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Magnitude of the prewetting boundary tension near wetting for short-range forces

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We determine in a mean field approximation the spin-$\frac{1}{2}$ Ising model line tension τ along the boundary between surface states at the prewetting transition in the neighborhood of the wetting transition at bulk phase coexistence. We find very close agreement with the predictions of the interface displacement model for short-range interactions, i.e., τ increases (with a square-root dependence on the bulk external field h) towards a finite limit with diverging slope at wetting. Our findings help both in settling the discussion on the limiting value of τ and in understanding the origin of its singular behavior.

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Recent studies [1–6] of the contact line where three coexisting phases meet have revealed interesting singular behavior for its associated excess free energy, or line tension τ, when a first-order wetting transition is approached. Evidence for a sharp increment in the value of τ in the neighborhood of wetting along both partial wetting [4,5] and prewetting states [4] has already been reported. These results were obtained from studies of microscopic models in a mean-field approximation. Moreover, a phenomenological interface displacement model [6] yields analytical predictions that depend crucially on the range of the molecular interactions: The positive limiting value for τ is finite only when the decay rate of the interactions exceeds r^{-6}. These predictions hint at novel surface critical phenomena associated with first-order wetting transitions, the framework of which we sketch briefly below. This, in turn, points out the relevance of the contact line in interfacial phenomena, e.g., τ appears to play a dominant role in the kinetics of phase change associated with wetting films [7,8], opening interesting possibilities for further characterization of the elusive prewetting transition [9], or, alternatively, for the measurement of τ itself [7]. Microscopic model studies capable of probing the behavior of τ have been unable to come close enough to wetting [4,5], since they encounter technical difficulties that originate from both the bidirectional nature of the line inhomogeneity and the singular behavior that takes place there. The purpose of this paper is to help establish the fate of τ at wetting and to examine quantitatively, and—if it is the case—substantiate, some of the above-mentioned phenomenological predictions.

Along prewetting coexistence states, τ is necessarily positive, since in this case the line inhomogeneity connects only two surface states that differ in thickness, i.e., τ is the tension of an interface between two, two-dimensional phases. The prewetting transition curve is bounded by a prewetting critical point, located away from bulk coexistence, where the two surface states become identical (the analog of bulk criticality where surface tension vanishes), and by the wetting transition at bulk coexistence where the two states differ most since the thickness of one of the interfaces becomes infinite. Thus, as the wetting transition is approached, it could be expected that the magnitude of τ would increase in value, and possibly diverge. When the wetting transition is approached along partial-wetting states, the contact angle between two interfaces tends to zero, and a situation similar to that obtained from the prewetting side develops. These two interfaces and the phase they bound turn out to be, at wetting, a surface state of infinite thickness, while the remaining interface, which has become parallel to the other two, is its coexisting surface state.

Now, the surface phase diagram associated with a first-order wetting transition can be seen to be analogous to that of a system exhibiting a critical end point. This can be appreciated when it is considered that the basic coexisting states are the interfacial states and not the bulk phases (so that Young's law, or Antonov's rule, appear in place of equality of free energies). Then, partial wetting would correspond to a line of triple points, complete wetting to a line of ordinary critical points, first-order wetting to the critical end point, and prewetting states to a two-phase continuation terminating at another ordinary critical point. In the context of this analogy the line tension τ would exhibit critical behavior singularities resembling those recently discussed for bulk critical end points [10]. The interface displacement model [6] predicts that along prewetting states and for short-ranged forces (i.e., a decay rate faster than r^{-6}), τ attains its finite value with a diverging slope that has an inverse square-root dependence on the (thermodynamic-field) distance from coexistence. Along partial-wetting states, τ approaches its finite limit also with divergent slope, a weak logarithmic divergence in terms of the contact angle. Further, it has also been found that the amplitudes of these singular terms have universal properties [6]. It is therefore of interest to compare these predictions with the outcome of calculations based on microscopic models in the neighborhood of the wetting transition.

Here we present results obtained from precise numerical calculations for the mean-field behavior of the line tension along prewetting states for the nearest-neighbor spin-$\frac{1}{2}$ Ising model on a cubic lattice. As we shall see, our results strongly support some of the conclusions obtained from the interface displacement model for short-ranged forces. We have employed a slab geometry with two parallel distant surfaces that introduce an asymmetry via surface fields with opposite signs. As described in more detail in Ref. 4, this is a convenient geometry to generate partial-wetting, complete-wetting, and prewetting equilibrium magnetization profiles. In the partial-wetting regime, the limiting factor in our calculations is the size of the lattice because this determines the smallest contact angle attainable. This limitation applies to a lesser extent to the prewetting states, and in this case it is possible to perform computations much closer to the wetting transition and therefore open the possibility for more stringent comparisons.

The Hamiltonian for the model is (with spins $S_i=\pm 1$)

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

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. The surface couplings are taken to be equal, $J_1=J_2>0$, and the surface fields of the same magnitude but opposite signs, $h_1=-h_2<0$. We denote by $(-)$ and $(+)$ the two phases that coexist with interfacial tension σ_0 when the temperature T is below the critical temperature T_c and $h=0$. The $(-)$ phase is favored by Γ_1 with surface free energy σ_{1-} and the $(+)$ phase is favored by Γ_2 with surface free energy $\sigma_{2+}=\sigma_{1-}$. When the $(+)$ phase develops close to Γ_1, or the $(-)$ phase develops close to Γ_2, a larger surface free energy $\sigma_{1+}=\sigma_{2-}$ is obtained. We choose the surfaces J_1 and J_2 to be oriented along the (100) lattice plane directions and to be rectangles of $N\times M$ lattice sites separated by L lattice sites. The model is translationally invariant with respect to the (001) plane direction where the lattice has a width of N sites. The magnetization is always uniform along this direction. At equilibrium, when $h>0$ and T and h_1 are chosen to position the system at a prewetting transition, both $(+)$ and $(-)$ phases can come close to the Γ_1 surface and two different surface states can coexist there, while only the $(+)$ phase can come close to the Γ_2 surface. In this case there is one contact line of length N on Γ_1 with tension τ [4].

The model mean-field free-energy functional $F[\{m_{i,j}\}]$ is written as

$$F/N=\frac{kT}{2}\sum_{i=0}^{L}\sum_{j=0}^{M}[(1+m_{i,j})\ln(1+m_{i,j})+(1-m_{i,j})\ln(1-m_{i,j})]-J\sum_{i=0}^{L}\sum_{j=0}^{M}m_{i,j}(m_{i,j+1}+m_{i+1,j}+m_{i,j})$$
$$-(J_1-J)\sum_{j=0}^{M}[m_{0,j}(m_{0,j+1}+m_{0,j})+m_{L,j}(m_{L,j+1}+m_{L,j})]-h\sum_{i=0}^{L}\sum_{j=0}^{M-1}m_{i,j}-(h_1-h)\sum_{j=0}^{M}(m_{0,j}-m_{L,j})\ , \tag{2}$$

where i and j are the column and row indexes, respectively, for a site in the lattice plane perpendicular to the planar surfaces; $i=0$ and $i=L$ define Γ_1 and Γ_2, respectively. The magnetization profiles $m_{i,j}$ are obtained as solutions of the Euler-Lagrange equations associated with the above equation with the additional boundary conditions $m_{i,j+1}=m_{i,j}$ at the free edges of the lattice. These equations are solved numerically by simple iteration methods and the equilibrium solutions are those which minimize F.

The locus of prewetting transitions that we determined for our study of the line tension is shown in Fig. 1. We chose $J_1=1.5J$ and a fixed working temperature $kT/J=5.46$, given that the critical temperature is $kT_c/J=6$; therefore, this locus lies on the $(h/J,h_1/J)$ plane. In the scale of the Figure, the prewetting line does not show [11] the tangential (and logarithmic) approach to bulk coexistence characteristic of short-range forces; the wetting transition has a surface field value of $h_1^w=-0.1256$. Then we determined the magnetization profiles for the surface states along this coexistence curve, first, as single surface phases occupying the whole of the lattice, and, secondly, in actual coexistence with each other via the line inhomogeneity. In all cases the global error at iteration n, measured as

$$\sum_{i,j}\{\text{abs}[m_{i,j}(n)-m_{i,j}(n-1)]\}\ ,$$

was less than 10^{-8} (like that for h_1/J for the prewetting

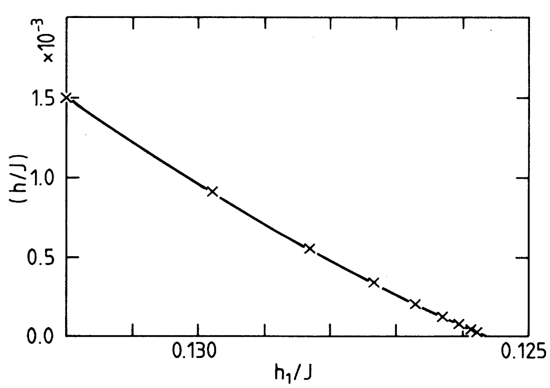

FIG. 1. Isothermal locus ($kT/J=5.46$) of prewetting transitions employed in the study of the boundary tension; the wetting transition has a surface field value of $h_1^w=-0.1256$.

transition locus in Fig. 1) for all lattices up to the maximum size considered ($L=50$ and $M=400$). The number of iterations necessary to reach convergence increased as the wetting transition was approached in a manner reminiscent of critical slowing down near critical states. (The smallest value for the bulk field considered was $h/J=2.75\times10^{-5}$ when it was necessary to perform over 5×10^5 iterations.)

The proximity to the wetting transition was monitored via the width W of the thick surface state at prewetting. This width is shown in Fig. 2(a) as a function of $\ln(h/J)$, where the linear behavior is indicative of that corresponding to short-range potentials in the neighborhood of the wetting transition. The stepwise behavior of W in this figure is due to our definition of this quantity as the number of lattice sites from the surface Γ_1 at which the absolute value of the magnetization is a minimum. We also found that as h is made to vanish, the line inhomogeneity extends faster along the direction parallel to the surfaces than in the direction normal to them. Therefore, it was necessary to consider lattices with large surface sizes (with M up to 400) for the profiles to become uniform along the direction parallel to the surfaces away from the central region of the lattice. The absence of finite-size effects was confirmed by reproduction of the profiles when only one surface phase is present by the wings $m_{i,0}$ and $m_{i,M}$ of the profiles with the contact line. In Fig. 2(b) we show a plot of the function

$$l(i)\equiv\min_j[\mathrm{abs}(m_{i,j})]\ , \qquad (3)$$

versus $\ln(i)$ for the interval $110<i<207$ for the smallest bulk field $h/J=2.75\times10^{-5}$ (the line inhomogeneity appears centered at $i=207$ and terminates roughly at $i=110$). The function $l(i)$ is analogous to the displacement profile $l(x)$ in the phenomenological theory of Ref. [6], which at wetting becomes proportional to $\ln x$ for short-ranged forces. Besides the stepwise nature of $l(i)$, introduced by the lattice, we observe from Fig. 2(b) that we obtain a close approximation to this logarithmic form close to wetting, and in support of the theoretical predictions mentioned.

We refer now to the results for the boundary tension itself. The bulk free energy was determined by solving the Euler-Lagrange equations for the uniform magnetization $m_{i,j}=m$ and substituting in the free-energy expression in Eq. (2). The surface free energies $\sigma_{1-}(T,h,h_1)=\sigma_{2+}$ and $\sigma_{1+}=\sigma_{2-}$ were obtained by subtraction of the bulk free energy from the total free energy calculated from the generated single-phase profiles. Finally, the line tension was determined by subtraction of bulk and surface terms from the free energy calculated from the generated double-phase profiles. Our results for the boundary tension are shown in Fig. 3 together with those from a minimum square fit of the formula

$$\tau/J=\tau_0/J-A(h/J)^{\phi} \quad \text{for } h\to0\ , \qquad (4)$$

with $\phi=\frac{1}{2}$ (as indicated by the asymptotic form obtained from the phenomenological theory). For $\phi=\frac{1}{2}$, we obtained $\tau_0/J=0.8180$ and $A=2.4878$, whereas if τ_0/J is given the value 0.8180, one obtains $\phi=0.5222$ and $A=2.9639$. Thus, from these data we are inclined to conclude that the predictions drawn in Ref. [6] from the interface displacement model appear to be confirmed for

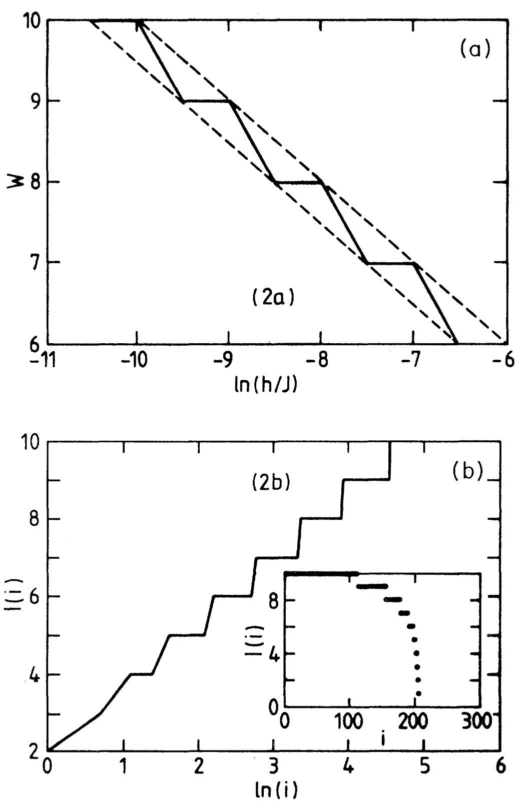

FIG. 2. (a) Width W of the thick film at prewetting vs logarithm of the bulk field h. Linear behavior is predicted near wetting. The stepwise behavior is due to the lattice and its definition (see text), while the straight lines are guides to the eye. (b) Displacement profile $l(i)$ of Eq. (3) vs logarithm of the wall coordinate i for $h/J=2.75\times10^{-5}$. Linear behavior is predicted at wetting. The inset shows the same profile as a function of i. The stepwise nature of $l(i)$ is introduced by the lattice.

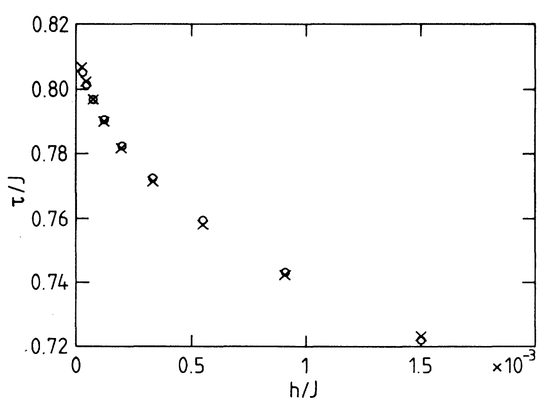

FIG. 3. The boundary tension τ as a function of the bulk external field (crosses), together with those from a minimum-square fit (circles) of the asymptotic form in Eq. (4) predicted by the phenomenological theory for the case of short-range forces.

short-ranged forces along prewetting states, leading to a finite line tension at the wetting transion. We note that in the global surface phase diagram [12], the extraordinary transition (occurring at $h=0$ and positive surface enhancement factor [12]) is a point on the first-order wetting transition locus and previous [3] results show a finite value of τ at this point.

Short-range forces seem therefore to provide an interesting limiting case in which, even though the thickness of one of the coexisting surface states becomes infinite at the wetting transition, the extent of the line inhomogeneity does not acquire the quality of area. The finiteness of τ results from the development of an inhomogeneous region that becomes much wider along the two coexisting interfaces (along the surface Γ_1) than in the direction normal to them, and leads to the specific logarithmic form of $l(i)$. This form for $l(i)$ is reminiscent of that for the order-parameter profiles at a critical end point for which is found a slow approach to its limiting value at the critical phase [13], in support of the analogy between these two problems mentioned above. Our confirmation of the inverse square-root divergent slope of τ strengthens the view that this quantity displays singular critical behavior at wetting. A similar situation takes place for long-range forces (with a decay rate not greater than r^{-6}) except that in this case the displacement profile $l(x)$ exhibits a faster growth, with x suggesting the divergence of τ itself at wetting [6]. The equilibrium fluctuations of this line are necessarily accompanied by bulk and surface fluctuations, and these are likely to determine the overall behavior. Thus, our mean-field analysis may not suffer radical modifications. The application of more powerful techniques to the analysis of the line inhomogeneity, like the Monte Carlo simulations already used to study the related surface states [14], will help in assessing the general validity of the results presented here.

Note added in proof. The prewetting boundary tension has been determined recently for a mean-field density functional [15]. This work reports a growth of τ compatible with a vanishing exponent as the distance to the wetting transition goes to zero. Their results are generally consistent with those reported here and in Ref. [4].

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