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# Order Parameter Profiles near Surfaces of Super-weak Ferrimagnetic Materials Exhibiting a Paramagnetic-Ferrimagnetic Transition

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**Abstract** The aim of this paper is to determine the full order parameter profiles close to the surface for a system made of two strongly coupled paramagnetic sublattices of respective moments $\varphi$ and $\psi$. The material exhibits a para-ferrimagnetic transition at some critical temperature $T_c$ greater than the room temperature. The free energy describing the physics of the system is of Landau type, and involves, beside quadratic and quartic terms in both $\varphi$ and $\psi$, a lowest-order coupling, $-C_o\varphi\psi$ where $C_o < 0$ is the coupling constant measuring the interaction between the two sublattices. We consider here below a film of thickness $L$, and the free energy is then a sum of bulk and surface contributions expanded in terms of the local order parameters. The magnetization at the surface are $\varphi_s$ and $\psi_s$. As in a recent paper (whom the present work is an extension), we first reduce the model to an effective $\varphi^4$ −theory written in terms of the overall magnetization $\phi = \varphi + \psi$ and the associated fraction of magnetization $\eta_\alpha = \varphi/(\varphi + \psi)$. For the ordinary transition where the extrapolation length is positive $\lambda_S > 0$, we determine the order parameter profile near surfaces. We show, in particular, that the magnetization behavior is governed, in addition of $\lambda_S$ and the bulk correlation length $\xi_b^-$, by a new length $L_\alpha$. We have interpreted this latter as the width of the ordered ferrimagnetic layer close to the surface. Finally, we examine the extraordinary $(\lambda_s < 0)$, special $(\lambda_s = \infty)$ and surface (at $T_{cs} > T_c$) transitions.

***Keywords:*** *sublattices, coupling, paramagnetism, ferrimagnetism, transition, order parameter profiles*

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## 1. Introduction

The so-called super-weak ferrimagnetic materials we consider here are of considerable technological importance, in particular, in the domain of energy stocking (long life lithium batteries). Their common feature is that they present a small magnetization at low temperatures, in contrary to the usual ferrimagnetic materials. As example of super-weak ferrimagnetic systems we can quote certain members of Heusler Pauli-paramagnetic alloys [1] based on the composition $X_2YZ$, with $(X = Pd, Cu;\ Y = T_i, V$ and $Z = Al, In, Sn)$ and lamellar Curie-Weiss paramagnetic compounds [2], like $AM_xM'_{1-x}O_2$ $(0 \le x < 1)$ with $(A = Li, Na, K; M, M' = N, Co, \dots)$. The lithium-nickel oxides are promising candidates for electrode materials in lithium batteries [3-5] and electro-chromic displays [6].

To describe the super-weak ferrimagnetism arising from this category of materials, Neumann and co-workers [7] have proposed a continuous model based on the landau theory [8,9,10]. In this model, the material consists of a lattice made up of two coupled Pauli or Curie-Weiss paramagnets sublattices [11,12], with respective local magnetizations $\varphi$ and $\psi$. Above the critical temperature $T_c$ both magnetizations vanish and the system is a paramagnet. Below this temperature an anti-parallel configuration of the magnetization is favored, but with non-vanishing overall magnetization. One can say that the material exhibits a *ferrimagnetic* state. In fact, the appearance of such an order is intimately related to the existence of a strong coupling between the two sublattices. This latter manifests itself through the introduction of an extra term $-C_o\varphi\psi$ in the free energy. Negative values of the coupling constant $C_o$ favor the anti-parallel alignment of the local moments $\varphi$ and $\psi$, and a ferrimagnetic order appears.

From a mean-field point of view and within the framework of this model the para-ferrimagnetic transition in the bulk arising from these materials was widely studied. The theory has been developed, first, through some numerical method [7], and second, through an exact analytic analysis [13,14,15]. As the mean-field approach underestimates the strong fluctuations of the local moments near the critical point, use also was be made of the Renormalization-Group techniques [16,17], as in the case of usual para-ferromagnetic transition [18,19,20].

Theoretical treatments of phase transitions usually consider ideal crystals of infinite extent. Experiments, however, are carried out on samples of finite size; there may be a need to consider the effects of both external surfaces of the system and internal ones such a grain boundaries and other kind of interface [21]. As is well known, the mean-field treatment of a second phase transition in the bulk is rather simple [9,22,23,24]. In contrast, the mean-field theory of critical behavior at surfaces is much more involved, although all properties of interest can still be calculated analytically. As a consequence, many authors have contributed to its development [25,26,27,28,29].

To take into account the surface effects on bulk properties, close to a second-order phase transition, we have investigated, in a recent work [30], the critical behavior of the system at surfaces. We have shown, in particular, that the model can be reformulated in terms of an effective $\varphi^4$-theory using the fraction of the magnetization $\eta_\alpha = \varphi/\phi$, and the order parameter of interest is then the overall magnetization $\phi = \varphi + \psi$. We have found that this approach leads to an effective extrapolation length $\lambda_s$. The critical behavior of all physical quantities of interest (like the overall magnetization at surface $\phi_s$, the local susceptibilities at the surface $\chi_s$ and $\chi_{s,s}$, etc…) was determined [30].

In the present work, which must be regarded as a natural extension of that specified above [30], we obtain the order parameter profiles near surfaces, and surface corrections to bulk quantities. We show, in particular, that the behavior of the magnetization $\phi_\alpha(z)$ close to the surface is governed by the magnetization $\tilde{\phi}_\alpha$ and a new length $L_\alpha$ (instead of the bulk magnetization $\phi_b$ and the correlation length $\xi_b^+$, in the usual $\varphi^4$-theory [21]). The length $L_\alpha$, represent, in fact, the width of the ordered layer near surface. In all the above situations the phase transition at surface is considered with $\lambda_s > 0$ called *ordinary transition*. We examine, finally, the special case $\lambda_s = \infty$ called the *special transition*, as well as the *extraordinary transition* which occurs, for $\lambda_s < 0$, in the surface layer at $T_c$, in addition to the *surface transition* at a temperature $T_{cs} > T_c$. In all these cases we determine the critical behavior of the surface magnetization $\phi_s$ and the local susceptibilities at surface $\chi_s$ and $\chi_{s,s}$. The first is the response $\chi_s$ of a surface spin to a uniform field acting throughout the system, and the second is the response $\chi_{s,s}$ to a field acting in a surface. Schematic magnetization profiles near a free surface are also presented.

This paper is organized as follows. Section 2 is devoted to a succinct presentation the used model, and the necessary back ground information. Section 3 is devoted to the determination of the full order parameter profiles close to the surface. We present, in section 4, the results dealt with the special, the surface and the extraordinary transitions. We draw some concluding remarks in section 5.

## 2. The Model

The physical system we consider here consists of two strongly coupled sublattices, of respective moments $\varphi$ and $\psi$. For small moments and in the presence of an applied external magnetic field $H$, in a Landau approximation, the bulk free energy allowing to investigate the para-ferrimagnetic transition within this system writes [7,13,14]

$$\begin{aligned}\frac{F_b}{T} = \int d\vec{r}\Big\{&\frac{1}{2}c_\varphi\left(\nabla\varphi(\vec{r})\right)^2 + \frac{1}{2}c_\psi\left(\nabla\psi(\vec{r})\right)^2 \\ &+\frac{a}{2}\varphi^2(\vec{r}) + \frac{A}{2}\psi^2(\vec{r}) - C_o\varphi(\vec{r})\psi(\vec{r}) \\ &+\frac{u}{4}\varphi^4(\vec{r}) + \frac{v}{4}\psi^4(\vec{r}) - H(\vec{r})\left(\varphi(\vec{r})+\psi(\vec{r})\right)\Big\}.\end{aligned} \tag{2.1}$$

The squared gradient terms on the right-hand side of relation (2.1) traduce the spatial variations of order parameters $\varphi$ and $\psi$. There, $\vec{r}$ stands for the $d$-dimensional position vector of the considered point. In relation (2.1), the coupling constants $u$ and $v$ are taken to be positive, to ensure the stability of the free energy. Coefficients $a$ and $A$ depend on temperature according to

$$a(T) = a_o + a_1T^2 > 0;\ A(T) = A_o + A_1T^2 > 0, \tag{2.2a}$$

for a Pauli paramagnet [7,8], or

$$a(T) = \bar{a}(T-\theta_1);\ A(T) = \bar{a}(T-\theta_2), \tag{2.2b}$$

for Curie-Weiss paramagnet [12,31]. $a_o$ and $a_1$ appearing in relation $(2.2a)$, have a simple dependence in both free electron density and Fermi energy relative to the two sublattices [32]. In relation $(2.2b)$, the Curie-Weiss temperatures $\theta_1$ and $\theta_2$ are proportional to exchange integrals $J_1 > 0$ and $J_2 > 0$, inside the sublattices [16]. The extra term $C_o$ in Eq. (2.1) represent the lowest-order coupling between the two sublattices. Such a term plays, in fact, the role of an internal magnetic field. For a negative coupling constant $C_o < 0$, an antiparallel configuration of magnetizations $\varphi$ and $\psi$ is favored, while $C_o > 0$ favors their parallel alignment. For Curie-Weiss materials like lamellar compounds [2,33], the coupling $C_o$ is proportional to the exchange integral $J_{12}$ between the two sublattices. In this work we are concerned only with negative values of $C_o$, in order to investigate the ferrimagnetic state of the system. $H(\vec{r})$ is a (suitable normalized) magnetic field. For a film of thickness $L$, the free energy writes as a sum a bulk part $F_b$ and a surface one $F_s$ $(F/T = F_b/T + F_s/T)$. The generalization of Eq. $(2.1)$ is then [30]

$$\begin{aligned}\frac{F}{TS} = \int_0^L dz\Big\{&\frac{1}{2}c_\varphi\left(\frac{\partial\varphi}{\partial z}\right)^2 + \frac{1}{2}c_\psi\left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{a}{2}\varphi^2(z) \\ &+\frac{A}{2}\psi^2(z) - C_o\varphi(z)\psi(z) + \frac{u}{4}\varphi^4(z) \\ &+\frac{v}{4}\psi^4(z) - H\left(\varphi(z)+\psi(z)\right)\Big\} \\ &+\Big\{\frac{1}{2}c_\varphi\lambda_\varphi^{-1}\left[\varphi^2(z=0)+\varphi^2(z=L)\right] \\ &+\frac{1}{2}c_\psi\lambda_\psi^{-1}\left[\psi^2(z=0)+\psi^2(z=L)\right] \\ &+c_{\varphi\psi}\lambda_{\varphi\psi}^{-1}\left[C_o\varphi(z=0)\psi(z=0)+C_o\varphi(z=L)\psi(z=L)\right] \\ &-H_s\left[\varphi(z=0)+\psi(z=0)+\varphi(z=L)+\psi(z=L)\right]\Big\}\end{aligned} \tag{2.3}$$

where, similarly, the surface free energy $F_s$ is expanded in terms of the local order parameters including terms up to second order-only. Since we wish to study the system close enough to $T_c$ we then neglect higher order terms in $F_s$ in Eq. (2.3). The linear term involves a field $H_s$ acting on spins in the surface plane only, and the constants of the quadratic terms were written arbitrarily as $(c_i \lambda_i^{-1}; \, i = \varphi, \psi \text{ or } \varphi\psi)$, where the parameters $\lambda_i$ have the dimension of a length and are called extrapolation lengths [21]. We consider that the fields $H$ and $H_s$ are homogeneous, and we disregard variations of the magnetization with the layers, hence we replace $\varphi(\vec{r})$ and $\psi(\vec{r})$ by their averages, which we denote by $\varphi(z)$ and $\psi(z)$ [30].

It is important to note that we can write the model as an effective $\varphi^4$-theory in terms of the fraction of magnetizations $\eta_\alpha = \varphi/(\varphi+\psi)$ and the overall magnetization $\phi = (\varphi+\psi)$. Indeed, under these considerations the free energy (2.3) reduce to [30]

$$\frac{F}{TS} = \int_0^L dz \left\{ \begin{array}{l} \frac{1}{2} c_\alpha \left( \frac{\partial \phi}{\partial z} \right)^2 + \frac{A_\alpha}{2} \phi^2(z) \\ + \frac{B_\alpha}{4} \phi^4(z) - H\phi(z) \end{array} \right\} + F_s, \tag{2.4}$$

with

$$A_\alpha = a\eta_\alpha^2 + A(1-\eta_\alpha)^2 - 2C_o\eta_\alpha(1-\eta_\alpha), \tag{2.5a}$$

$$B_\alpha = u\eta_\alpha^4 + v(1-\eta_\alpha)^4, \tag{2.5b}$$

$$c_\alpha = c_\varphi \eta_\alpha^2 + c_\psi (1-\eta_\alpha)^2, \tag{2.5c}$$

and

$$\begin{aligned} F_s = &\frac{1}{2}\frac{c_s}{\lambda_s}\left[\phi^2(z=0) + \phi^2(z=L)\right] \\ &- H_s\left[\phi(z=0) + \phi(z=L)\right], \end{aligned} \tag{2.6}$$

where $c_s$ is an effective constant and $\lambda_s$ the effective extrapolation length, which write

$$c_s = c_\varphi \eta_s^2 + c_\psi (1-\eta_s)^2, \tag{2.7a}$$

and

$$\lambda_s = \frac{c_\varphi \eta_s^2 + c_\psi (1-\eta_s)^2}{\frac{c_\varphi}{\lambda_\varphi}\eta_s^2 + \frac{c_\psi}{\lambda_\psi}(1-\eta_s)^2 + 2\frac{c_{\varphi\psi}}{\lambda_{\varphi\psi}}\eta_s(1-\eta_s)}. \tag{2.7b}$$

Functional differentiation of Eq. (2.4) yields an equation due to Ginsburg Landau [34] and familiar from theory of superconductivity, but with the effective phenomenological parameters $A_\alpha$, $B_\alpha$ and $c_\alpha$

$$A_\alpha \phi(z) + B_\alpha \phi^3(z) - c_\alpha \left( \frac{\partial^2 \phi}{\partial z^2} \right) = H, \tag{2.8}$$

for which the surface term in Eq. (2.4) supply the boundary conditions

$$\frac{\partial \phi}{\partial z} - \frac{\phi}{\lambda_s} = \frac{H_s}{c_s}, \, z = 0, \tag{2.9a}$$

$$\frac{\partial \phi}{\partial z} + \frac{\phi}{\lambda_s} = \frac{H_s}{c_s}, \, z = L. \tag{2.9b}$$

From Eq. (2.8) one obtains the standard results for the bulk magnetization $\phi_b = \varphi_b + \psi_b$ and the overall susceptibility $\chi_b$, for a homogeneous system where $\left(\frac{\partial^2 \phi}{\partial z^2}\right)$ can be omitted [30]

$$\phi_b = \sqrt{-\frac{A_b}{B_b}} \cong (T - T_c)^{\frac{1}{2}}, T \to T_c^-, H = 0, \tag{2.10a}$$

$$\phi_b = \left(\frac{H}{B_b}\right)^{\frac{1}{3}}, H \to 0^+, T = T_c \tag{2.10b}$$

with

$$A_b = a\eta_b^2 + A(1-\eta_b)^2 - 2C_o\eta_b(1-\eta_b), \tag{2.11a}$$

$$B_b = u\eta_b^4 + v(1-\eta_b)^4, \tag{2.11b}$$

where the fraction $\eta_b$ is given by: $\eta_b = \varphi_b/\phi_b$. Note that close to the critical temperature $T_c$, the effective phenomenological parameter $A_b$ behaves as: $A_b \cong (aA - C_o^2) \cong (T - T_c)$ [30]. The overall susceptibility $\chi_b$ above and below $T_c$, can be obtained directly by taking the first derivative of Eq. (2.8) with respect of the magnetic field $H$, and setting $H = 0$, one finds [30]

$$\begin{aligned} \chi_b^+ &= A_b^{-1} \cong \chi_o^+ (T - T_c)^{-1}, \\ \chi_b^- &= -\frac{1}{2A_b} \cong \chi_o^- (T - T_c)^{-1}. \end{aligned} \tag{2.12}$$

Expressions of the correlation length $\xi_b$ above and below $T_c$ can also be extracted

$$\begin{aligned} \xi_b^+ &= \sqrt{\frac{c_b}{A_b}} \cong \xi_o^+ (T - T_c)^{-\frac{1}{2}}, \\ \xi_b^- &= \sqrt{\frac{c_b}{2A_b}} \cong \xi_o^- (T - T_c)^{-\frac{1}{2}}, \end{aligned} \tag{2.13}$$

where $c_b = c_\varphi \eta_b^2 + c_\psi (1-\eta_b)^2$. It is also important to note that for a semi-infinite system, $L \to \infty$, we may replace the boundary condition Eq. $(2.9b)$, by

$$\left.\frac{\partial \phi}{\partial z}\right|_{z \to \infty} = 0, \phi(z \to \infty) = \phi_b, \tag{2.14}$$

and the magnetization at the surface is given by: $\phi_s = \phi(z = 0)$. Multiplying Eq. (2.8) by $\left(\frac{\partial \phi}{\partial z}\right)$ and integrating over $z$ from zero to infinity, whereby the boundary conditions Eqs. $(2.9a)$ and $(2.14)$, can be used, this yields [30]

$$\begin{aligned} &\frac{B_b}{4}\phi_b^4 + \frac{A_b}{2}\phi_b^2 - \frac{B_s}{4}\phi_s^4 - \frac{A_s}{2}\phi_s^2 \\ &+ \frac{1}{2}c_s\left(\frac{\phi_s}{\lambda_s} - \frac{H_s}{c_s}\right)^2 = H(\phi_b - \phi_s). \end{aligned} \tag{2.15}$$

Relation (2.15) is the state equation containing all information about critical behavior of the system in the bulk and at surface.

## 3. Order Parameter Profiles near Surfaces

We consider here next the full profile of the magnetization $\phi_\alpha(z)$ close to the surface and corrections to bulk quantities. To this end we return to Eq. (2.8) and neglect the non-linear term in $\phi(z)$ for $T > T_c$, and small enough fields (linear response to $H$, $H_s$). In these conditions Eq. (2.8) writes

$$\phi(z)-L_\alpha^2\frac{\partial^2\phi}{\partial z^2}=\tilde{\phi}_\alpha, \tag{3.1}$$

where $L_\alpha=\sqrt{\frac{c_\alpha}{A_\alpha}}$ and $\tilde{\phi}_\alpha=\frac{H}{A_\alpha}$. In terms of a scaled coordinate $\zeta=\frac{z}{L_\alpha}$; one obtain

$$\phi(\zeta)-\frac{\partial^2\phi(\zeta)}{\partial\zeta^2}=\tilde{\phi}_\alpha. \tag{3.2}$$

Notice for the usual $\varphi^4$-theory, the magnetization $\tilde{\phi}_\alpha$ and the length $L_\alpha$ are nothing else but the bulk magnetization $\phi_b$ $\left(\phi_b=\chi_b^+H=\frac{H}{A_b}\right)$ and the correlation length $\xi_b^+$ $\left(\xi_b^+=\sqrt{\frac{c_b}{A_b}}\right)$ respectively [21]. The length $L_\alpha$ can be interpreted, in fact, as the width of the ordered ferrimagnetic layer near surface. Remark that this length $L_\alpha$, as it should do, is an increasing function of $-C_o$ (strong coupling), and it decreases with increasing temperature. For a film of thickness $L$ with the boundary conditions $(2.9a-b)$, this equation is readily solved as

$$\phi(\zeta)=\tilde{\phi}_\alpha-\left(\tilde{\phi}_\alpha-\phi_s\right)\left(\frac{\cosh\left(\zeta-\frac{L}{2L_\alpha}\right)}{\cosh\left(\frac{L}{2L_\alpha}\right)}\right), \tag{3.3a}$$

where

$$\phi_s=\frac{\left\{\tilde{\phi}_\alpha\frac{\lambda_s}{L_\alpha}\tanh\left(\frac{L}{2L_\alpha}\right)+\frac{H_s\lambda_s}{c_s}\right\}}{\left\{1+\frac{\lambda_s}{L_\alpha}\tanh\left(\frac{L}{2L_\alpha}\right)\right\}}, \tag{3.3b}$$

which for $L\to\infty$ becomes

$$\phi(\zeta)=\tilde{\phi}_\alpha-\left(\tilde{\phi}_\alpha-\phi_s\right)e^{-\zeta},\ \phi_s=\frac{\left\{\tilde{\phi}_\alpha\frac{\lambda_s}{L_\alpha}+\frac{H_s\lambda_s}{c_s}\right\}}{\left\{1+\frac{\lambda_s}{L_\alpha}\right\}}. \tag{3.3c}$$

For $T<T_c$, one can also find and explicit solution of Eq. (2.8) by first multiplying it by $\frac{d\phi}{dz}$ and integrating over $z$ from 0 to $z$ to get

$$\begin{aligned}&\frac{B_\alpha}{4}\phi^4+\frac{A_\alpha}{2}\phi^2-\frac{1}{2}c_\alpha\left(\frac{\partial\phi}{\partial z}\right)^2-H\phi\\&=\frac{B_s}{4}\phi_s^4+\frac{A_s}{2}\phi_s^2-\frac{1}{2}c_s\left(\frac{\phi_s}{\lambda_s}-\frac{H_s}{c_s}\right)^2-H\phi_s.\end{aligned} \tag{3.4}$$

Using Eq. (2.15) once more for $(L\to\infty)$ and scaling variables as $z=\xi_b^-\zeta$, $\phi(z)=\phi_b\Omega(\zeta)$, $h=\frac{H\chi_b^-}{\phi_b}$, one finds

$$\zeta=\int_{\Omega_s}^{\Omega}\frac{d\Omega}{\sqrt{\left[\frac{1}{4}\frac{c_b}{c_\alpha}\left(\frac{B_\alpha}{B_b}\Omega^4-1\right)-\frac{1}{2}\frac{c_b}{c_\alpha}\left(\frac{A_\alpha}{A_b}\Omega^2-1\right)-2\frac{c_b}{c_\alpha}h(\Omega-1)\right]}}, \tag{3.5a}$$

the solution of this kind of integrals is given by

$$\begin{aligned}&\zeta(\Omega,h=0)\\&=\frac{L_\alpha}{\xi_b^+}\left[arctg\left\{\left(\frac{1}{4}\frac{A_b}{A_\alpha}-\frac{1}{2}\Omega^2+\frac{1}{4}\frac{A_b}{A_\alpha}\frac{B_\alpha}{B_b}\Omega^4\right)^{-\frac{1}{2}}\right\}\right.\\&\left.-arctg\left\{\left(\frac{1}{4}\frac{A_b}{A_\alpha}-\frac{1}{2}\Omega_s^2+\frac{1}{4}\frac{A_b}{A_\alpha}\frac{B_\alpha}{B_b}\Omega_s^4\right)^{-1/2}\right\}\right],\end{aligned} \tag{3.5b}$$

where $\frac{L_\alpha}{\xi_b^+}=\sqrt{\frac{c_\alpha}{A_\alpha}\frac{A_b}{c_b}}$ and $\Omega_s=\phi_s/\phi_b$ ($\phi_s$ being the solution of Eq. (2.15)).

Finally we consider the case $T=T_c$, $H=0$ but $H_s\neq 0$; in order to find the magnetization behavior induced in the bulk due to the field at the surface. Multiplying Eq. (2.8) by $\frac{d\phi}{dz}$ and integrating it over z, one finds

$$\frac{A_\alpha}{2}\phi^2+\frac{B_\alpha}{4}\phi^4-c_\alpha\left(\frac{\partial\phi}{\partial z}\right)^2=0. \tag{3.6}$$

Close to the surface where the variation of $\phi$ with $z$ is small, the solution of this differential equation writes then

$$\phi(z)=\frac{H_s}{c_s}\left(\frac{1}{\lambda_s}-\frac{1}{\sqrt{2}L_\alpha}\right)^{-1}exp\left(z/\sqrt{2}L_\alpha\right). \tag{3.7}$$

Both equations (3.3) and (3.7) show that the variation of the order parameter $\phi(z)$ depends on the scaled variable $z/L_\alpha$ only. For $H_s=0$, this variation of $\phi(z)$ results as an interplay of the two lengths $L_\alpha$ and $\lambda_s$, as illustrated in Figure 2(a). It is clear from Eqs. $(3.3c)$ that $\phi(z)$ varies linearly with $z$ near $z=0$, $\phi(\zeta)=\phi_s+\zeta(\tilde{\phi}_\alpha-\phi_s)$; if one extrapolates this linear variation to negative $z$, $\phi(z)$ vanishes for $z = -\lambda_s$. This fact explains the interpretation of $\lambda_s$ as an extrapolation length.

In order to introduce correction to bulk quantities we first obtain the average magnetization of a film of thickness $L$ for $T > T_c$, by averaging of Eq. $(3.3a)$. The results is

$$\tilde{\phi} = \frac{1}{L}\int_0^L \phi(z)dz = \frac{L_\alpha}{L}\int_0^{\frac{L}{L_\alpha}} \phi(\zeta)d\zeta = \left\{\tilde{\phi}_\alpha - \frac{2L}{L_\alpha}\left(\tilde{\phi}_\alpha - \phi_s\right)tanh\left(\frac{L}{2L_\alpha}\right)\right\}, \quad (3.8)$$

using Eq. $(3.3b)$, one obtain

$$\bar{\phi} = \tilde{\phi}_\alpha - 2\left(\tilde{\phi}_\alpha - \frac{H_s\lambda_s}{c_s}\right)\frac{\left(\frac{L_\alpha}{L}\right)}{coth\left(\frac{L}{2L_\alpha}\right) + \frac{\lambda_s}{L_\alpha}}. \quad (3.9)$$

Since the film has two surfaces, we define the surface magnetization $\tilde{\phi}_s$ as follows

$$\bar{\phi} = \tilde{\phi}_\alpha - \left(\frac{2}{L}\right)\tilde{\phi}_s, \tilde{\phi}_s = \frac{1}{2}\int_0^L dz\left[\tilde{\phi}_\alpha - \phi(z)\right]; \quad (3.10a)$$

while in the limit $L \to \infty$, where only the effect of the surface at $z = 0$ is considered, $\tilde{\phi}_s$ becomes

$$\tilde{\phi}_s = \int_0^\infty dz\left[\tilde{\phi}_\alpha - \phi(z)\right]. \quad (3.10b)$$

From Eq. $(3.3c)$, one then finds that

$$\tilde{\phi}_s = L_\alpha\left(\tilde{\phi}_\alpha - \phi_s\right) = \frac{L_\alpha^2}{L_\alpha + \lambda_\alpha}\left(\tilde{\phi}_\alpha - \frac{H_s\lambda_s}{c_s}\right). \quad (3.11)$$

Remembering that $\tilde{\phi}_\alpha = \frac{H}{A_\alpha}$ for $T > T_c$, Eq. (3.11) is actually an expression for a surface susceptibility $\tilde{\chi}_s$, defined in analogy to Eq. $(3.10a)$:

$$\bar{\chi} = \tilde{\chi}_\alpha - \left(\frac{2}{L}\right)\tilde{\chi}_s, \tilde{\chi}_s = \int_0^\infty dz\left[\tilde{\chi}_\alpha - \chi(z)\right], \quad \chi(z) = \frac{\partial\phi(z)}{\partial H}, \quad (3.12)$$

which for $H_s = 0$ and $t \to 0^+$ yields (using relation $(3.3c)$)

$$\tilde{\chi}_s^+ = L_\alpha\left(\tilde{\chi}_\alpha^+ - \chi_s^+\right) = \frac{L_\alpha^2}{\left(L_\alpha + \lambda_s\right)}\tilde{\chi}_\alpha^+, \quad \tilde{\chi}_\alpha^+ = \left(\frac{\partial\tilde{\phi}_\alpha}{\partial H}\right)_{H=0}, \quad (3.13)$$

the surface susceptibility $\tilde{\chi}_s^+$ finally writes

$$\tilde{\chi}_s^+ = \frac{L_\alpha^2}{\left(L_\alpha + \lambda_s\right)}A_\alpha^{-1}. \quad (3.14)$$

Notice that for a vanishing coupling constant $(C_o = 0)$ (case of the usual $\varphi^4$-theory), one has [20]:

$$\tilde{\chi}_s^+ \to \chi_b^+\xi_b^+ \sim t^{-3/2}.$$

# 4. The "extraordinary", "special" and "surface transitions"

In the previous sections treatment has been restricted to the case $0 < \lambda_s < \infty$, however, there is no physical reason to assume that the extrapolation length necessarily is positive. In fact, for the usual $\varphi^4$-theory, it has been shown [35] that a suitable enhancement of the interactions close to the surface can lead to $\lambda_s < 0$, and the special case $\lambda_s = \infty$ is also possible. Following Lubensky and Rubin [29] the previous case of a phase transition at a surface with $\lambda_s > 0$ is called the "*ordinary transition*", while the special case $\lambda_s = \infty$ will be called the "*special transition*". For $\lambda_s < 0$, the "*extraordinary transition*" occurs in the surface layer at $T_c$ due to the onset of order in the bulk, in addition to "*the surface transition*" at $T_{cs}$.

## 4.1. The Special Transition

For this case $(\lambda_s = \infty)$ it is only the surface field $H_s$ which provides a non trivial boundary condition at the surfaces. Indeed, for $H_s = 0$, we just have $\frac{\partial\phi}{\partial z} = 0$ (Eqs. (2.9)), and then the minimum of the free energy is reached if $\frac{\partial\phi}{\partial z} = 0$ everywhere in the system. In this trivial situation, $\phi_s$ and $\chi_s$ are equal to their bulk counterparts

$$\phi_s = \phi_b = \sqrt{-\frac{A_b}{B_b}} \cong \left(T - T_c\right)^{\frac{1}{2}}, \quad T \to T_c^-, H = 0, H_s = 0, \quad (4.1a)$$

$$\phi_s = \phi_b = \left(\frac{H}{B_b}\right)^{\frac{1}{3}} = \left(\frac{H}{u\eta_b^4 + v\left(1-\eta_b\right)^4}\right)^{\frac{1}{3}}, \quad T = T_c, H_s = 0, H \to 0^+ \quad (4.1b)$$

$$\chi_s^+ = \chi_b^+ = A_b^{-1} \cong \chi_o^+\left(T - T_c\right)^{-1}, \quad T \to T_c^+, H = 0, H_s = 0 \quad (4.1c)$$

$$\chi_s^- = \chi_b^- = -\frac{1}{2A_b} \cong \chi_o^-\left(T - T_c\right)^{-1}, \quad T \to T_c^-, H = 0, H_s = 0. \quad (4.1d)$$

From Eq. (2.15), in the limit $\lambda \to \infty$ and for $T > T_c$, we now obtain the response to the surface field $H_s$,

$$\phi_s \cong \left(\frac{1}{A_s c_s}\right)^{\frac{1}{2}} H_s, T \to T_c^+, \quad (4.2a)$$

$$\chi_{s,s}^+ \cong \left(\frac{1}{A_s c_s}\right)^{\frac{1}{2}}, T \to T_c^+, \quad (4.2b)$$

for $T < T_c$ the response of surface magnetization $\phi_s$ to the surface field $H_s$, writes,

$$\phi_s \cong \left(\frac{A_s}{B_s}\right)^{\frac{1}{2}} \left\{-1+\sqrt{1-\left(\frac{B_s A_b^2}{B_b A_s^2}-\frac{2B_s}{A_s^2 c_s}H_s^2\right)}\right\}^{\frac{1}{2}}, \quad (4.2c)$$

$T \to T_c^-$,

and at the critical temperature $T = T_c$ ($A_b = 0$), the surface magnetization becomes

$$\phi_s \cong \left(\frac{A_s}{B_s}\right)^{\frac{1}{2}} \left\{-1+\sqrt{1+\frac{2B_s}{A_s^2 c_s}H_s^2}\right\}^{1/2}, \quad T = T_c. \quad (4.2d)$$

The same result is obtained if one considers the response to a local field deep in the bulk (which then is independent of the extrapolation length $\lambda_s$). Notice finally that the "*special*" or $(\lambda_s = \infty)$-*transition* is sometimes called "*surface bulk*" (*SB*)-transition.

## 4.2. The Surface Transition

For negative extrapolation length $\lambda_s < 0$ the surface layer orders at a temperature $T_{cs} > T_c$. In the regime $T_c < T < T_{cs}$ the bulk correlation length $\xi_b$ is finite, and the order decays exponentially fast from its maximum value $\phi_s$ at the surface towards zero in the bulk (see Figure 1(c)). Recall that, in a previous work [30], we have shown that above the critical temperature and from Eq. (2.15), surface susceptibility $\chi_{s,s}^+$ is given by

$$\chi_{s,s}^+ = \left(\frac{\partial \phi_s}{\partial H_s}\right) \cong \frac{\lambda_s}{c_s}\left(\frac{1}{1-\lambda_s\sqrt{\frac{A_s}{c_s}}}\right), T > T_c, \quad (4.3)$$

we find $T_{cs}$ most easily from Eqs. (3.3$c$) and (4.3), noting that both $\chi_s^+$ and $\chi_{s,s}^+$ will diverge when $|\lambda_s| = \sqrt{\frac{c_s}{A_s}}$. The parameter $A_s$ behaves as:

$$A_s \cong \left(a(T_{cs})A(T_{cs}) - C_o^2\right) \sim \left(\frac{T_{cs}}{T_c} - 1\right),$$

which yields

$$t_{cs} = \left(\frac{T_{cs}}{T_c} - 1\right) = c_s \lambda_s^{-2}. \quad (4.4)$$

Using expressions of $\chi_s^+$ and $\chi_{s,s}^+$ yields, for small $t_s = \left(\frac{T}{T_{cs}} - 1\right)$,

$$\chi_s^+ \sim t_s^{-1}, \ \chi_{s,s}^+ \sim \left(\frac{1}{2c_s} t_{cs}^{1/2}\right) t_s^{-1}. \quad (4.5)$$

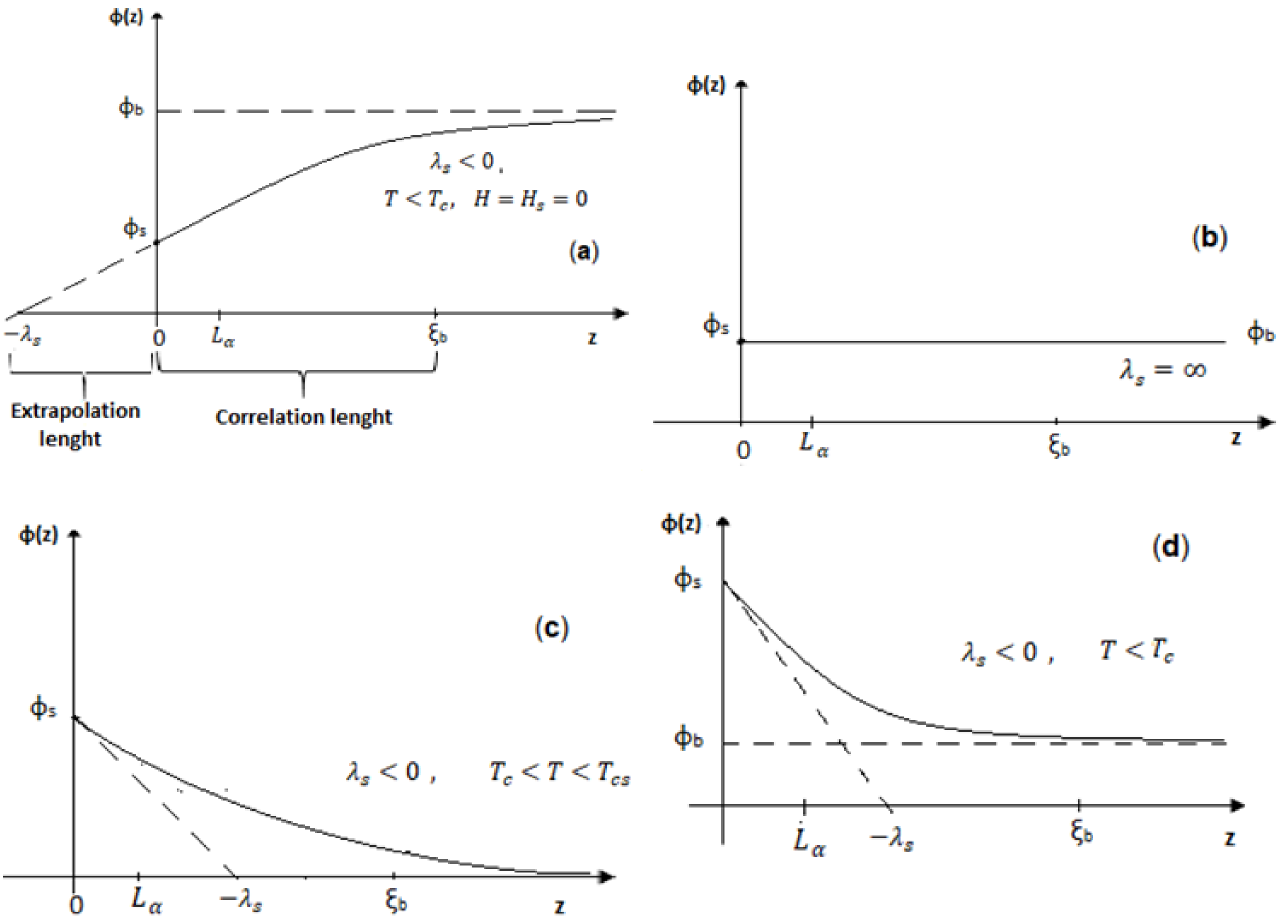


**Figure 1.** Schematic magnetization profiles near a free surface, according to the model which is of Ginzburg-Landau type. **(a)** Extrapolation length $\lambda_s > 0$ (ordinary transition). **(b)** Extrapolation length $\lambda_s = \infty$ (special transition). **(c)** Extrapolation length $\lambda_s < 0$, $(T > T_c)$ (surface transition). **(d)** Extrapolation length $\lambda_s < 0$, $(T < T_c)$ (extraordinary transition).

For $t_s < 0$ we immediately find from Eq. $(2.15)$ that, for $H_s = 0, H = 0$ and small $|\lambda_s^{-1}|$,

$$\phi_s \sim \sqrt{\frac{2}{B_s}}\left(-t_s\right)^{1/2}, t_s \to 0^-, \qquad (4.6)$$

while at $T = T_{cs}$ we have

$$\phi_s \sim \left(\frac{4}{B_s}\sqrt{\frac{t_{cs}}{c_s}}\right)^{1/3} H_s^{1/3},\ H_s \to 0,\ H = 0, \qquad (4.7a)$$

and

$$\phi_s \sim \left(\frac{4}{B_s}\right)^{1/3} H^{1/3},\ H \to 0,\ H_s = 0. \qquad (4.7b)$$

As expected, at the surface transition the surface layer shows the critical behavior of a bulk system, just the prefactors in the asymptotic laws, Eqs. $(4.5) - (4.7)$, differ from those of Eqs. $(2.10a - b)$ and $(2.12)$.

## 4.3. The Extraordinary Transition

At the surface and for $\lambda_s < 0$ and $T_c < T < T_{cs}$ $\left(or\ 0 < t = \frac{T - T_c}{T_c} < t_{cs} = \frac{T_{cs} - T_c}{T_c}\right)$, order already exists; but the divergence of bulk correlation length at $T_c$ and the onset of order in the bulk induce singularities in the behavior of surface quantities. Using Eq. $(2.30)$, we once again analyse these singularities. At critical temperature $T_c$ the bulk magnetization is zero, we have then for $H_s = 0$ and $H = 0$

$$\phi_s^2 \cong \frac{2c_s}{B_s\lambda_s^2} - \frac{2}{B_s}t,\ 0 < t < t_{cs} = c_s\lambda_s^{-2}, \qquad (4.8a)$$

$$\phi_s^2 \cong \frac{2c_s}{B_s\lambda_s^2} - \frac{2}{B_s}t - \frac{1}{2}\frac{\lambda_s^2}{B_s c_s}t^2,\ t \to 0^-. \qquad (4.8b)$$

At $T_c$ the order parameter profile decays algebraically from $\phi_s = \sqrt{2c_s/B_s\lambda_s^2}$ at the surface to zero in the bulk. The susceptibilities $\chi_s$ and $\chi_{s,s}$ near $T_c$ become

$$\chi_s \sim \left(\frac{c_s}{\lambda_s^2} - t\right)^{-1},\ t > 0, \qquad (4.9a)$$

$$\chi_s \sim \left(\frac{c_s}{\lambda_s^2} - t\right)^{-1}\left[1 + \frac{\lambda_s}{\sqrt{2c_s}}(-t)^{1/2}\right],\ t < 0, \qquad (4.9b)$$

and

$$\chi_{s,s} \sim \left|\lambda_s^{-1}\right|\left(\frac{c_s}{\lambda_s^2} - t\right)^{-1},\ t > 0, \qquad (4.10a)$$

$$\chi_{s,s} \sim \left|\lambda_s^{-1}\right|\left(\frac{c_s}{\lambda_s^2} - t\right)^{-1}\left[\frac{c_s}{\lambda_s^2} - t - \frac{\lambda_s^2}{2c_s}t^2\right]^{-1},\ t \to 0^-. \qquad (4.10b)$$

# 5. Concluding Remarks

In this work, which is an extension of a previous one dealt with the critical properties at surfaces of strong coupling paramagnetic systems undergoing a para-ferrimagnetic transition, we have investigated the full order parameter profiles of the system close to the surface. We have, foremost, used the model written as an effective $\varphi^4$-theory, in terms of the overall magnetization $\phi$ and the fraction of the magnetization $\eta$. In this context, all information about the system like the dependence in temperature (through $a(T)$ and $A(T)$), the coupling constant $C_o$ and the competition between them are involved in the phenomenological constants of the model.

In order to get correction to bulk quantities, we have considered the full profile of the magnetization $\phi_\alpha(z)$ close to the surface. We have, in particular, determined the order parameter near surface $\phi_s$, and found that, in addition to the thickness $L$ of the film and the extrapolation length $\lambda_s$, $\phi_s$ depend also on a length $L_\alpha = \sqrt{c_\alpha/A_\alpha}$. This latter is interpreted as the width of the ordered ferrimagnetic layer near surface. For a zero coupling constant ($C_o = 0$), where the two sublattices are decoupled (case of the usual $\varphi^4$-theory), $L_\alpha$ reduces to the bulk correlation length $\xi_b^-$. Note that this length $L_\alpha$ increases for a strong coupling $C_o$ ($C_o > aA$), and conversely it decreases for a high temperature (weak coupling $(C_o < aA)$). We have also derived the expression of the surface susceptibility $\chi_s$ and found that it not depend on the shift to critical temperature $(T - T_c)$.

Finally we have considered the *special* $(\lambda_s = \infty)$, *surface* $(\lambda_s < 0)$ and *extraordinary* transitions. At the surface transition, the surface layer shows a critical behavior similar to that of the bulk system, the main difference lies only in the amplitudes in the asymptotic laws. For all cases, we have derived the expressions of surface magnetization $\phi_s$ and the surface susceptibility $\chi_s$ and $\chi_{s,s}$.

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