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Surface melting and surface-induced-disorder transitions in thin films: The effect of hidden variables

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Surface melting and interface delocalization transitions are studied in films of finite thickness L, for systems in which more than one density is needed to describe the ordered state. Since the system is closed, there is the constraint of fixed concentration. For short-range (exponential) interactions, a Ginzburg-Landau model is used to show that the finite-size effects are different from those of a system without constraints. For long-range (e.g., van der Waals) interactions, we derive a simple two-component order-parameter model for surface melting from the density-functional theory. For large L, the shift in the transition temperature is found to be proportional to $L^{-1/2}$ in both cases.

I. INTRODUCTION

The theoretical description of phase transitions is necessarily restricted to simple idealized models. The "real" system has extra "hidden" variables or nonordering densities which are often ignored. Real fluids, for example, always contain impurities at some level. One form of "impurity" that is normally unavoidable is that deriving from isotopic composition. In the usual experiment the number of impurity atoms does not change. As another example, consider ordering binary alloys. Two densities are needed to describe the ordered state, the order parameter, and the concentration (given by differences and sums of the sublattice concentrations, respectively). Experimental studies of the order-disorder transition in these systems are generally carried out at fixed overall composition. Furthermore, the constituent atoms of the binary alloy are usually of different size. The sample may be surrounded by a medium of low compressibility, which in the extreme case corresponds to an experiment at constant volume. In the situations described above, the nonordering densities are subject to a constraint of some sort. At second-order bulk phase transitions, constraints of this kind lead to what is commonly known as the Fisher renormalization of the critical exponents.[1]

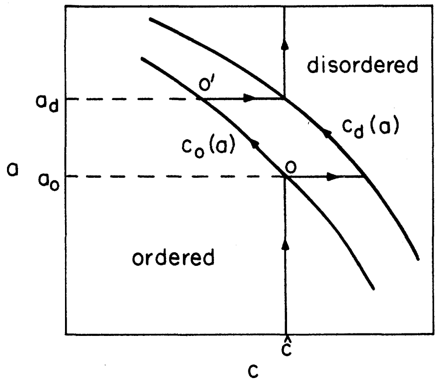

FIG. 1. Schematic bulk temperature-concentration phase diagram of Cu_cAu_{1-c} near $c=0.75$. The boundaries of the two-phase region with the ordered and the disordered phases are labeled by $c_o(a)$ and $c_d(a)$, respectively. For further discussion, see the text.

In this paper we consider the effect of constrained nonordering densities on interface delocalization transitions which occur when the bulk transition is *first* order.[2] A constraint on the nonordering density commonly leads to the appearance of a two-phase region in the bulk phase diagram (see Fig. 1): The nonordering density (here the "concentration" c) takes on different values in the ordered and the disordered phases. This does *not* change the critical behavior at interface delocalization transitions in semi-infinite systems, since the bulk acts as a reservoir, which can absorb (or supply) an arbitrary number of atoms. The surface-induced-disorder transition occurs in this case as the boundary of the two-phase region is approached from below.[3,4] In contrast, the effect of constraints on the nonordering density becomes important in *finite* systems. The question is then, "What are the finite-size effects in these systems?" We will consider surface-induced-disorder (SID) transitions in this paper, because examples of wetting transitions with conserved nonordering densities seem to be harder to find. However, our results are equally applicable to the corresponding wetting transitions.[5]

II. SHORT-RANGE FORCES

One essential feature of the systems described in the Introduction is that more than one density is needed to describe the ordered state. In addition, there is a constraint on the nonordering density. A simple continuum model which contains these essential features is described by the Landau free-energy functional

$$F\{\phi,c\}=\int d^{d-1}\rho\int_0^L dz\{\tfrac{1}{2}(\nabla\phi)^2+f_b(\phi,c)+[\delta(z)+\delta(L-z)]\tfrac{1}{2}a_1\phi^2\} \qquad (1)$$

for a scalar order parameter $\phi(\boldsymbol{\rho},z)$ and "concentration" $c(\boldsymbol{\rho},z)$. For the free-energy density we take

$$f_b(\phi,c)=\tfrac{1}{2}a\phi^2-\tfrac{1}{3}b\phi^3+\tfrac{1}{4}g\phi^4+\beta c\phi^2+\tfrac{1}{2}\alpha c^2-\mu c\ . \qquad (2)$$

This model can be used to describe, for example, the order-disorder transition in thin-film fcc Ising antiferromagnets and binary alloys with *short-range forces.* In particular, this explicit form of (1), (2) can be derived from a short-range lattice-gas model for Cu_3Au films with (111)-free surfaces.[3] The two densities in this case are (i) the order parameters (OP) ϕ [given by the difference of the sublattice concentrations in the (111) planes], and (ii) the nonordering density c [identified with the deviation of the average Cu concentration of the (111) planes from stoichiometry]. For Cu_3Au, it turns out that $\beta>0$ (Ref. 3) so that $c_d(a)>c_o(a)$ in the two-phase region of the phase diagram, as in Fig. 1. There is no $(\nabla c)^2$ term in (1) because the range of the concentration interactions in the (111) direction turns out to be shorter than that of the OP interactions. The OP mode determines the wetting behavior in this case so that the interaction term involving the concentration field does not influence the universal features of the critical behavior, and can therefore be ignored. For similar reasons, no c-dependent surface term has been included in (1). The effect of such a term has been absorbed in a renormalization of a_1. See Ref. 3 for a further discussion of these points.

In the bulk, this model has a first-order phase transition. For fixed chemical potential $\mu=\mu_o$ there is a transition at $a_c=2b^2/9g_{\text{eff}}-2\beta\mu_o/\alpha$, where $g_{\text{eff}}=g-2\beta^2/\alpha$, from a homogeneous, ordered low-temperature phase with $\phi(a_c^-)\equiv\bar{\phi}=2b/3g_{\text{eff}}$ and $c(a_c^-)=(\mu_o-\beta\bar{\phi}^2)/\alpha$ to a homogeneous, disordered high-temperature phase with $\phi\equiv0$ and $c\equiv\mu_0/\alpha$. The finite-size effects which arise in thin-film geometries in this case have been analyzed in Refs. 6 and 7.

In many cases, however, experiments are performed at *fixed total concentration* so that the integral of $c(\mathbf{r})$ over the system volume V is fixed. The bulk phase diagram in this case exhibits regions of two-phase coexistence (see Fig. 1). Assume that the average concentration density is fixed to be

$$\hat{c}=\frac{1}{V}\int d^d r\, c(\mathbf{r})\ . \qquad (3)$$

At high temperatures,

$$a>a_d=2b^2/9g_{\text{eff}}-2\beta\hat{c}\ ,$$

the system is in a homogeneous disordered phase, and at low temperatures,

$$a<a_o=a_d-2\beta^2\bar{\phi}^2/\alpha\ ,$$

in a homogeneous ordered phase. However, for $a_o<a<a_d$, the system breaks up into domains with concentrations

$$c_o(a)=\hat{c}+(a_o-a)/2\beta$$

and

$$c_d(a)=\hat{c}+(a_d-a)/2\beta$$

of relative volume such that (3) is fulfilled. In the present model, the bulk order parameter $\phi(a)=\bar{\phi}$ in the two-phase region of the phase diagram (i.e., along the line $o-o'$ in Fig. 1).

Returning now to the finite system, we shall consider a film geometry of thickness L. There are two free surfaces at $z=0$ and L, and the system is infinite and homogeneous in the direction perpendicular to z. In the present mean-field (MF) analysis, the dependence of ϕ and c on $\boldsymbol{\rho}$ can therefore be ignored. Incorporating the constraint $\int_0^L c(z)dz=L\hat{c}$ of fixed average concentration $\hat{c}$ and integrating out $c(z)$ we arrive at a *nonlocal* free-energy density[8]

$$f(\phi)=\tfrac{1}{2}(a+2\beta\hat{c})\phi^2-\tfrac{1}{3}b\phi^3+\tfrac{1}{4}\left[g-\frac{2\beta^2}{\alpha}\right]\phi^4+\frac{\beta^2}{2\alpha L}\phi^2\int_0^L dz\,\phi^2(z)\ . \qquad (4)$$

In (4), we have dropped terms independent of ϕ. From (1) and (4) we obtain the MF equation for the order-parameter profile

$$-\frac{d^2\phi}{dz^2}+(a_{\text{eff}}\{\phi\}\phi-b\phi^2+g_{\text{eff}}\phi^3)=0\ , \qquad (5)$$

with the coefficients

$$a_{\text{eff}}=a+2\beta\hat{c}+2\frac{\beta^2}{\alpha L}\int_0^L dz\,\phi^2(z)\ ,$$

$$g_{\text{eff}}=g-\frac{2\beta^2}{\alpha}\ ,$$

and the boundary conditions

$$\left.\frac{d\phi}{dz}\right|_{z=0}=a_1\phi(z=0)$$

and

$$\left.\frac{d\phi}{dz}\right|_{z=L}=-a_1\phi(z=L)\ .$$

The concentration profile has the form

$$c(z)=\hat{c}-\frac{\beta}{\alpha}\phi^2(z)+\frac{\beta}{\alpha L}\int_0^L dz\,\phi^2(z)\ .$$

For fixed a_{eff}, Eq. (5) is identical to the MF equation of the single OP model.[6,7] We therefore solve (5) with a_{eff} constant and use the solution $\phi(z)$ to calculate the real "temperature" a. Since we are interested in continuous SID transitions, we assume $a_1>(a_{\text{eff}}^*)^{1/2}$, where

$a^*_{\text{eff}}=2b^2/(9g_{\text{eff}})$, throughout this paper.

We have analyzed the MF equations by direct numerical integration, as well as using asymptotic estimates, and a piecewise linear approximation. To determine the phase diagram, two solutions, denoted $m(z)$ and $M^L(z)$, have to be compared.[9] The profile $m(z)$ describes the disordered film and therefore vanishes identically for all z. The profile $M^L(z)$ is monotonically increasing for $0<z<L/2$. For $L\to\infty$, $M^L(L/2)$ approaches ϕ_b, the bulk order parameter in the ordered state. As already noted, $\phi_b=\bar{\phi}$ in the two-phase region of the phase diagram, so that $M^L(L/2)=\bar{\phi}$ (up to exponentially small corrections) for $a>a_o$.

The main result of our calculations is that in the limit $L/\xi\to\infty$, where ξ is the bulk correlation length, the free energy of the ordered state and the equilibrium thickness $\hat{l}$ of the disordered surface layer can be obtained by minimizing the function

$$F_{\text{ord}}(l)=2\sigma^*+(L-2l)f(\phi_b)+c_1e^{-2l/\xi_d}-c_2e^{-(L-2l)/\xi_o}\ , \tag{6}$$

where c_1 and c_2 are constants[10] and $f(\phi_b)$ is given by (4) with

$$\int_0^L dz\,\phi^2(z)=(L-2l)\phi_b^2\ .$$

In the two-phase region, this can be written as

$$f(\phi_b)=f(\bar{\phi})=\tfrac{1}{2}(a-a_d)\bar{\phi}^2+\frac{\beta^2}{2\alpha L}\bar{\phi}^4(L-2l)\ . \tag{7}$$

For $a\lesssim a_o$, (7) is correct to leading order in (a_o-a). In (6), ξ_o and ξ_d denote the correlation lengths of the ordered and the disordered bulk phases, respectively, and σ^* is the surface tension of a free interface between the ordered and the disordered phases in the infinite system. The equilibrium state is determined by comparing the free energy of the completely disordered state, $F_{\text{dis}}=0$, with $F_{\text{ord}}(\hat{l})$.

For systems with a relatively large surface tension, the disordered state can become thermodynamically stable at a temperature $a_t(L)<a_o$. The necessary condition for this to occur is that

$$L/\xi_d<\frac{8\sigma^*}{(a_d-a_o)\xi_d\bar{\phi}^2}\ , \tag{8}$$

or equivalently, L/ξ_d must be small compared to $(a_d-a_o)^{-1}$. In this case,

$$a_t(L)=\tfrac{1}{2}(a_o+a_d)-\frac{4\sigma^*}{\bar{\phi}^2L}\ ,$$

so that the shift of the transition temperature is proportional to $1/L$, just as in the single OP case.[6,7] For $a\to a_t(L)$, the coverage begins to diverge as $\hat{l}/\xi_d\sim-\ln(a_o-a)$ and attains a maximum value $\hat{l}/\xi_d\propto\ln L$ at $a_t(L)$. This behavior persists until $a_t(L)=a_o$, i.e., when (8) becomes an equality. For larger values of L, a_t is greater than a_o. In this case the thickness $\hat{l}$ of the disordered surface phase begins to diverge as a_o is approached from below. Above a_o, $\hat{l}\sim O(L)$. Extremizing (6), one finds that both the wetting and crossover behavior in the neighborhood of a_o are described [to lowest order in $e^{-\hat{l}/\xi_d}$ and $(\hat{l}/L)$] by

$$A_1e^{-2\hat{l}/\xi_d}+(a-a_o)=A_2\frac{2\hat{l}}{L}\ , \tag{9}$$

where $A_1=2c_1/(\xi_d\bar{\phi}^2)$ and $A_2=(a_d-a_o)$ are constants. Thus, for $L=\infty$, $\hat{l}$ diverges as $a\to a_o^-$, while for finite L, $\hat{l}\sim\ln(L)$ at a_o (see Fig. 2). For $a_o<a<a_t$, $\hat{l}$ is $O(L)$ and the surface order parameter is $O(e^{-L})$. The surface transition is thus *very weakly* first order in this case. The temperature dependence of $\hat{l}$ for $a>a_o$ is determined by the "lever rule" for two-phase coexistence, i.e., by the condition

$$2\hat{l}c_d+(L-2\hat{l})c_o=L\hat{c}\ ,$$

where c_o and c_d are the values of the nonordering density in the ordered and disordered bulk phases, respectively. Since c_o and c_d depend linearly on temperature in our model, we obtain immediately the linear temperature behavior of $\hat{l}$ in Eq. (9). This result is a consequence of the quadratic approximation for the concentration field $c(z)$ in (2). Higher-order terms would give rise to a more realistic temperature dependence; however, the leading temperature dependence would still be linear so that the conclusions obtained using the present simple model remain unchanged.

For $L\to\infty$, $a_t\to a_d$. Using (6) and (9), one finds that the temperature dependence of the free energy of the ordered profile is given by

$$F_{\text{ord}}(a)=2\sigma^*-\tfrac{1}{4}\bar{\phi}^2\frac{(a_d-a)^2}{(a_d-a_0)}L\ .$$

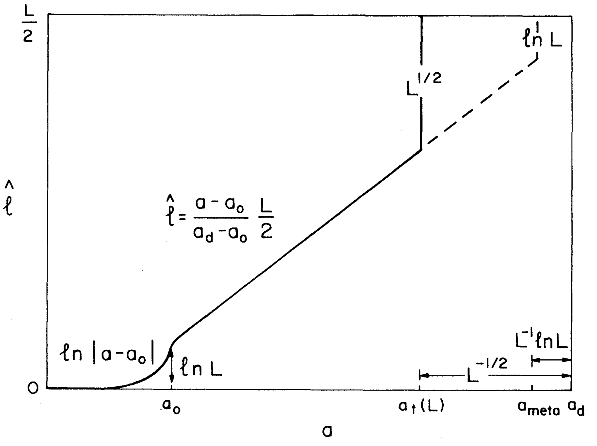

FIG. 2. Temperature dependence of the thickness $\hat{l}$ of the disordered surface layer, for the case of short-range interactions. The dependence of various quantities as a function of the film thickness L is indicated. Four different regimes have to be distinguished: (i) a SID regime $(a<a_o)$, where $\hat{l}$ increases logarithmically with temperature; (ii) a crossover regime $(a\simeq a_o)$; (iii) a lever-rule regime $[a_o<a<a_t(L)]$; and (iv) a metastable regime $[a_t(L)<a<a_{\text{meta}}(L)]$. For further discussion, see the text.

Comparing with $F_{\rm dis}(a)=0$, this leads to the shift in the transition temperature

$$a_t(L)-a_d=-\left[\frac{8\sigma^*(a_d-a_o)}{\bar{\phi}^2}\right]^{1/2}L^{-1/2}\,. \tag{10}$$

The *quadratic* dependence of $F_{\rm ord}(a)$ on a_d-a described above occurs in the two-phase region of the bulk phase diagram. In contrast, when there is no constraint on the nonordering density (i.e., for the single OP model), $F_{\rm ord}(a)$ is a linear function of $(a-a_d)$, so that $a_t(L)-a_d\sim L^{-1}$.[6,7] This difference in the finite-size behavior is a direct consequence of the different ensembles realized in these two cases. Note that the entropy, i.e., the derivative of the free energy with respect to temperature, is a *continuous* function of temperature when the transition occurs in the two-phase region of the bulk phase diagram.

Although the ordered profile is no longer the state of lowest free energy for $a>a_t(L)$, it still exists as a metastable state and may be observed experimentally because the relaxation time to the true equilibrium state may be very large. It is therefore interesting to find the limit of metastability, $a_{\rm meta}(L)$, of the ordered state. Using (6) and (9) we obtain

$$\frac{[a_d-a_{\rm meta}(L)]}{(a_d-a_o)}=\frac{\xi_o}{L}\ln\frac{L}{\xi_o}+O(L^{-1})\,,$$

which implies that the thickness of the ordered layer in the center of the film is

$$(L-2\hat{l})/\xi_o=\ln(L/\xi_0)+\text{const}$$

at $a_{\rm meta}(L)$. The temperature dependence of $\hat{l}$ as a function of L is summarized in Fig. 2.

As already noted, models (1) and (2) should describe SID behavior in short-range lattice-gas models for fcc alloys in thin-film geometries. In particular, it has been argued in Ref. 3 that the explicit form of the model we apply is the correct continuum generalization of short-range models of $\rm Cu_3Au$ films with (111)-free surfaces. A recent numerical analysis[11] of one such model using a discrete Bragg-Williams approximation (although restricted to relatively thin films) does indeed exhibit certain aspects of the behavior predicted above: in particular, the behavior of the surface OP, $\phi(z=0)\sim O(e^{-L})$ for $a_t(L)>a_o$, is clearly visible in the data presented in Ref. 11. The data for the transition temperature, on the other hand, seem *not* to follow the $L^{-1/2}$ law (10). We do not have any good explanation for this discrepancy.

III. LONG-RANGE FORCES—SURFACE MELTING

The wetting behavior in many experimental systems is determined by long-range power-law interactions. This occurs, for example, in simple liquids, where van der Waals forces dominate. Our analysis will be based on a simple two-component OP model for the surface melting[12–14] of crystalline films, where such forces are expected to be important asymptotically.

Let $n(\mathbf{r})$ denote the atomic number density. In the bulk solid phase, $n(\mathbf{r})$ can be expanded in the form

$$n(\mathbf{r})=n_o+\sum_{\mathbf{K}}n_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}\,,$$

where

$$n_o=\frac{1}{V}\int_V d^dr\,n(\mathbf{r})$$

is the mean density of the solid and $\mathbf{K}$ is a reciprocal-lattice vector. The sum runs over all $\mathbf{K}$. In the film, we write

$$\begin{aligned}n(\boldsymbol{\rho},z)&=n_o(z)+\sum_{\mathbf{K}}n_{\mathbf{K}}(z)e^{i\mathbf{K}\cdot\mathbf{r}}\\&=\bar{n}\left[1+\phi_0(z)+\sum_{\mathbf{K}}\phi_{\mathbf{K}}(z)e^{i\mathbf{K}\cdot\mathbf{r}}\right]\,,\end{aligned} \tag{11}$$

where $\bar{n}$ is a convenient reference density (see the Appendix).

Here we consider only a simple, truncated version of the expansion (11). Namely, we assume that one set of nonzero reciprocal-lattice vectors of equal length, denoted by $\{\mathbf{G}\}$, is dominant in the solid phase. In general, the dominant set $\{\mathbf{G}\}$ is the smallest nonzero set, e.g., the 12 [110] reciprocal-lattice vectors in a bcc crystal.[13] Our order parameter is therefore

$$\phi=\sum_{n}(\phi_{\rm G}+\phi_{-\rm G})/2$$

(Ref. 15), where the sum runs over the elements of $\{\mathbf{G}\}$, and the nonordering density $c=\phi_0$. In general, c is different in the solid (c_o) and liquid (c_d) phases; we shall assume here that $c_o>c_d$. Finally, we consider here the case in which solid-liquid coexistence is approached from the solid side, and ignore any possible evaporation process at the surface; this is certainly correct for low vapor pressure substances such as lead (Pb).

Assuming that the asymptotic form of the interatomic interaction is of van der Waals type, it is shown in the Appendix that the appropriate coarse-grained free-energy functional [for bcc crystals with (111)-free surfaces] is given by (1) and (2), with the additional term

$$F_{\rm LR}\{c\}=\tfrac{1}{2}\int_0^L dz\int_0^L dz'\,c(z)w(|z-z'|)c(z')\,, \tag{12}$$

where

$$w(x)=-w_0x^{-p}\quad\text{for } x\to\infty$$

describes the long-range (LR) interactions of the concentration c. $w_0>0$ is constant, and for nonretarded van der Waals interactions, $p=4$. In the simple MF approximation we apply, there is no long-range interaction between the OP fields (see the Appendix for a discussion of this point). We have ignored a term of the type $(\nabla c)^2$ in (1) because, while present, it is expected to be much weaker than the $(\nabla\phi)^2$ coupling.[13] Note furthermore that $\beta<0$, since we require $c_0>c_d$ in the two-phase region of the phase diagram.

The Euler-Lagrange equations for this model are

$$-\frac{d^2\phi}{dz^2}+[a\phi(z)-b\phi^2(z)+g\phi^3(z)+2\beta c(z)\phi(z)]=0 \tag{13a}$$

and

$$-\mu+\beta\phi^2(z)+\alpha c(z)+\int_0^L dz'\, w(|z-z'|)c(z')=0\ . \tag{13b}$$

If the thickness of the film is free to adjust itself, the transition occurs at constant chemical potential μ and the finize-size effects are the same as in the single OP case.[6,7] However, for L fixed, we have the constraint $\int_0^L dz\, c(z)=L\hat{c}$, and μ is therefore both temperature and size dependent. This is the case we consider here.

In a sharp-kink approximation, ϕ_b, c_o, c_d, and μ are given by the solutions of the equations

$$c_o=(\mu-\beta\phi_b^2)/(\alpha+w_b)\ ,$$

$$c_d=\mu/(\alpha+w_b)\ ,$$

$$(a+2\beta c_o)-b\phi_b+g\phi_b^2=0\ ,$$

and

$$\mu=(\alpha+w_b)\hat{c}+\phi_b^2\frac{\beta}{L}(L-2l)\ ,$$

where

$$w_b=\int_{-\infty}^{\infty}dx\, w(|x|)<0\ .$$

In the limit $L/\xi\rightarrow\infty$ it is straightforward to show that the free energy of the ordered state can be obtained in this approximation by minimizing the function

$$F_{\text{ord}}(l)=2\sigma^*+(L-2l)f(\phi_b)+\lambda_1 l^{-p+2}-\lambda_2(L-2l)^{-p+2} \tag{14}$$

with the Hamaker constants

$$\lambda_1=+\frac{w_0}{(p-1)(p-2)}2c_d(c_o-c_d)\ ,$$

$$\lambda_2=+\frac{w_0}{(p-1)(p-2)}(c_o-c_d)^2\ .$$

In the two-phase region, $f(\phi_b)$ is given by (7) as before, with $\bar{\phi}=2b/3\bar{g}_{\text{eff}}$ and

$$\bar{g}_{\text{eff}}=g-2\beta^2/(\alpha+w_b)\ .$$

In (14), terms of order $(L-l)^{-p+2}$ and L^{-p+2} have been neglected, because they do not become singular in the limits $l\rightarrow 0$ or $(L-2l)\rightarrow 0$. Note that (14) is the naive generalization of (6) one would expect for long-range interactions: all one has to do is to substitute the correct form of the effective interface potential for the interaction between the various interfaces. For $c_o>c_d$, both λ_1 and λ_2 are positive; for $c_o<c_d$, however, λ_1 changes sign and there can be no continuous SID transition in this case. For $c_o=c_d$ one expects, in general, higher-order terms of the type l^{-p+1} and $(L-2l)^{-p+1}$.

Minimizing (14), we find that both wetting and the crossover behavior near a_o are described (to lowest order) by

$$A_3\hat{l}^{-p+1}+(a-a_o)=A_2\frac{2\hat{l}}{L}\ , \tag{15}$$

where

$$A_3=-2w_0\beta c_d/(p-1)(\alpha+w_b)>0\ .$$

Thus, for $L=\infty$, $\hat{l}$ diverges as $a\rightarrow a_o^-$ as $(a_o-a)^{-1/(p-1)}$, while for finite L, $\hat{l}\sim L^{1/p}$ at a_o. For $a_o<a<a_t$, $\hat{l}$ is $O(L)$, just as in the case of short-range interactions considered before.

The shift in transition temperature is given by (10), *independent* of the range of the interactions (as long as w_b is finite). However, when the system is taken into the metastable regime, the interactions start to become important again. The limit of metastability is given by

$$a_d-a_{\text{meta}}(L)\sim L^{-1+1/p}$$

in the long-range case, which implies

$$(L-2\hat{l})\sim L^{1/p}$$

at $a_{\text{meta}}(L)$. These results are summarized in Fig. 3.

Going beyond the sharp-kink approximation, it is straightforward to show, using (13b) and arguments similar to those applied in Ref. 16, that the concentration profile $c(z)$ develops a long-range tail of the form

$$c(z)-c_d\sim 1/z^{p-1}$$

in the disordered surface layer, i.e., for $0\ll z\ll\hat{l}$, as well as a similar tail in the ordered phase. Using this result in (13a), however, one finds that this does not change the exponential behavior of the tails of $\phi(z)$, so that

$$\phi(z)\sim\exp[-(\hat{l}-z)/\xi_d] \tag{16}$$

in the surface layer. Our model therefore predicts that

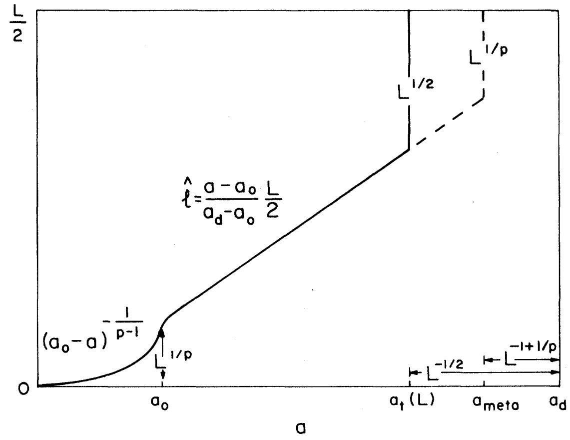

FIG. 3. Temperature dependence of the thickness $\hat{l}$ of the disordered surface layer, for the case of long-range (power-law) interactions. The dependence of various quantities as a function of the film thickness L is indicated. For further discussion, see the text.

the order-parameter decays exponentially, whereas the concentration approaches its bulk value with a power law. This kind of behavior has been postulated in order to interpret surface melting experiments in thin films.[17]

It is easy to show that the tails of the concentration profile do not change the leading contributions to the effective interface potentials, so that (14) is correct beyond the sharp-kink approximation.[16,18,19] Because the concentration interactions are of longer range than those of the OP, the concentration mode determines the wetting behavior in the present case. This implies a rather unusual, nonuniversal temperature dependence of the surface OP as $a \to a_o^-$.[14] However, in the two-phase region, Eq. (16) implies that the surface order parameter is $O(e^{-L})$, just as in the case of short-range interactions. The surface concentration at the transition temperature a_t, on the other hand, approaches its value in the infinite system, $c_\infty(z=0)$, as

$$c(0)-c_\infty(0)\sim L^{-p+1} .$$

IV. SUMMARY

The presence of conserved nonordering densities drastically alters the finite-size behavior at interface delocalization transitions in films of finite thickness L. The reason for this is that the constraints lead to a two-phase region in the bulk phase diagram. For small L, the disordered phase can become thermodynamically stable before this two-phase region is reached. In this case the shift of the transition temperature is proportional to L^{-1}, just as in systems without constraints. However, for L sufficiently large, the thickness of the disordered surface layer begins to diverge as the two-phase region is approached from below. In the two-phase region, the thickness of the wetting layer is determined by the constraint (lever-rule regime). With increasing temperature, the thickness of the wetting layer continues to grow until close to the upper boundary of the two-phase region, only a thin ordered layer of thickness $O(L^{1/2})$ remains at the center of the film. At this point, the ordered profile becomes thermodynamically unstable, resulting in a shift of the transition temperature proportional to $L^{-1/2}$, *independent* of the range of interactions. The different finite-size behavior in systems with and without constraints is thus a direct consequence of the different ensembles realized in these two cases. Finally, it was shown that the ordered profile is metastable above the thermodynamic transition temperature up to a temperature $a_{\mathrm{meta}}(L)$, the value of which depends on the explicit form of the interaction potential.

Two models were analyzed in detail; the first describes surface-induced-disorder transitions in binary alloys with short-range (exponential) interactions, and the other, surface melting with long-range van der Waals interactions. In both cases, constraints of the type we consider are expected to occur in many experimental situations. Explicit results for the finite-size behavior summarized in the last paragraph were presented. In addition, new results for the decay of the order-parameter profiles at the surface melting transition were derived.

Accurate experimental studies of wetting behavior in thin-film geometries have become increasingly feasible in the last few years.[17,20] It is hoped that the present work will be of use in the interpretation of those experiments in which "hidden" variables play an important role.

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APPENDIX

According to the density-functional formalism, the Helmholtz free energy $\mathcal{F}$ on an inhomogeneous system can be expressed as a functional of the atomic number density $n(\mathbf{r})$. If the elementary interatomic interaction potential $v(r)$ can be divided into a short-range repulsive part $u(r)$ and a long-range attractive tail $w(r)$, the mean-field grand potential functional can be written as[21]

$$\Omega[n]=\mathcal{F}_u[n]+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,w(|\mathbf{r}-\mathbf{r}'|)n(\mathbf{r})n(\mathbf{r}') + \int d\mathbf{r}[V(\mathbf{r})-\mu]n(\mathbf{r}) , \qquad \text{(A1)}$$

where μ is the chemical potential, $V(\mathbf{r})$ an external potential, and $\mathcal{F}_u[n]$ the free energy functional of the reference system with potential $u(r)$. Without loss of generality, $u(\mathbf{r})$ can be approximated by a hard-sphere potential which is infinite for $r \le d$ and zero for $r > d$, where d is an effective hard-sphere diameter approximately equal to r_o, the position of the minimum of the full interaction potential $v(r)$. Equation (A1) contains only the lowest-order mean-field-like contribution of $w(r)$. This will be sufficient for our purposes.

For small inhomogeneities, it is convenient to expand the grand potential about some homogeneous reference state.[22] If we take this reference state to be the equilibrium liquid phase at uniform density $n(\mathbf{r})=\bar{n}$, we obtain

$$\Omega[n]=\Omega[\bar{n}]+\Delta\mathcal{F}+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,w(|\mathbf{r}-\mathbf{r}'|)\Delta n(\mathbf{r})\Delta n(\mathbf{r}') + \int d\mathbf{r}\,V(\mathbf{r})\Delta n(\mathbf{r}) \qquad \text{(A2)}$$

where

$$\Delta\mathcal{F}=\beta^{-1}\int d\mathbf{r}\{n(\mathbf{r})\ln[n(\mathbf{r})/\bar{n}]-[n(\mathbf{r})-\bar{n}]\} - \frac{\beta^{-1}}{2}\int d\mathbf{r}\int d\mathbf{r}'\,c_{\mathrm{HS}}^{(2)}(|\mathbf{r}-\mathbf{r}'|;\bar{n})\Delta n(\mathbf{r})\Delta n(\mathbf{r}') , \qquad \text{(A3)}$$

with $\Delta n(\mathbf{r})=n(\mathbf{r})-\bar{n}$ and $\beta^{-1}=k_BT$. $c_{\mathrm{HS}}^{(2)}(r;\bar{n})$ is the hard-sphere (HS) direct correlation function of the homogeneous reference liquid. In deriving (A2) and (A3) we have used the fact that $\delta\Omega/\delta n|_{\bar{n}}=0$ for $V(\mathbf{r})=0$. The first term in (A3) is the ideal-gas contribution; the second term results from truncating the functional Taylor expansion of the excess Helmholtz free energy at second order in the density difference $\Delta n(\mathbf{r})$.

In the film, a convenient parametrization for the density is

$$n(\mathbf{r})=\bar{n}\left[1+\phi_0(z)+\sum_{\mathbf{K}}\phi_{\mathbf{K}}(z)e^{i\mathbf{K}\cdot\mathbf{r}}\right], \tag{A4}$$

where the sum runs over the nonzero reciprocal-lattice vectors $\mathbf{K}$ of the solid. In the bulk, $\{\phi_{\mathbf{K}}\}$ is the set of order parameters characterizing the solid phase. Here, it is sufficient to consider only a simple, truncated version of (A4) in which only one set of reciprocal-lattice vectors of equal length is included. This set, denoted by $\{\mathbf{G}\}$, is the smallest nonzero set, e.g., the 12 [110] reciprocal-lattice vectors in a bcc crystal.

To be specific, we shall assume in the following that the solid is a bcc crystal. As already noted, the set $\{\mathbf{G}\}$ contains 12 elements in this case. A suitable choice of basis vectors is

$$\mathbf{a}_1=\frac{a}{2}(-\hat{\mathbf{e}}_1+\hat{\mathbf{e}}_2+\hat{\mathbf{e}}_3)\ ,$$

$$\mathbf{a}_2=\frac{a}{2}(\hat{\mathbf{e}}_1-\hat{\mathbf{e}}_2+\hat{\mathbf{e}}_3)\ ,$$

and

$$\mathbf{a}_3=\frac{a}{2}(\hat{\mathbf{e}}_1+\hat{\mathbf{e}}_2-\hat{\mathbf{e}}_3)\ ,$$

where a is the next-nearest-neighbor distance. The corresponding reciprocal-lattice vectors are

$$\mathbf{b}_1=\frac{2\pi}{a}(\hat{e}_2+\hat{e}_3)\ ,$$

$$\mathbf{b}_2=\frac{2\pi}{a}(\hat{e}_1+\hat{e}_3)\ ,$$

and

$$\mathbf{b}_3=\frac{2\pi}{a}(\hat{e}_1+\hat{e}_2)\ ,$$

so that the 12 elements of $\{\mathbf{G}\}$ are $\pm\mathbf{b}_1$, $\pm\mathbf{b}_2$, $\pm\mathbf{b}_3$, $\pm(\mathbf{b}_1-\mathbf{b}_2)$, $\pm(\mathbf{b}_1-\mathbf{b}_3)$, and $\pm(\mathbf{b}_2-\mathbf{b}_3)$.

In the bulk, the coefficients ϕ_{G} of all the [110] reciprocal-lattice vectors must be of equal magnitude in order for the resulting solid to have the proper cubic point-group symmetry. Near a surface, however, this is not so; in this case they divide into several different classes depending on the direction cosine between the particular [110] vector and the surface normal. Within each class the amplitudes are the same.

In the following, we consider films with (111) surfaces, and take the z direction to be parallel to $\mathbf{a}_1$. In this case, the set $\{\mathbf{G}\}$ divides into two classes, each consisting of six elements. The first class, $\{\mathbf{G}_1\}\equiv\{\pm\mathbf{b}_2,\pm\mathbf{b}_3,\pm(\mathbf{b}_2-\mathbf{b}_3)\}$ consists of those reciprocal-lattice vectors which are perpendicular to $\mathbf{a}_1$. The second class, $\{\mathbf{G}_2\}=\{\pm\mathbf{b}_1,\pm(\mathbf{b}_1-\mathbf{b}_2),\pm(\mathbf{b}_1-\mathbf{b}_3)\}$ consists of those elements of $\{\mathbf{G}\}$ which have a finite projection on the z direction.

The interaction terms in (A2) and (A3) can be combined and written as

$$I\equiv-\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\Theta(|\mathbf{r}-\mathbf{r}'|)\Delta n(\mathbf{r})\Delta n(\mathbf{r}')\ , \tag{A5}$$

where

$$\Theta(|\mathbf{r}-\mathbf{r}'|)=\beta^{-1}c_{\mathrm{HS}}^{(2)}(|\mathbf{r}-\mathbf{r}'|;\bar{n})-w(|\mathbf{r}-\mathbf{r}'|)\ .$$

Substituting (A4) in (A5), we find $I=I_0+I_1+I_2$, with

$$I_i=-A\frac{\bar{n}^2}{2N_i}\int dz\int dz'\,\phi_i(z)\Theta_i(|z-z'|)\phi_i(z')\ ,$$

where A is the area of one surface of the film, N_i is the number of reciprocal-lattice vectors in $\{\mathbf{G}_i\}$, and

$$\phi_i\equiv\sum_{N_i}(\phi_{\mathbf{G}_i}+\phi_{-\mathbf{G}_i})/\sqrt{2}$$

for $i=1,2$. The functions $\Theta_i(z)$ are given by

$$\Theta_0(z)=\int d\rho\,\Theta[(\rho^2+z^2)^{1/2}]\ ,$$

$$\Theta_1(z)=\sum_{\mathbf{G}_1}\int d\rho\,\Theta[(\rho^2+z^2)^{1/2}]e^{i\mathbf{G}_1\cdot\rho}\ ,$$

and

$$\Theta_2(z)=\sum_{\mathbf{G}_2}e^{iG_2^{\perp}z}\int d\rho\,\Theta[(\rho^2+z^2)^{1/2}]e^{i\mathbf{G}_2^{\parallel}\cdot\rho}\ ,$$

where $G_2^{\perp}$ is the magnitude of the component of $\mathbf{G}_2$ perpendicular to the surface (i.e., parallel to z) and $\mathbf{G}_2^{\parallel}$ is the component of $\mathbf{G}_2$ in the (111) plane.

First, note that for nonretarded van der Waals forces, $\Theta_0(z)$ is asymptotically proportional to $1/z^4$ in $d=3$ dimensions. On the other hand, both $\Theta_1(z)$ and $\Theta_2(z)$ are *short range*, even though $\Theta(r)$ has a long-range tail. To see this, consider $\Theta_1(z)$. First of all,

$$\int d\rho\,e^{i\mathbf{G}_1\cdot\rho}=\int_0^{\infty}\rho\,d\rho\int_0^{2\pi}d\theta\,e^{iG_1\rho\cos\theta}$$

$$=2\pi\int_0^{\infty}\rho\,d\rho\,J_0(G_1\rho)$$

so that

$$\Theta_1(z)=12\pi\int_0^{\infty}\rho\,d\rho\,\Theta[(\rho^2+z^2)^{1/2}]J_0(G_1\rho)\ .$$

The essential features of the large-z behavior of $\Theta_1(z)$ can be determined by assuming an analytically tractable form for $\Theta(r)$ which exhibits the correct large-r behavior. A particularly simple choice, appropriate for van der Waals forces, is $\Theta(r)=\gamma/(\alpha^2+r^2)^3$, where α and γ are constants. With this choice we find

$$\int_0^{\infty}\rho\,d\rho\,\Theta[(\rho^2+z^2)^{1/2}]J_0(G_1\rho)$$

$$=\frac{\gamma}{8}\left[\frac{G_1}{\alpha^2+z^2}\right]^2K_2[G_1(\alpha^2+z^2)^{1/2}]$$

so that $\Theta_1(z)\sim e^{-G_1|z|}$ asymptotically. Similar arguments can be applied to analyze $\Theta_2(z)$.

Because both $\Theta_1(z)$ and $\Theta_2(z)$ are short ranged, I_1 and I_2 can be simplified further by performing a gradient expansion. Expanding $\phi_1(z')$ and $\phi_2(z')$ to second order in $(z'-z)$ about z, we find

$$I_i=-\frac{\bar{n}A}{2N_i}\bar{J}_{i,0}\int dz\,\phi_i^2(z)+\frac{\bar{n}A}{2N_i}\bar{J}_{i,2}\int dz\left[\frac{d\phi_i}{dz}\right]^2$$

for $i=1,2$, where

$$\bar{J}_{i,m}=\bar{n}\int_{-\infty}^{\infty} dz\, z^m\Theta_i(z)=\bar{n}\sum_{\mathbf{G}_i}\int d\mathbf{r}\, z^m\Theta(r)e^{i\mathbf{G}_i\cdot\mathbf{r}} .$$

Since $G_1=G_2=G$, we see that

$$\bar{J}_{1,0}=\bar{J}_{2,0}=6\Theta(G)>0 ,$$

where $\Theta(G)$ is the Fourier transform of the direct correlation function. Also, note that

$$\bar{n}\int d\mathbf{r}\, r_\alpha r_\beta\Theta(r)e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$=-\left[\frac{1}{k}\left[\delta_{\alpha,\beta}-\frac{k_\alpha k_\beta}{k^2}\right]\frac{d\Theta(k)}{dk}+\frac{k_\alpha k_\beta}{k^2}\frac{d^2\Theta(k)}{dk^2}\right]$$

and that $\Theta(k)=1-1/S(k)$, where $S(k)$ is the liquid structure factor. Quite generally, we expect G to be the approximate position of the first peak in $S(k)$ (Ref. 23) so that

$$\bar{J}_{1,2}=-\frac{6}{G}\frac{d\Theta(k)}{dk}\bigg|_G\approx 0 ,$$

and

$$\bar{J}_{2,2}=-\frac{4}{G}\frac{d\Theta(k)}{dk}\bigg|_G-2\frac{d^2\Theta(k)}{dk^2}\bigg|_G$$

$$\approx -2\frac{d^2\Theta(k)}{dk^2}\bigg|_G>0 .$$

The contribution of the ideal-gas term in (A3) can be determined as follows. Substituting (A4) in the first term on the right-hand side of (A3) one obtains

$$\int d\mathbf{r}\{n(\mathbf{r})\ln[n(\mathbf{r})/\bar{n}]-[n(\mathbf{r})-\bar{n}]\}$$

$$=\bar{n}\sum_{k=2}^{\infty}\frac{(-1)^k}{(k^2-k)}\int d\mathbf{r}\left[\phi_0(z)+\sum_{\mathbf{G}}\phi_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{r}}\right]^k . \tag{A6}$$

The right-hand side of (A6) can be written as

$$\bar{n}\int d\mathbf{r}\left[\sum_{\mathbf{K}}a_{\mathbf{K}}\phi_{\mathbf{K}}(z)\phi_{-\mathbf{K}}(z)\right.$$

$$\left.+\sum_{\mathbf{K},\mathbf{K}',\mathbf{K}''}a_{\mathbf{K},\mathbf{K}',\mathbf{K}''}\phi_{\mathbf{K}}\phi_{\mathbf{K}'}\phi_{\mathbf{K}''}+\cdots\right] ,$$

where the K sums run over zero and the elements of $\{\mathbf{G}_1\}$ and $\{\mathbf{G}_2\}$. In the third-order term, only those reciprocal-lattice vectors contribute which satisfy the condition $\mathbf{K}+\mathbf{K}'+\mathbf{K}''=0$, and, in general, the condition that the nth order term does not vanish is $\mathbf{K}+\mathbf{K}'+\cdots+\mathbf{K}^{(n)}=0$.

Since ϕ_0 is a nonordering density, we shall keep only the lowest-order contributions ϕ_0^2 and $\phi_0\phi_{\mathbf{G}}\phi_{-\mathbf{G}}$. Doing this we finally obtain

$$\bar{n}\int d\mathbf{r}[\tfrac{1}{2}a_2(\phi_1^2+\phi_2^2)+\tfrac{1}{2}b_2\phi_0^2-b_3\phi_0(\phi_1^2+\phi_2^2)-\tfrac{1}{4}a_3(\phi_1^3+3\phi_1\phi_2^2)+\tfrac{1}{9}a_4(2\phi_1^4+2\phi_2^4+5\phi_1^2\phi_2^2)+\cdots] . \tag{A7}$$

In writing (A7) we have followed the procedure used in Ref. 13. At any (e.g., nth) power of order parameters ϕ_1 and ϕ_2, there exist several symmetry classes of polygons with n sides which can be constructed from the elements of $\{\mathbf{G}\}$. All the polygons in a given symmetry class can be transformed into one another by an operation of the cubic point group. We make the ansatz that all polygons with the same number of sides have the same coefficients. This is not, however, required by symmetry. Nevertheless, the essential physics would not change if different coefficients were allowed for, and furthermore, there is no convenient empirical procedure for determining the values of these coefficients.

Denoting the integrand of (A7) by $f(\{\phi_i\})$, our free-energy functional has the form

$$\int dz\left[\frac{1}{2}\left[\frac{d\phi_2}{dz}\right]^2+f(\{\phi_i\})\right]$$

$$-\tfrac{1}{2}\int dz\int dz'\,\Theta(|z-z'|)\phi_0(z)\phi_0(z') , \tag{A8}$$

where unimportant constants have been dropped. The Euler-Lagrange equations for this model contain no gradient term involving $\phi_1(z)$. $\phi_1(z)$ is therefore determined by the local values of $\phi_0(z)$ and $\phi_2(z)$; in particular, it is easy to see that $\phi_1(z)\sim\phi_2^2(z)$ for $\phi_2(z)\to 0$ so that the surface critical exponent for the ϕ_1 mode is just twice that of the ϕ_2 mode. In the bulk, however, $\phi_1(\infty)\equiv\phi_2(\infty)$ in order that the bulk crystal exhibits cubic point-group symmetry. As shown in Ref. 3, the ϕ_1 mode does not affect the universal features of the SID transition in this case. ϕ_1 can therefore be integrated out, leaving a two-component order-parameter model. The resulting model is given by Eqs. (1), (2), and (12) with $\phi\equiv\phi_2$ and $c\equiv\phi_0$.

The same procedures can be applied in other crystal directions. For example, in the [110] direction, $\{\mathbf{G}\}$ divides into three classes, two of which have a nonzero projection of the z direction.[13] The resulting model is somewhat more complicated in that four fields must be considered, three of which have nontrivial interaction terms. Note that two elements of $\{\mathbf{G}\}$ (say $\pm\mathbf{g}$) are, in fact, parallel to the z direction in this case. This leads to the novel situation that *both* ϕ_0 and $\phi_{\mathbf{g}}$ have long-range interactions in the z direction.[24] All other fields have effective exponential interactions; for these fields a gradient expansion can again be made.

One general feature which has emerged from the present analysis should be emphasized, namely, that the range of the effective interaction in the z direction of some component $\phi_{\mathbf{k}}$ of the order parameter depends on the value of $\hat{\mathbf{z}}\cdot\mathbf{k}$. Quite generally, the smaller the projection of $\mathbf{k}$ on $\hat{\mathbf{z}}$, the shorter the range of the interaction. In particular, for $\mathbf{k}\|\hat{\mathbf{z}}$, one obtains long-range power-law interactions.

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