Possibility of Surface Magnetic Order Above the Bulk Ordering Temperature: A Response to a Comment by Sukiennicki and Wojtczak*

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We point out an error in the argument advanced recently by Sukiennicki and Wojtczak which suggests that the molecular-field theory applied to a magnetic film gives no ordered state above the bulk ordering temperature, no matter what the value of the surface exchange. When the surface exchange J_s is considerably larger than the bulk exchange constant J, we discuss the properties of the ordered suface state predicted by molecular-field theory.

In an earlier paper,[1] the present author examined the effect of a surface on a number of properties of a simple Heisenberg ferromagnet and antiferromagnet, for temperatures close to the bulk Curie temperature. In that paper, the temperature dependence of the order parameter near and in the surface was examined, along with the behavior of the static spin-correlation function. Our discussion was based on the use of the Landau-Ginzburg theory for the semi-infinite material.

In a recent comment, Sukiennicki and Wojtczak[2] have suggested a reinterpretation of one point in the earlier paper. The purpose of this note is to present an expanded discussion of the point in question, and also to note that an unphysical assumption introduced by these authors invalidates their principal conclusion.

In my earlier paper, I examined the properties of a semi-infinite Heisenberg magnet with nearest-neighbor exchange, where all spins except those within the surface layer are coupled by the bulk exchange interaction J, and those within the surface are coupled by exchange interactions $J_s \neq J$. Upon examining the response of the spin system to a dc external magnetic field, it was found that when J_s exceeded J by a certain amount, the surface susceptibility, which gives the moment induced within the surface layer by the field, diverged at a temperature T_s greater than the bulk ordering temperature, while the bulk susceptibility remained well behaved at this temperature. It was suggested that when $T_0 < T < T_s$, where T_0 is the bulk ordering temperature, the molecular-field theory predicts magnetic order within and near the surface layer. In the earlier paper, no detailed discussion of the variation of the order parameter with temperature or distance from the surface was presented, although it was remarked that except for special values of J_s very near the critical value required for the presence of surface order above T_0, the order parameter decays to zero within a distance the order of a lattice constant of the surface.

Sukiennicki and Wojtczak[2] offer a very simple proof which suggests that above T_0 in the Heisenberg ferromagnet, mean-field theory predicts no magnetically ordered region near the surfaces of a film of thickness L, no matter what the value of the surface exchange constant J_s. Since their proof is valid for any L, they argue that their conclusion is valid also for the semi-infinite case. They do accept the divergence in the surface susceptibility, and offer the suggestion that the theory predicts that a phase transition of the Stanley-Kaplan type occurs.[3]

The theory presented in my earlier work,[1] in the note by Sukiennicki and Wojtczak,[2] and in the references cited by them, is based on the use of the molecular-field theory. It may well be that an investigation of the question of whether surface magnetic order may occur above T_0 by a theory more sophisticated than molecular-field theory will show that singular behavior of the Stanley-Kaplan type indeed occurs, as Sukiennicki and Wojtczak conjecture. My only point here is that the *molecular-field theory* does indeed predict long-range order in and near the surface above T_0 when J_s exceeds J by a sufficient amount, as we previously noted. There is an overly restrictive assumption in the proof offered by Sukiennicki and Wojtczak which leads to its inapplicability to this question, and earlier workers cited in their work apparently overlooked this possibility.

Since Sukiennicki and Wojtczak claim to have demonstrated quite generally that the molecular-field theory does not predict surface magnetism above T_0 for any value of J_s, it is sufficient in our case to examine only a special limit where the solution may be exhibited in a simple analytic form. Examination of this solution will lead us to the overly restrictive assumption introduced in Ref. 2. We consider the case $J_s \gg J$ for a film made from a simple cubic Heisenberg ferromagnet, with nearest-neighbor exchange interactions. We presume the film to have $2N+3$ layers, with the layer $l = 0$ at the film center, $l = \pm N$ are the two atomic

layers immediately below the surface, and quantities which refer to the surface layer will have the subscripts s_1 and s_2 attached to them.

We proceed in a manner similar to Ref. 1. The order parameter in layer l is $\eta_l = \langle S_z(l) \rangle / S$. If surface magnetism occurs in the theory, then just below the transition temperature T_s where the surface spins order, the order parameter η_{s_1} and η_{s_2} in the two surfaces, and also in the vicinity of the surfaces is very small. Thus, we write down the equations of the molecular-field theory, and expand the Brillouin function assuming η_l is small. If $\tau = T/T_0$, $r_s = J_s/J$, and the remaining notation is the same as Ref. 1, then proceeding as we did earlier, the order parameter η_{s_1} for the right-hand surface obeys

$$\eta_{s_1} - \frac{1}{6\tau}(4r_s\eta_{s_1} + \eta_N) + \frac{\beta}{216\tau^3}(4r_{s_1}\eta_{s_1} + \eta_N)^3 = 0, \quad (1)$$

with a similar equation for the left-hand surface. For the first layer below the surface ($l = N$), the order parameter obeys

$$\eta_N - \frac{1}{6\tau}(\eta_{s_1} + 4\eta_N + \eta_N - 1) + \frac{\beta}{216\tau^3}(\eta_{N-1} + 4\eta_N + \eta_{s_1})^3 = 0. \quad (2)$$

with a similar equation for η_{-N}. For the interior layers $-(N-1) \le l \le (N-1)$ we have

$$\eta_l - \frac{1}{6\tau}(\eta_{l-1} + 4\eta_l + \eta_{l+1}) + \frac{\beta}{216\tau^3}(\eta_{l-1} + 4\eta_l + \eta_{l+1})^3 = 0. \quad (3)$$

When $r_s \gg 1$, just below T_s we will have η_{s_1} and η_{s_2} large compared to the bulk order parameter η_l for $-N \le l \le N$, since T_s will be large compared to T_0, and while the surface layers spontaneously order (in the molecular-field description), the second layer will have a much smaller magnetization. We use this assumption to obtain a simple solution to the equations, and we shall see that the solution is in accord with this assumption.

When $r_s \gg 1$ and T is just below T_s, the cubic terms in Eq. (2) and Eq. (3) may be ignored, and these equations replaced by

$$\eta_N - \frac{1}{6\tau}(4\eta_N + \eta_{N-1}) = \frac{\eta_{s_1}}{6\tau} \quad (4)$$

and

$$\eta_l - \frac{1}{6\tau}(\eta_{l+1} + 4\eta_l + \eta_{l+1}) = 0. \quad (5)$$

Then quite clearly η_N is proportional to η_{s_1}, so we write

$$\eta_N = \gamma\eta_{s_1}. \quad (6)$$

Equation (1) then becomes

$$\left[1 - \frac{2r_s}{3\tau}\left(1 + \frac{\gamma}{4r_s}\right)\right]\eta_{s_1} + \frac{8\beta r_s^3}{27\tau^3}\left(1 + \frac{\gamma}{4r_s}\right)^3\eta_{s_1}^3 = 0. \quad (7)$$

Equation (7) has a nonzero solution for η_{s_1} when $\tau < \tau_s$, where

$$\tau_s = \frac{2r_s}{3}\left(1 + \frac{\gamma}{4r_s}\right) \equiv \frac{T_s^{(0)}}{T_0}\left(1 + \frac{\gamma}{4r_s}\right). \quad (8)$$

In Eq. (8), $T_s^{(0)}$ is the transition temperature provided by molecular-field theory for the two-dimensional square lattice with exchange interaction J_s, and the factor $\gamma/4r_s$ shows that the coupling of surface to bulk spins raises the temperature at which the surface spins order.[4] Actually, γ depends on temperature, as we shall see, although it is positive definite, so Eq. (8) always predicts $\tau_s > \tau_s^{(0)}$. For $\tau < \tau_s$, the solution to Eq. (7) for the order parameter in the surface layer has the familiar Landau-Ginzburg temperature dependence

$$\eta_{s_1} = \beta^{-1/2}(1 - \tau/\tau_s)^{1/2}. \quad (9)$$

It is a straightforward matter to show that Eq. (5) has the solution

$$\eta_l = \eta_B \frac{\cosh ql}{\cosh qN}, \quad (10)$$

where q is found from

$$\cosh q = 3\tau - 2, \quad (11)$$

and $\eta_B = \gamma\eta_s$, with γ determined by substitution of Eq. (6) into Eq. (4). Unless τ is close to unity, the parameter q is some small number comparable to unity in value. This means that unless J_s is very close to the critical value $J_s^{(c)}$ required for the surface order to occur above T_0 (then T_s is close to T_0, and the values of τ of interest are close to unity), the function in Eq. (10) assumes its maximum value at $l = N$, and decays to zero exponentially fast as one moves to the center of the film, with a characteristic length the order of the lattice constant. For γ one finds, in the limit $qN \gg 1$, the result

$$\gamma = (6\tau - 5)^{-1}.$$

If we set $\tau = \tau_s \gg 1$, then we see γ is small compared to unity, as we have assumed.

In the discussion above, we have examined the molecular-field equations for a film of thickness L, and in the limit $J_s \gg J$, and for T just below T_s, we have explicitly exhibited the form of the magnetization in the ordered surface magnetic state which occurs in the temperature region $T_0 < T < T_s$. Since Sukiennicki and Wojtczak claim to have demonstrated that no such solution to the equations can exist, there must be an error in their proof. The error is in fact in their initial assumption about the form of the solution. They write down the full equations of the molecular-field theory, and inquire about the possibility of obtaining a solution with the following two properties: (i) the order parameter is even under reflection through the midpoint of the film, and (ii) the order parameter vanishes *identically* at the midpoint of the film.

Our solution satisfies assumption (i) but violates (ii).[5] Thus, while the argument presented by Sukiennicki and Wojtczak indeed rules out the existence of a certain class of solutions to the molecular-field equations, the class of functions excluded by the argument does not include the ordered surface state mentioned earlier.[2] At present, there is no theoretical basis for the assertion that at T_s, a transition of the Stanley-Kaplan kind is predicted by the theory.

We conclude with a few brief remarks. We have confined our attention to the limit $J_s \gg J$ since we can easily exhibit the form of the solution in this limit, to provide an explicit counter example to the conclusion reached by Sukiennicki and Wojtczak. However, as long as the order parameter is even under reflection through the midpoint of the film, and as long as $qN \gg 1$, the functional form in Eq. (10) describes the behavior of η_l near the midpoint of the film for all temperatures $T_0 < T < T_s$. This is because η_l will be exponentially small near the midpoint, and Eq. (5) describes the variation of the order parameter everywhere it is small compared to unity. Thus, we can conclude that for a film with $qL \gg 1$, assumption (ii) of the argument of Sukiennicki and Wojtczak will always be violated, not only for $J_s \gg J$, but for any J_s that gives use to the ordered surface magnetic state above T_0. Indeed, for any value of L, quite clearly any even parity solution will violate this assumption.

Quite recently, Wiener[6] has carried out an investigation of the properties of the surface magnetic state more complete than the rather restricted one reported here. Wiener explores the form of the solution for all values of J_s above the critical value $\frac{5}{4}J$ obtained previously[1] for the semi-infinite geometry. He has also explicitly compared the free energy of the surface state to that of the paramagnetic state in the temperature region $T_0 < T < T_s$ to verify that the free energy of the crystal in the presence of the surface state is indeed lower than that of paramagnetic state, in this temperature region. We refer the reader to Wiener's paper for a more complete discussion of this problem.

I am grateful to Professor R. A. Weiner for a summary of his work in advance of publication.

Note added in proof. After this note was submitted for publication, a very complete study of the semi-infinite Ising model with $J_s \neq J$ has been reported by Binder and Hohenberg (K. Binder and P. Hohenberg, report of work prior to publication). These authors find, in accord with the conclusion in Ref. 2, that surface order indeed appears above T_c when J_s exceeds a certain critical value which, of course, differs somewhat than the critical value $\frac{5}{4}J$ provided by the Landau-Ginzburg theory.

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[1]D. L. Mills, Phys. Rev. B **3**, 3887 (1971).

[2]A. Sukiennicki and L. Wojtczak, Phys. Rev. B **7**, 2205 (1973).

[3]H. E. Stanley and T. A. Kaplan, Phys. Rev. Lett. **17**, 913 (1966).

[4]The reader should keep in mind that the present discussion is valid only for $J_s \gg J$. The discussion in our earlier paper is not valid in this limit, since in Ref. 2 it was presumed that the order parameter varies slowly everywhere, even when one is close to the surface. When $J_s \gg J$, η_{s1} differs by a considerable amount from η_N, so the order parameter suffers a large jump near the surface. Our earlier discussion is applicable to the case where J_s is close to, but a bit larger than the critical value $J_s^{(c)}$ for surface order to occur above T_0. Then the bulk coherence length $\zeta(T)$ is considerably larger than the lattice constant, and η_{s_1} is close to η_N for T above T_0, but below T_s. Our earlier discussion, while it is valid only in this limited regime, is useful in the one regard that it provides an explicit expression for $J_s^{(c)}$. We found $J_s^{(c)} = (5/4)J$ for the semi-infinite simple cubic model. Equation (8) yields the same value for $J_s^{(c)}$ if we look for the value of J_s required to rase T_s above T_0. However, when γ is near unity (as is the case when J_s is near $J_s^{(c)}$), then it may be necessary to include the cubic terms neglected in Eqs. (4) and (5) to properly analyze the spatial variation of the order parameter near the surface.

[5]There is a solution with $\eta_{s_1} = -\eta_{s_2}$ and $\eta(l) = \eta_B \times \sinh(ql)/\sinh(qN)$. This solution satisfies assumption (ii) but violates (i). It also has a transition temperature lower than ours, and in the ordered state a free energy larger than ours by an amount that vanishes exponentially as $L \to \infty$.

[6]R. A. Weiner, following paper, Phys. Rev. B 8, 4427 (1973).