# Contact angle for two-dimensional Ising ferromagnets

D. B. Abraham,* J. De Coninck, and F. Dunlop†
*Faculté des Sciences, Université de l'Etat à Mons, B-7000 Mons, Hainaut, Belgium*
(Received 22 July 1988)

The contact angle of a sessile drop on a wall is considered within a modified planar Ising model. The thermal variation of this contact angle is computed exactly, and it is shown how a simple thermalization of the boundaries (wall) may lead to an exact treatment of multiple wetting transitions.

## I. INTRODUCTION

Consider a binary mixture which separates into two immiscible phases labeled + and − and let the wall of the container differentially wet the components. Provided the + and − phases coexist, the system should undergo a phase transition from a partially wet to a totally wet state at a temperature $T_W$ below the critical value $T_c$, but dependent on the degree of differential wetting. Such a conclusion was suggested in the seminal phenomenological theory of Cahn[1] for the contact angle displayed by a macroscopic drop of one-phase sessile on the wall. For the planar case in which the binary mixture is modeled by the spin-$\frac{1}{2}$ Ising ferromagnet there is an exact solution[2] which has been interpreted and extended in terms of the solid-on-solid (SOS) or random walk arguments (Ref. 3 and references therein).

A natural order parameter in this problem is the contact angle: A *macroscopic* droplet of the minus phase has a well-defined shape and, in particular, a well-defined contact angle with the wall. This contact angle $\theta_c$ is a function of temperature and wall interaction; it goes to zero when approaching the wetting transition, where droplets spread and cover the wall completely. The shape of a macroscopic droplet can be obtained by minimizing the surface free energy at constant volume;[4] the contact angle $\theta_c$ is then found to obey the equation

$$\cos\theta_c \tau_{+-}(\theta_c) - \sin\theta_c \frac{d\tau_{+-}}{d\theta}(\theta_c) = \tau_{+w} - \tau_{-w} , \quad (1)$$

where $\tau_{+-}(\theta)$ is the interfacial surface tension for an interface at angle $\theta$ with respect to the underlying lattice, and $\tau_{+w}$, $\tau_{-w}$ are the wall free energies of the plus and minus phases. This is the modified Young rule,[5] applicable to anisotropic media [in three dimensions we should write $\tau_{+-}(\theta,\phi)$ and $\theta_c = \theta_c(\phi)$, but the equatorial angle $\phi$ plays a dummy role].

The thermodynamical variational argument leading to (1) has been justified in statistical mechanics only for 1+1 dimensional SOS models.[5,6] A proof for more general systems would be very welcome, but the result can already be used to predict contact angles, whenever the interfacial and wall free energies are known. It should be kept in mind that the concept of a contact angle is valid only for macroscopic droplets—a metastable situation.

In the present paper, we give the temperature dependence of this contact angle for a droplet within the Ising model with various wall interactions.

## II. THE RESULTS

For the planar Ising model shown in Fig. 1(a), with $K_1 = \beta J_1 \geq 0$, $K_2 = \beta J_2 \geq 0$, $\beta = 1/kT$ and with a surface field $aK_1$ we can grow a sessile drop of the minus phase with either minus favored at the wall ($a < 0$, wetting) or with plus favored at the wall ($a > 0$, drying). The two cases are related by reversing the sign of $\tau_{+w} - \tau_{-w}$ in (1), thus $\theta_c$ is replaced by $\pi - \theta_c$. Thus, we can treat both wetting and drying transitions in this way.

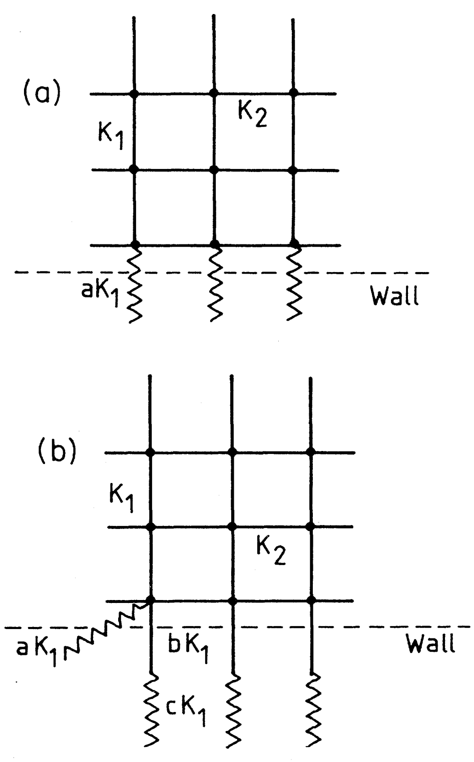


FIG. 1. (a) The planar Ising ferromagnet with an external field $aK_1$ on one edge. (b) A decorated planar Ising ferromagnet.

 

The exact calculation[7] of the wall free energies gives for $a \le 0$,

$$\beta\tau_{+w} - \beta\tau_{-w} = \hat{\gamma}(i\Psi(a,T)) \quad (2)$$

where $\Psi(a,T)$ is given by

$$\exp[\Psi(a,T)] = \exp(2K_2)(\cosh 2K_1 - \cosh 2aK_1)/\sinh 2K_1 , \quad (3)$$

and the Onsager function $\hat{\gamma}(\;)$ is defined by

$$\cosh[\hat{\gamma}(\omega)] = \cosh 2K_1 \cosh 2K_2^* - \sinh 2K_1 \sinh 2K_2^* \cos\omega \quad (4)$$

with $\hat{\gamma}(\omega) \ge 0$ for real $\omega$. Finally, we need the interfacial tension which has been computed in Ref. 8 and equals

$$\beta\tau_{+-}(\theta) = \cos\theta\, \hat{\gamma}(\omega(\theta)) - i \sin\theta\, \omega(\theta) \quad (5)$$

for $0 \le \theta \le \pi/2$ with $\omega = \omega(\theta)$ a solution of

$$i \tan\theta = \frac{\partial \hat{\gamma}}{\partial \omega} . \quad (6)$$

Inserting (5) and (6) into the modified Young equation gives, with (2), (3), and (4),

$$\tan\theta_c(a,T) = \sinh 2K_1 \sinh 2K_2^* \sinh\Psi / \sinh(\beta\tau_{+w} - \beta\tau_{-w}) \quad (7)$$

for the contact angle $\theta_c(a,T)$ in the partially wet case. Evidently $\theta_c(a,0_+) = \pi/2$, and $\theta_c(a,T) \to 0$ as $\Psi(a,T) \to 0$, which corresponds to the already known[2] wetting transition line $T_W = T_W(a)$ (dashed curve in Fig. 3 below). Near the transition, we obtain

$$\theta_c(a,T) \sim 2 \frac{T_W - T}{T_W} \left\{ K_2 + K_1 \frac{\sinh 2K_1 - a \sinh 2aK_1}{\cosh 2K_1 - \cosh 2aK_1} - K_1 \coth 2K_1 \right\} . \quad (8)$$

This linear vanishing is characteristic of second-order phase transitions, with an amplitude which takes into account the angular dependence of the surface tension $\tau_{+-}(\theta)$.[9] Notice that $\beta\tau_{+w} - \beta\tau_{-w} (\ge 0)$ is a monotone function of $a$ [this follows from Fortuin, Kasteleyn, and Ginibre (FKG) inequalities[10]]. Thus, $\theta_c(a,T)$ is also monotone in $a$ and $0 \le \theta_c(a,T) \le \pi/2$ for $a \le 0$. Some solutions of (7) for $\theta_c(a,T)$ are shown in Fig. 2.

The theory has an SOS limit with $K_1 \to \infty$, $(1-a)K_1 \to \delta$ where $\delta > 0$ is a pinning potential. Then (7) simplifies to give

$$\tan\theta_c(\delta,T) = \sinh\phi / (\cosh K_2 - \cosh\phi) , \quad (9)$$

where

$$e^{\phi} = e^{2K_2}(1 - e^{-\delta}) , \quad (10)$$

and the transition condition is $\phi = 0$.

We now turn to the question of multiple wetting transitions. In Fig. 1(b), each spin near the wall is subjected to a surface field $aK_1$ as in Fig. 1(a), but is also coupled, via $bK_1$, to a spin in the wall, which in turn is subjected to a different field $cK_1$. The wall is thus given a thermal structure, chosen here to be as simple as possible for illustrative purposes, but still exactly solvable. The sum over the spins in the wall can be carried out and the result is as in Fig. 1(a), but with a temperature-dependent $a_{\rm eff}(T)$ given by

$$a_{\rm eff}(T) = a + \frac{1}{K_1} \tanh^{-1}[\tanh(bK_1)\tanh(cK_1)] . \quad (11)$$

Suppose that $b = \pm c$ for simplicity, then $a_{\rm eff}(\infty) = a$ and, for $b > 0$, as $T \to 0$

$$a_{\rm eff}(T) \sim a \pm b \mp (\ln 2)/2K_1 + O(e^{-2K_1 b}) . \quad (12)$$

Inspection of Eq. (3) at the transition $\Psi = 0$ near $a \to -1$, $T \to 0$ gives

$$a \sim -1 + (e^{-2K_2})/2K_1 . \quad (13)$$

Choose $a$ and $b = -c$ so that $a \gtrsim -1$, $a - b \lesssim -1$. Then there exists a (wet-partially wet-wet) sequence of phase transitions on raising $T$. We give in Figs. 3 and 4 $a_{\rm eff}(T)$ for some values of $a$, $b$, and $c$ and the corresponding con-

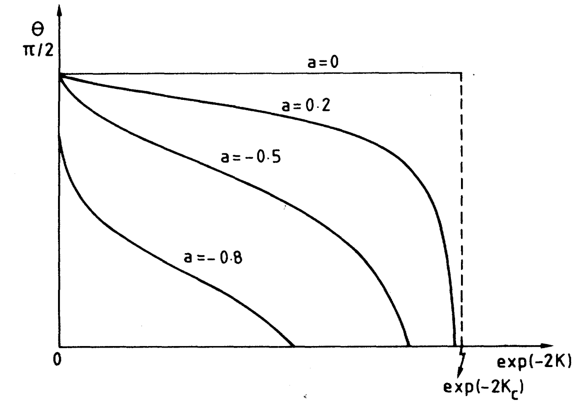


FIG. 2. The contact angle $\theta$ as a function of $\exp(-2K)$ for a drop within a planar Ising ferromagnet with external field $aK_1$ on one edge ($K_1 = K_2 = K$). $K_c$ denotes the critical value of the coupling [$\exp(-2K_c) = \sqrt{2} - 1$].

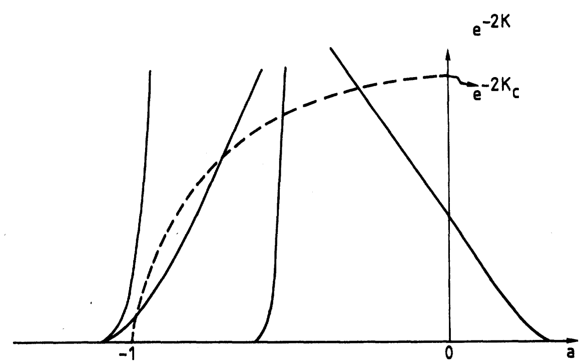


FIG. 3. $a_{\rm eff}(T)$ as given in (11) for various values of $a$, $b$, and $c$ with $K_1 = K_2 = K$. From left to right, we have $a = -0.9$, $b = -c = 0.3$; $a = -0.2$, $b = -c = 1.0$; $a = -0.5$, $b = -c = 0$; $a = -2.7$, $b = c = 3.0$. One can see zero, one, or two intersections with the transition line (dashed curve) calculated from (3) with $\Psi = 0$.

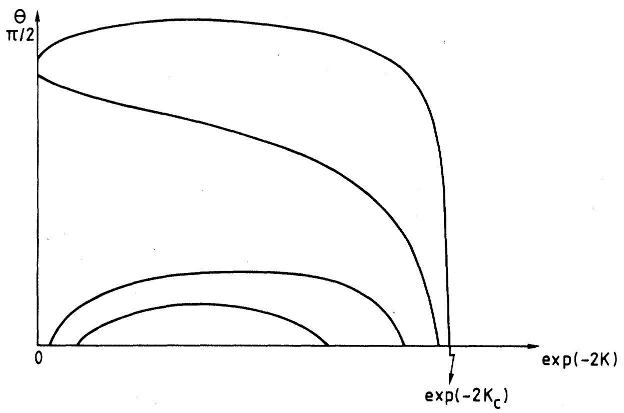


FIG. 4. The contact angle $\theta$ as a function of $\exp(-2K)$ for various values of $a$, $b$, and $c$ with $K_1=K_2=K$. From top to bottom we have one wetting transition $a=-2.3$, $b=c=3.0$ and $a=-0.3$, $b=-c=0.1$ and two wetting transitions $a=1.85$, $b=-c=3$ and $a=-0.2$, $b=-c=1$.

tact angles $\theta_c$. This extends results of Chalker and Sluckin[11] on a similar but more complicated model, and a mean-field study of Ebner and Saam[12] on a model with long-range wall potential.

It is also worth noting that (11) and (12) also hold in three dimensions; the results of Fröhlich and Pfister [Ref. 13, Eq. (2.23)] give

$$-1 \geq a \geq -\beta\tau_{+-}(\theta=0)/2K_1 , \quad (14)$$

and a low-temperature expansion of $\tau_{+-}$ leads to

$$\beta\tau_{+-}(\theta=0)=2K_1-2e^{-4(K_2+K_3)}+\cdots , \quad (15)$$

where the ellipsis represents higher-order terms so that the analog of Eq. (13) reads

$$-1 \geq a \geq -1+\frac{e^{-4(K_2+K_3)}}{K_1}+\cdots . \quad (16)$$

If we now choose again $b=-c$ and $a \geq -1$, $a-b \leq 1$, the wall will be wet near $T=0$ and will undergo a wet-partially wet transition within the low-temperature regime. Raising even more the temperature should then yield a partially wet-wet transition before reaching $T_c$ because of entropic repulsion; this second transition is the usual one, but a rigorous proof of its occurrence is still lacking in dimension greater than 2, at least to our knowledge.

The possibility of a (wet-partially wet-wet) sequence on raising $T$ has also been found for continuous SOS models.[5,9] Comparing that case with the discrete SOS model as obtained in (9) and (10), which has only one transition, we conclude that the continuous character of the variables may also induce multiple wetting transitions. The results of the present paper for a discrete model with a thermalized wall show that the possibility of two wetting transitions is a rather general phenomenon. It may be useful in the interpretation of experiments.[14]

## ACKNOWLEDGMENTS

F. Dunlop and D. B. Abraham are respectively grateful to Communauté Française de Belgique and Université de l'Etat à Mons for financial support which made this collaboration possible. Two of us (J.D.C. and F.D.) would like to thank M. P. Gelfand for correspondence about Ref. 5. We would also like to thank C.-E. Pfister for interesting discussions regarding Ref. 13.

*On leave from Department of Theoretical Physics, University of Oxford, 1 South Parks Road, Oxford 0X1 3TG, Oxfordshire, United Kingdom.

†On leave from Centre de Physique Théorique, Ecole Polytechnique, 91128 Palaiseau CEDEX, France.

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

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

[3]M. E. Fisher, J. Stat. Phys. **34**, 667 (1984); D. B. Abraham, in *Surface Structures and Phase Transitions—Exact Results, Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1986), Vol. 10.

[4]H. van Beijeren and I. Nolden, in *Structure and Dynamics of Surfaces II,* edited by W. Schommers and P. von Blanckenhagen (Springer, New York, 1987), p. 259; C. Rottman and M. Wortis, Phys. Rep. C **103**, 59 (1984).

[5]J. De Coninck and F. Dunlop, J. Stat. Phys. **47**, 827 (1987).

[6]J. De Coninck, F. Dunlop, and V. Rivasseau (unpublished).

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

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

[9]J. De Coninck and F. Dunlop, Europhys. Lett. **4**, 1291 (1987).

[10]C. M. Fortuin, P. W. Kasteleyn, and J. Ginibre, Commun. Math. Phys. **22**, 89 (1971).

[11]J. T. Chalker and T. J. Sluckin, J. Phys. (Paris) Lett. **45**, L863 (1984).

[12]C. Ebner and W. F. Saam, Phys. Rev. Lett. **58**, 587 (1987).

[13]J. Fröhlich and C.-E. Pfister, Commun. Math. Phys. **112**, 51 (1987).

[14]J. Kolaczkiewicz and E. Bauer, Phys. Rev. Lett. **54**, 574 (1985).