Divergence of the Point Tension at Wetting

D. B. Abraham, F. Latrémolière,* and P. J. Upton
Department of Physics, Theoretical Physics, 1, Keble Road, Oxford, OX1 3NP, England
(Received 12 April 1993)

To determine the behavior of the *line-point tension* $\hat{\tau}$ at the wetting transition, we consider a two-dimensional Ising model with appropriate boundary conditions and investigate suitable definitions of $\hat{\tau}$ associated with the junction of an interface tilted with average angle θ_c and another lying along the substrate. Size-dependent fluctuations in the *point of contact* require that $\hat{\tau}$ be defined through a convolution sum. Hence $\hat{\tau} \approx \ln(1/\theta_c)$ as $\theta_c \to 0$ (wetting transition), which can be understood as a consequence of the *entropic repulsion* of the tilted part of the interface against the substrate.

PACS numbers: 68.45.Gd, 05.50.+q, 05.70.−a, 82.65.Dp

Consider the common situation where two phases α and β meet at a wall (or third phase) ω with an angle of contact of θ_c between the $\alpha\beta$ interface and the $\beta\omega$ interface. As one approaches the surface wetting transition (for reviews, see, e.g., Refs. [1,2]), where, say, the β phase wets the $\alpha\omega$ interface at a temperature T_w, $\theta_c \to 0$ as temperature $T \to T_w$ from below, and the surface excess free energy (per area) $f^\times$ will have a singular part of the form $f^\times_{\text{sing}} \sim t^{2-\alpha_s}$, with $t=(T_w-T)/T_w$. Suppose one is able to associate a free energy per length, $\hat{\tau}$, called the *line tension* [3], with the *line of contact* of the $\alpha\beta$ interface and ω. An intriguing question to ask is whether $\hat{\tau}$ has any interesting singular behavior as $T \uparrow T_w$ analogous to that of the interfacial and surface tensions as the bulk critical point is approached. This has been the subject of much recent work which has been largely mean-field-like in character [4,5]. A mean field theory involving an interfacial displacement model [5], which fixes the line of contact in some laboratory frame, predicts that $\hat{\tau} \propto -\theta_c$ as $\theta_c \to 0$ for critical wetting. A *nonclassical scaling hypothesis* has recently been proposed [6] where if $\hat{\tau}_{\text{sing}} \sim t^{2-\alpha_l}$ as $t \downarrow 0$ and the correlation length parallel to the wall $\xi_\parallel$ diverges like $\xi_\parallel \sim t^{-\nu_\parallel}$ as $t \downarrow 0$, then the following exponent relation holds:

$$\alpha_l = \alpha_s + \nu_\parallel . \tag{1}$$

Line tensions have also been considered experimentally [7] including in recent studies of the decay time of surface metastable states via nucleation near wetting [8].

A Gibbs' thermodynamic argument [3] implies that $\hat{\tau}$ stays invariant under parallel translations of the arbitrary Gibbs' dividing surfaces. However, with some exceptions [9,10], very little has been said about the effect of fluctuations in the *tilt* of the $\alpha\beta$ interface around θ_c or in transverse (capillary-wave-like) fluctuations in the contact line itself. Such fluctuations may prevent one from uniquely defining a line tension that stays finite in the thermodynamic limit. With these issues in mind, it seems timely to present the results of a treatment based on an *exactly* solved two-dimensional model where the line tension is replaced by a "point" tension—i.e., a free energy associated with the point of contact between a sloping interface (now a line) and a wall.

Consider a nearest-neighbor Ising ferromagnet on a square lattice with zero bulk field but with spins fixed on the boundary so that a domain wall crosses the system as shown in Fig. 1. By weakening the vertical bonds contiguous with fixed spins on the lower boundary a wetting transition can be induced as has been shown by studying the thermodynamics [11] and spin [11] and excess-energy-density distributions [12]. The exact mean shape of the interface is also given by a Wulff construction and is composed of two line segments, the one crossing the strip being inclined on average at a contact angle θ_c, the value of which is given by the following Young equation, modified by the inclusion of the second term on the left-hand side which takes into account the anisotropy of the surface tension $\sigma(\theta)$ on the lattice [12]

$$\sigma(\theta_c)\cos\theta_c - \sigma'(\theta_c)\sin\theta_c = f^\times . \tag{2}$$

The crucial fact which has to be added to the thermodynamic picture is the existence of large fluctuations in the interface as it crosses the strip, growing as $\sqrt{L}$. In the associated solid-on-solid (SOS) model [13], the point

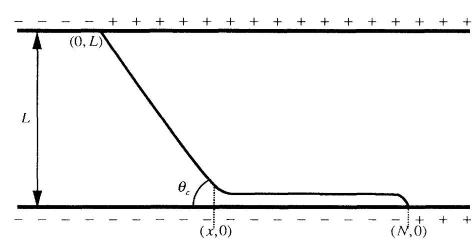

FIG. 1. Phase separation by fixed-spin boundary conditions, equivalent to a surface field acting on the spins next to the boundary. The bottom edge of the strip has bonds of *reduced strength* in the (0,1) direction abutting the line $y=0$. Provided the temperature is low enough, the interface stays near the bottom edge as it moves from right to left until it crosses the strip at a mean angle of θ_c. The partially wet layer well to the right of $(x,0)$ behaves exactly like the wetting film in Ref. [11]; it is characterized by length scales parallel and perpendicular to the edge, $\xi_\parallel$ and $\xi_\perp$, respectively.

0031-9007/93/71(3)/404(4)$06.00

of first contact of the domain wall with the line $y=0$ given by x_0 fluctuates about its mean value x_c (given by the Wulff shape, $x_c = L\cot\theta_c$) asymptotically as

$$\langle (x_0 - x_c)^2 \rangle \approx \frac{L}{\sin^3\theta_c \tilde{\Sigma}(\theta_c)}, \tag{3}$$

where $\tilde{\Sigma}(\theta_c) = \sigma(\theta_c) + \sigma^{(2)}(\theta_c)$ is the surface stiffness [14]. This can be seen more simply from an argument based on fluctuation theory [13] analogous to that of Ref. [14].

As explained in the introduction, we want to associate a free energy with the joining of the two linear portions of the mean interface shape. Our definition of the *point tension* $\hat{\tau}$ is

$$\exp\hat{\tau} = \lim_{L\to\infty}\lim_{N\to\infty}\sum_{x=-\infty}^{\infty} Q_L(x) Z(N-x)/Z_L(N), \tag{4}$$

where $Z_L(N)$ is the exact partition function (PF) for the boundary condition shown in Fig. 1, $Z(N-x)$ is the PF with the interface beginning at (0,0) and ending at $(N-x,0)$ with the same wetting boundary field as in $Z_L(N)$. The reason we have a sum over x is that, as Eq. (3) suggests, the point of first contact of the domain wall with the bottom face x_0 fluctuates strongly. Although values of x_0 which deviate from x_c by more than $\mathcal{O}(\sqrt{L})$ are relatively unimportant, the unrestricted summation makes the calculations easier.

We have investigated four choices of $Q_L(x)$, the PF for the interface crossing from $(0,L)$ to $(x,0)$: These are illustrated in Fig. 2. Definitions (i) and (ii) are of Dobrushin type [2,15]; (iii) is due to Fisher and Ferdinand [16]; and (iv) is a hybrid of (i) and (iii) of our own devising. The Fisher-Ferdinand definition inserts into a system, which is either up or down magnetized, a "connected" ladder of exactly reversed bonds, L horizontal and x vertical ones joining the two points $(0,L)$ and $(x,0)$. The surface tension is then extracted from a quotient of partition functions in the usual way [16]. The interface becomes a path of frustrated bonds with no geometrical restriction, unlike cases (i) and (ii). That the surface tension should be the same follows from duality arguments, but the finite-size corrections differ significantly. In case (iv), we want the domain wall restriction to be the same at the upper point $(0,L)$ as in Fig. 1, but to allow any approach to the final point $(x,0)$. We do this by bringing the reversed-bond ladder up to an edge of the system, where the spins are forced to be up, containing the point $(0,L)$. The dual of the partition function ratio is then a pair-spin correlation function for a half plane with one spin in a free edge but the other tending to the bulk, something which we have determined exactly.

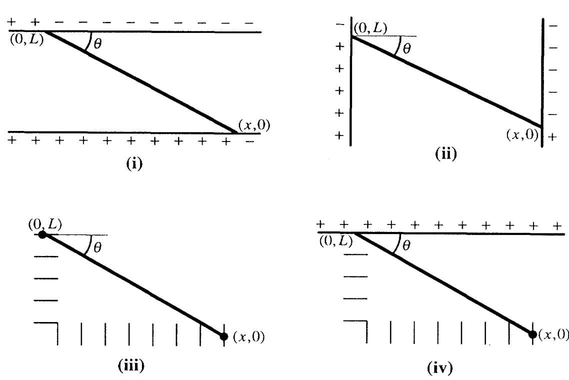

FIG. 2. Schematic picture showing the average location of the interface as a thick line for the four cases considered for $Q_L(x)$: (i) and (ii) are definitions after Dobrushin, with (i), but not (ii), retaining entropic repulsion with the boundary walls of the original strip in Fig. 1. (iii) shows the Fisher-Ferdinand definition where the interface is induced by the ladder of reversed bonds as indicated, and (iv) is a hybrid which does not restrict the interface at its lower end, but the restriction at the upper end "cancels" with that in Fig. 1 when the angle of tilt is the same.

The crucial ingredient of $\hat{\tau}$ is the *entropic repulsion* from the substrate line [17]; this vanishes when (i) is used since the entropic repulsion in the denominator is completely canceled by the numerator. This is a most unifying concept in this field. The results near wetting are (i) $\hat{\tau}$ is analytic in θ_c at wetting; (ii) and (iii) $\hat{\tau} \approx 2\times\ln(1/\theta_c)$; (iv) $\hat{\tau} \approx \ln(1/\theta_c)$ (the symbol "$\approx$" denotes the *exact* asymptotic form, prefactors included). Recall that in two dimensions $\theta_c \sim t$ as $t \downarrow 0$ as a detailed analysis of Eq. (2) shows. We make the following remarks:

(1) Ignoring all terms in the convolution sum (4) apart from the maximal one given by the Wulff value x_c gives a *divergent* $\hat{\tau}$ for any $0<\theta_c<\pi/2$; fluctuations in the point of contact cannot be ignored, even at a thermodynamic level. This is a crucial point, the details of which will be published at length elsewhere [13].

(2) In the calculations of $\hat{\tau}$, the convolution sum in (4) was evaluated exactly *before* taking the limits (further details of this are given below). However, we also confirmed that performing the sum around the maximal values of the partition functions for large L and N, which are peaked at the Wulff value $x=x_c$, and including only Gaussian corrections (as in the usual Laplace method for asymptotic analysis of sums) gives *identical* results for $\hat{\tau}$. Thus, only quadratic fluctuations in the Wulff shape are needed in the determination of $\hat{\tau}$.

(3) In the associated SOS model, the two linear pieces of the interface are independent and the PF can be written

$$Z_L(N) \equiv \sum_{x=1}^{N} Q_L^{(\mathrm{i})}(x) Z(N-x) \tag{5}$$

with the (i) indicating that definition (i) is being used. Thus, Eq. (4) gives a point tension that is zero when using definition (i) for $Q_L(x)$. For case (iv), the entropic repulsion of the tilted part of the interface against the wall is contained within $\hat{\tau}$. For cases (ii) and (iii) we get *twice* this entropic repulsion (coming from both the upper and lower walls) and hence the results differ from (iv) by a factor of 2. We have calculated this entropic repulsion in the SOS model and it behaves like $\ln(1/\theta_c)$ near wetting. This indicates that in the Ising model the dominant part of the point tension near wetting comes from the entropic interaction of the long contour with the wall.

(4) The logarithmic anomaly $\hat{\tau} \approx \ln(1/t)$ as $t \downarrow 0$ is consistent with the scaling ansatz of Indekeu and Robledo [6]. This is because the result $\alpha_l = 2(\log)$ together with the known results $\alpha_s = 0$ [11] and $\nu_\parallel = 2$ [18] satisfy the required exponent relation Eq. (1).

(5) The correlation length $\bar{\xi}_\parallel$ for the axial pair-energy function has been obtained for an Ising strip with boundary conditions as shown in Fig. 3, where a typical domain wall configuration induced by the opposed surface fields is also shown. An energy-entropy balance argument of the type first used in this field by Privman and Fisher [19] allows estimation of the mean spacing between consecutive unbound parts of the domain wall. Making the reasonable assumption that this is the correlation length $\bar{\xi}_\parallel$ gives us

$$\begin{aligned}\bar{\xi}_\parallel &\approx \exp(\Delta F/k_B T) \\ &= \exp\{2\hat{\tau} + L[\sigma(\theta_c)\csc\theta_c - f^\times \cot\theta_c]\}\,, \end{aligned} \tag{6}$$

where ΔF is the free energy fluctuation of a single unbound segment as given in the succeeding equation. An *exact* result for $\bar{\xi}_\parallel$ is known [20] from which, using (6), one can identify $\hat{\tau}$ which has a logarithmic divergence *identical* to that calculated directly from (4) using the hybrid definition (iv) for $Q_L(x)$. These ideas also extend to higher dimensions. Consider, for example, pair correlations in a pore for a system isomorphic to the uniaxial ferromagnet. The asymptotic behavior of the pair correlation function is given by a correlation bubble [20]; suppose the bubble is typically bound to the cylindrical surface of the pore. Then the decay is generated by a free energy fluctuation of the bubble which contains surface tension generated area contributions from the sides of the cylinder and the conical end caps *and* two contributions from the line tension proportional to the circumference of the pore. The fluctuations in the joining of the conical and cylindrical parts are, of course, taken up in the line tension definition.

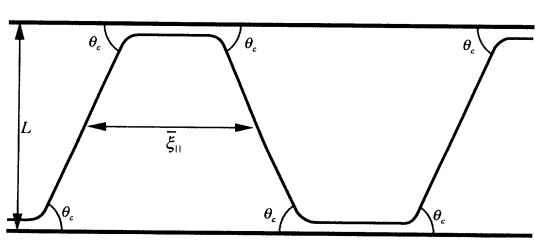

FIG. 3. Ising strip at coexistence with equal and opposite fields on the boundary of such a magnitude that the induced domain wall is pinned, but jumps from edge to edge, crossing at an angle θ_c and giving a long correlation length $\bar{\xi}_\parallel$. The bends at the ends of the bound portions give a point tension contribution to the free energy fluctuation.

(6) In *three dimensions,* a model for the line of contact which imposes the SOS constraint on the interface in directions parallel to the substrate [13], along with more phenomenological "capillary wave" models [10], gives a root-mean-square deviation of the contact line going like $\sqrt{\ln L}$ for a wedge of height L. Such models are expected to give the correct size-dependent statistics of the contact line (as they do for the contact point in two dimensions). Thus, although weaker in three dimensions, large fluctuations in the contact line are still present, indicating that a convolution definition of the line tension, analogous to Eq. (4), may still be necessary. Previous studies of the line tensions, supposedly applicable to three dimensions, have ignored this question. These considerations are, of course, relevant only in the case of a *rough* interface. Interfaces in the three-dimensional Ising model are known to be *smooth* at low temperatures [21]. Therefore, resolving this issue using the Ising model is likely to be very difficult.

The key to the calculation of $\hat{\tau}$ is that for definition (iv) duality with a pair-spin correlation function [16,22] gives

$$\begin{aligned} Q_L(x) = \frac{c}{2\pi}\int_0^{2\pi} d\omega \frac{e^{-L\gamma(\omega)} e^{ix\omega}[D_-(\omega) - D_+(\omega)]}{1 + e^{-i\delta^*(\omega)}} \\ + O(e^{-3L\gamma(0)})\,, \end{aligned} \tag{7}$$

where

$$D_+(\omega) = \left[\frac{e^{i\omega} - B}{e^{i\omega} - A}\right]^{1/2}, \quad D_-(\omega) = \left[\frac{e^{i\omega} - A^{-1}}{e^{i\omega} - B^{-1}}\right]^{1/2} \tag{8}$$

with $A = \exp 2(K_1 + K_2^*)$, $B = \exp 2(K_1 - K_2^*)$ and K_1 and K_2 the coupling constants along bonds in the (0,1) and (1,0) directions, respectively. Here we use the duality relation $\exp(-2K_j^*) = \tanh K_j$. The prefactor c depends only on K_1 and K_2. Also we have used the Onsager functions [23]

$$\begin{aligned} \cosh\gamma(\omega) = \cosh(2K_1^*)\cosh(2K_2) \\ - \sinh(2K_1^*)\sinh(2K_2)\cos\omega\,, \end{aligned} \tag{9}$$

$$e^{-i\delta^*(\omega)} = (A/B)^{1/2} D_+(\omega) D_-(\omega)\,. \tag{10}$$

From Ref. [11],

$$Z(x) = \frac{ie^{2K_2}}{2\pi}\int_0^{2\pi} d\omega \frac{e^{ix\omega}C(\omega)}{A(\omega)} + O(e^{-2L\gamma(0)})\,, \tag{11}$$

where

$$A(\omega) = \sinh 2K_1 \cos[\delta^*(\omega)/2](e^{\gamma(\omega)} - w)/\sinh 2h\,, \tag{12}$$

$$C(\omega) = \sinh 2K_1 \sin[\delta^*(\omega)/2](e^{\gamma(\omega)} - e^{-4K_2}w)/\sinh 2h \tag{13}$$

with

$$w = e^{2K_2}(\cosh 2K_1 - \cosh 2h)/\sinh 2K_1 \tag{14}$$

and h is the (lower) edge field. The asymptotics for the partially wet case are given by a simple pole coming from the nearest zero of $A(\omega)$ to the real axis in the upper half plane. Implementing the convolution sum in (4) gives a Dirac delta function and the remaining integral is dominated by the pole. The partition function $Z_L(N)$ is already known [12],

$$Z_L(N) = \frac{1}{2\pi}\int_0^{2\pi} d\omega \frac{e^{iN\omega}e^{-L\gamma(\omega)}}{A(\omega)\cos[\delta^*(\omega)/2]} + O(e^{-3L\gamma(0)}) , \tag{15}$$

whose asymptotics are given by the complex conjugate of the pole dominating (11).

To summarize, we find that large size-dependent fluctuations in the point of contact force us to define a point tension $\hat{\tau}$ through a convolution sum. This procedure was carried out on an exactly soluble model. Four choices of the convolution function, $Q_L(x)$, were considered, although only one of them, definition (iv), takes proper account of the entropic repulsion of the tilted part of the interface against the wall. Entropic repulsion gives rise to a logarithmic divergence of $\hat{\tau}$ at wetting. This property of $\hat{\tau}$ is consistent with an indirect identification of $\hat{\tau}$ through the correlation length $\xi_{\parallel}$ parallel to the edges of an Ising strip with opposite aligned edge fields of equal magnitude. Although our results are confined to two dimensions, some of the basic issues raised here may well be important in three dimensions (since here the line of contact also has size-dependent fluctuations, albeit weaker) and these need to be addressed before one can be confident in one's definition of the line tension.

We wish to thank H. Dobbs, A. O. Parry, A. Robledo, and B. Widom for interesting discussions and J. O. Indekeu for motivating us towards this problem. D.B.A and P.J.U. acknowledge support from the Science and Engineering Research Council (United Kingdom) under Grants No. GR/H73028 and No. B/92/RF/1420.

*On leave from Ecole Normale Supérieure, 45, rue d'Ulm, 75005 Paris, France.

[1] S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1988), Vol. 12.

[2] D. B. Abraham, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1986), Vol. 10.

[3] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1989).

[4] J. F. Joanny and P. G. de Gennes, J. Colloid Interface Sci. **111**, 94 (1986); B. Widom and A. S. Clarke, Physica (Amsterdam) **168A**, 149 (1990); B. Widom and H. Widom, Physica (Amsterdam) **173A**, 72 (1991); C. Varea and A. Robledo, Phys. Rev. A **45**, 2645 (1992); A. Robledo, C. Varea, and J. O. Indekeu, Phys. Rev. A **45**, 2423 (1992); I. Szleifer and B. Widom, Mol. Phys. **75**, 925 (1992); C. Varea and A. Robledo, Physica (Amsterdam) **183A**, 12 (1992).

[5] J. O. Inkekeu, Physica (Amsterdam) **183A**, 439 (1992).

[6] J. O. Indekeu and A. Robledo, Katholieke Universiteit Leuven report, 1993 (to be published).

[7] See, e.g., P. A. Kralchevsky, A. D. Nikolov, and I. B. Ivanov, J. Colloid Interface Sci. **112**, 132 (1986); B. V. Toshev, D. Platikanov, and A. Scheludko, Langmuir **4**, 489 (1988); D. Li and A. W. Neumann, Colloids Surf. **43**, 195 (1990); J. A. Wallace and S. Schürch, Colloids Surf. **43**, 207 (1990).

[8] P. Muller and F. Gallet, Phys. Rev. Lett. **67**, 1106 (1991); B. M. Law, Phys. Rev. Lett. **69**, 1781 (1992).

[9] J. F. Joanny and P. G. de Gennes, J. Chem. Phys. **81**, 552 (1984).

[10] A. S. Clarke, J. Chem. Phys. **96**, 9073 (1992).

[11] D. B. Abraham, Phys. Rev. Lett. **44**, 1165 (1980).

[12] D. B. Abraham and L.-F. Ko, Phys. Rev. Lett. **63**, 275 (1989).

[13] D. B. Abraham, F. Latrémoleière, and P. J. Upton (unpublished).

[14] D. S. Fisher, M. P. A. Fisher, and J. D. Weeks, Phys. Rev. Lett. **48**, 369 (1982).

[15] D. B. Abraham and P. Reed, Commun. Math. Phys. **49**, 35 (1976); D. B. Abraham, Phys. Rev. Lett. **47**, 545 (1981).

[16] M. E. Fisher and A. E. Ferdinand, Phys. Rev. Lett. **19**, 169 (1967).

[17] M. E. Fisher and D. S. Fisher, Phys. Rev. B **25**, 3192 (1982).

[18] D. B. Abraham and L.-F. Ko, Phys. Rev. B **39**, 12341 (1989).

[19] V. Privman and M. E. Fisher, J. Stat. Phys. **33**, 385 (1983).

[20] D. B Abraham, N. M. Švrakić, and P. J. Upton, Phys. Rev. Lett. **68**, 423 (1992).

[21] R. L. Dobrushin, Theory Prob. Appl. **17**, 582 (1972); **18**, 253 (1973).

[22] D. B. Abraham, G. Gallavotti, and A. Martin-Löf, Physica (Utrecht) **65**, 73 (1973).

[23] L. Onsager, Phys. Rev. **65**, 117 (1944).