Evidence for the divergence of the line tension at the wetting transition

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We calculate, for a spin-$\frac{1}{2}$ Ising model within the mean-field approximation, the line tension along partial-wetting surface states up to a first-order wetting transition where the line disappears. We likewise calculate the line tension of the boundary between the two coexisting surface states at the prewetting transition and follow its behavior into the neighborhood of bulk wetting. In both cases we find evidence for the *divergence* of the line tension.

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The macroscopic one-dimensional locus where two or more interfaces meet, known as the contact line [1] is a complex type of equilibrium inhomogeneity that is currently attracting attention [2–5], and some of the properties of its excess free energy per unit length, or line tension τ, have begun to be revealed. An interesting, and potentially important, question posed by Widom and coworkers [2] is the fate of the line tension at a first-order wetting transition. A system exhibiting such a transition can be taken from three-phase partial-wetting states to two-phase prewetting-transition states, with the virtue that along this path of states the contact line is well defined except at the first-order wetting transition. Experimentally, the line tension τ is not easily accessible, since the contact line is a delicate object and its properties appear overwhelmed by surface and bulk effects. The magnitude of τ is presumably very small in general, and therefore its role in many interfacial phenomena, e.g., spreading, contact-angle hysteresis, etc., although largely unknown, might only be a secondary one. The possibility of the divergence of τ at the wetting transition would bring into the forefront the consideration of the line inhomogeneity in descriptions of aspects of the wetting phenomenon itself, and may also provide the conditions at which the properties of the contact line may become conspicuous and observable in macroscopic systems.

Phenomenological studies [2] have probed the behavior of τ along the above mentioned path of states, and the preliminary evidence gathered has provided arguments for its vanishing there. A similar result has been found [3] for the line tension associated with surface critical phenomena (specifically, at the ordinary, special, and pure surface transitions [6,7]). Other situations that may lead to experimentally observable properties of the contact line involve phase-coexistence configurations where several lines are present, for example, when, say, two immiscible liquids both partially wet a solid substrate. Such a multiple-line problem has been analyzed [4] and the one-dimensional analog for line tensions of the partial- to perfect-wetting transition leading to Antonov's rule [1] has been found to occur and to determine equilibrium line structures. Finally, general microscopic expressions for τ have been derived in terms of the density [5], the pressure tensor [5] and the direct-correlation function [3] appropriate for this type of inhomogeneity.

Here we present evidence for the divergence of the line tension at a first-order wetting transition. (Recent work [8] on a more general line-tension model of the type studied in Ref. [2] indicates, in agreement with our findings, the divergence of τ when complete wetting is approximated from partial-wetting three-phase states.) Our evidence is obtained from the consideration of a simple spin-$\frac{1}{2}$ Ising model in the mean-field approximation, and we find $\tau \to \infty$ at wetting, both from the three-phase side and from the prewetting line. We determine first the equilibrium magnetization inhomogeneities that correspond to a slab geometry with two parallel, but distant, surfaces that introduce an asymmetry via surface fields equal in magnitude but with opposite sign. With this geometry, partial wetting, complete wetting, and prewetting states are conveniently generated via minimization of the lattice free-energy functional (and access to the spatial variation of the magnetization allows also for the direct measurement of contact angles when applicable). We then analyze bulk, surface, and line free-energy contributions.

The macroscopic condition for the existence of a contact line at which three phases, say, α, β, and γ, and three interfaces $\alpha\beta$, $\alpha\gamma$, and $\beta\gamma$, meet is easily visualized in terms of the Neumann triangle construction [1]. In this construction the three tensions σ_{ij} $(i,j=\alpha,\beta,\gamma)$ are related to the sides of the triangle and the dihedral angles occupied by the three phases are related to the angles of the triangle. In our case, where one of the phases is taken to be inert and its interface with the other two is taken to be a planar surface, the Neumann triangle reduces to Young's law $\sigma_{\alpha\beta}=\sigma_{\beta\gamma}+\sigma_{\alpha\beta}\cos\vartheta$ where ϑ is the contact angle. The Neumann triangle collapses into a line when the largest of the tensions, say, $\sigma_{\alpha\gamma}$, is equal to the sum of the other two; then, the equilibrium configuration of the three phases is that in which the β phase completely wets the interface between the α and the γ phases. The wetting condition among the three interfacial tensions is known as Antonov's rule [1] and when it is satisfied, the three-phase line disappears.

Our numerical calculations correspond to a nearest-neighbor spin-$\frac{1}{2}$ Ising model on a cubic lattice confined by two parallel planar surfaces, separated by a distance large enough for finite-size effects to be negligible. Each surface represents the interface with an inert phase, and two other phases correspond to two oppositely magnetized domains when the temperature T is below the Curie temperature T_c. The Hamiltonian for the model is (with spins $S_i = \pm 1$)

$$H(\{S_i\}) = -J\sum_{\langle i,j\rangle} S_iS_j - J_1 \sum_{\langle i,j\rangle \in \Gamma_1} S_iS_j - J_2 \sum_{\langle i,j\rangle \in \Gamma_2} S_iS_j - h\sum_i S_i - h_1 \sum_{i\in\Gamma_1} S_i - h_2 \sum_{i\in\Gamma_2} S_i \ , \quad (1)$$

where J is the bulk (or interior) coupling; J_1 and J_2 the surface couplings on the two parallel planar surfaces Γ_1 and Γ_2, respectively; h is the bulk (or interior) magnetic field; and h_1 and h_2 are the surface magnetic fields on Γ_1 and Γ_2, respectively. This spin lattice is shown in Fig. 1(a). The total free energy of the system,

$$F = fV + \sigma_0 A_0 + \sigma_1 A_1 + \sigma_2 A_2 + \tau_1 L_1 + \tau_2 L_2 \ , \quad (2)$$

contains bulk (fV), surface ($\sigma_0 A_0 + \sigma_1 A_1 + \sigma_2 A_2$) and line ($\tau_1 L_1 + \tau_2 L_2$) contributions, where f is the bulk free-energy density in a volume V, σ_0 the interfacial tension of a domain wall with area A_0 that develops when $h=0$ between the two coexisting phases (+) and (−), σ_1 and σ_2 are the tensions at the walls with areas A_1 and A_2, and τ_1 and τ_2 are the line tensions of lengths L_1 and L_2 that may form on Γ_1 and Γ_2. We choose the surfaces Γ_1 and Γ_2 to be oriented along the (100) lattice-plane directions and to be rectangles of $N \times M$ lattice sites separated by L sites. The magnetization is always uniform along the k direction in Fig. 1(a). The surface couplings are taken to be equal, $J_1 = J_2$, and the surface fields of the same magnitude but opposite signs, $h_1 = -h_2$. Thus, when $h_1 > 0$, the (+) phase is favored by Γ_1 with tension σ_{1+}, the (−) phase is favored by Γ_2 with tension $\sigma_{2-} = \sigma_{1+}$. The (−) phase close to Γ_1 or the (+) phase close to Γ_2 have a larger tension $\sigma_{1-} = \sigma_{2+}$.

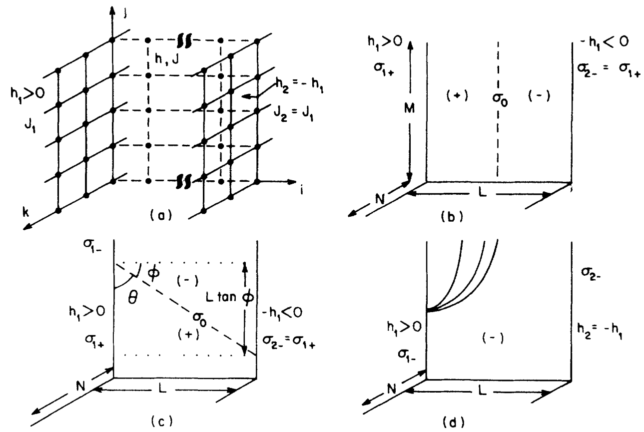

FIG. 1. (a) The two-surface-lattice geometry, (b) a complete wetting state, (c) a partial-wetting state, and (d) a prewetting state.

When $h=0$ and $T<T_c$, the complete wetting condition is $\sigma_{1-} = \sigma_{1+} + \sigma_0$ or $\sigma_{2+} = \sigma_{2-} + \sigma_0$, and the configuration of the system is as shown in Fig. 1(b). When this condition is not fulfilled, the equilibrium partial-wetting configuration is as shown in Fig. 1(c), where the contact angle is $\vartheta = \pi/2 - \varphi$, and there are two contact lines of length N on Γ_1 and Γ_2 with the same tension $\tau_1 = \tau_2$. When $h \neq 0$ and T and h_1 are chosen to lock the system at a prewetting transition, the configuration of the system is as shown in Fig. 1(d), where the lines represent contours of equal magnetization; there is one contact line of length N on Γ_1 with tension τ_1. The values of L, M, N of the system are large enough to ensure semi-infinite surface behavior. In our lattice model the interfacial and line tensions are anisotropic, i.e., they have a dependence on lattice directions, and our results exhibit the particular anisotropy of the line tensions that correspond to the fixed orientations of Γ_1 and Γ_2.

As mentioned, the model is translationally invariant with respect to the direction k [perpendicular to the plane of Figs. 1(b) to 1(d)], and its mean-field free energy per unit length (along that direction) can be written as

$$F = kT\sum_{i=0}^{L}\sum_{j=0}^{M}(1+m_{i,j})\ln(1+m_{i,j}) + \sum_{i=0}^{L}\sum_{j=0}^{M}(1-m_{i,j})\ln(1-m_{i,j}) - J\sum_{i=0}^{L}\sum_{j=0}^{M} m_{i,j}(m_{i,j+1}+m_{i+1,j}+m_{i,j})$$
$$-(J_1-J)\sum_{j=0}^{M}\left[m_{0,j}(m_{0,j+1}+m_{0,j}) + m_{L,j}(m_{L,j+1}+M_{L,j}) - h\sum_{i=0}^{L}\sum_{j=0}^{M-1} m_{i,j} - h_1\sum_{j=0}^{M}(m_{0,j}-m_{L,j})\right] , \quad (3)$$

where i and j are the column and row indexes, respectively, for a site in the lattice; $i=0$ defines Γ_1 and $i=L$ defines Γ_2. The magnetization profiles $m_{i,j}$ are obtained as solutions of the Euler-Lagrange equations associated with Eq. (3) with appropriate boundary conditions. These equations are solved numerically by simple iteration methods in 200×50 and 200×52 lattices with additional boundary conditions $m_{i,j+1} = m_{i,j}$ at the free edges of the lattice. The equilibrium solutions are those which minimize F.

The line tension $\tau = \tau_1 = \tau_2$ is determined by evaluating, first, bulk and surface contributions in the absence of contact lines, followed by a subtraction of these terms from the total free energy of the system configurations where these contact lines are present. As we see below, it is not necessary to evaluate the interfacial tension σ_0 of (+ −) two-phase-coexistence states if two different calculations are performed for systems where the two walls are separated by two different distances L and $L+\Delta L$. (Partial-wetting states necessarily introduce contact-line inhomogeneities and the discrimination between interfacial and line-tension terms introduces practical difficulties that we avoid via the variation of the size of the system.) The bulk density $f(T,h)$ is first determined by solving the Euler-Lagrange equations for the uniform magnetization $m_{i,j}=m$ and substituting in the free-energy expression Eq. (3). Then the surface tensions $\sigma_{1+}(T,h,h_1)=\sigma_{2-}$ and $\sigma_{1-}=\sigma_{2+}$ are obtained by generation of single-phase structures, $(+)$ or $(-)$, between the two walls and by subtraction of the bulk free energy from their total free energy.

Consider the partial-wetting configuration shown in Fig. 1(c). The total free energy of the system (per unit length along the k direction) can be written as

$$F(L)=fLM+(\sigma_{1+}+\sigma_{1-})(M-L\tan\varphi)+(\sigma_{1+}+\sigma_{2-})L\tan\varphi+\sigma_0 L(\cos\varphi)^{-1}+2\tau\ , \quad (4)$$

and the change in total free energy when the surfaces Γ_1 and Γ_2 are separated an additional distance ΔL is

$$\frac{\Delta F}{\Delta L}=\frac{F(L+\Delta L)-F(L)}{\Delta L}=fM-(\sigma_{1+}+\sigma_{1-}-\sigma_{1+}-\sigma_{2-})\tan\varphi+\sigma_0(\cos\varphi)^{-1}\ . \quad (5)$$

Therefore, the line tension is obtained as

$$\tau=\frac{1}{2}\left[F(L)-\frac{\Delta F}{\Delta L}L-(\sigma_{1+}+\sigma_{1-})\right]\ . \quad (6)$$

Our results for the contact line along partial-wetting states ($J_1=1.5$ J, $L=50$, $\Delta L=2$, and $M=200$) are shown in Fig. 2. The initial configuration was always that of a $(+-)$ interface perpendicular to Γ_1 and Γ_2 and iteration led to a well-defined contact angle (this angle was found to be independent of L for L larger than 20). Figure 2(a) shows magnetization contours for one such state. From these contours the contact angle can be clearly seen when the $(+-)$ interface is viewed as a whole, i.e., considering a "macroscopic length scale." On the other hand, close to the walls, at shorter or molecular length scales, the magnetization inhomogeneity that gives rise to the line tension shows an inwardly bent shape for the boundary where the three phases meet. The possible forms of this boundary have been discussed [9] in the context of intermediate length scales for the case of long-ranged van der Waals forces. Here, of course, the interactions are short ranged, but nevertheless we are able to show the actual shape of the boundary in our problem. Figure 2(b) shows the divergence of τ as the first-order wetting transition is approached (the surface field at the transition is approximately $h_1^w=0.1264$) Measurement of the contact angle as a function of h_1 leads to the plot of $\ln\tau$ versus $\ln(1-\cos\vartheta)$ shown in the inset in Fig. 2(b).

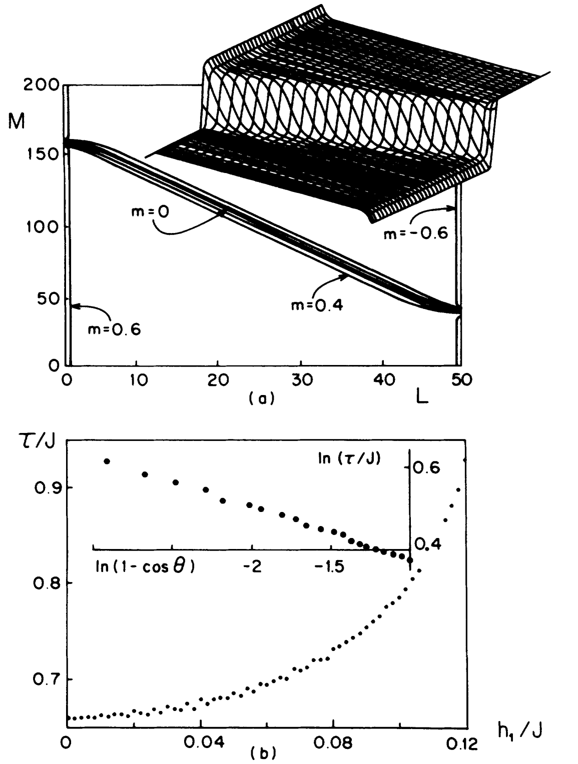

FIG. 2. (a) Magnetization contours of a partial-wetting state with $kT/J=2.73$ and $h_1/J=0.12$. The inset is a three-dimensional plot of the magnetization. (b) The line tension τ along partial wetting states as a function of the surface field h_1 (the wetting transition occurs approximately at $h_1^w/J=0.1264$). The inset shows $\ln\tau$ vs $\ln(1-\cos\vartheta)$, where ϑ is the contact angle.

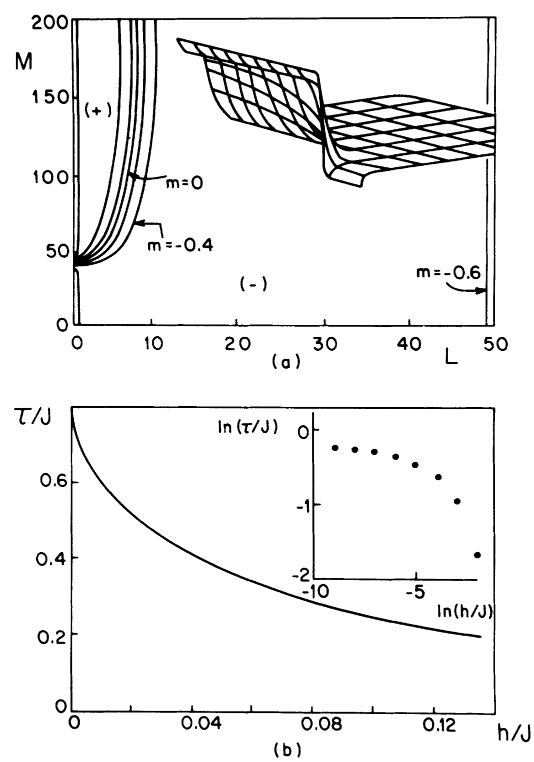

FIG. 3. (a) Magnetization contours of a prewetting state with $kT/J=2.73$, $h/J=-4.5\times10^{-5}$, and $h_1/J=0.1263$. The inset is a three-dimensional plot of the magnetization. (b) The dependence of the line tension τ, along prewetting transition states, on the bulk field h. The inset shows $\ln\tau$ vs $\ln h$.

The exponent for the divergence of τ with ϑ appears to be very small, and it might approach zero for smaller values of ϑ (notice that the smallest ϑ^2 obtained is of $\sim(10^{-2})$.

Our results for the contact line along the prewetting transition states ($J_1=1.5$ J, $L=50$, $\Delta L=2$, and $M=200$) are shown in Fig. 3. The starting trial magnetization was that corresponding to one of the surface states that coexist at prewetting, except that, at Γ_1, half of the plane was given the opposite sign of the magnetization, and iteration led to the contours shown in Fig. 3(a). In Fig. 3(b) we show the tension τ as a function of the bulk field h. There, the increment in τ leading to its divergence, as bulk wetting is approached, can be clearly seen. The inset in Fig. 3(b) shows a plot of $\ln\tau$ versus $\ln h$, from which the exponent for the divergence of τ with h appears also to be very small, or zero. Here it was possible to obtain magnetization profiles and line tensions without much computational effort down to bulk fields h that are (10^{-4}).

We have obtained the equilibrium spatial inhomogeneities in mean-field approximation generated at the planar surface of a spin-$\frac{1}{2}$ Ising model. The choice of surface couplings and fields for a slab geometry facilitated the evaluation of the line-tension terms. The line tension τ for both partial-wetting and prewetting states was found to increase in value without bound as the first-order wetting transition is approached from either end and therefore provides indications for its divergence there. This behavior is contrary to the evidence obtained from previous model predictions of this quantity that suggested the vanishing of τ at the wetting transition [2], but it is in agreement with more recent work [8] on a more general line-tension model of the type studied in Ref. [2]. This divergence appears plausible when one recalls that the contact line in this limit becomes the boundary that joins a microscopically thin interface with another, the wetting layer, of macroscopic thickness. The exponents with which τ diverges as a function of the distance to the wetting transition were determined, for both partial-wetting and prewetting states. We found that τ grows slowly, perhaps logarithmically, as wetting is approached. This behavior was most clearly observed from the prewetting side. Our findings correspond to the numerical solution of our model, and analytical evidence for the divergence of τ, even in mean-field theory is a challenging problem due to the complex type of inhomogeneity involved. Our results correspond to short-ranged interactions and the fluctuations that we ignored are expected to be important for the line inhomogeneity. The effects of long-ranged interactions and of fluctuations are not expected to remove the divergence of τ, but are likely to modify its exponents. It should be recalled that the inhomogeneity that gives rise to the contact line is not a purely one-dimensional object, but is embedded within the boundaries of bulk and surface phases. The equilibrium fluctuations of this line are necessarily accompanied by bulk and surface fluctuations [3], and these are likely to determine the overall behavior. Thus, our mean-field analysis may not suffer the radical modifications expected for a truly one-dimensional system.

Note added in proof. The interaction decay conditions for the divergence of τ at wetting have been analyzed by J. O. Indekeu (unpublished).

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