Nonuniversal anisotropy dependence of critical-wetting exponents in a vector model

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A Landau theory of critical wetting is discussed for two anisotropic vector models of a semi-infinite ferromagnet. In one case (cubic anisotropy) the existence of two competing length scales leads to mean-field critical exponents which are nonuniversal and depend on the anisotropy constant. This behavior is determined by the form of the tails of the magnetization profiles at the free interfaces of the model. In the second case, a model with uniaxial anisotropy, the particular form of the free interfacial profiles is governed by a single length scale and yields only universal wetting behavior at the mean-field level.

I. INTRODUCTION

A wetting transition[1] may be described as the intrusion at the interface between two bulk phases B and C of a third phase, A, as some thermodynamic field is varied at bulk three-phase coexistence. It is often convenient to consider C to be an inert, spectator phase which simply exerts a potential on the A-B system. In the present context we employ magnetic terminology and C is a flat substrate, taken to exert a localized magnetic field on the spins in the surface layer of a semi-infinite ferromagnet, so as to favor one of the bulk phases A. The system is prepared such that the bulk phase far from the substrate is B. On raising the temperature in zero applied bulk field the thickness of the layer of A "wetting" the substrate-B interface may diverge at some (wetting) temperature T_W. Depending on the particular system this transition may be either first order or continuous (critical wetting), in which case it is accompanied by a diverging transverse correlation length $\xi_{\parallel}$, associated with capillary-wave-like fluctuations in the depinning A-B interface.[1,2] Critical wetting has been the subject of considerable theoretical attention, although the difficulties inherent in experimental studies mean that there has so far been no unambiguous observation thereof.

Wetting is commonly encountered in the study of fluids in contact with solid substrates, where A and B refer to bulk-liquid and gas phases, respectively. In such situations the order parameter associated with the bulk transition is a scalar quantity. A mean-field analysis of wetting transitions in a system with a two-component order parameter has been provided by Hauge,[3] wherein it was shown that the existence of two competing length scales provided a regime in which $\nu_{\parallel}$, the exponent associated with the divergence of $\xi_{\parallel}$, was nonuniversal. In particular, $\nu_{\parallel}$ was shown to depend on the ratio of the two length scales.

The purpose of this communication is to draw attention to a model in which this ratio depends on a single temperature-independent parameter, the anisotropy coefficient. This is the case for a semi-infinite two-component vector model with cubic anisotropy, although the arguments could easily be applied to models with more components. In Sec. II we introduce the model concerned and demonstrate, following the arguments of Hauge,[3] the anisotropy dependence of $\nu_{\parallel}$ at the level of Landau theory. Section III then contrasts this case with that of a model with uniaxial anisotropy, for which an increase in temperature is accompanied by a change in the nature of the A-B interface which precludes the possibility of nonuniversal mean-field exponents.

II. CUBIC ANISOTROPY

The model we consider has been studied in the context of free interfaces in a system of infinite extent by Subbaswamy and Trullinger.[4] In applying it here, we simply include some plausible surface-free-energy terms along the lines of those usually derived from a lattice-gas (Ising model) treatment of a fluid in contact with an inert substrate.[1]

If we take the surface of the substrate ("the wall") to be the $z=0$ plane, then, provided surface and bulk magnetic fields do not depend on the transverse position (x,y), a mean-field analysis will yield extremal solutions for the magnetization which depend only on the coordinate z perpendicular to the wall. It is then convenient to consider the one-dimensional problem described by the following functional, the minimum value of which is the excess free energy per unit area:

$$\tilde{\sigma}_s[\mathbf{M}(z)]=u\left[\int_0^{\infty}dz\left[\frac{\xi_0^2}{2}\left|\frac{d\mathbf{M}(z)}{dz}\right|^2+f(\mathbf{M}(z))-f(\mathbf{M}_b)\right]+\xi_0 f_s(\mathbf{M}(0))\right], \qquad (1)$$

where

$$f(\mathbf{M})=\frac{t}{2}(M_x^2+M_y^2)+\tfrac{1}{4}(M_x^4+M_y^4)+\frac{\lambda}{2}M_x^2M_y^2-\mathbf{H}\cdot\mathbf{M}, \qquad (2)$$

$$f_s(\mathbf{M})=\frac{\xi_0 c}{2}(M_x^2+M_y^2)-\mathbf{H}^s\cdot\mathbf{M}, \qquad (3)$$

and t is the usual reduced temperature $(T-T_c)/T_c$. $\mathbf{H}$ is a uniform bulk magnetic field, while ξ_0 and u are constants with dimensions of length and energy per unit volume, respectively. λ is a measure of the anisotropy and equals unity in the isotropic limit. $\lambda>1$ favors alignment of the spins along a crystal axis, as opposed to along a body diagonal, which is preferred for $\lambda<1$. The surface terms may be interpreted as follows. That involving c accounts for a possible enhancement (or dehancement, according to the value of c) of the interaction between spins in the surface layer (i.e., at $z=0$), while $\mathbf{H}^s$ is the localized field acting on spins in this layer. In the Ising case it is the value of c which determines the order of the wetting transition,[1] which, if continuous, occurs as $\tau\equiv\xi_0 cM_b-H^s\to0^+$. We shall see that the anisotropy parameter λ also plays an important role in the present model.

Notice that in the intgrand of Eq. (1) we have subtracted the free-energy density of a uniform bulk magnetization $\mathbf{M}_b$ so that $\tilde{\sigma}_s$ is a functional representing the excess free energy over and above that obtained if the bulk phase approached right up to the wall.

On minimization $\tilde{\sigma}_s[\mathbf{M}(z)]$ yields

$$\xi_0^2\frac{d^2M_\alpha}{dz^2}=\frac{\partial f}{\partial M_\alpha}\quad(\alpha=x,y)\ , \tag{4}$$

with the boundary conditions

$$\xi_0\frac{dM_\alpha}{dz}\bigg|_{z=0}=\frac{\partial f_s}{\partial M_\alpha(0)}\ , \tag{5}$$

$$\lim_{z\to\infty}\frac{\partial f}{\partial M_\alpha}=0\ . \tag{6}$$

The solution of these could be achieved on obtaining two separate first integrals of Eq. (4). Unfortunately, these equations are coupled owing to the term involving λ in $f(\mathbf{M})$. However, one integral obtainable for all values of λ is

$$\frac{\xi_0^2}{2}\left|\frac{d\mathbf{M}(z)}{dz}\right|^2=f(\mathbf{M}(z))-f(\mathbf{M}_b)\ . \tag{7}$$

At best one can hope to proceed further for a specific value of λ by a judicious change of variables. Indeed, we have shown previously[5] that, for $\lambda=3$, using $P\equiv M_x+M_y$ and $Q\equiv M_x-M_y$, one may decouple the equations into forms identical to those previously obtained in the Ising model case.

For general λ we employ a different approach. Figure 1 is a schematic contour map (for $\mathbf{H}=0$) of $V(\mathbf{M})\equiv f(\mathbf{M}_b)-f(\mathbf{M})$. The four peaks A, B, D, and E, correspond to coexisting uniform bulk solutions, for which $V=0$. To be specific, let us consider wetting of the wall-B interface by phase A. When the wall is completely wet by A, the projection of the profile $\mathbf{M}(z)$ onto the M_xM_y-plane passes through the peak at A, where, by Eq. (7), $dM/dz=0$. Hence, $M(z)$ maintains the value $\mathbf{M}_A$ over an infinite distance. For partial wetting by A the projection of $\mathbf{M}(z)$ no longer passes through, but only close to A, and the distance over which the profile differs

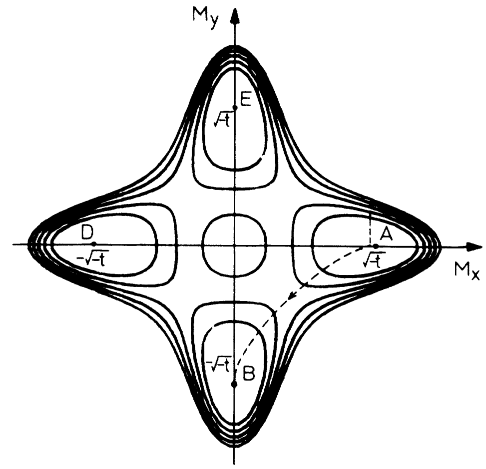

FIG. 1. Schematic contour map of $V(\mathbf{M})=f(\mathbf{M}_b)-f(\mathbf{M})$ for the model with cubic anisotropy, and for $\mathbf{H}=0$. The peaks at A, B, D, and E correspond to the coexisting bulk phases. The dashed line denotes a typical projection of $\mathbf{M}(z)$ just below T_W.

from M_B is finite.

Clearly, as pointed out by Hauge,[3] the form of $\mathbf{M}(z)$ is decided in the vicinity of peak A. One is therefore prompted to expand V about M_A, where the principal axes are M_x and M_y. To quadratic order this gives

$$V(\mathbf{M})\approx-\tfrac{1}{2}\sum_\alpha\left[\frac{\xi_0}{\xi_\alpha}\right]^2(M_\alpha-M_{A,\alpha})^2\ , \tag{8}$$

where

$$\left[\frac{\xi_0}{\xi_\alpha}\right]^2=\frac{\partial^2 f}{\partial M_\alpha^2}\bigg|_{\mathbf{M}_A}=t+3M_{A,\alpha}^2+\lambda M_{A,B\neq\alpha}^2\ . \tag{9}$$

In terms of this approximate $V(\mathbf{M})$, solution of Eq. (4) yields

$$M_\alpha(z)=M_{A,\alpha}+a_\alpha e^{z/\xi_\alpha}+b_\alpha e^{-z/\xi_\alpha}\ . \tag{10}$$

The coefficients a_α and b_α may be determined from the boundary conditions. However, those at $z=\infty$ lie outside the region over which the above approximation is valid, and one must therefore find some alternative prescription for imposing the condition that the solution approaches M_B as $z\to\infty$. If the profile took the form of part of a free A-B interface, this would be guaranteed. In general, this will not be the case. However, just below T_W, $\mathbf{M}(z)$ will approach sufficiently close to A, so that beyond some finite distance z_0 one may, to a good approximation, replace it by $\mathbf{M}_0(z-l)$. This represents the profile of a free interface centered at $z=l$, where l is the (yet to be determined) thickness of the wetting layer.

For the purposes of determining the exponents associated with a critical wetting transition, we are interested in the large-l asymptotics of Eq. (1). In particular, the exponents depend on the direction of approach (in the M_xM_y-plane) of $M(z_0)$ to $\mathbf{M}_A$. Hence, approximating the entire profile by $\mathbf{M}_0(z-l)$ should not alter the critical exponents, although it will affect the actual wetting temperature.

Solving for $\mathbf{M}_0(z-l)$ near A and substituting the resulting approximation for $\mathbf{M}(z)$ in (1), we readily find

$$\sigma_s(l)=\sigma_{wA}+\sigma_{AB}-u\xi_0\sum_\alpha(\xi_0 cM_{A,\alpha}-H_\alpha^s)a_{0\alpha}e^{-l/\xi_\alpha}+\frac{u\xi_0^2}{2}\sum_\alpha(c-\xi_\alpha^{-1})a_{0\alpha}^2e^{-2l/\xi_\alpha}+O(e^{-3l/\xi_\alpha}) , \quad (11)$$

where σ_{wA} and σ_{AB} are the excess free energies per unit area of the wall-A and A-B interfaces, respectively, and $a_{0\alpha}$ are positive constants.

This constitutes a restricted Landau theory, in terms of the scalar order parameter l. The equilibrium solution will be obtained by minimizing with respect to l. The important terms will be the leading two, a critical wetting transition being characterized by the vanishing of the coefficient of the leading term. However, which of the above constitute the leading two terms depends on the ratio of the two lengths ξ_x and ξ_y. For our choice of wetting by phase A, we have from Eq. (9)

$$\frac{\xi_x}{\xi_y}=\sqrt{(\lambda-1)/2} , \quad (12)$$

where we have used $M_A=(\sqrt{-t},0)$. This provides us with three distinct regimes which will be discussed in Secs. II A–II C.

A. $\lambda>9$

In this region of large anisotropy the tail of the free interfacial profile approaches $\mathbf{M}_A$ (in the M_xM_y plane) along a path exponentially close to the M_x axis, and the behavior is governed by one length scale ξ_x. We have for $\Delta\sigma_s(l)\equiv[\sigma_s(l)-\sigma_{wA}-\sigma_{AB}]/u$,

$$\Delta\sigma_s(l)\approx-\xi_0(\xi_0cM_{A,x}-H_x^s)a_{0x}e^{-l/\xi_x}+\frac{\xi_0^2}{2}(c-\xi_x^{-1})a_{0x}^2e^{-2l/\xi_x}+\cdots . \quad (13)$$

We assume here, and in the remainder of Sec. II, that $c>\xi_x^{-1}$. This then implies a critical wetting transition as $\tau\equiv\xi_0M_{A,x}-H_x^s\rightarrow0^+$ (cf. the Ising case[1]). It is a simple matter to show that the equilibrium thickness l_0 of the layer of phase A wetting the wall diverges as

$$l_0\sim-\ln\tau , \quad (14)$$

i.e., $l_0\sim(T_W-T)^{-\beta_s}$ with $\beta_s=0$. The transverse correlation length $\xi_\parallel$ associated with fluctuations of $l(x,y)$ is given by

$$\xi_\parallel^{-2}\sim\left.\frac{\partial^2\Delta\sigma_s}{\partial l^2}\right|_{l_0}\sim\tau^2 , \quad (15)$$

which implies

$$\nu_\parallel=1 . \quad (16)$$

The predominance of only one length scale in this regime thus yields exponents identical to those obtained in the one-component Ising case.

B. $3<\lambda<9$

Here,

$$\Delta\sigma_s(l)\approx-\tau\xi_0a_{0x}e^{-l/\xi_x}+\xi_0H_y^sa_{0y}e^{-l/\xi_y}+\cdots . \quad (17)$$

As Hauge[3] notes, $H_y^sa_{0y}\geq0$ is necessary for a continuous transition. Leaving aside the equality for the moment, one finds the following exponents:

$$\beta_s=0 \text{ (logarithmic growth)} ,$$
$$\nu_\parallel=\tfrac{1}{2}[1-\sqrt{2/(\lambda-1)}]^{-1} . \quad (18)$$

In other words one obtains exponents which vary continuously with the anisotropy λ.

C. $\lambda<3$

Provided that $H_y^s\neq0$, the leading term is now

$$\xi_0H_y^sa_{0y}e^{-l/\xi_y} \quad (19)$$

which does not change sign with temperature, thus precluding the possibility of a continuous transition. The global nature of $\Delta\sigma_s(l)$ is required to determine the details of any wetting transition, which, if it exists, must necessarily be first order in nature.

The special case of $\lambda=3$ would then represent a tricritical point. In any case, whatever the nature of the transition for $\lambda<3$, the exponents for $\lambda=3$ are found to be universal and equivalent to those of regime A.

Let us now briefly consider how the aforementioned is modified for the special case $H_y^s=0$. Regimes A and B now both exhibit the same (universal) mean-field exponents, while critical wetting becomes possible in regime C. The exponents in this latter case are

$$\beta_s=0 \text{ (logarithmic)} ,$$
$$\nu_\parallel=[2-\sqrt{2/(\lambda-1)}]^{-1} , \quad (20)$$

i.e., nonuniversal but with a modified dependence of λ.

As mentioned earlier, $H_y^sa_{0y}<0$ requires any wetting transition to be first order in regime B. It is of interest to note that if $\mathbf{H}^s$ makes a sufficiently small angle with the y axis, the transition involving wetting by phase A may be followed, on further increasing the temperature, by a second corresponding to wetting of the wall-A interface by phase E (see Fig. 1). Above the temperature at which A wets the wall-B interface, one has a situation wherein there is an A-B interface infinitely removed from the wall. Thus, the growth of a new phase at the wall can essentially be viewed in terms of wetting of the wall-A interface. If one now subtracts out from Eq. (1) the contribution from a free A-B interface, wetting by phase E can be considered in the presence of an effective bulk A. The above analysis then follows with the roles of the x and y components interchanged, and with a_{0x} now a negative constant. The large anisotropy regime A permits this second transition to be critical. However, one now has $H_x^sa_{0x}\leq0$ and, unless the equality holds, such a phase transition must be first order in regime B. We thus have the possibility of a system which exihibits a continuous followed by a first-order wetting transition. The only case in this regime for which wetting by phase E may proceed via a continuous transition is when $H_x^s=0$. However, the lack of a symmetry-breaking field in the x direction leads to the existence of only one wetting transition, viz., that corresponding to wetting by phase E of the wall-B interface. For $\lambda=3$, on the other hand, it is not difficult to demonstrate the possibility (for suitably chosen c) of two critical wetting transitions, provided $0<\theta_s<\pi/4$, where θ_s is the angle between $\mathbf{H}^s$ and the y axis.

III. UNIAXIAL ANISOTROPY

We now turn to a model given by the functional (1), but with

$$f(\mathbf{M})=\frac{t}{2}(M_x^2+M_y^2)+\tfrac{1}{4}(M_x^2+M_y^2)^2+\frac{\kappa}{4}M_x^2-\mathbf{H}\cdot\mathbf{M} \ . \tag{21}$$

For $\mathbf{H}=0$ there are only two coexisting bulk states given by $\mathbf{M}_b=(0,\pm\sqrt{-t}\,)$.

It has been previously shown[6] that the free interfaces of this model adopt forms in one of two possible classes. The class-1 solutions involve variation of only M_y:

$$M_x^{(1)}(z)=0 \ ,$$

$$M_y^{(1)}(z)=\pm\sqrt{-t}\ \tanh\left[\frac{z}{\xi_0}\sqrt{-t/2}\right] , \tag{22}$$

the sign depending on the boundary conditions at $z=\pm\infty$. The class-2 solutions come in two homotopic varieties (chiralities), and exist only for $\kappa<-t$:

$$M_x^{(2)}(z)=\sqrt{(-t-\kappa)}\operatorname{sech}\left[\frac{z}{\xi_0}\sqrt{\kappa/2}\right] ,$$

$$M_y^{(2)}(z)=\pm\sqrt{-t}\ \tanh\left[\frac{z}{\xi_0}\sqrt{\kappa/2}\right] , \tag{23}$$

and

$$M_x^{(2^*)}(z)=-\sqrt{(-t-\kappa)}\operatorname{sech}\left[\frac{z}{\xi_0}\sqrt{\kappa/2}\right] ,$$

$$M_y^{(2^*)}(z)=\pm\sqrt{-t}\ \tanh\left[\frac{z}{\xi_0}\sqrt{\kappa/2}\right] . \tag{24}$$

Thus for a given κ there will be a chiral-symmetry-breaking transition as the temperature is lowered. The important point to note, in the present context, is that within each class the solutions are governed by a single length scale.

Performing the analysis of Sec. II for each class of solution (with the added advantage of an explicit form for the entire free interface) one finds

$$\Delta\sigma_s(l)\approx-2\xi_0\sqrt{-t}\,(\xi_0c\sqrt{-t}-H_y^s)e^{-l/\xi}+2\xi_0\sqrt{-t}\,[(2\xi_0c-\sqrt{-2t}\,)\sqrt{-t}-H_y^s]e^{-2l/\xi} \tag{25}$$

with $\xi=\xi_0/\sqrt{-2t}$ and

$$\Delta\sigma_s(l)\approx-2\xi_0H_x^s\sqrt{(-t-\kappa)}e^{-l/2\xi}-\xi_0[2\xi_0c\kappa-\sqrt{2\kappa}(\kappa+t)-\sqrt{-t}\,H_y^s]e^{-l/\xi}$$
$$+2\xi_0H_x^s\sqrt{(-t-\kappa)}e^{-3l/2\xi}+\xi_0[4\xi_0c\kappa-\sqrt{2\kappa}(t+3\kappa)-2\sqrt{-t}\,H_y^s]e^{-2l/\xi} \tag{26}$$

with $\xi=\xi_0/\sqrt{2\kappa}$ for class 1 and 2 solutions, respectively. Hence, for the class-1 solutions, there exists the possibility of a critical wetting transition with universal exponents. On the other hand, for the class-2 solutions, the leading order term is

$$-2\xi_0H_x^s\sqrt{(-t-\kappa)}e^{-l/2\xi} \ .$$

This vanishes only at $-t=\kappa$, at which point the class-2 degenerates to a class-1 solution. Thus, in the regime where class-2 solutions are stable, any wetting transition must have a first-order character (unless $H_x^s=0$). In conclusion then we have found for this uniaxial model, the particular form of the free-interfacial profiles reduces the number of relevant length scales to 1, and leads to only universal mean-field wetting exponents.

Finally, in view of the fact that for continuous wetting with short-range forces $d=3$ is known to be the upper critical bulk dimension[7] we should mention how the behavior in Secs. II and III is expected to be modified by fluctuations. From the analysis of Subbaswamy and Trullinger,[4] one can deduce that the lowest-lying band of excitations associated with the free interface are of a capillary-wave-like nature. Indeed, the only relevant $q=0$ mode is the Goldstone mode associated with the breaking of translational invariance in the z direction. Spin-wave-like fluctuations may be expected to change the shape of the magnetization profile, but the associated spectrum exhibits a gap due to the presence of anisotropy. These excitations are thus noncritical at the wetting transition. Hence, capillary waves may be expected to be the only relevant critical fluctuations, and one expects that renormalization of the critical exponents will be along the lines of that found previously by Hauge and Olaussen[8] in terms of an interface displacement model.[9,10]

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