SURFACE REENTRANCE IN THE
SEMI-INFINITE SPIN-1 ISING MODELS

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ABSTRACT

The critical behavior of the semi-infinite Blume-Capel and Blume-Emery-Griffiths models is investigated in the pair approximation of the Cluster Variation Method. Equations for bulk and surface order parameters and n.n. correlation functions are given, from which analytical expressions for the second order bulk and surface critical temperatures are derived. The phase diagrams of the Blume-Capel model are classified, and the existence of a surface first order transition is discussed. This transition is shown to be, under certain conditions, slightly reentrant, and the behavior of the surface order parameters and correlation functions is given for such a case. The extension of our results to the Blume-Emery-Griffiths model is briefly discussed.
1. Introduction

The spin-1 Ising models have been originally proposed to describe the critical behavior of magnetic systems[1], and have subsequently been applied to He$^3$-He$^4$ mixtures[2] and to multicomponent fluids[3]. The most common and most extensively studied among these models are the Blume-Capel (BC) model[1] and the Blume-Emery-Griffiths (BEG) model[2], the former being but a special case, with no biquadratic exchange interaction, of the latter.

These models are not exactly solvable in more than one dimension (one exception being the BEG model in a particular subspace of the phase space[4]), but they have been studied over infinite $d$-dimensional lattices with a lot of different approximation techniques, and their phase diagrams are well-known.

In the last few years some attention has been devoted to the study of these models over semi-infinite lattices, with different couplings at the surface and in the bulk. Benyoussef, Boccara and Saber[5] have investigated the BC model in the mean field approximation (MFA), giving a complete classification of the possible types of phase diagrams, while Benyoussef, Boccara and El Bouziani[6] have carried out the same investigation on the BEG model in a real-space renormalization group (RG) framework. A few other papers have been devoted to the application of the semi-infinite BEG model to the study of surface superfluidity in He$^3$-He$^4$ mixtures, both with RG[7,8] and MFA[9], and a particular investigation of the BC model, in the effective field approximation (EFA), in the case of equal bulk and surface exchange interactions is due to Tamura[10].

As in the case of the spin-1/2 Ising model, it is possible to have an ordered surface even when the bulk is disordered. When such a situation occurs, it is customary to speak of extraordinary (i.e. bulk) and surface transition, and the temperature of the extraordinary transition is lower than the surface one. Otherwise, bulk and surface disorder at the same temperature and with the same critical exponents and the transition is said to be ordinary. Finally, in the limiting case between the two situations above, one has a special transition, with bulk and surface disordering at the same temperature but with different critical exponents.
While these results are well-established, the literature shows a controversy about the order of these transitions. Some papers, where MFA[5,9] or RG[7,8] are employed, indicate clearly that the surface transition (and thus also the extraordinary one) can be either second or first order; on the contrary, there are authors who exclude the possibility of a first order surface or extraordinary transition, both in a RG[6] and in an EFA[10] approximation scheme.

In this paper we investigate the semi-infinite spin-1 Ising models in the pair approximation of the cluster variation method (CVM), which has been introduced by Kikuchi[11] and has subsequently been reformulated by An[12], who put it into a much simpler form resorting to the Möbius inversion.

In order to allow for the spatial variation of the local quantities which this method introduces, we divide the lattice into an infinite set of layers which are parallel to the free surface: since this procedure leads to an infinite number of equations, we make another approximation, which consists in treating the first layer below the surface as if it was bulk; this way we obtain only two finite sets of equations: one for the bulk, which is not coupled to the surface one, and one for the surface, which contains the bulk variables as parameters.

The use of the CVM has two main advantages: it allows us to obtain the correlation functions in a quite straightforward way and to distinguish easily between second and first order transitions, the former being located analytically. Furthermore, we overtake the problem of dealing with a great number of variables and equations by considering a minimal set of independent functions (the order parameters and the correlation functions) of the elements of the reduced density matrices, and by developing moreover a procedure which allows us to solve the equations for the correlation functions, leaving us with only two coupled equations for the order parameters. These equations, when solved numerically by iteration, give always thermodynamically stable solutions, i.e. minima of the free energy. From the equations for the order parameters we deduce an equation for the second order critical temperature, while first order transitions are determined numerically.

The analysis, in the whole phase space of the BC model, shows two new
types of phase diagrams and a reentrant first order surface transition. For
the latter, we give qualitative conditions about the region of the phase space
where it occurs and an example of behavior of the order parameters and of
the correlation functions.

The paper is organized as follows: in Sec. 2 we determine the CVM
free energy, the equations for the order parameters and the second order
critical temperatures; in Sec. 3 we describe our main results: the classification
of the phase diagrams for the BC model and the analysis of the reentrant
phenomenon in the first order surface transition. In Sec. 4 we discuss the
extension of our results to the BEG model and some conclusions are drawn
in Sec. 5.

2. The model and the approximation.

The semi-infinite BEG model has hamiltonian

\[
\beta H_{\text{BEG}} = - J_S \sum_{(ij)} S_i S_j - J_B \sum_{(kl)} S_k S_l + \Delta_S \sum_i S_i^2 + \Delta_B \sum_k S_k^2 \\
- K_S \sum_{(ij)} S_i^2 S_j^2 - K_B \sum_{(kl)} S_k^2 S_l^2,
\]

where \(i, j, k, l\) are site labels, \(S_i\) is the \(z\)-component of a spin-1 operator at site
\(i\), \(\sum_{(ij)}\) denotes a sum over all nearest neighbors (n.n.) with both sites lying
on the surface, \(\sum_{(kl)}\) denotes a sum over the remaining n.n., and \(\beta = (k_B T)^{-1}\)
(with \(k_B\) Boltzmann constant and \(T\) absolute temperature). \(J_S\) and \(J_B\)
(both positive, since we study the ferromagnetic case) are reduced exchange
interactions, while \(\Delta_S\) and \(\Delta_B\) are reduced crystal fields and \(K_S\) and \(K_B\) are
reduced biquadratic exchange interactions, respectively at the surface and in
the bulk.

As we mentioned in the introduction, we divide our lattice into layers,
parallel to the surface, labeled by an integer \(n\), \(n = 1\) being the surface layer.
For the sake of simplicity in the following we will consider a simple cubic
lattice with a (100) free surface.
The CVM is based on an approximate expression of the entropy of the model as a sum of contributions by all the elements of a set $\mathcal{M}$ of maximal clusters and all their subclusters. In the pair approximation, one chooses as $\mathcal{M}$ the set of all n.n. pairs.

Thus our entropy will be the sum of contributions of three different kinds: one due to one-site clusters on layer $n$, denoted by $\sigma_s^{(n)}$; one from two-site clusters with both sites in layer $n$, denoted by $\sigma_p^{(n)}$ and one from two-site clusters with a site in layer $n$ and another in layer $n+1$, denoted by $\sigma_{p'}^{(n)}$. All these contributions will be weighted appropriately yielding, for the total entropy $\sigma$

$$\sigma/N_S = \sum_\gamma a_\gamma (N_\gamma/N_S) \sigma_\gamma,$$

(2)

where $N_S$ is the number of sites in a layer and $\gamma$ ranges over all the clusters above. The weights $a_\gamma$ can be determined by means of An’s equations[12] and, as well as the multiplicities $N_\gamma/N_S$, are lattice dependent. In our case we obtain

$$a_s^{(1)} = -4, \quad a_s^{(n)} = -5, \quad n \geq 2, \quad N_s^{(n)}/N_S = 1, \quad n \geq 1$$

$$a_p^{(n)} = a_{p'}^{(n)} = 1, \quad N_p^{(n)}/N_S = 2, \quad N_{p'}^{(n)}/N_S = 1, \quad n \geq 1.$$  

(3)

Finally, $\sigma_\gamma$ is the entropy associated to the cluster $\gamma$ and is given by

$$\sigma_\gamma = -k_B \text{Tr}(\rho_\gamma \ln \rho_\gamma),$$

(4)

where $\rho_\gamma$ is the reduced density matrix for cluster $\gamma$, which has to be determined by minimization of the free energy.

Since the model hamiltonian is diagonal the reduced density matrices turn out to be diagonal as well. Furthermore, they must obey the following constraints:

$$\text{Tr} \rho_\gamma = 1, \quad \sum_\epsilon \rho_p^{(n)}_{\delta \epsilon} = \sum_\epsilon \rho_{p'}^{(n)}_{\epsilon \delta} = \rho_s^{(n)}_{\delta}$$

$$\sum_\epsilon \rho_p^{(n)}_{\delta \epsilon} = \rho_s^{(n)}_{\delta}, \quad \sum_\epsilon \rho_{p'}^{(n)}_{\epsilon \delta} = \rho_s^{(n+1)}_{\delta}.$$  

(5)
where $\rho_p^{(n)}_{\delta \epsilon} = \langle \delta \epsilon | \rho_p^{(n)} | \delta \epsilon \rangle$ and so on, with $\delta$ and $\epsilon$ taking values $+ , 0 , -$ , and it is assumed for $\rho_p^{(n)}$ that the first index refer to the site in layer $n$ and the second one to the site in layer $n+1$.

These constraints allow us to re-express the density matrices as functions of a reduced (with respect to the set of the elements of the matrices themselves) set of order parameters and correlation functions; this is the first step in lowering the number of equations one must deal with when minimizing the free energy. Upon defining the order parameters ($\langle \rangle$ denotes now thermal average and $S_i^{(n)}$ stands for a spin in the $n$th layer)

$$y_1^{(n)} = \langle S_i^{(n)} \rangle \quad \text{and} \quad y_2^{(n)} = \langle S_i^{(n)^2} \rangle,$$

and the n.n. two-points correlation functions

$$y_3^{(n)} = \langle S_i^{(n)} S_j^{(n)} \rangle, \quad y_3'(n) = \langle S_i^{(n)} S_j^{(n+1)} \rangle;$$

$$y_4^{(n)} = \langle S_i^{(n)} S_j^{(n)^2} \rangle, \quad y_4' = \langle S_i^{(n)} S_j^{(n+1)^2} \rangle ; \quad y_4'' = \langle S_i^{(n)^2} S_j^{(n+1)^2} \rangle;$$

one obtains the following expressions for the elements of the density matrices:

$$\rho_s^{(n)}_{\pm} = \frac{y_2^{(n)} \pm y_1^{(n)}}{2}, \quad \rho_s^{(n)}_{0} = 1 - y_2^{(n)};$$

$$\rho_p^{(n)}_{\delta \epsilon} = \frac{y_5^{(n)} + \delta \epsilon y_3^{(n)} + (\delta + \epsilon)y_4^{(n)}}{4}; \quad \rho_p^{(n)}_{00} = 1 + y_5^{(n)} - 2y_2^{(n)};$$

$$\rho_p^{(n)}_{\pm 0} = \rho_p^{(n)}_{0 \pm} = \frac{y_2^{(n)} - y_5^{(n)} \pm y_1^{(n)} \mp y_4^{(n)}}{2};$$

$$\rho_p^{(n)}_{\pm \epsilon} = \frac{y_5^{(n)} + \delta \epsilon y_3^{(n)} + \delta y_4^{(n)} + \epsilon y_4^{(n)}}{4};$$

$$\rho_p^{(n)}_{\pm 0} = \frac{y_2^{(n)} - y_5^{(n)} \pm y_1^{(n)} \mp y_4^{(n)}}{2};$$

$$\rho_p^{(n)}_{0 \pm} = \frac{y_2^{(n+1)} - y_5^{(n)} \pm y_1^{(n+1)} \mp y_4^{(n)}}{2};$$
where now $\delta$ and $\epsilon$ take values $+,$ $-.$

We are now able to write down our approximate expression for the reduced free energy density $f = \beta(U - T\sigma)/N_S$; we obtain

\[
f = \Delta_S y_2^{(1)} - 2K_S y_5^{(1)} - 2J_S y_3^{(1)} + \sum_{n=2}^{\infty} \left[ \Delta_B y_2^{(n)} - 2J_B y_3^{(n)} - 2K_B y_5^{(n)} \right] - \sum_{n=1}^{\infty} \left[ J_B y_3^{(n)} + K_B y_5^{(n)} \right] + \sum_{n=1}^{\infty} \left[ 2\text{Tr} \left( \rho_p^{(n)} \ln \rho_p^{(n)} \right) + \text{Tr} \left( \rho_{p'}^{(n)} \ln \rho_{p'}^{(n)} \right) \right] - 4\text{Tr} \left( \rho_s^{(1)} \ln \rho_s^{(1)} \right) - 5 \sum_{n=2}^{\infty} \text{Tr} \left( \rho_s^{(n)} \ln \rho_s^{(n)} \right).
\]

Requiring that $f$ is a minimum with respect to all the $y$'s yields an infinite set of coupled equations, which we report making use of the notation $\lambda_s^{(n)} = \ln \rho_s^{(n)}, \lambda_p^{(n)} = \ln \rho_p^{(n)}, \lambda_{p'}^{(n)} = \ln \rho_{p'}^{(n)},$ and indices have the same meaning as in (8):

\[
\begin{align*}
4(\lambda_p^{(n)} + 0 - \lambda_p^{(n)} - 0) + \\
(\lambda_{p'}^{(n)} + 0 - \lambda_{p'}^{(n)} - 0) + \lambda_p^{(n-1)} 0_+ - \lambda_p^{(n-1)} 0_+ + a_s^{(n)}(\lambda_s^{(n)} + - \lambda_s^{(n)} -) &= 0 \\
2D_n + 4(\lambda_p^{(n)} + 0 + \lambda_p^{(n)} - 0 - 2\lambda_p^{(n)} 0_0) + \\
(\lambda_{p'}^{(n)} + 0 + \lambda_{p'}^{(n)} - 0 - 2\lambda_{p'}^{(n)} 0_0 + \lambda_{p'}^{(n-1)} 0_+ - 2\lambda_{p'}^{(n-1)} 0_+) + \\
a_s^{(n)}(\lambda_s^{(n)} + + \lambda_s^{(n)} - - 2\lambda_s^{(n)} 0) &= 0 \\
-4J_n + (\lambda_p^{(n)} + + + \lambda_p^{(n)} - - - 2\lambda_p^{(n)} + -) &= 0 \\
-4J_B + (\lambda_{p'}^{(n)} + + + \lambda_{p'}^{(n)} - - - \lambda_{p'}^{(n)} + +) &= 0 \\
\lambda_p^{(n)} + + - \lambda_p^{(n)} - - - 2(\lambda_p^{(n)} + 0 - \lambda_p^{(n)} - 0) &= 0 \\
(\lambda_{p'}^{(n)} + + + \lambda_{p'}^{(n)} - - - \lambda_{p'}^{(n)} + +) - 2(\lambda_{p'}^{(n)} + 0 - \lambda_{p'}^{(n)} - 0) &= 0
\end{align*}
\]

(10)
\[
(\lambda^{(n)}_{p^{++}} - \lambda^{(n)}_{p^{+-}} + \lambda^{(n)}_{p^{--}} - \lambda^{(n)}_{p^{+-}}) - 2(\lambda^{(n)}_{p^{0+}} - \lambda^{(n)}_{p^{0-}}) = 0
\]

\[-4K_n + (\lambda^{(n)}_{p^{++}} + \lambda^{(n)}_{p^{--}} + 2\lambda^{(n)}_{p^{+-}}) + 4\lambda^{(n)}_{p^{00}} - 4(\lambda^{(n)}_{p^{0+}} + \lambda^{(n)}_{p^{0-}}) = 0
\]

\[-4K_B + (\lambda^{(n)}_{p^{++}} + \lambda^{(n)}_{p^{--}} + \lambda^{(n)}_{p^{+-}} + \lambda^{(n)}_{p^{00}} - 2(\lambda^{(n)}_{p^{0+}} + \lambda^{(n)}_{p^{0-}}) + 4\lambda^{(n)}_{p^{00}} = 0.
\]

Here \(n\) ranges from 1 to \(\infty\), \(J_1 = J_S\), \(J_n = J_B\) for \(n \geq 2\) and similarly for \(D_n\) and \(K_n\), and \(\lambda^{(0)}_{p^{0}} = 0\).

Letting \(n\) go to \(\infty\) in the equations above one obtains the bulk equations, which are only five, since in the bulk correlations like \(y_3\) and \(y'_3\) coincide. We have already solved the bulk equations in Ref. 13 and here we report the two coupled equations for the bulk order parameters

\[
y^{(B)}_1 = \frac{[(V_+ - V_-) + \eta(V^2_+ - V^2_-)]}{W}
\]

\[
y^{(B)}_2 = \frac{[(V_+ + V_-) + \eta(V^2_+ + V^2_-) + 2\gamma V_+ V_-]}{W}
\]

and the expressions for the correlation functions given as functions of the order parameters

\[
y^{(B)}_3 = \frac{\eta(V^2_+ + V^2_-) - 2\gamma V_+ V_-}{W}
\]

\[
y^{(B)}_4 = \frac{\eta(V^2_+ - V^2_-)}{W}
\]

\[
y^{(B)}_5 = \frac{\eta(V^2_+ + V^2_-) + 2\gamma V_+ V_-}{W}
\]

where \(\eta = \exp(J_B + K_B)\), \(\gamma = \exp(-J_B + K_B)\),

\[
V_\pm = e^{-\Delta_B/6} \left[ \frac{y^{(B)}_2 \pm y^{(B)}_1}{2(1 - y^{(B)}_2)} \right]^{\frac{1}{2}},
\]

\[
W = \eta(V^2_+ + V^2_-) + 2\gamma V_+ V_- + 2(V_+ + V_-) + 1 \text{ and } y^{(B)}_i = \lim_{n \to \infty} y^{(n)}_i.
\]

From equations (11) one can easily derive the equation for the second order critical temperature, which reads[13]

\[
e^{\Delta_B} = 2\zeta(\gamma_0 - 1) \left[ \frac{\zeta \gamma_0}{\zeta(\gamma_0 - 1) + 1} \right]^5,
\]
where $\zeta = e^{K_B} \cosh J_B$ and $\gamma_0 = 5 \tanh J_B$.

Turning to the whole set of equations (10) let us observe that, since is not possible to decouple different layers, some sort of approximation is in order; one can, for example, choose a maximum number $\bar{n}$ of layers and then solve numerically the equations for $n = 1, 2, \ldots \bar{n}$ using the bulk solutions as boundary conditions, i.e. as if they were the solutions for layer $\bar{n} + 1$. We choose the crudest approximation, $\bar{n} = 1$, which allows us to obtain analytical results for the second order transition. The same assumption has been made in Refs. 5-8.

The procedure we follow to determine the equations for the surface $(n = 1)$ order parameters (which is analogue to that used in [13] for the bulk ones) can easily be shown to be equivalent to the natural iteration method (NIM) by Kikuchi[14], in the sense that the resulting equations, when solved by numerical iteration, give always thermodinamically stable solutions. Moreover, our procedure has the advantage of dealing with a considerably lower number of equations (only two, in the present case).

From now on we will suppress the index $(1)$, which has become redundant; furthermore, instead of $(2)$ we will write $(B)$, because layer 2 now plays the role of the bulk.

In order to determine the surface equations we express $\rho_{p'} \equiv \rho_{p'}^{(1)}$ and $\rho_p \equiv \rho_p^{(1)}$ as functions of $\rho_s \equiv \rho_s^{(1)}$ and of the bulk quantities; to this aim we consider a set of equations formed by the four equations in the set (10) for $n = 1$ which contain only elements of $\lambda_{p'}$, the first two equations of that set for $n = 2$, and the three equations given by the first of the constraints (5) for $\rho_{p'}$. This way we obtain a system which (recalling that $\lambda_{p'} = \ln \rho_{p'}$) can be solved for the elements of $\rho_{p'}$, obtaining

$$\rho_{p'}^\delta \epsilon = \exp \left[ \delta \epsilon J_B + (\delta \epsilon)^2 K_B \right] \frac{c_\epsilon}{d \delta} \rho_{s \delta}, \quad \delta, \epsilon = +, 0, -, \quad (15)$$

where

$$c_\pm = e^{-\Delta_B/6} \left( \frac{\rho_{s(B)}^\pm}{\rho_{s(B)}^0} \right)^{5/6} \quad c_0 = 1 \quad (16)$$
\[ d_\delta = \sum_\epsilon \exp \left[ \delta \epsilon J_B + (\delta \epsilon)^2 K_B \right] c_\epsilon \quad \delta = +, 0, - \]  
\[ \text{(17)} \]

The remaining five equations for \( n = 1 \), together with the normalization condition \( \text{Tr}(\rho_p) = 1 \) can now be used to obtain the elements of \( \rho_p \); one finds

\[ \rho_{p \delta \epsilon} = \exp \left[ \delta \epsilon J_S + (\delta \epsilon)^2 K_S \right] \gamma_\delta \gamma_\epsilon G^{-1}, \quad \delta, \epsilon = +, 0, - \]  
\[ \text{(18)} \]

where

\[ \gamma_\pm = e^{-\Delta S/4} \left( \frac{\rho_{s \pm}}{\rho_{s 0}} \right)^{3/4} \left( \frac{d_{\pm}}{d_0} \right)^{1/4} \quad \gamma_0 = 1 \]  
\[ \text{(19)} \]

and

\[ G = \sum_\delta \exp \left[ \delta \epsilon J_S + (\delta \epsilon)^2 K_S \right] \gamma_\delta \gamma_\epsilon. \]  
\[ \text{(20)} \]

Since the surface order parameters are related to \( \rho_p \) by the equations

\[ y_1 = \rho_{p++} - \rho_{p--} + \rho_{p+0} - \rho_{p-0} \]  
\[ y_2 = \rho_{p++} + \rho_{p--} + \rho_{p+0} + \rho_{p-0} + 2 \rho_{p+-} \]  
\[ \text{(21)} \]

they must satisfy the following equations

\[ y_1 = \left[ e^{J_S + K_S \left( \gamma_+^2 - \gamma_-^2 \right)} + (\gamma_+ - \gamma_-) \right] / G \]  
\[ y_2 = \left[ e^{J_S + K_S \left( \gamma_+^2 + \gamma_-^2 \right)} + 2e^{-J_S + K_S \gamma_+ \gamma_-} + (\gamma_+ + \gamma_-) \right] / G. \]  
\[ \text{(22)} \]

Once one has solved (22), using (8), (15) and (18) it is immediate to obtain explicit expressions for the n.n. two-points correlation functions.

It is easy to check that, when \( y_1 = 0 \), then \( y_1^{(B)} = 0 \) too, that is, if the surface is paramagnetic, the bulk must also be paramagnetic. On the contrary, if the bulk is paramagnetic \( (y_1^{(B)} = 0) \), the equation for \( y_1 \) has always the paramagnetic solution \( y_1 = 0 \), but can also have a ferromagnetic solution \( y_1 \neq 0 \). It means that in the paramagnetic region of the bulk phase diagram one can have a surface transition line. The first order part of this line must be evaluated numerically, by comparison of the free energies of the two phases, while the second order one can be determined analytically by expanding (22) in powers of \( y_1 \) (the order parameter \( y_2 \) must be expanded as well, and one must remember that \( y_1^{(B)} = 0 \), because we are in the bulk
paramagnetic region of the phase diagram) around the solution $y_1 = 0$, and then requiring that the resulting equations are satisfied to the 3rd order in $y_1$ (going to the 5th order would give a set of equations for the tricritical point). One finds, for the surface second order transition

$$2^{-8} e^{K_S} \frac{c}{c_0} x \left[ 3 \frac{3x + \sqrt{x^2 + 8}}{e^{-K_S} + x} \right]^3 = e^{\Delta S},$$

(23)

where $x = e^{J_S} - 2e^{-J_S} > 0$, $c_0 = 1 + 2V$ and $c = 1 + 2V e^{K_B} \cosh J_B$, with

$$V = e^{-\Delta_B / 6} \left[ \frac{y_2(B)}{2(1 - y_2(B))} \right] \frac{1}{2}.$$

(24)

3. Phase diagram and reentrant phenomenon

In the present section we turn to the Blume-Capel model: thus we set $K_B = K_S = 0$.

Following [5] we define the ratios $R = J_B / J_S$ and $D = \Delta_B / \Delta_S$ and classify the possible phase diagrams at fixed $R, D$ in the plane $(d, \tau)$, where $d = \Delta_B / 6J_B$ and $\tau = 1 / 6J_B$. As in [5] we obtain four main types of phase diagrams, which we report in Figs. 1-4; solid and dashed lines represent respectively second and first order transitions, and the thinner lines, when present, refer to the surface. B and S stand for bulk and surface respectively, while P and F stand for para- and ferromagnetic.

The type-A diagram, reported in Fig. 1, is characterized by the presence of only ordinary transitions; the type-B diagram (Fig. 2) shows an ordinary transition at high temperatures, while in the low temperature region one has extraordinary and surface transitions: the three transition lines meet at the special point $X$; in the type-C diagram (Fig. 3) the situation is reversed, and finally, in the type-D diagram (Fig. 4) one has no ordinary transition but two non-intersecting, extraordinary and surface, transition lines. Type-B and type-C diagrams could be classified with even more detail, because in both cases the surface tricritical point can be either present or absent, but we do not enter into these point.
It is possible to distinguish between these four types by means of analytic conditions. First of all one must determine the bulk and surface critical temperatures at \( d = -\infty \), respectively denoted by \( \tau_B^{(\infty)} \) and \( \tau_S^{(\infty)} \) (the latter is determined under the assumption of paramagnetic bulk), and the bulk and surface critical values of \( d \) at \( \tau = 0 \), respectively denoted by \( d_B^{(0)} \) and \( d_S^{(0)} \), and then compare these values, recalling that, if \( \tau_B^{(\infty)} > \tau_S^{(\infty)} \) or \( d_B^{(0)} > d_S^{(0)} \), the corresponding transition must be necessarily an ordinary one, because in the bulk ferromagnetic region of the phase diagram the surface is always ferromagnetic and surface transitions are forbidden.

By means of (14) and (23) one obtains \( \tau_B^{(\infty)} = (3 \ln \frac{3}{2})^{-1} \approx 0.822 \) and \( \tau_S^{(\infty)} = (3 R \ln 2)^{-1} \approx 0.481 R^{-1} \) respectively; the condition \( \tau_B^{(\infty)} = \tau_S^{(\infty)} \) gives the critical value

\[
R_c = \frac{\ln 3}{\ln 2} - 1 \approx 0.585, \tag{25}
\]

above which the \( d = -\infty \) transition is ordinary (the corresponding MFA value is \( R_c = 2/3 \)). Furthermore, simple analytic considerations on the ground state yield \( d_B^{(0)} = 1/2 \) and \( d_S^{(0)} = \frac{1}{3} DR^{-1} \), from which the critical value

\[
D_c \equiv D_c(R) = \frac{3}{2} R \tag{26}
\]

(equal to the corresponding MFA value), below which the zero temperature transition is ordinary, can be derived. Thus, the four main phase diagrams are characterized by the following conditions:

Type-A diagram: \( R > R_c \) and \( D < D_c \),
Type-B diagram: \( R > R_c \) and \( D > D_c \),
Type-C diagram: \( R < R_c \) and \( D < D_c \),
Type-D diagram: \( R < R_c \) and \( D > D_c \).

Notice that type-B and type-C have not been found in the RG-based classification of Ref. 6, although a different renormalization group scheme[7,8] gives a phase diagram which is similar to our type B.

To this fundamental classification we must add two new cases, which appear in the CVM treatment when \( D \) is just below \( D_c \) and are illustrated in Figs. 5-6 for \( R \) above and just below \( R_c \), respectively. The new feature
of these diagrams is the presence of two or more special (i.e. multicritical points where surface and bulk transition lines meet) points.

In Figs. 2, 4 and 5 it is possible to observe a reentrant phenomenon in the ferromagnetic-paramagnetic (order-disorder) surface transition. In fact, for fixed $R$, there is a range of values of $D$ for which one has such a phenomenon. The lower and upper limits depend on $R$, and the former is, of course, just below $D_c$. In Figs. 7-10 we report the behavior of the order parameters and of the correlation functions for a set of values of the parameters corresponding to the dotted line in Fig. 4. As can be expected, the surface-bulk n.n. correlation functions are very small (even if non-zero) in the temperature range where the bulk is paramagnetic and the surface ferromagnetic.

Finally, it is noteworthy that the surface reentrant phenomenon is not revealed by a MFA analysis: in Fig. 11 we compare the MFA phase diagram corresponding to Fig. 4 to that obtained in our approximation.

4. The surface reentrance in the BEG model

Let us now briefly consider the BEG model in the case $\xi > -1$, being $\xi = K_B/6J_B$ (the case $\xi < -1$, where a staggered quadrupolar phase can occur, would require the introduction of two sublattices, with different order parameters to allow for the symmetry breaking between them). The results of the previous section can be easily extended to this case; the only change that is needed in the classification is that one finds, for the critical value of the ratio of crystal fields,

$$D_c = \frac{3}{2} R \frac{1 + \xi}{1 + \xi R \Gamma^{-1}},$$

(27)

where $\Gamma = K_B/K_S$. Furthermore, since for the BEG model the bulk phase diagram can exhibit reentrance (see [13] and references therein) both for $\xi < 0$ and for $\xi > 3$, it is interesting to know what happens in these cases for the semi-infinite model.

For $\xi < 0$ one can easily find cases of reentrant ordinary transitions, where the bulk and the surface are simultaneously interested by the reentrant phenomenon, as in Fig. 12.
The most interesting situations occur for $\xi > 3$. When $D$ is slightly less than $D_c$ the surface reentrant transition already seen for the BC model, together with the ordinary reentrant transition, give rise to a double reentrant phenomenon, as shown in Fig. 13. Another double reentrant phenomenon can be obtained for $D$ slightly greater than $D_c$: in this case (Fig. 14) one has two successive reentrances on the surface transition line, the highest temperature transition being now second order.

5. Final remarks

We have investigated the semi-infinite spin-1 Ising models, devoting particular attention to the BC model, in the framework of the pair approximation of the CVM. We have classified the possible phase diagrams at fixed $R, D$, finding two new types of diagrams and showing that, at least in the present approximation, the first order surface transition do occur and exhibits reentrant phenomenon; finally, we have given qualitative conditions for this phenomenon and have discussed the extension of our results to the BEG model.

The surface reentrant phenomenon we have found in the BC model is not revealed by a MFA analysis. It would be interesting to check our results by other high-precision methods.

Our analysis has led to a classification scheme with four fundamental types of phase diagram, depending on the values of $R$ and $D$. Two of them, namely type-B and type-C, have not been found in the approximations of Refs. 6 and 10, while Refs. 7 and 8 present a phase diagram like our type-B. This point is worth of a further investigation, in order to establish whether the first order surface transition exists or it is only an effect due to the approximation method adopted. We conjecture that this transition is a real feature of the model, and give the following argument in support.

Let us consider the BC model again: at $T = 0$, and for $d > 1/2$, the bulk ground state is paramagnetic, i.e. $S_k = 0$ for all bulk sites $k$. Then all the interaction terms between bulk and surface vanish and the surface behaves like a BC model on an infinite square lattice, thus exhibiting a first order
transition (if $D > D_c$) at $d = d_s^{(0)}$ (indeed, this zero temperature transition is found also in [5]). Similarly, at a very low but finite temperature, only a small fraction of the bulk spins will be different from zero and the surface will be only weakly coupled to the bulk, this resulting in a slight change of the critical value of $d$, giving a smooth surface first order transition line in the $(d, \tau)$ plane starting from the point $(d_s^{(0)}, 0)$. Work is in progress to confirm the conjecture and the results we have obtained.
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Figure captions

Fig. 1: Phase diagram of the semi-infinite BC model for $R > R_c$ and $D < D_c$. Solid and dashed lines denote second and first order transitions, respectively; $X$ is the special point; B = bulk, S = surface, P = paramagnetic, F = ferromagnetic.

Fig. 2: Phase diagram for $R = 1$ and $D = 1.8$. Symbols as in Fig. 1.

Fig. 3: Phase diagram for $R = 0.4$ and $D = 0.5$. Symbols as in Fig. 1.

Fig. 4: Phase diagram for $R = 0.4$ and $D = 0.8$. Symbols as in Fig. 1.

Fig. 5: Phase diagram for $R = 1$ and $D = 1.49$. Symbols as in Fig. 1.

Fig. 6: Phase diagram for $R = 0.56$ and $D = 0.8$. Symbols as in Fig. 1.

Fig. 7: Behavior of the order parameters $y_1$ (solid line) and $y_2$ (dashed line) for the case corresponding to the dotted line in Fig. 4.

Fig. 8: Behavior of $y_3$ (solid line) and $y'_3$ (dashed line) in the case of Fig. 7.

Fig. 9: Behavior of $y_4$ (solid line), $y'_4$ (dashed line) and $y''_4$ (dot-dashed line) in the case of Fig. 7.

Fig. 10: Behavior of $y_5$ (solid line) and $y'_5$ (dashed line) in the case of Fig. 7.

Fig. 11: Comparison between the phase diagram of Fig. 4 (denoted by CVM) and the corresponding one obtained in MFA (denoted by MFA).

Fig. 12: Phase diagram of the BEG model for $\xi = -0.5$, $R = 0.5$, $D = 0.4$ and $\Gamma = 1$.

Fig. 13: Phase diagram of the BEG model for $\xi = 3.6$, $R = 0.5$, $D = 1.22$ and $\Gamma = 1$.

Fig. 14: Phase diagram of the BEG model for $\xi = 3.6$, $R = 0.5$, $D = 1.26$ and $\Gamma = 1$. 

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