Exact Derivation of the Modified Young Equation for Partial Wetting

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We examine a planar wetting model which exhibits a sessile drop and microscopic droplets. The contact angle of the sessile drop obeys the modified Young equation. The microscopic droplets diverge in size and the contact angle vanishes at a single wetting temperature.

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The study of wetting received new impetus about a decade ago in the works of Cahn[1] and Ebner and Saam;[2] the substantial progress made since has been reviewed recently.[3,4] Cahn[1] drew attention to the phenomenological interpretation in terms of thermodynamic parameters and the contact angle θ_c of sessile drops which satisfies (or could be defined by) the modified Young equation

$$\tau_{AB}(\theta_c)\cos\theta_c - \tau'_{AB}(\theta_c)\sin\theta_c = \tau_{AW} - \tau_{BW}\,, \qquad (1)$$

where τ_{ij} is the interfacial free energy for an interface between phases i and j; W denotes the wall. The second term on the left-hand side is not usually present and is included to allow for an angle-dependent surface tension such as occurs in lattice models. In the simplest situation, on raising T we expect θ_c to decrease, vanishing at the wetting temperature T_w above which a macroscopic film of B phase is intercalated between the bulk phase A and the wall. In the case of the planar Ising model in the binary-mixture analogy with the suitable boundary conditions, the first model for which wetting was derived exactly[5] by analysis of correlation functions as well as the free energy, the least temperature for which (1) is solved with $\theta_c = 0$ does indeed give the wetting temperature.[6]

The relationship, noted by many authors, of the solid-on-solid (SOS) approximation to the planar Ising model has been reviewed and extended by Fisher.[7] By applying the theory of recurrent events it has been shown[6] that *there are no macroscopic sessile drops at equilibrium.* Further, a Peierls contour analysis of the planar Ising model with wetting boundary conditions shows that for $T \ll T_w$ there are no such drops either, a point of view extended recently by an exact solution of a 3D system.[8] In view of the phenomenological picture, and indeed elementary experimental observation, this is rather perplexing. We conjecture that the resolution of this problem lies partly in the choice of ensembles; the following remarks illustrate this for the planar case, and we shall obtain a partial resolution.

Consider an $L \times L$ lattice with $T < T_c(2)$ so that the ferromagnet supports two coexisting oppositely magnetized pure phases in the limit as $L \rightarrow \infty$. Let the bonds pointing in from the boundary be reduced in strength and suppose the magnetization per spin denoted by m satisfies

$$m = \alpha m^* + (1-\alpha)(-m^*)\,, \qquad (2)$$

where $0 < \alpha < 1$, m^* being the spontaneous magnetization. This is a canonical prescription with a fraction α of plus-magnetized phase. If all the boundary spins are fixed in value at $+1$, then the phase should reside at the boundary as a sessile drop, which satisfies the Wulff construction[9] and has a contact angle given by (1), in equilibrium with a gas of microscopic droplets like that given in the grand-canonical analysis.[5,6] Both of these entities should undergo wetting transitions, but perhaps not necessarily at the same temperature, a matter to which we shall return later. The same description should hold if (2) has $\alpha = cL^{\delta-1}$ with $0 < \delta < 1$ and c a large enough constant, since then we have an amount of the plus phase proportional to the perimeter but with the microscopic droplets overcompressed to form a macroscopic sessile one.

To date, the planar Ising model has been solved neither in a field nor a fixed magnetization. Thus the analysis of the canonical drop shape would appear a hopeless task. Nevertheless, in this Letter we circumvent

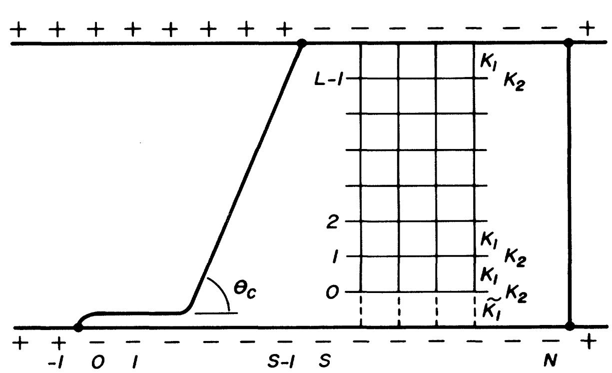

FIG. 1. A strip of an Ising lattice (only part of the lattice is shown) with reduced nearest-neighbor couplings K_1 and K_2. A row of vertical bonds at the bottom are weakened to $\tilde{K}_1 < K_1$ and represent the wall interactions. The boundary conditions impose an inclined interface, which is partially pinned and forms a contact angle θ_c with the wall.

the problem by introducing a specially restricted grand-canonical, or zero-field, ensemble which has $\alpha \sim \frac{1}{2}$, being essentially canonical in a way described below.

Consider an Ising lattice with $\sigma_{i,j} = \pm 1$, $-M \le i \le M$, $-1 \le j \le L$. The nearest-neighbor reduced couplings are K_1 and K_2 for the vertical and the horizontal directions, respectively. In addition, there is a row of weakened bonds $\tilde{K}_1$ in the bottom row to simulate an attracting wall. Periodic boundary conditions are taken for the horizontal direction. The boundary spins at the bottom row are all up except between the 0th and the Nth columns; similarly the top spins are all up except between the Sth and the Nth columns. We consider the limit $N \to \infty$ and concentrate on the long contour extending from $i = -\frac{1}{2}$, $j = -1$ to $i = S - \frac{1}{2}$, $j = L$ (see Fig. 1). It is evident in the limit of a strip of infinite length that we have an equal admixture of the two extremal phases, that is $\alpha = \frac{1}{2}$.

In the case where there is no attracting bonds at the bottom, i.e., if $\tilde{K}_1 = K_1$, the interfacial tension of the inclined interface[10] $\tau_{AB}(\theta)$ for inclination $\tan\theta_0 = L/S$ has been calculated; it satisfies

$$\tau_{AB}(\theta_0) = \sin\theta_0\, \gamma(iv_s(\theta_0)) + v_s(\theta_0)\cos\theta_0 ,$$
$$\gamma'(iv_s(\theta_0)) = i \cot\theta_0 , \tag{3}$$

where $\gamma'(w) \equiv d\gamma(w)/dw$ and $\gamma(w)$ is the well known function introduced by Onsager,[11]

$$\sinh 2K_1 \cosh\gamma(w) = \cosh 2K_1 \cosh 2K_2 - \sinh 2K_2 \cos w . \tag{4}$$

However, if $\tilde{K}_1 < K_1$, under appropriate conditions, which we shall make precise below, a portion of the interface will be pinned to the wall; and the interfacial free energy for this part of the interface, $\tau_p = \tau_{AW} - \tau_{BW}$, is given by[5]

$$\cosh\tau_p = \cosh\tau_{AB}(0) - \frac{[e^{K_2}(\cosh 2K_1 - \cosh 2\tilde{K}_1) - \sinh 2K_1 e^{-K_2}]^2}{\sinh 2K_1 (\cosh 2K_1 - \cosh 2\tilde{K}_1)} , \tag{5}$$

where the free energy for a bulk interface in the horizontal direction is $\tau_{AB}(0) = 2K_1 + \ln(\tanh K_2)$. The interface cannot be entirely pinned because of the boundary condition imposed; as it turns upward, a contact angle θ_c is defined by the inclination of departure, as depicted in Fig. 1.

The picture for the behavior of the interface described above implies that the associated free energy is the sum of that of the pinned portion and that of the inclined portion,

$$f = (S - L\cot\theta_c)\tau_p + L\tau_{AB}(\theta_c)/\sin\theta_c . \tag{6}$$

Comparing this with the exact calculation of the interfacial free energy to be presented yields an equation for θ_c. This derivation is of course based on a picture of how the interface behaves which needs to be justified. We shall confirm this picture, and at the same time give another derivation for θ_c which turns out, as it should, to be identical with the one derived from free-energy considerations by computing the energy-density profile. An energy density $\epsilon_{n,m} = \sigma_{n,m-1}\sigma_{n,m}$ takes the value -1 only when it is exactly at a contour. If $\langle \epsilon_{n,m} \rangle$ is properly subtracted so as to isolate the contribution from the long contour, it is a very sensitive probe for the location of the interface, for it should decay exponentially away from the average positions of the interface in the partially wet phase; it is far easier to calculate than the magnetization density.

We shall derive an equation satisfied by θ_c by computing the interfacial free energy and the energy-density profile. We use the method of the transfer matrix to compute these two objects. Let V_1, V_2, and $\tilde{V}_1$ denote the row-to-row transfer matrices corresponding to K_1, K_2, and $\tilde{K}_1$, respectively. In terms of the Pauli matrices σ_j^a, $a = x,y,z$,

$$V_1 = \exp\left(-K_1^* \sum_j \sigma_j^z\right) ,$$
$$V_2 = \exp\left(K_2 \sum_j \sigma_j^x \sigma_{j+1}^x\right) , \tag{7}$$

where the dual of K_j satisfies $\coth K_j^* = \exp 2K_j$; and $\tilde{V}_1$ is the same as V_1 except K_1^* is replaced by $\tilde{K}_1^*$. Let $|+\rangle$ denote the state with all spins in a row pointing up. We imposed the desired boundary conditions by operating on the state $|+\rangle$ with the spin-reversal operator $P_k^j = \prod_{i=k}^{j}(-\sigma_i^z)$, which reverses the spins from the kth to the jth column.

We denote the partition function for this lattice by Z, and that of the lattice with plain boundary conditions, i.e., all the spins at the top and bottom rows point up, by Z_0. Then

$$Z_0 = \langle + | \tilde{V}_1 (V_2 V_1)^L | + \rangle ,$$
$$Z = \lim_{n \to \infty} \langle + | P_0^N \tilde{V}_1 (V_2 V_1)^L P_S^N | + \rangle . \tag{8}$$

The energy-density correlation is given in terms of the operator $\epsilon_j^x = \sigma_{j-1}^x \sigma_j^x$ by

$$\langle \epsilon_{n,m} \rangle = \lim_{n \to \infty} \langle + | P_0^N \tilde{V}_1 V_2 (V_1 V_2)^n \epsilon_m^x (V_1 V_2)^{L-n} V_1 P_S^N | + \rangle / Z . \tag{9}$$

Our result for the free energy is given by

$$\frac{Z}{Z_0}=\frac{1}{2\pi}\int_{-\pi}^{\pi}dw\frac{e^{-L\gamma(w)+iSw}}{E(w)A(w)}\frac{1}{2\pi}\int_{-\pi}^{\pi}dw'\frac{e^{-L\gamma(w')}}{E(w')A(w')}=\frac{Z_1}{Z_0}\frac{Z_2}{Z_0}, \tag{10}$$

where Z_1/Z_0, the first integral, corresponds to the interface from $(-1,-\frac{1}{2})$ to $(L,S-\frac{1}{2})$ on which we focus, while the second factor is related to the other interface infinitely far away as $N\to\infty$ and does not concern us. The functions $E(w)$ and $A(w)$ will be given shortly. The result for the subtracted profile $\langle\epsilon_{n,m}\rangle_c=\langle\epsilon_{n,m}\rangle_Z-\langle\epsilon_{n,m}\rangle_{Z_0}$ is the following:

$$\langle\epsilon_{n,m}\rangle_c=\frac{Z_0}{Z_1}\frac{1}{(2\pi)^2}\int\int_{-\pi}^{\pi}dw\,dw'\frac{e^{-n\gamma(w)-imw}}{A(w)}\frac{e^{-L\gamma(w')+i(S-m)w'}}{E(w')}$$
$$\times 2\left\{-\cos\left[\frac{\delta^*(w)}{2}-\frac{\delta^*(w')}{2}\right]e^{n\gamma(w')}+\frac{B(w')}{A(w')}\sin\left[\frac{\delta^*(w)}{2}-\frac{\delta^*(w')}{2}\right]e^{-n\gamma(w')}\right\}, \tag{11}$$

where $\delta^*(w)$ is another well known function of Onsager,[11]

$$\sinh 2K_1\sinh\gamma(w)\cos\delta^*(w)=\sinh 2K_2\cosh 2K_1-\cosh 2K_2\cos w, \tag{12}$$

and the definitions for $A(w)$, $B(w)$, and $E(w)$ are[6]

$$\sinh 2\tilde{K}_1 A(w)=(\cosh 2\tilde{K}_1-\cos w)e^{K_2}\cos\frac{\delta^*(w)}{2}+\sin w\, e^{-K_2}\sin\frac{\delta^*(w)}{2}, \tag{13}$$

$$\sinh 2\tilde{K}_1 B(w)=-(\cosh 2\tilde{K}_1-\cos w)e^{K_2}\sin\frac{\delta^*(w)}{2}+\sin w\, e^{-K_2}\cos\frac{\delta^*(w)}{2}, \tag{14}$$

and

$$E(w)=e^{-K_2}\cos\frac{\delta^*(w)}{2}. \tag{15}$$

If $\tilde{K}_1=K_1$, $A(w)=e^{\gamma(w)}E(w)$. Equation (13) vanishes at $w=\pm i\tau_p$, giving two poles to the integrals in (10) and (11); this produces the pinning mechanism. As the transition temperature is approached, i.e., as $T\to T_w^-$, these poles merge with the branch points from $\gamma(w)$ and $\delta^*(w)$ at $w=\pm i\tau_{AB}(0)$.

By choosing S sufficiently large or $\tilde{K}_1$ sufficiently weak, or $\tau_p<v_s(\theta_0)$ to be precise, $-\ln Z_1/Z_0$ has the following asymptotic behavior:

$$f=L\gamma(i\tau_p)+S\tau_p. \tag{16}$$

Comparing with (6), and using (3), this gives a contact angle θ_c satisfying

$$\gamma(iv_s(\theta_c))+\cot\theta_c v_s(\theta_c)=\gamma(i\tau_p)+\cot\theta_c\tau_p. \tag{17}$$

Clearly θ_c is independent of L or S; hence the contact angle is well defined.

The result above which is derived from the thermodynamic considerations can be justified by investigating the energy-density profile in (11). A similar steepest-descent analysis gives the following exponential behavior for the energy density:

$$\langle\epsilon_{m,n}\rangle_c\sim\exp\Big(-(L-n)\{\gamma(iv_s(\theta))-\gamma(i\tau_p)+[v_s(\theta)-\tau_p]\cot\theta\}\Big), \tag{18}$$

where

$$\cot\theta=(S-m)/(L-n),\quad \gamma'(iv_s(\theta))=i\cot\theta. \tag{19}$$

Assume $m\to\infty$ with S as expected, but $n\to\infty$ less fast so that the pole dominates in the integral. Maximizing the exponent of the right-hand side of (18) defines a line along which the interface is predominantly located, and gives an equation for θ_c identical to (17). Hence we have shown both from macroscopic and microscopic viewpoints that the contact angle is defined by the solution of (17), $\tau_p=v_s(\theta_c)$. This solution can be shown to be equivalent to (1). The maximal exponent in (18) is zero, as expected. The width of the profile then diverges as $\sqrt{L}$. When $T_c(2)>T>T_w$ the mean interface is a straight line connecting $(-\frac{1}{2},0)$ to $(S-\frac{1}{2},L)$, with fluctuations as predicted in Ref. 12. Both this and the $T<T_w$ result for the mean interface are as the Wulff construction would predict with suitable boundary conditions at the variational problem for free-energy minimization.

Thus the $T<T_w$ interface has two portions which are on average straight: one along, and bound to, the surface, and the other crossing the strip at the mean slope given by the contact-angle value. The correlation functions in the portion along the surface can be shown, as $s\to\infty$, to be precisely those calculated in the original grand-canonical wetting model,[5] which does not display macroscopic droplets. The wetting temperature for the bound part of the interface, which is established through the growth of the microscopic droplets, is exactly the temperature at which the contact angle, as we have defined it, vanishes.

It seems likely that the planar-Ising conjecture based on (2) will be confirmed for very low temperatures.[13] The analogous problem for the SOS model has already been solved[14] but we believe ours is the first analysis of this problem at a molecular level. An additional bonus is that we shall be able to analyze the rounding between the bound part of the interface and the part which crosses the strip.

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[1]J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[2]C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

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

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

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

[6]D. B. Abraham and J. J. De Coninck, J. Phys. A **16**, L333 (1983).

[7]M. E. Fisher, J. Stat. Phys. **34**, 667 (1984).

[8]D. B. Abraham and C. M. Newman, Phys. Rev. Lett. **61**, 1969 (1988).

[9]For recent reviews, see C. Rottman and M. Wortis, Phys. Rep. **103**, 59 (1984); H. van Beijeren and I. Nolden, in *Structure and Dynamics of Surfaces II,* edited by W. Schommers and P. Von Blanckenhagen, Topics in Current Physics Vol. 43 (Springer-Verlag, Berlin, 1987).

[10]D. B. Abraham and P. Reed, J. Phys. A **10**, L121 (1977).

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

[12]D. B. Abraham and P. J. Upton, Phys. Rev. B **37**, 3835 (1988).

[13]R. Kotecky and Ch. Pfister (private communication).

[14]J. De Coninck, F. Dunlop, and V. Rivasseau, Commun. Math. Phys. **121**, 401 (1989).