

## Existence of Surface Phase Transitions in Molecular-Field Theory

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It is shown that molecular-field theory predicts a surface spontaneous magnetization at temperatures higher than the bulk Curie temperature if the surface exchange coupling is sufficiently larger than that in the bulk. Furthermore, this solution of the molecular-field equations is thermodynamically stable, whereas the no spontaneous magnetization solution is thermodynamically unstable.

In a discussion of surface effects in magnetic crystals Mills<sup>1</sup> has noted that if the exchange coupling between the spins in the surface layer is sufficiently larger than that in the bulk the surface susceptibility obtained by molecular-field theory will diverge at a temperature  $T_C^s$  above the bulk Curie temperature  $T_C$ . As a Heisenberg ferromagnet does not order in two dimensions,<sup>2</sup> it has been assumed that this behavior is an artifact of the use of molecular-field theory which ignores the effects of fluctuations on the phase transition. In a recent paper Sukiennicki and Wojtczak<sup>3</sup> claim to have shown that the surface spontaneous magnetization obtained from molecular-field theory is zero for  $T$  between  $T_C^s$  and  $T_C$  and hence that molecular-field theory does imply that the entire semi-infinite crystal will order, in the sense of a nonzero spontaneous magnetization, at a single temperature  $T_C^s$  which may be greater than the bulk  $T_C$ . However, their argument is incorrect: It equally well gives no spontaneous magnetization for  $T < T_C$  in an infinite crystal and corresponds to a thermodynamically unstable solution of the molecular-field equations, whereas the familiar nonzero spontaneous magnetization solution is thermodynamically stable. In this paper we shall explicitly obtain a nonzero result for the spontaneous magnetization for  $T_C^s > T > T_C$  and show that it is the thermodynamically stable solution of the molecular-field equations, while the zero spontaneous magnetization solution is thermodynamically unstable.

We consider a simple cubic lattice with a free (100) surface and nearest-neighbor ferromagnetic coupling between the spins. Using the cubic approximation to the Brillouin function for spin  $S$ , the molecular-field equations in the presence of an external magnetic field  $H$  are

$$\eta(1) = \{h + [4(J_s/J)\eta(1) + \eta(2)]/6\}/\tau - \beta \{h + [4(J_s/J)\eta(1) + \eta(2)]/6\}^3/\tau^3, \quad (1)$$

$$\eta(l) = \{h + [\eta(l-1) + 4\eta(l) + \eta(l+1)]/6\}/\tau - \beta \{h + [\eta(l-1) + 4\eta(l) + \eta(l+1)]/6\}^3/\tau^3, \quad l \geq 2 \quad (2)$$

where

$$\eta(l) = \langle S^z(l) \rangle / S$$

is a measure of the magnetization,  $\tau = T/T_C$ ,  $h = (S+1)g\mu_B H/3kT_C$ ,  $\beta = \frac{3}{5}[S(S+1) + \frac{1}{2}]/(S+1)^2$ ,  $J_s$  and  $J$  are the exchange couplings in the surface layer and the bulk, respectively, and  $l$  is an index labeling the crystal planes parallel to the surface.

The spontaneous magnetization is found by setting  $h$  equal to zero. A closed form solution can be obtained by discarding the cubic term in Eq. (2); this approximation should be valid for  $T$  quite close to  $T_C^s$  where the spontaneous magnetization will be quite small. The resulting equation,

$$\eta(l) = [\eta(l-1) + 4\eta(l) + \eta(l+1)]/6\tau, \quad (2')$$

has a solution in a semi-infinite crystal,

$$\eta(l) = \eta(l-1)/d, \quad (3a)$$

$$d = 1 + (6\epsilon + 9\epsilon^2)^{1/2} + 3\epsilon, \quad (3b)$$

where  $\epsilon = \tau - 1$  is the reduced temperature ( $T - T_C$ )/ $T_C$ . As  $d > 1$ , Eq. 3(a) implies that  $\eta(l)$  decays exponentially as  $l$  increases. Using Eqs. (3) for  $l=2$  gives a cubic for the surface spontaneous magnetization  $\eta(1)$ ,

$$\eta(1) = B\eta(1) - \beta B^3\eta(1)^3, \quad (4)$$

$$B = [4(J_s/J) + 1/d]/[6(1 + \epsilon)].$$

For  $B - 1 > 0$ , which defines a temperature range  $0 < \epsilon < \epsilon^*$  if  $J_s/J > \frac{5}{4}$ , there is a nonzero spontaneous magnetization

$$\eta(1) = [(B - 1)/\beta B^3]^{1/2}, \quad (5)$$

as well as the  $\eta(1)$ -equal-zero solution found by Sukiennicki and Wojtczak.<sup>3</sup>

For systems in which the magnetic field enters the Hamiltonian only linearly (thereby excluding diamagnetic behavior) the criterion for thermodynamic stability is  $(\partial M/\partial H)_T > 0$ .<sup>4</sup> The restriction holds for our model and hence the thermodynamic stability of the two solutions for  $\eta(1)$  will depend on the sign of

$$\chi_l \equiv \left. \frac{\partial \eta_l}{\partial h} \right|_{h=0}. \quad (6)$$

For the almost linearized approximation, Eqs. (1) and (2'), we find

$$\chi(l) = \chi_\infty(1 + u(l)), \quad l \geq 2 \quad (7)$$

where

$$\chi_\infty = 1/\epsilon$$

is the bulk susceptibility and

$$u(l) = u(l-1)/d, \quad (8)$$

$d$  given by Eq. (3b). Hence

$$\begin{aligned} \chi(1) &= A[1 - 3\beta B^2 \eta(1)^2] / [1 - B + 3\beta B^3 \eta(1)^2], \\ A &= [1 + (d-1)/6d\epsilon] / (1 + \epsilon). \end{aligned} \quad (9)$$

If  $\eta(1) = 0$ ,  $\chi(1)$  is negative for  $0 < \epsilon < \epsilon^s$  and the zero spontaneous magnetization solution is thermodynamically unstable. However, using Eq. (5),

$$\chi(1) = A(3 - 2B) / 2B(B - 1)$$

is positive for  $0 < \epsilon < \epsilon^s$  if  $3 - 2B$  is positive. The possibility of  $3 - 2B < 0$  can be traced back to a negative derivative of the cubic approximation to the Brillouin function. Since the Brillouin function itself always has a positive derivative, this problem with our result is due to our use of the cubic approximation and is no indication that the full molecular-field equations do not have a thermodynamically stable solution for  $0 < \epsilon < \epsilon^s$  if  $J_s/J > \frac{5}{4}$ .

If the cubic term in Eq. (2) is retained a closed form solution is not possible. Numerical solutions of Eqs. (1) and (2) have been investigated for various  $\epsilon$  and  $J_s/J$ . While there are quantitative changes from the approximate solution found above,

all of its qualitative features are retained: For  $0 < \epsilon < \epsilon_s$ ,  $J_s/J > \frac{5}{4}$ , there is a nonzero spontaneous magnetization at the surface, decaying exponentially into the bulk, with a positive susceptibility in all the crystal planes, while the zero spontaneous magnetization solution has a negative susceptibility near the surface. Hence the solution found by Sukiennicki and Wojtczak<sup>3</sup> is an unstable solution of molecular-field theory and the original conclusion that molecular-field theory leads to an unphysical phase transition near the surface if the surface exchange coupling is sufficiently larger than the bulk stands.

We note, in passing, that the method of solution of the nonlinear difference equations used above can also be applied when  $J_s/J < \frac{5}{4}$  and gives results in complete agreement with those obtained by Mills<sup>1</sup> from a Landau-Ginsberg equation when  $\epsilon$  is sufficiently small so that the range of the surface effects is much larger than the lattice spacing, the condition under which the derivation of the Landau-Ginsberg equation is valid. Furthermore, if this analysis is applied to the case of magnetic thin films we find that molecular-field theory, contrary to the suggestion of Sukiennicki and Wojtczak,<sup>3</sup> gives a depression of the thin film Curie temperature below the bulk  $T_C$  if  $J_s/J < \frac{5}{4}$ , as has been noted before.<sup>5</sup> If  $J_s/J > \frac{5}{4}$  the thin film Curie temperature is greater than the bulk  $T_C$ , but just as in the semi-infinite case this phenomenon is clearly associated with a two-dimensional surface phase transition which is an artifact of the use of molecular-field theory and hence corresponds to an unphysical phase transition.

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