Interfacial Structural Changes and Singularities in Nonplanar Geometries

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We consider phase coexistence in a thin-film Ising magnet with opposing surface fields and nonplanar walls. We show that the loss of translational invariance has a strong and unexpected nonlinear influence on the interface structure and phase diagram. We identify four nonthermodynamic singularities, where there is a qualitative change in the interface shape. In addition, at the finite-size critical point, the singularity in the interface shape is characterized by two critical exponents in contrast to the planar case (which is characterized by one). Similar effects should be observed for prewetting at a corrugated substrate. Analogy is made with the behavior of a nonlinear oscillator showing chaotic dynamics. [S0031-9007(98)06836-7]

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There are a number of well-studied examples of fluid interfacial phenomena for planar systems in which surface phases with distinct adsorptions coexist along a line of first-order phase transitions which terminates at a surface critical point. Examples include the prewetting transition associated with first-order wetting [1] and also interfacial localization in thin-film magnets (with opposite surface fields) associated with confinement effects at critical wetting [2]. In both cases, the difference in adsorption between the two phases vanishes continuously as the critical point, signifying the end of a two-phase coexistence, is approached. This second-order phase transition is characterized by the critical exponents belonging to the two-dimensional Ising universality class (for three-dimensional bulk systems) since the adsorption difference acts as a scalar order parameter [3,4]. In this Letter, we describe a wealth of new interfacial structural changes and singularities which emerge when the analogous phenomena are considered in slightly nonplanar geometries and which are intimately associated with nonlinear behavior. In addition to a shift in the finite-size (FS) critical point (compared to the planar confined system), the shape of the nonplanar interface undergoes a number of structural changes as we move along and beyond the line of coexistence. This behavior has no counterpart in the planar geometry, and has not been reported previously. Moreover, as the shifted surface critical point is approached, the function describing the shape of the nonplanar interface shows nonanalyticities which are characterized by two critical exponents. While one of these appears to be identical with the usual critical exponent describing the singularity in the total (or average) adsorption, the general identification of the second is a more difficult problem, although scaling arguments (consistent with our explicit results) suggest that its value is related to the energy density. Our predictions are based on a detailed numerical analysis of a simple mean-field (MF) model of interfacial behavior which we believe is qualitatively correct beyond MF approximation (in three dimensions). These rather dramatic effects emanating from the introduction of a slight nonplanar perturbation to the interface can be viewed profitably by making an analogy with the classical mechanics of an extremely sensitive nonlinear dynamical system exhibiting chaotic behavior [5]. As we will see, the interface behavior may be elegantly portrayed as the temperature evolution of a phase plane plot, similar to that employed in dynamical systems, allowing us to distinguish different qualitative types of interface shapes separated by nonthermodynamic singularities.

To begin, we recall the relevant properties and phase diagram of the planar system prior to a discussion of the nonplanar generalization. The transition that we concentrate on occurs in a thin-film magnet with opposing surface fields, but the phenomena are generic to other situations such as prewetting at a planar wall. Consider then an Ising-like thin-film magnet of width L_z and infinite transverse area in zero bulk field and below the bulk critical temperature T_c^{bulk} with surface fields h_1 and $h_2 = -h_1$ acting on the spins in the $z = 0$ and $z = L_z$ planes, respectively. We further suppose (through a judicial choice of surface enhancement [4]) that in the semi-infinite limit $L_z \to \infty$ each surface undergoes a critical wetting transition at temperature T_w. For such a system, MF [2] and simulation studies [3] show that the finite-size phase diagram is dominated by wetting effects which are able to suppress bulklike coexistence over a large temperature regime. At sufficiently low temperatures $T < T_c(L_z)$, with the finite-size critical temperature satisfying $T_c(L_z) < T_w$, phase coexistence is possible between phases corresponding to an interface being bound to either wall. As the temperature increases, the interface position moves continuously to the middle of the system and for $T > T_c(L_z)$ only one phase is possible. Thus, in the temperature window $T_c^{\mathrm{bulk}} > T > T_w$, the FS effects suppress bulklike phase coexistence for all L_z. This temperature range is also characterized by a near soft-mode phase since the transverse correlation length $\xi_\parallel$ is extremely large due to capillary-wave-like excitations. These features can be most easily understood using a simple effective interfacial

Hamiltonian model [2]:

$$H[\ell] = \int d\mathbf{r} \left[\frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell; L_z) \right], \qquad (1)$$

where $\ell(\mathbf{r})$ is the collective coordinate describing the interface position at vector displacement $\mathbf{r} = (x, y)$ along the wall and Σ is the stiffness coefficient of the up-spin–down-spin interface. The total finite-size binding potential $W(\ell; L_z)$ acting on the interface (whose minima determine the MF location/s of the interface) is the sum of the two contributions from each wall:

$$W(\ell; L_z) = W_\infty(\ell) + W_\infty(L_z - \ell), \qquad (2)$$

where $W_\infty(\ell)$ is the appropriate semi-infinite binding potential for the ranges of forces in the model. For systems with short ranged forces this is usually specified as [1]

$$W(\ell) = a_0(T - T_w)e^{-\kappa\ell} + b_0 e^{-2\kappa\ell}, \qquad \ell > 0, \quad (3)$$

with a_0, b_0 positive constants and κ being the inverse bulk correlation length. For $T < T_c(L_z)$, with $T_c(L_z) = T_w - 4(b_0/a_0)e^{-\kappa L_z/2}$ in MF approximation, the total potential $W(\ell; L_z)$ has a double well structure with two equal minima at $\ell_\pi < L_z/2$ and $\ell_\pi^* = L_z - \ell_\pi$. As $T \to T_c(L_z)^-$, the adsorption difference $\Delta\Gamma = 4m_0(L_z/2 - \ell_\pi)$ (with m_0 the bulk magnetization) vanishes like $\Delta\Gamma \sim [T_c(L_z) - T_c]^{1/2}$, corresponding to a standard order-disorder transition. For $T > T_c(L_z)$, the potential $W(\ell; L_z)$ has only one minimum at $\ell_\pi = L_z/2$ and the correlation length $\xi_\parallel \sim e^{\kappa L_z/4}$. Interestingly, most of these quantitative MF predictions are confirmed by extensive Monte Carlo simulation studies which established that the true asymptotic critical regime, where we can expect Onsager-like behavior $\Delta\Gamma \sim [T_c(L_z) - T_c]^{1/8}$, is extremely small [3]. All these facts support MF theory as an excellent quantitative description of the thin-film system.

We now wish to consider the MF phase diagram for the analogous phase transition in a slightly nonplanar geometry. We will take as our starting point the simplest possible phenomenological model of this system which generalizes (1) and will suppose that the configuration energy is specified by

$$H[\ell; z_w^{(1)}, z_w^{(2)}] = \int d\mathbf{r} \times \left[\frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell; L_z, z_w^{(1)}, z_w^{(2)}) \right], \qquad (4)$$

where $z_w^{(1)}(\mathbf{r})$ and $z_w^{(2)}(\mathbf{r})$ describe the (small) deviations of the walls near the $z = 0$ and $z = L_z$, respectively, and $W(\ell; L_z, z_w^{(1)}, z_w^{(2)}) = W_\infty(\ell - z_w^{(1)}) + W_\infty(L_z + z_w^{(2)} - \ell)$. While the model could certainly be improved by including further coupling terms involving $\nabla\ell \cdot \nabla z_w$ with associated position dependent (stiffness) coefficients, we do not expect these to make any significant difference to the interfacial behavior described here [6]. In any case, even with the further assumption of corrugated walls such that $z_w^{(1)}$ and $z_w^{(2)}$ depend only on a single coordinate (x, say), the interfacial behavior generated is sufficiently complex to warrant attention within the simple model above. Writing $z_w^{(1)}(x) = a\sqrt{2}\sin(qx)$, we have considered the geometry for which $z_w^{(1)} = z_w^{(2)}$ although, of course, many other choices are possible [6]. The rms width a and wavelength $L_x = 2\pi/q$ of the wall corrugation are assumed to be small and large, respectively, in comparison with the bulk correlation length. With these assumptions, the wetting transition remains second order and located at T_w in the semi-infinite limit [7].

The equilibrium nonplanar interfacial profile/s $\ell_\nu(x)$ satisfies the Euler-Lagrange equation

$$\Sigma\ddot{\ell}_\nu(x) = W_\infty'(\ell_\nu - z_w^{(1)}) - W_\infty'(L_z + z_w^{(2)} - \ell_\nu), \quad (5)$$

where the dot and prime signify differentiation with respect to x and argument, respectively. Periodic boundary conditions are imposed after a large multiple of wavelengths L_x. Two preliminary remarks are as follows: Firstly, the Euler-Lagrange equation is inversion symmetric so that, if $\ell_\nu(x)$ is a solution, $\ell_\nu^*(x) = L_z - \ell_\nu(x + \pi/q)$ is also a solution with the same free energy and is distinct from $\ell_\nu(x)$ in the two-phase regime. Secondly, we have established numerically that the stable phases all have the same wavelength as the wall corrugation L_x. However, this is not the case for the metastable states [6]. Finally, we note that an elegant description of the interfacial shape is afforded by a reduced phase plane plot $\ell/\sqrt{2}a$ vs $\dot{\ell}/\sqrt{2}aq$ and helps distinguish different types of structural regimes. A section of the equilibrium phase diagram, with suitable reduced units [8], is shown in Fig. 1 and shows a critical line (corresponding to an order-disorder transition) and four nonthermodynamic singularities where there is a qualitative change of interfacial structure. In this way, we are able to distinguish five different interfacial types (see Fig. 2).

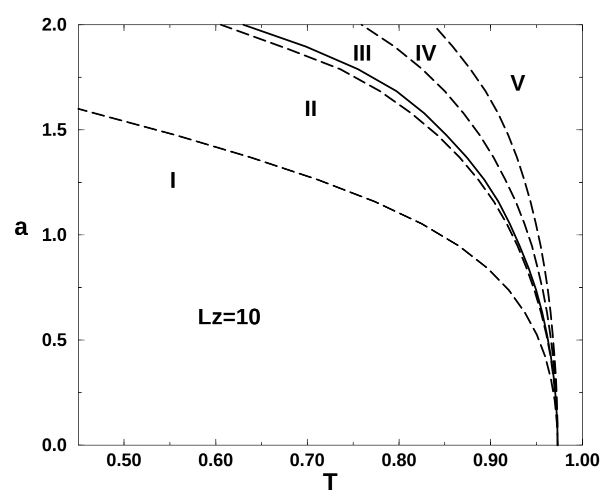

FIG. 1. Phase diagram for $L_z = 10$ and $q = 2\pi/10$ in reduced units [8]. The solid line separates the ordered and the disordered phases. The dashed lines show the location of the nonthermodynamic singularities and divide the phase diagram into five regions.

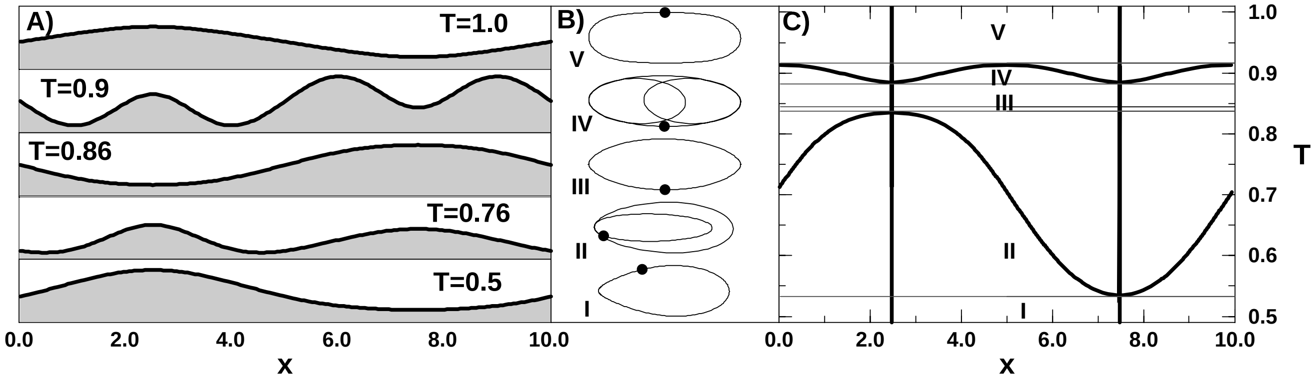

FIG. 2. Behavior of the system for $L_z = 10$, $a = 1.5$, and $q = 2\pi/10$ showing the shape of the interface in the different regimes (A) and their corresponding phase portraits $\dot{\ell}$ vs ℓ (B). The circle represents the point $x = 0$. For clarity, scales related to ℓ are omitted but can be checked in Fig. 3. The loci of the interface minima and maxima are represented as a function of the temperature (C). The FS critical temperature $T_c(L_z, a, q) \approx 0.845$ is represented by a thin line and is within regime III.

Phase coexistence and order are most easily revealed through the mean interfacial height

$$\ell_0 \equiv \frac{1}{L_x} \int_0^{L_x} dx\, \ell_\nu(x) \tag{6}$$

which is single valued ($\ell_0 = L_z/2$) in the disordered regime above the critical temperature $T_c(L_z, a, q)$, but is double valued (with $\ell_0^* = L_z - \ell_0$) in the order regime, analogous to ℓ_π and ℓ_π^* for the planar system. Our numerics indicate that the singularity in ℓ_0 is of the expected type:

$$\frac{L_z}{2} - \ell_0 \simeq \begin{cases} t^{1/2} & \text{if } t > 0 \\ 0 & \text{if } t < 0 \end{cases}, \tag{7}$$

where we have introduced the scaled temperature variable $t \equiv [T_c(L_z, a, q) - T]/T$. In addition to the mean interface height, however, the shape function shows a number of qualitative changes with temperature. At very low temperatures, the interface is closely bound to one of the walls and follows the corrugation [see Fig. 2(A)]. Over one period L_x, the graph $\ell_\nu(x)$ has one maximum and one minimum which are in phase with the wall function $z_w^{(1)}(x)$. For this case, the phase plane plot is a simple loop. Nevertheless, notice that its form is not precisely circular, indicating that nonlinear effects are important even when the interface is close to the wall. On increasing the temperature, the interface smoothly deforms and shows a number of nonthermodynamic singularities, where the minima and maxima of the graph undergo a series of *bifurcations*. These reveal themselves as the appearance/disappearance of loops in the phase plane portrait, as illustrated in Fig. 2(B), which also shows the locus of the maxima/minima with temperature [Fig. 2(C)]. Corresponding profiles are shown in Fig. 2(A). Two counterintuitive features are worth emphasizing here. Firstly, there are two regimes, II and IV, where the interface shape has two and three maxima per wavelength of the wall corrugation. Secondly, in the vicinity of the order-disorder transition, regime III, the interface shape is similar to the wall (i.e., there is only one max/min pair per period) but is *out of phase* with it. Finally, at high temperatures above the two supercritical nonthermodynamic singularities, the interface shape returns to that of a simple sinusoidal-like function in phase with the wall, and the phase portrait is basically a circle of radius $(1 + q^2\xi_\parallel^2)^{-1}$ centered at $L_z/2$.

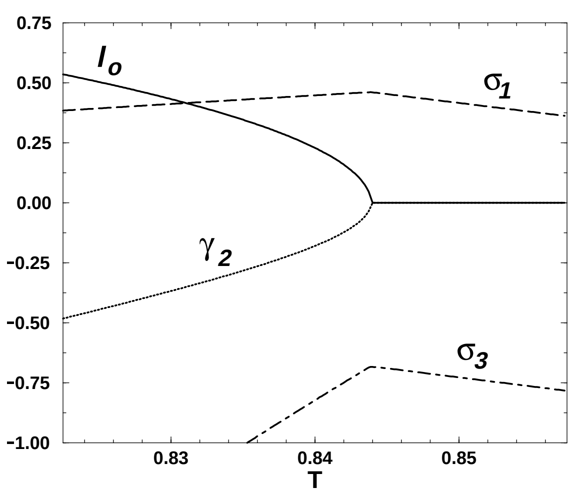

FIG. 3. Behavior of the coefficients $L_z/2 - \ell_0$, σ_1, γ_2, and σ_3 of Eq. (8) near $T_c(L_z, a, q)$ for $L_z = 10$, $a = 1.5$, $q = 2\pi/10$. They are multiplied by 1, $10L_x$, 10^2L_x, and 10^3L_x, respectively.

Next, we focus on the singularity in the shape profile at the order-disorder transition. We have established that the stable phase/s can be represented by a Fourier series

$$\ell_\nu(x) = \ell_0 + \sigma_1 \sin(qx) + \sum_{k=1}^{\infty} \{\sigma_{2k+1} \sin[(2k + 1)qx] + \gamma_{2k} \cos(2kqx)\} \tag{8}$$

throughout the phase diagram. In this expression, ℓ_0 is the mean interface position [given by Eq. (6)], while the second term is the harmonic response to the wall corrugation. The final term represents the higher-order harmonic excitations arising from the nonlinearity of the Euler-Lagrange equation which are responsible for the complicated evolution of the interface structure with temperature. We stress that, without this term (i.e., just considering linear response), the phase plane portrait would be simply circular. Note that there are no even sine terms and no odd cosine terms. The temperature dependence of the two sets of coefficients $\{\sigma_{2k-1}\}$ and $\{\gamma_{2k}\}$ is extremely involved, but near $T_c(L_z, a, q)$ only two types of singularity are observed in our numerical analysis (See Fig. 3). The coefficients $\{\gamma_{2k}\}$ all vanish above $T_c(L_z, a, q)$ and behave precisely as the mean order parameter $\frac{L_z}{2} - \ell_0$, i.e., they are characterized by the usual MF order-parameter critical exponent $\beta = 1/2$. In contrast, the terms $\{\sigma_{2k-1}\}$ all have a cusplike singularity

$$\sigma_{2k-1} - \sigma_{2k-1}^c \simeq |t|^\theta, \qquad t \to 0^\pm, \tag{9}$$

where σ_{2k-1}^c is the value at criticality and the critical exponent $\theta = 1$. There is no analogy of this singularity in the planar system. Furthermore, while it is natural to identify the cosine term singularities with the order-parameter exponent β of the $(d-1)$-dimensional bulk universality class ($\beta = 1/2$ in MF, $\beta = 1/8$ beyond MF for three-dimensional thin films), a similar identification for θ is not as obvious. Nevertheless, we have constructed scaling arguments which suggest that $\theta = 1 - \alpha$, where α is the specific heat critical exponent, consistent with our numerical results [6]. Similarly, we have also established that, for fixed L_z, the critical line is consistent with the scaling law

$$T_c(L_z, a, q) - T_c(L_z, 0, 0) \simeq a^2 \Lambda\left(\tfrac{a}{q}\right), \tag{10}$$

where Λ is an appropriate scaling function. This behavior can be understood using finite-size scaling ideas with MF critical exponents and indicates that the effective width of the system is reduced by corrugation [6].

In conclusion, we make some pertinent remarks. Firstly, the interfacial structural changes reported here are not peculiar to short-ranged forces with the exponential binding potential Eq. (3), and also emerge if long-ranged forces are considered instead [6]. Also, we emphasize that in previous studies of the effect of roughness on wetting transitions most authors have considered binding potentials with a single minimum which do not exhibit the same subtle nonlinear behavior discussed here [7,9]. Next, we note that, on making a change of variable $\eta(x) \equiv \ell(x) - L_z - z_w^{(1)}$ and expanding to appropriate (cubic) order, the Euler-Lagrange equation can be written as

$$\Sigma \ddot{\eta} = -\tilde{t}\eta + \tilde{u}\eta^3 + aq^2 \sin(qx), \tag{11}$$

where $\tilde{t} \propto [T_c(L_z) - T]$ and $\tilde{u}$ is positive in the region of interest. This is essentially equivalent to the Duffing equation of a soft-polynomial oscillator (without a damping term) which is known to yield extremely rich (including chaotic) dynamics [5]. In this context, the nonthermodynamic singularities described above are analogous to the harmonic excitations of the nonlinear oscillator (however, this analogy does not shed any light on the nature of the singularities near the order-disorder transition and their identification beyond MF).

We have shown from a simple MF model of interfacial behavior in a slightly nonplanar geometry that new types of structural phase changes and additional critical singularities can emerge which are intimately related to nonlinear phenomena. Similar behavior is also expected for prewetting at a nonplanar substrate [6]. Also of interest is the structure of metastable states in this system which we do not discuss here [6]. We believe that future studies of improved models which include thermal fluctuations and different types of nonplanarity will also uncover new structural and fluctuation related behavior.

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[1] For a review of wetting, see, for example, S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J.L. Lebowitz (Academic Press, London, 1988), Vol. 12, p. 1.
[2] A. O. Parry and R. Evans, Phys. Rev. Lett. **64**, 439 (1990); Physica (Amsterdam) **181A**, 250 (1992).
[3] K. Binder, D. P. Landau, and A. M. Ferrenberg, Phys. Rev. Lett. **74**, 298 (1995).
[4] H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).
[5] See, for instance, S. Wiggins, *Introduction to Applied Nonlinear Dynamical Systems and Chaos* (Springer-Verlag, New York, 1990).
[6] C. Rascón and A. O. Parry (to be published).
[7] A. O. Parry, P. S. Swain, and J. A. Fox, J. Phys. Condens. Matter **8**, L659 (1996).
[8] Throughout the paper, lengths are measured in (dimensionless) units of the bulk correlation length and temperature in units of T_w (the wetting temperature of the semi-infinite system).
[9] S. Nechaev and Y.-C. Zhang, Phys. Rev. Lett. **74**, 1815 (1995); M. Napiórkowski and K. Rejmer, Phys. Rev. E **53**, 881 (1996); R. R. Netz and D. Andelman, Phys. Rev. E **55**, 687 (1997); G. Sartoni, A. L. Stella, G. Giugliarelli, and M. R. D'Orsogna, Europhys. Lett. **39**, 633 (1997).