Surface states in nearly modulated systems

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A Landau model is used to study the phase behavior of the surface layer for magnetic and cholesteric liquid-crystal systems that are at or near a Lifshitz point marking the boundary between modulated and homogeneous bulk phases. The model incorporates surface and bulk fields and includes a term in the free energy proportional to the square of the second derivative of the order parameter in addition to the usual term involving the square of the first derivative. In the limit of vanishing bulk field, three distinct types of surface ordering are possible: a wetting layer, a nonwet layer having a small deviation from bulk order, and a different nonwet layer with a large deviation from bulk order that decays nonmonotonically as the distance from the wall increases. In particular, the large deviation nonwet layer is a feature of systems at the Lifshitz point and also those systems having only homogeneous bulk phases.

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I. INTRODUCTION

The interaction of a bulk system with a wall may give rise to a large variety of surface phenomena, associated with the thermodynamic behavior of the surface layer adjacent to the wall. For example, in ferromagnetic systems, when the interaction with the wall is such that it enhances local order, it may happen that a surface transition takes place at temperatures above the critical temperature of the bulk. In such a transition, the layers close to the wall become ordered although the bulk remains disordered. Depending on the nature of the interactions within the bulk and the interactions between the bulk and the wall, the system may exhibit phenomena such as wetting, critical wetting, prewetting, and other surface phase transitions. These phenomena have been extensively studied both theoretically and experimentally in recent years (for a review, see [1]).

A study of the global phase diagram for surface critical phenomena in ferromagnetic and other homogeneously ordered systems has been carried out by Nakanishi and Fisher [2]. In this study, a Landau phenomenological approach has been applied and the phase diagram has been analyzed in the space of temperature, surface enhanced interactions, and bulk and surface ordering fields. For example, it has been found that for finite positive surface field and no surface enhanced interactions, and in the limit of a vanishingly small negative bulk field, the system exhibits a wetting transition as the temperature is varied below the bulk ordering temperature. At low temperatures, the surface field induces a local order in a layer of finite thickness l near the wall. However, at temperatures just below the bulk ordering temperature, the thickness of the surface layer is infinite, yielding a ''wet'' state. The two regimes are separated by a first-order transition in which the thickness of the layer undergoes a discontinuous jump. This is known as the wetting transition.

More recently, surface phenomena in *modulated systems* have been considered. These systems are characterized by a periodic spatial variation of the order parameter in the bulk. Examples are magnetic spirals, cholesteric liquid crystals, amphiphilic systems, diblock copolymers, and many others. In many cases, the modulated phase is driven by a gradient-squared term with negative coefficient in the Landau free energy. The system is then stabilized by terms quadratic in the second derivative. Studies of surface phenomena in such systems suggest that surface phase diagrams are rather rich, exhibiting novel surface states [3] and complicated surface structures [4–6]. However, the possible global phase diagrams of these systems have not been fully explored.

Systems exhibiting a Lifshitz point may be considered as intermediate between ferromagnetic and modulated [7–9]. In the Landau free energy of such systems, the coefficient of the gradient-squared term vanishes, making the quadratic term in the second derivatives the leading-order interaction term. Surface phase diagrams of these systems have not been explored so far and it would be of interest to study them in some detail.

In this paper, we study the surface states and the surface phase diagram corresponding to a model of a Lifshitz point within the Landau approach. The phase diagram is studied in the space of temperature, bulk, and surface fields. It is found that unlike the ferromagnetic case, these systems do not exhibit a wet phase in which the thickness of the surface layer diverges. It rather exhibits a transition from one surface state to another, as the temperature is varied, where *both* surface states have a finite thickness.

We also consider the surface phase diagram of a ferromagnetic system, which is characterized by higher-order interaction terms. Specifically, we consider a Landau free energy which includes terms quadratic in the gradient and in the second derivatives of the order parameter, both with positive coefficient. As is well known, the quadratic term in the second derivatives does not affect the bulk phase diagram as long as the sign of its coefficient is positive. However, we find, rather surprisingly, that although this term does not introduce any competing with the gradient-squared term, it affects the surface diagram in a profound way. In particular, we find that in addition to the usual wet and nonwet states that exist in the model of Nakanishi and Fisher, the model exhibits a second nonwet state with a distinct structure of the order parameter near the surface. Numerical studies yield the global phase diagram of the model.

The paper is organized as follows. In Sec. II, we review the model of Nakanishi and Fisher, and present analytic expressions for the location of the wetting and the critical prewetting points. Results of a numerical study of the surface phase diagram corresponding to the model with a Lifshitz point are presented in Sec. III. The surface states and the surface phase diagram of the generalized ferromagnetic model are discussed in Sec. IV. Finally, a short summary is given in Sec. V.

II. FERROMAGNETIC MODEL

In this section, we consider the surface phase diagram of a ferromagnetic system in the space of temperature and bulk and surface ordering fields. The phase diagram exhibits wetting, prewetting, and critical prewetting transitions. The Landau phenomenological model of Nakanishi and Fisher is reviewed, and analytic expressions for the wetting and the critical prewetting points are given. In this model, the ferromagnetic interaction is simply introduced by a gradient-squared term with a positive coefficient. Extensions of this model to other ferromagnetic systems with higher-order ferromagnetic interactions and to systems exhibiting Lifshitz points will be discussed in the following sections.

Let $\phi(x)$ be the scalar order parameter that corresponds to the ferromagnetic order. The wall is taken to be in the y-z plane, and the order parameter is assumed to depend only on the coordinate x perpendicular to the wall. The Landau free energy is given by

$$F=\int_0^L dx[-h\phi+\tfrac{1}{2}r\phi^2+\tfrac{1}{4}\phi^4+\tfrac{1}{2}(\phi')^2]-h_s\phi_s, \quad (1)$$

where $\phi_s=\phi(0)$ denotes the value of the order parameter at the wall and $\phi'=d\phi/dx$. The system is assumed to be of length L in the x direction. In calculating the surface free energy, we will take the limit $L\to\infty$. We have scaled the order parameter, the energy, and the unit of length to simplify the coefficients, and so the bulk field h, the temperature r, and the surface field h_s are rescaled variables.

The (r,h) phase diagram of this model for nonvanishing surface field $h_s>0$ is given schematically in Fig. 1 [2]. The order parameter away from the wall is not affected by the surface field. For a negative bulk field, $h<0$, it approaches a negative value characteristic of the bulk. On the other hand, the surface field enhances the order within a layer of thickness l. The thickness of this layer undergoes a discontinuous change along the prewetting transition line in the figure. For $h=0$, this becomes the first-order wetting transition (WT). The line ends at some critical point (CP) known as the critical prewetting point. The low-temperature surface state, existing to the left of the line, is the prewet state (PW). It is characterized by a surface layer with a finite width. The state to the right of the line is the wet state (W), in which the width of the surface layer diverges in the limit of vanishing bulk field. In the following, we analyze the Landau free energy (1) and obtain analytic expressions for the wetting WT and the critical prewetting CP points.

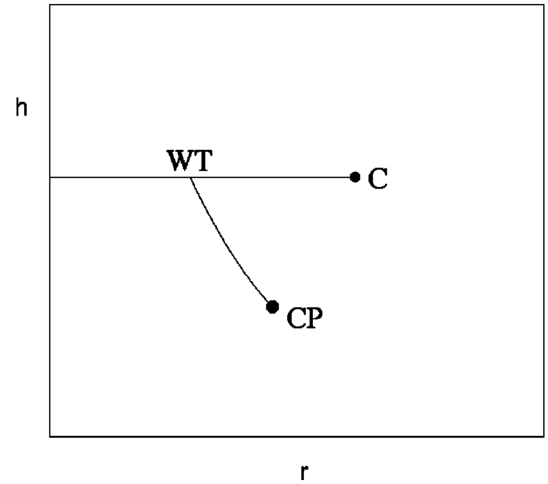

FIG. 1. A schematic (r,h) phase diagram of the Nakanishi-Fisher model for $h_s>0$. The horizontal line represents the bulk coexistence line, which terminates at an ordinary critical point C. The curved line at negative bulk fields is the prewetting transition line on which the two types of surface solutions coexist. This line intersects the $h=0$ axis at the wetting point WT, which separates the dry phase existing at large negative r [known as the prewet phase (PW)] from the wet phase (W), which exists close to the critical point. The prewetting transition line terminates at the critical prewetting point CP, where the two surface solutions become identical. The width l of the surface layer of the wet and the prewet phases is finite for nonvanishing bulk field. However, l diverges in the limit $h\to0^-$ in the wet phase.

The Euler-Lagrange equation corresponding to the free energy (1) is

$$\phi''+h-r\phi-\phi^3=0 \quad (2)$$

with the boundary condition at $x=0$,

$$h_s=-\phi_s'. \quad (3)$$

We are interested in calculating the order-parameter profile and free energy for negative bulk field $h<0$ and positive surface field $h_s>0$. We thus expect that for large x, the order parameter approaches the bulk value $-\phi_B$, where $\phi_B>0$ satisfies

$$h+r\phi_B+\phi_B^3=0. \quad (4)$$

Multiplying Eq. (2) by ϕ', this equation may be integrated to yield

$$\tfrac{1}{2}r\phi^2+\tfrac{1}{4}\phi^4-h\phi-\tfrac{1}{2}(\phi')^2=C, \quad (5)$$

where C is a constant. This constant may be evaluated by noting that at large x, the order parameter asymptotically approaches $-\phi_B$. Thus

$$C=\tfrac{1}{2}r\phi_B^2+\tfrac{1}{4}\phi_B^4+h\phi_B. \quad (6)$$

Using this result, the first integral of the Euler equation (2) becomes

$$\frac{d\phi}{dx} = -|\phi+\phi_B|\sqrt{\frac{1}{2}(\phi-\phi_B)^2-\frac{h}{\phi_B}}, \tag{7}$$

where the $-$ sign on the right-hand side is taken since for the choice of the bulk and surface fields in this problem the order parameter is expected to decrease with x.

In order to locate the wetting point WT, we take the limit $h \to 0^-$ in Eq. (7),

$$\frac{d\phi}{dx} = -\frac{1}{\sqrt{2}}|\phi^2-\phi_B^2|. \tag{8}$$

In order to evaluate the surface free energy F_s associated with the local surface order, we note that the free-energy density of the bulk state is given by C. Thus $F_s = F - CL$. Using Eqs. (1), (4), and (6), one obtains

$$F_s = F - CL = \int_0^L dx(\phi')^2 - h_s\phi_s \tag{9}$$

or

$$F_s = \int_{\phi_s}^{-\phi_B} d\phi \frac{d\phi}{dx} - h_s\phi_s. \tag{10}$$

We proceed by evaluating the order-parameter profile obtained from Eq. (8). Two distinct types of profiles are found: $\phi_1(x)$ for negative and large r and $\phi_2(x)$ for negative and small r, close to the bulk critical point. These profiles are schematically given in Fig. 2. For large r, the surface field does not affect the local surface order in a substantial way and thus the surface order parameter ϕ_{s1} remains close to the bulk value, satisfying $-\phi_B < \phi_{s1} < \phi_B$. Integrating Eq. (8), one finds the surface free energy for this type of solution,

$$F_{s1} = \frac{\sqrt{2}}{3}(\phi_B^3 + \phi_{s1}^3), \tag{11}$$

where the surface order parameter, ϕ_{s1}, is determined by the boundary equation

$$h_s = \frac{1}{\sqrt{2}}(\phi_B^2 - \phi_{s1}^2). \tag{12}$$

On the other hand, for small r the local order is highly susceptible to the local ordering field and one obtains an order-parameter profile $\phi_2(x)$ that at the surface is considerably different from the bulk value, satisfying $\phi_{s2} > \phi_B$. Integrating Eq. (8) for this solution, one obtains the surface free energy,

$$F_{s2} = \sqrt{2}\phi_B^3 - \frac{\sqrt{2}}{3}\phi_{s2}^3 \tag{13}$$

with the surface order parameter satisfying

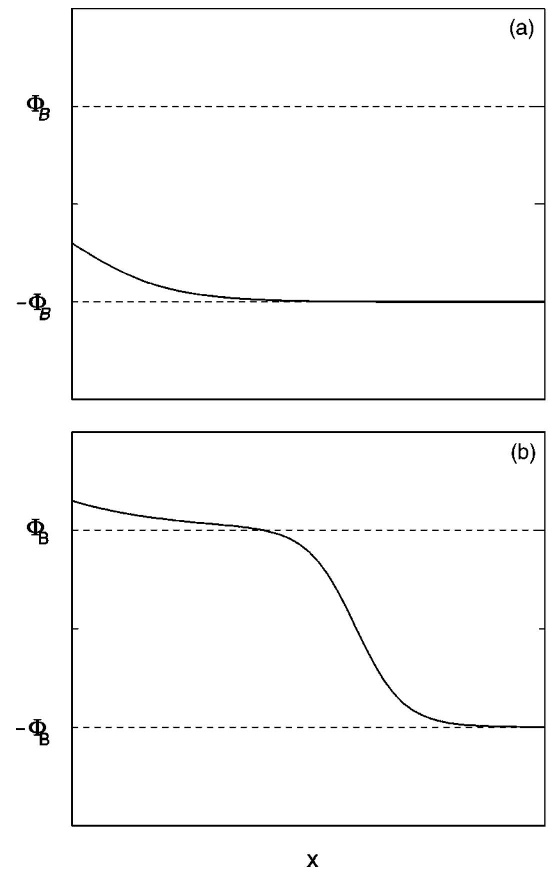

FIG. 2. Schematic order-parameter profiles for $h<0$ and $h_s>0$, (a) at large negative r and (b) close to the bulk critical line. In the limit $h \to 0^-$, the width of the surface layer of solution (b) diverges, leading to a wet state.

$$h_s = \frac{1}{\sqrt{2}}(\phi_{s2}^2 - \phi_B^2). \tag{14}$$

At the wetting transition, the two types of solutions have the same free energy. To find the transition point, we define $y_1 = \phi_{s1}/\phi_B$, $y_2 = \phi_{s2}/\phi_B$. At the coexistence point, one has

$$y_1^3 + y_2^3 = 2. \tag{15}$$

In addition, the boundary condition equations (12) and (14) impose the following relation between y_1 and y_2:

$$y_1^2 + y_2^2 = 2. \tag{16}$$

To solve Eqs. (15) and (16), we use the substitutions $y_1^2 = 1 - u$ and $y_2^2 = 1 + u$, where $u = h_s\sqrt{2}/\phi_B^2$. Equation (15) is then readily solved, yielding $u^2 = \sqrt{12} - 3$. The wetting transition thus takes place at

$$h_s = -\frac{r}{\sqrt{2}}\sqrt{\sqrt{12}-3}. \tag{17}$$

To locate the critical prewetting CP point, we consider the boundary equation (3). Combining it with the expression for the order-parameter derivative (7), it may be written as

$$G(\phi_s)\equiv\phi_s^4+2r\phi_s^2-4h\phi_s+(\phi_B^4-2h\phi_B-2h_s^2)=0. \tag{18}$$

This equation determines the surface order parameter ϕ_s for given r, h, and h_s. At the critical prewetting point, the two solutions of this equation, which correspond to the two coexisting states on the prewetting line, become identical. The conditions for this to take place are $\partial G/\partial\phi_s=\partial^2G/\partial\phi_s^2=0$. These equations together with Eq. (18) yield the critical prewetting point

$$r=-\sqrt{\tfrac{2}{3}}h_s,\qquad h=-2(\tfrac{2}{27})^{3/4}h_s^{3/2}. \tag{19}$$

It is of interest to explore the general validity of this global phase diagram by considering Landau free energies with different nonlinear terms. To this end, we studied the phase diagram of a Landau model with piecewise parabolic potential,

$$F=\int_0^L dx[-h\phi+f(\phi)+\tfrac{1}{2}(\phi')^2]-h_s\phi_s, \tag{20}$$

where

$$f(\phi)=\begin{cases}\tfrac{1}{2}a^2(\phi-\phi_0)^2, & \phi\geqslant 0\\ \tfrac{1}{2}a^2(\phi+\phi_0)^2, & \phi<0\end{cases} \tag{21}$$

and the parameters a and ϕ_0 are dependent on r. The analysis presented above for the Nakanishi-Fisher model may be extended to study the phase diagram of the Landau free energy (20). It is found that the (r,h) phase diagram of the two models exhibits the same qualitative features. The wetting transition takes place at

$$h_s=\tfrac{1}{2}a\phi_0 \tag{22}$$

while the critical prewetting point is found to be located at

$$h_s=2a\phi_0,\qquad h=-a^2\phi_0. \tag{23}$$

III. LIFSHITZ POINT MODEL

In this section, we study the surface phase diagram corresponding to a model of a Lifshitz point in the presence of a surface ordering field. We consider the Landau free energy

$$F=-h_s\phi_s+\int_0^L dx[-h\phi+\tfrac{1}{2}r\phi^2+\tfrac{1}{4}\phi^4+\tfrac{1}{2}v(\phi')^2+\tfrac{1}{2}(\phi'')^2] \tag{24}$$

with $v=0$. This model for $v>0$ will be considered in the next section. The Euler-Lagrange equation corresponding to this free energy is

$$\phi''''-v\phi''-h+r\phi+\phi^3=0 \tag{25}$$

with the boundary equations at

$$-v\phi_s'+\phi_s'''-h_s=0,\quad \phi_s''=0. \tag{26}$$

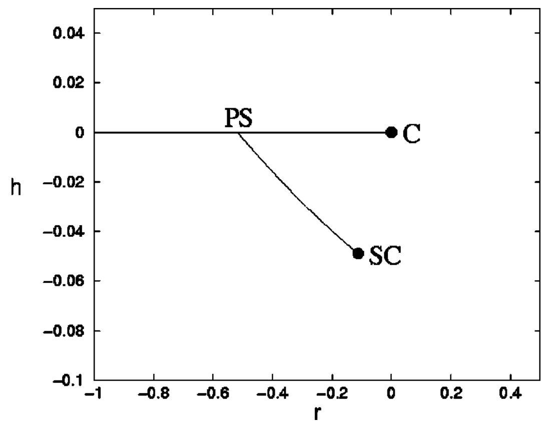

FIG. 3. The (r,h) phase diagram corresponding to the Lifshitz point model for $h_s=0.1$. The phase diagram displays two nonwet states: a prewet state (PW) and a state with surface enhanced order (S). The two phases are separated by a first-order line. This line intersects the $h=0$ axis at the point PS. It terminates for finite h at a surface critical point SC.

We have integrated numerically Eq. (25) with the boundary conditions (26) for $v=0$, corresponding to the case of a Lifshitz point. We find that, unlike the ferromagnetic case, the model does *not* exhibit a wet phase. Rather it exhibits two distinct phases [a prewet state (PW) and a state (S) with surface enhanced order] both characterized by surface states with a finite width. Here, in analogy with the phase diagram of the Nakanishi-Fisher model, we keep referring to the low-temperature state as the prewet phase, although the phase diagram does not exhibit a wet state at all. The resulting (r,h) phase diagram for $h_s=0.1$ is given in Fig. 3. The diagram displays a first-order transition line separating the two surface phases PW and S. The line terminates at a surface critical point SC. This line intersects the $h=0$ axis at the point PS.

Representative order-parameter profiles in the two nonwet phases are given in Fig. 4 for small bulk field h. At low temperatures $(r\ll-1)$, the surface field introduces only a

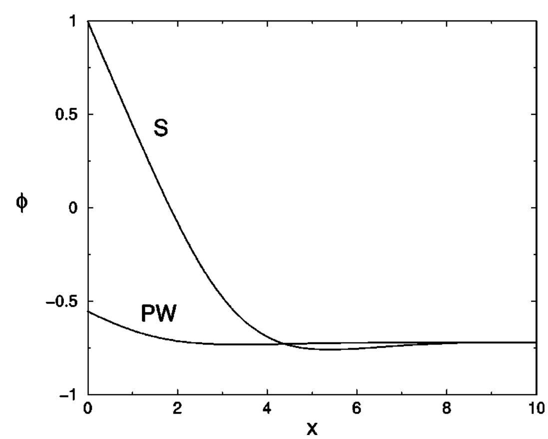

FIG. 4. Characteristic profiles of the order parameter of the two nonwet states PW and S. The profiles are given at a point on the coexistence line of the two states, close to the point PS of Fig. 3, where $h\to0^-$, $r=-0.520\,08$, $h_s=0.1$, and $h=-10^{-6}$.

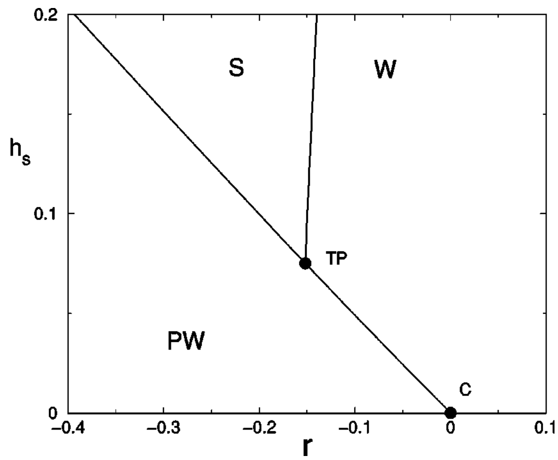

FIG. 5. The (r,h_s) phase diagram of the extended ferromagnetic model in the limit $h\rightarrow 0^-$. It displays three distinct states: a wet state (W) and two nonwet states $(PW$ and $S)$. The state S is characterized by surface enhanced order (see Fig. 6). The phases are separated by three first-order lines, which intersect at a triple point TP. The bulk critical point is denoted by C.

weak local order near the surface, and the order parameter decays monotonically to its bulk value as one moves away from the wall. This is very similar to the low-temperature phase of the ferromagnetic case. However, at higher temperatures, just below the bulk critical point, the order parameter becomes highly susceptible to the local surface field, the surface order parameter is much larger than the bulk value, and it decays in a nonmonotonic way to the bulk value away from the wall. The width of the surface layer remains finite even in the limit $h\rightarrow 0^-$. This is in sharp contrast to the ferromagnetic case, in which the width diverges in this limit, leading to a wet state.

IV. EXTENDED FERROMAGNETIC MODEL

In this section, we consider the extended ferromagnetic model (24) with $v=1$. We restrict this study to negative bulk fields in the limit $h\rightarrow 0^-$ and evaluate the (r,h_s) phase diagram.

For small surface fields, the model is found to yield surface phenomena similar to the model of Nakanishi and Fisher. It exhibits a wet phase (W) at temperatures below the bulk critical point and a prewet state (PW) at low temperatures. The two states are separated by a first-order wetting transition.

However, the phase diagram becomes rather different for large h_s. Here, in addition to the wet state existing at high temperatures, one finds *two* distinct surface phases at lower temperatures: a phase with a surface enhanced order (S) and a prewet phase (PW). The two phases are separated from each other by a first-order transition. The resulting (r,h_s) phase diagram is given in Fig. 5. We also display some characteristic order-parameter profiles of the three phases. Figure 6 gives the profiles at a point on the PW-S coexistence line, while the profiles at a point on the PW-W line are given in Fig. 7.

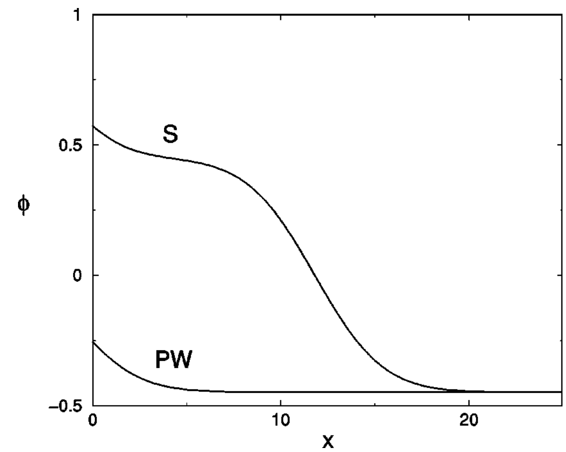

FIG. 6. Characteristic profiles of the order parameter at a point along the PW-S coexistence line for $h\rightarrow 0^-$. The profiles are given for $r=-0.2$, $h_s=0.099\,67$, and $h=-10^{-10}$. It is evident that while in the S state the surface order is highly susceptible to the surface field, the surface order in the PW state is affected only mildly by this field.

V. SUMMARY

Using a general Landau model, we have studied the surface phase diagrams that result from the effect of a wall bounding a semi-infinite sample that exhibits homogeneous bulk phases. The model is applicable to a wide variety of systems including magnetic materials and cholesteric liquid crystals.

Choosing coefficients to simplify the model to the ferromagnetic model studied by Nakanishi and Fisher, we obtained analytic expressions for the temperature and bulk field co-ordinates of the wetting transition point and the critical prewetting point as functions of the surface field. We also demonstrated that the general surface phase diagram is not highly sensitive to the precise form of the nonlinear terms.

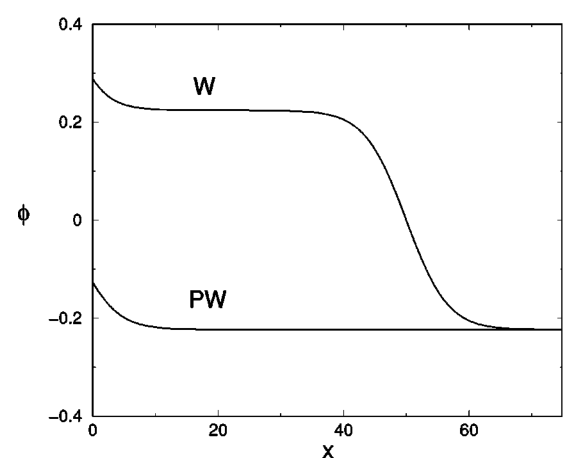

FIG. 7. Characteristic profiles of the order parameter at a point along the PW-W coexistence line for $h\rightarrow 0^-$. The profiles are given for $r=-0.05$, $h_s=0.024\,33$, and $h=-10^{-10}$. Note that in this figure the flat part of the W state has been truncated, as the width of the surface layer of this state diverges in the limit of vanishing bulk field.

In contrast, we found that a system at the Lifshitz point is similar to the case of modulated bulk phases where a wetting layer does not form. Instead, a nonwet surface state forms that decays nonmonotonically. The wetting transition is replaced by a transition between the two types of nonwet states and the critical prewetting point becomes a surface critical point.

In the extended ferromagnetic model, we examined only the case of vanishing bulk field and found that all three types of surface layers develop if the surface field is not too weak. As temperature is reduced from the bulk critical point, a wetting transition occurs, followed at even lower temperatures by a transition from a highly deviated to a weakly deviated nonwet layer. Unfortunately, we are not aware of any experimental observations of such a transition so far. This is, however, not surprising because it is a subtle change that has not been expressly looked for.

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