + 1/4\Delta) A_l + A_{l+1} + 6\epsilon(4\Delta)^{-l} - 6\epsilon X B(4\Delta)^{-3l} = 0.\]  

(24)

The solution of (24) with the boundary condition \(A_0 = 0\) is

\[A_l = \frac{6l(4\Delta)^{-l}}{4\Delta - 1/4\Delta} + \frac{6\epsilon X B[(4\Delta)^{-3l} - (4\Delta)^{-l}]}{(4\Delta - 1/4\Delta)^2(4\Delta + 1/4\Delta)}.\]  

(25)
Combining (22), (25) and the boundary condition (21b), we obtain for the surface magnetization the expression

\[ m_0^2 = [1 + (4\Delta)^{-2}] (\tau_c X)^{-1} \epsilon. \] (26)

The critical exponent associated with the surface magnetization is the same as that in the bulk. Again, for \( \Delta \to \infty \), (26) reduces to the result for the two-dimensional square lattice.

5. Low-field magnetization at the critical temperature

We now examine the low-field magnetization at the critical temperature. For \( 4\Delta < 1 \), we know from §3 that \( \tau_c = 1 \). In a small field, equations (14) reduce to

\[ a^2 m''(z) + h - 6Xm^3(z) = 0 \] (27a)

and

\[ -(1 - 4\Delta)m(0) + am'(0) + h - 6Xm^3(0) = 0. \] (27b)

In the bulk \( m''(\infty) = 0 \), equation (27a) reduces to the bulk result

\[ h = 6Xm^3(\infty). \] (28)

Multiplying (27a) by \( m(z) \) and integrating, one finds

\[ [am'(z)]^2 + 2m(z)h - 3Xm^4(z) - (3h/2)(h/6X)^{1/3} = 0. \] (29)

Here the constant term is obtained from the boundary conditions \( m'(\infty) = 0 \) and \( m(\infty) = (h/6X)^{1/3} \). Combining (27b) and (29) (evaluated at \( z = 0 \)) and neglecting higher-order terms in \( m(0) \) and \( h \), we find that

\[ (1 - 4\Delta)^2 m^2(0) + 8\Delta m(0)h = (3h/2)(h/6X)^{1/3}. \] (30)

Since \( (4\Delta - 1) \neq 0 \), the term \( 8\Delta m(0)h \) is of higher order and can be neglected. Equation (30) then reduces to

\[ (1 - 4\Delta)m(0) = (9/16X)^{1/6}h^{2/3}. \] (31)

At the critical temperature the surface magnetization varies as \( h^{2/3} \), in contrast to the behaviour \( h^{1/3} \) in the bulk. For \( 4\Delta > 1 \), equations (14) are not valid as mentioned above. We have to solve equations (5) for the low-field magnetization. At \( \tau_c = (4 + 4\Delta + 1/4\Delta)/6 \), equations (5) become

\[ m_{i-1} - (4\Delta + 1/4\Delta)m_i + m_{i+1} + h - 6\tau_c Xm_i^3 = 0 \] (32a)

and

\[ m_i - (4\Delta)^{-1}m_0 + h - 6\tau_c Xm_0^3 = 0. \] (32b)

Similar to (22), we can assume that

\[ m_i = m_0[(4\Delta)^{-i} + C_i h^q + \ldots] \]

where \( C_0 = 0 \) and \( C_i \) and \( q \) are constants to be determined. Substituting (33) into (32a) and keeping the leading terms, we obtain

\[ [C_{i-1} - (4\Delta + 1/4\Delta)C_i + C_{i+1}]m_0 h^q + h - 6\tau_c Xm_0^3(4\Delta)^{-3i} = 0. \] (34)
The above equation should be satisfied for all values of \( l \) in the leading power in \( h \). It follows that \( q = \frac{3}{2} \) and \( m_0 \) is of order \( h^{1/3} \). Setting \( m = Dh^{1/2} \), we obtain the equation

\[
D[C_{i-1} - (4\Delta + 1/4\Delta)C_i + C_{i+1}] + 1 - 6\tau_c XD^3(4\Delta)^{-3l} = 0. \quad (35)
\]

The solution of (35) with the consistency condition \( C_0 = 0 \) is

\[
C_i = \frac{1 - (4\Delta)^{-l}}{D(4\Delta + 1/4\Delta - 2)} + \frac{6\tau_c XD^2[(4\Delta)^{-3l} - (4\Delta)^{-l}]}{(4\Delta - 1/4\Delta)^2(4\Delta + 1/4\Delta)}. \quad (36)
\]

From (33), (36) and the boundary condition (27b), we find that

\[
m_0^3 = D^3h = h(4\Delta + 1/4\Delta)(4\Delta + 1)(96\tau_c X\Delta^2)^{-1}. \quad (37)
\]

When \( \Delta \to \infty \), equation (37) reduces to that expected for the plane square lattice.

6. Zero-field susceptibility below and near the critical temperature

At a temperature below \( T_c^s \), the magnetizations are nonzero. For \( 4\Delta < 1 \), \( \tau = \tau_c - \epsilon = 1 - \epsilon \). By differentiating equations (14) with respect to \( h \), we obtain the equation for the zero-field susceptibility below \( T_c^s \), that is,

\[
-6\epsilon\chi(z) = a^2\chi''(z) + 1 - 18Xm^2(z)\chi(z). \quad (38a)
\]

The boundary condition for \( \epsilon \ll 1 \) is

\[
(1 - 4\Delta)\chi(0) = a\chi'(0). \quad (38b)
\]

In the bulk \( \chi'(\infty) = 0 \) and \( m^2(\infty) = \epsilon/X \) (equation (16)), and equation (38a) reduces to the bulk result \( \chi(\infty) = (12\epsilon)^{-1} \). To determine the surface susceptibility \( \chi(0) \), we adopt the approach which was used by Mills (1971) to obtain the surface spontaneous magnetization. We define a function \( \chi^0(z) \) with the properties that \( \chi^0(0) = 0, \chi^0(\infty) = \chi(\infty) \) and, for a finite value of \( z \), \( |\chi^0(z) - \chi(z)| \ll \chi(\infty) \). With the transformations \( x = (3\epsilon)^{1/2} z/a \) and \( \chi(x) = 12\epsilon \chi^0(z) \), we obtain from (38a) the equation for \( \chi(x) \):

\[
\frac{d^2\chi(x)}{dx^2} + 2\chi(x) - 6\chi(x)\tanh^2x + 4 = 0. \quad (39)
\]

Here, to the first approximation, we have replaced \( m^2(x)/m^2(\infty) \) by \( \tanh^2x \). The boundary condition (38b) now becomes

\[
(1 - 4\Delta)\chi(0) = a\chi'(0) = a\left. \frac{d\chi^0(z)}{dz} \right|_{z=0} = \frac{1}{12} \left( \frac{3\epsilon}{\chi(x)} \right)^{1/2} \frac{d\chi(x)}{dx} \bigg|_{x=0}. \quad (40)
\]

We have solved (39) numerically. With the boundary conditions \( \chi(0) = 0 \) and \( \chi(\infty) = 1 \), we find that \( (d\chi(x)/dx)|_{x=0} = 4.0 \). Therefore,

\[
\chi(0) = (1 - 4\Delta)^{-1} (3\epsilon)^{-1/2}. \quad (41)
\]

We notice that \( \chi(x) \) has a maximum of 1.64 at \( x = 0.9 \). This means that the layer susceptibility increases as \( \epsilon \) increases and reaches its maximum at the layer \( \epsilon = 0.9(3\epsilon)^{-1/2} \), and then decreases to the bulk susceptibility. Here we find again that the thermal variation of the surface susceptibility \( \epsilon^{-1/2} \) is different from that of the bulk susceptibility \( \epsilon^{-1} \).
For $4\Delta > 1$, \( \tau = (4 + 4\Delta + 1/4\Delta) - \epsilon \). Differentiating (5a) with respect to \( h \), we have

\[
\chi_{l-1} - (4\Delta + 1/4\Delta - 6\epsilon)\chi_{l} + \chi_{l+1} + 1 - 18X\tau_m^2\chi_{l} = 0
\]

(42a)

with the boundary condition

\[
\chi_1 - (1/4\Delta - 6\epsilon)\chi_0 + 1 - 18X\tau_m^2\chi_0 = 0.
\]

(42b)

For small \( \epsilon \), similar to (22), we assume that

\[
\chi_l = \chi_0[(4\Delta)^{-l} + P_l\epsilon^r + \ldots]
\]

(43)

where \( P_0 = 0 \) and \( P_l \) and \( r \) are constants to be determined. Substituting (43), (22) and (26) into (42a) and neglecting high-order terms, we arrive at

\[
[P_{l-1} - (4\Delta + 1/4\Delta)P_l + P_{l+1}]\epsilon^r\chi_0 + 6\epsilon\chi_0(4\Delta)^{-l} + 1 - 18\epsilon\chi_0(4\Delta)^{-3}\left[1 + (4\Delta)^{-2}\right] = 0.
\]

(44)

By the same argument used in (23) and (34), the above equation requires that \( r = 1 \) and \( \chi_0 \) is of order \( \epsilon^{-1} \). Assume that \( \chi_0 = (Q\epsilon)^{-1} \). Equation (45) then reduces to

\[
P_l = 6l(4\Delta - 1/4\Delta)^{-l}(4\Delta)^{-l} + Q(4\Delta + 1/4\Delta - 2)^{-1}\left[1 - (4\Delta)^{-l}\right]
\]

\[+ 18(4\Delta)^{-1}(4\Delta - 1/4\Delta)^{-2}\left[(4\Delta)^{-3l} - (4\Delta)^{-l}\right].
\]

(46)

From (42a), (43) and (46) we find that

\[
\chi_0 = (1 + 1/4\Delta)(12\epsilon)^{-1}.
\]

(47)

For $4\Delta > 1$, \( \chi_0 \) as well as \( \chi_\infty \) varies as \( \epsilon^{-1} \) near the critical temperature. In the limit \( \Delta \to \infty \), equation (47) is consistent with the two-dimensional result.

7. Conclusions

We have considered a semi-infinite Heisenberg ferromagnet on a simple cubic lattice with the exchange constant \((1 + \Delta)J\) in the surface layer and \( J \) elsewhere. By use of the molecular-field approximation we determine the thermodynamic properties associated with the surface layer: the zero-field susceptibility above the surface critical temperature \( T_c^s \), the spontaneous magnetization and the zero-field susceptibility below and near \( T_c^s \), and the low-field magnetization at \( T_c^s \).

For $4\Delta < 1$ the surface critical temperature is identical with the bulk critical temperature \( T_c^b \). Near the critical temperature thermal variations of the magnetization and susceptibility of the surface layer are qualitatively different from those of the bulk. The surface magnetization is much smaller than the bulk magnetization. This is due to the shortage of one neighbouring spin for each spin in the surface layer. Therefore, the effective magnetic field at the surface is smaller than that in the bulk. For $4\Delta = 1$ thermodynamic properties of each layer are exactly the same. This is expected in the molecular-field approximation since for each spin in the surface the enhancement of the surface exchange interaction compensates the shortage of one interacting neighbour spin exactly for $4\Delta = 1$. For $4\Delta > 1$ the surface critical temperature is higher than the bulk critical temperature. Thermal variations of the surface magnetization and susceptibility
near $T_c$ are qualitatively similar to the variations of the bulk magnetization and susceptibility near $T_c^b$.

In the molecular-field approximation the Ising model behaves in exactly the same way as the Heisenberg model. It is expected that the surface magnetization of a semi-infinite three-dimensional Ising ferromagnet can order at a temperature higher than $T_c^b$, if the surface exchange constant is large enough, since it is shown exactly that a two-dimensional Ising model has a phase transition. For a Heisenberg model, although it is rigorously proved that a two-dimensional system with finite-range interaction cannot have a spontaneous magnetization at any finite temperature (Mermin and Wagner 1966), it may not be appropriate to conclude that a surface phase transition will not occur in a semi-infinite three-dimensional system, because Weiner (1973b) has shown that surface magnetic order is not a purely two-dimensional phenomenon. Whether surface magnetic order can occur above $T_c^b$ in a Heisenberg model required a more exact theoretical treatment than the molecular-field approximation.

In the previous sections we have only studied the surface magnetization and the surface susceptibility. Other extensive quantities associated with the surface layer can be defined, although they probably cannot be measured experimentally. For instance, the zero-field internal energy associated with the surface layer can be defined as

$$E_0 = -\frac{1}{2}(4Jm_0^2 + Jm_0m_1)(g\mu_B)^{-2}. \tag{48}$$

For $4\Delta < 1$, $m_1 = m(0) + am'(0) = (2 - 4\Delta)m(0)$ and therefore $E_0 = -3J(m_0/g\mu_B)^2$. From (19) we see that the zero-field specific heat of the surface layer $C_0 = \partial E_0/\partial T$ varies linearly in $\epsilon$ and vanishes at $T_c^b$. For $4\Delta > 1$, $m_1 = m_0/4\Delta$ and $E_0 = -J(2 + 2\Delta + 1/8\Delta)(m_0/g\mu_B)^2$. We find from (26) that the specific heat has a discontinuity at $T_c^b$.

In this paper various thermodynamic properties of a semi-infinite Heisenberg ferromagnet are studied by means of the molecular-field approximation. As it is well-known that this approximation does not predict the bulk critical temperature and bulk critical exponents correctly, it is expected that the surface critical temperature, surface critical exponents and the critical value of $\Delta(=\frac{1}{4})$, which are obtained from the molecular-field approximation, are not exact. It will be interesting to see what these critical parameters are in a more exact theory.

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References
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