Journal of Statistical Physics, Vol. 61, Nos. 5/6, 1990

Exact Results for a Meniscus in a Three-Phase System Within an SOS-Type Approximation

Joël De Coninck,[1] François Dunlop,[2] and Frédéric Menu[1]

Received June 20, 1989; final July 18, 1990

The shape of a meniscus of one phase between two others is studied in two dimensions using random walk models. An interface with a meniscus is approximated by two random walks forming microscopic droplets of the intruding phase before and after a macroscopic lens. Within this class of models, we establish a Wulff construction and prove the Herring relations between contact angles. We give explicit formulas for the contact angles as functions of temperature, both at low temperatures and near the wetting transition.

KEY WORDS: Contact angle; wetting transition; Wulff construction; Herring relations.

1. INTRODUCTION

The coexistence of three or more phases is a common phenomenon in nature. From a theoretical point of view, this subject has motivated in particular the Potts and Blume–Capel models. The geometrical features of this coexistence have, however, been considered only recently in statistical mechanics.[(1)] The shape of a lens of one phase between two others has been studied in two dimensions using a three-random-walk model: the first two walks serve as upper and lower boundaries to the lens; they meet only at the endpoints of the lens, where the third walk starts. The aim of the present paper is to provide exact results for a meniscus within a two-random-walk model, where the two walks can meet and separate as often as they like, thus forming many microscopic droplets of the intruding phase before and after a macroscopic lens.

[1] Université de Mons-Hainaut, Faculté des Sciences, 7000 Mons, Belgium.
[2] Centre de Physique Théorique (CNRS-UPR14), École Polytechnique, 91128 Palaiseau, France.

822/61/5-6-11

The paper is organized as follows: in Section 2 we introduce the problem in terms of SOS (solid-on-solid) models[2] and describe the Wulff construction for a meniscus in a three-phase system. In Section 3 we derive technical results based on the reflection principle and the necklace representation[3,4] for a pair of restricted SOS models as in ref. 5. In Section 4 we use these results and the Herring relations[6] to discuss contact angles both near the second-order wetting transition and at low temperatures. A comparison is given with a three-random-walk model, as in ref. 1, which has a first-order transition. In Section 5 we prove the microscopic validity of the Wulff construction and of the Herring relations for the above models, following the method of ref. 7.

2. SOS MODELS AND THE WULFF CONSTRUCTION FOR A MENISCUS

From a macroscopic point of view, a meniscus is characterized in particular by two contact angles θ_1 and θ_2 (see Fig. 1), which should obey the thermodynamic Herring relations[6]:

$$\sigma_{AB}(\theta_1)\cos\theta_1 - \sigma'_{AB}(\theta_1)\sin\theta_1 + \sigma_{BC}(\theta_2)\cos\theta_2 - \sigma'_{BC}(\theta_2)\sin\theta_2 = \sigma_{AC}(0) \tag{2.1}$$

$$\sigma_{AB}(\theta_1)\sin\theta_1 + \sigma'_{AB}(\theta_1)\cos\theta_1 = \sigma_{BC}(\theta_2)\sin\theta_2 + \sigma'_{BC}(\theta_2)\cos\theta_2 \tag{2.2}$$

where σ_{xy} denotes the interfacial tension between X and Y and σ'_{xy} denotes its derivative with respect to the angle between the XY interface and a fixed given direction.

The validity of these relations has been proved in ref. 1 for a Gaussian three-random-walk model in a canonical ensemble where the volume of the intruding phase is a fixed fraction of the total volume. It has also been shown in ref. 1 that such a meniscus may be viewed as a superposition of two droplets of appropriate volume (as Fig. 1 cut along the dashed line), of respective shapes given by the Wulff construction for droplets on a wall. We give here the thermodynamic argument which underlies this double Wulff construction in general.

Figure 2a shows a droplet of B above a horizontal line (dashed line) with the appropriate values for the coordinates (x_M, y_M) of the contact point M in a frame of reference centered at the Wulff point 0, as functions of the contact angle θ_1. The value $\cos\theta_1\,\sigma_{AB}(\theta_1) - \sin\theta_1\,\sigma'_{AB}(\theta_1)$ for y_M follows from the Wulff construction, as shown in ref. 8. The value $\sin\theta_1\,\sigma_{AB}(\theta_1) + \cos\theta_1\,\sigma'_{AB}(\theta_1)$ for x_M follows by rotation by $\pi/2$. Comparing now with the Herring relations yields the double construction for a meniscus as indicated in Fig. 2b. The method is also valid in dimension 3.

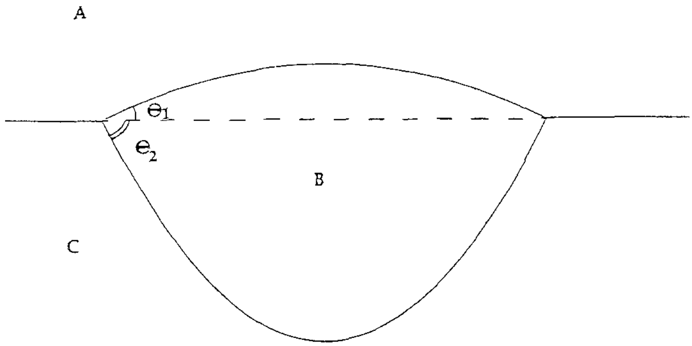

Fig. 1. A meniscus of phase B between A and C characterized by two contact angles θ_1 and θ_2.

The SOS-type models we shall consider can be defined as follows. For one-dimensional interfaces characterized by heights $h_0,..., h_N$, the surface tension at angle θ is given by

$$\beta\sigma(\theta) = \lim_{N \to \infty} -\frac{\cos\theta}{N} \log \sum_{h_0,..., h_N} e^{-\beta E(h_0,..., h_N)} \delta(h_0)\, \delta(h_N - N\tan\theta) \qquad (2.3)$$

where $E(h_0,..., h_N)$ defines the energetic cost of the interface. We assume a general form

$$E(h_0,..., h_N) = \sum_1^N P(h_{i-1} - h_i) \qquad (2.4)$$

where $P(x)$ is an even function on $\mathbb{Z}$ such that

$$-\infty < P(x) \leqslant +\infty$$

and

$$\lim_{x \to +\infty} \frac{P(x)}{x} = c_{\max} \qquad (2.5)$$

with

$$0 < c_{\max} \leqslant +\infty$$

Let us now formulate a general lemma.

Lemma. For the models defined in (2.3)–(2.5), for all θ with $0 \leqslant \theta < \theta_{\max}$, there exists a unique c_θ with $0 \leqslant c_\theta < c_{\max}$ such that

$$\tan\theta = \frac{\sum_x x e^{-\beta P(x) + c_\theta x}}{\sum_x e^{-\beta P(x) + c_\theta x}} \qquad (2.6)$$

where $\theta_{\max}$ is obtained from the above expression with c_θ replaced by $c_{\max}$. This leads to

$$\beta\sigma(\theta) = -\cos\theta \log \sum_x e^{-\beta P(x) + c_\theta(x - \tan\theta)} \tag{2.7}$$

$$\beta \cos\theta\, \sigma(\theta) - \beta \sin\theta\, \sigma'(\theta) = -\log \sum e^{-\beta P(x) + c_\theta x} \tag{2.8}$$

$$\beta \sin\theta\, \sigma(\theta) + \beta \cos\theta\, \sigma'(\theta) = c_\theta \tag{2.9}$$

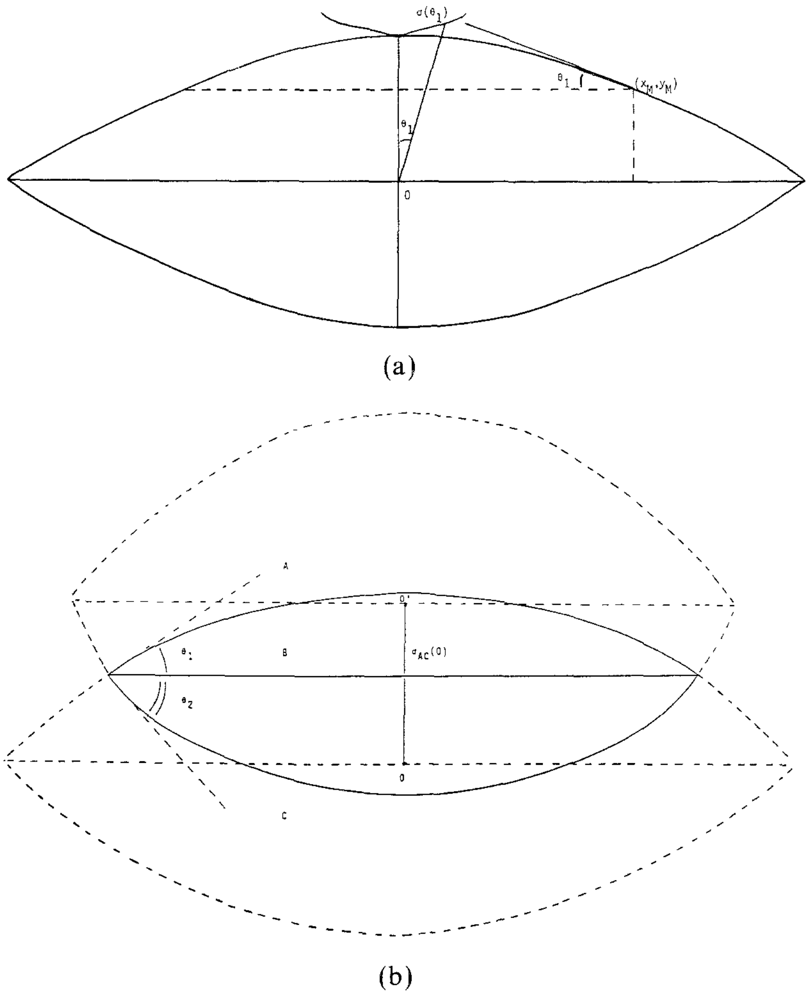

Fig. 2. (a) A sessile drop in the RSOS model and sketch of the Wulff construction. (b) Double Wulff construction for a meniscus in the double RSOS model.

Proof. Equations (2.6) and (2.7) were proven in ref. 8 for continuous SOS models. The proof here is similar and (2.8) and (2.9) follow easily.

Suppose now that the AB and BC interfaces are given by restricted SOS models, defined by

$$P_{AB}(x)=\begin{cases} J(1+|x|) & \text{if } \ |x|=0 \text{ or } 1 \\ +\infty & \text{otherwise}\end{cases}$$

and similarly for $P_{BC}(x)$ with J replaced by J'. The lemma then gives, with $\beta J=K$ and $\beta J'=K'$,

$$\tan\theta_1=e^{-K}(e^{c_{\theta_1}}-e^{-c_{\theta_1}})/[1+e^{-K}(e^{c_{\theta_1}}+e^{-c_{\theta_1}})] \tag{2.10}$$

$$\tan\theta_2=e^{-K'}(e^{c'_{\theta_2}}-e^{-c'_{\theta_2}})/[1+e^{-K'}(e^{c'_{\theta_2}}+e^{-c'_{\theta_2}})] \tag{2.11}$$

where c_θ and c'_θ are associated, as in the lemma, to $P_{AB}(\cdot)$ and $P_{BC}(\cdot)$, respectively. The second Herring relation (2.2), together with (2.9), implies

$$c_{\theta_1}=c'_{\theta_2}\equiv c \tag{2.12}$$

The first Herring relation then becomes, using (2.8),

$$[e^{-K}+e^{-2K}(e^c+e^{-c})][e^{-K'}+e^{-2K'}(e^c+e^{-c})]=e^{-\beta\sigma_{AC}(0)} \tag{2.13}$$

The quadratic equation (2.13) can now be solved for e^c+e^{-c}, which yields the angles θ_1 and θ_2 from (2.12), (2.10), and (2.11). The result is particularly simple if $K=K'$:

$$\tan^2\theta_1=\tan^2\theta_2=1-2e^{[\beta\sigma_{AC}(0)-2K]/2}+e^{\beta\sigma_{AC}(0)-2K}-4e^{\beta\sigma_{AC}(0)-4K} \tag{2.14}$$

The difficult part of the problem remains, namely to study the interfacial tension $\sigma_{AC}(0)$ of the AC interface in the presence of B. We shall compute $\sigma_{AC}(0)$ in a model where the system is described by two random walks h_i and h'_i with $h_i\geqslant h'_i$. Phase A lies above h_i, phase C lies below h'_i, and "phase" B is between h_i and h'_i and is present at i only if $h_i>h'_i$. The two random walks are chosen as restricted SOS models so as to obtain a solvable model. Other cases have been considered in ref. 4, where the bubble partition function is considered as a combination of one random walk for the center-of-mass motion and another one for the relative motion. This point of view is exact within a Gaussian model, but can only be an approximation for non-Gaussian SOS models such as the one considered in the present paper.

Our two interfaces (see Fig. 3) are characterized by heights

$$h_0=0;\qquad h_i\in\mathbb{Z},\qquad h_i-h_{i-1}=1,0,-1,\quad i=1,\dots,N$$

$$h'_0=0;\qquad h'_i\in\mathbb{Z},\qquad h'_i-h'_{i-1}=1,0,-1,\quad i=1,\dots,N;\qquad h'_N=h_N \tag{2.15}$$

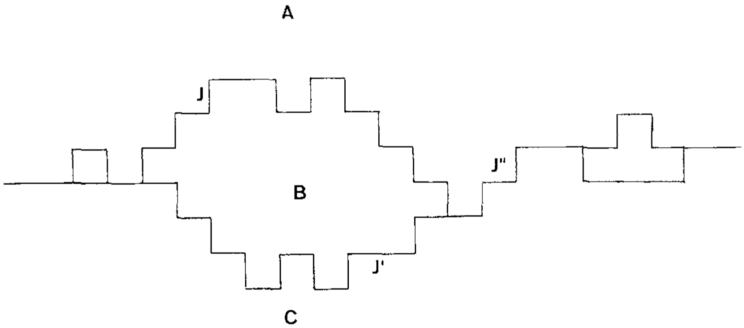

Fig. 3. A typical configuration in the two-random-walk model.

with the restriction

$$h_i \geqslant h_i' \qquad \forall i \tag{2.16}$$

The Boltzmann factor is then

$$\exp\left\{-K\sum_1^N (1+|h_i-h_{i-1}|-K'\sum_1^N (1+|h_i'-h_{i-1}'|) - (K''-K-K')\sum_1^N \delta_{h_i,h_i'}(1+|h_i-h_{i-1}|\,\delta_{h_{i-1},h_{i-1}'})\right\} \tag{2.17}$$

3. METHOD

Let Q_N be the partition function obtained by summing up (2.17) with the constraints (2.15) and (2.16). The corresponding interfacial tension $\sigma_{AC}(0)$ is given by

$$\beta\sigma_{AC}(0)=\lim_{N\to\infty} -\frac{1}{N}\log Q_N$$

We shall compute $\sigma_{AC}(0)$ near the wetting transition and near $T=0$ using the technique developed in ref. 5. The reader who is interested in the physical results may skip this technical section. For simplicity, we now fix $K'=K$. Let

$$Q_N^b=\sum{}' \exp\left\{-K\sum_1^N (2+|h_i-h_{i-1}|+|h_i'-h_{i-1}'|)\right\} \tag{3.1}$$

where the sum is over the configurations (2.15) with the restriction

$$h_i > h_i', \qquad i = 1,..., N-1$$

Let

$$Q_N^a = \sum'' \exp\left\{-K'' \sum_1^N (1 + |h_i - h_{i-1}|)\right\}$$

where the sum is over the configurations (2.15) with the restriction

$$h_i = h_i' \qquad \forall i = 0,..., N$$

Let us define the generating functions

$$G(z) = \sum_{N=0}^{\infty} z^N Q_N$$

$$G_b(z) = \sum_{N=2}^{\infty} z^N Q_N^b$$

$$G_a(z) = \sum_{N=2}^{\infty} z^N Q_N^a = [1 - z(e^{-K''} + 2e^{-2K''})]^{-1}$$

It is then straightforward to obtain

$$G(z) = \frac{G_a(z)}{1 - v^2 G_a(z)\, G_b(z)} \tag{3.2}$$

with $v^2 = e^{-K'' + 2K}$. It can be derived that $G_b(z)$ is analytic in the disk

$$|z| < z_b = (e^{-K} + 2e^{-2K})^{-2} \tag{3.3}$$

and is singular but finite at $z = z_b$. The quantity $e^{\beta\sigma_{AC}(0)}$ must equal the closest singularity of $G(z)$. Therefore

$$e^{\beta\sigma_{AC}(0)} = \text{Min}\{z_b, z_{ab}\}$$

where z_{ab} is the root of the equation

$$1 = v^2 G_a(z)\, G_b(z) \tag{3.4}$$

More precisely, we have

$$e^{\beta\sigma_{AC}(0)} = \begin{cases} z_b & \text{for} \quad T \geq T_w \\ z_{ab} & \quad\quad T \leq T_w \end{cases}$$

and the wetting transition line $z_{ab}=z_b$ is given by the equation[5]

$$m(K,K'')=\frac{3e^{-K}+e^{-2K}-e^{-K}(1+2e^{-K})^{1/2}}{e^{K''}[(e^{-K}+2e^{-2K})^2-(e^{-K''}+2e^{-2K''})]}=1 \tag{3.5}$$

and is reproduced in Fig. 4.

In the present paper, we are interested in partial wetting, i.e., $z_{ab}<z_b$, and we shall estimate z_{ab} near the wetting transition and at low temperatures. In order to find z_{ab} from (3.4), we start from the exact formula[5]

$$G_b(z)=\frac{C_0(z)-C_0^d(z)-2ze^{-4K}C_0(z)\,C_1(z)\,G_b(z;1,0)}{2C_0(z)\,C_0^d(z)} \tag{3.6}$$

where

$$C_x(z)=\int_0^{2\pi}\frac{d\theta}{2\pi}\frac{e^{-ix\theta}}{1-ze^{-2K}(1+2e^{-K}\cos\theta)^2} \tag{3.7}$$

$$C_0^d(z)=\frac{1}{1-z(e^{-2K}+2e^{-4K})}$$

$$G_b(z;1,0)=\frac{C_1(z)-ze^{-4K}[C_1(z)\,C_0(z)-C_2(z)\,C_1(z)]}{C_0(z)+ze^{-4K}[C_2(z)\,C_0(z)-C_1^2(z)]} \tag{3.8}$$

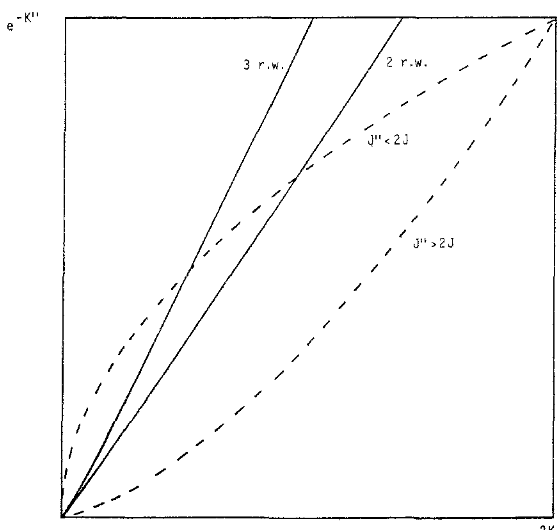

Fig. 4. Phase diagram for the two-random-walk model [2 r.w.; cf. Eq. (3.5)] and three-random-walk approximation [3 r.w.; cf. Eq. (4.11)]. The dashed lines represent trajectories as the temperature is varied for fixed values of J and J''.

By isolating the singular part of C_x,

$$C_x(z) = C_0(z) - d_x(z) \tag{3.9}$$

we get

$$\begin{aligned}
&G_b(z; 1, 0)\\
&= [1 - ze^{-4K} d_2(z)][1 - C_0^{-1}(z)\, d_1(z)]\\
&\times \left(\{1 + ze^{-4K}[2d_1(z) - d_2(z)]\} \left\{ 1 - C_0^{-1}(z) \frac{ze^{-4K} d_1^2(z)}{1 + ze^{-4K}[2d_1(z) - d_2(z)]} \right\} \right)^{-1}
\end{aligned} \tag{3.10}$$

Near the wetting transition, we can expand $G_b(z)$ in powers of $(z_b - z)^{1/2}$. We have

$$C_0^{-1}(z) = 2^{3/2} e^{-3K/2}(1 + 2e^{-K})(z_b - z)^{1/2} + O(z_b - z)^{3/2}$$

and

$$d_x(z) = d_x(z_b) - \delta_x (z_b - z)^{1/2} + O(z_b - z)$$

with

$$\begin{aligned}
\delta_x &= x^2 2^{-7/2} e^{K/2}(1 + 2e^{-K})^{5/2}\\
d_1(z_b) &= 2^{-2} e^K (1 + 2e^{-K})^{3/2}\\
d_2(z_b) &= 2^{-1} e^{2K}(1 + 2e^{-K})^{3/2}\, [(1 + 2e^{-K})^{1/2} - 1]
\end{aligned}$$

It may be worth pointing out that $d_1(z_b)$ and $d_2(z_b)$ happen to be directly computable from (3.6) and (3.9), whereas δ_x can be extracted from the divergence of $(d/dz)\, d_x(z)$ as $z \uparrow z_b$. Expanding $G_b(z; 1, 0)$ to first order in $(z_b - z)^{1/2}$ now gives

$$\begin{aligned}
G_b(z; 1, 0) = G_b(z; 1, 0)[1 &- 2^{-3/2} e^{-K/2}\\
&\times \{(1 + 2e^{-K})^2 + (1 + 2e^{-K})^{3/2}\}(z_b - z)^{1/2} + O(z_b - z)]
\end{aligned}$$

from which we get

$$\begin{aligned}
G_b(z) = G_b(z_b) &- 2^{-3/2} e^{-3K/2}(1 + 2e^{-K})^{1/2}\\
&\times [2 + 3e^{-K} + (2 - e^K)(1 + 2e^{-K})^{1/2}](z_b - z)^{1/2} + O(z_b - z)
\end{aligned}$$

which we use to solve (3.4) near T_w. We obtain

$$z_{ab} = z_b - \left(\frac{m - 1}{m} \right)^2 \frac{G_b(z_b)^2}{B(z_b)^2} + O(m - 1)^3 \tag{3.11}$$

with m given by (3.5) and

$$G_b(z_b) = e^{-K}(1+2e^{-K})^{-2}\,[3+e^{-K}-(1+2e^{-K})^{1/2}]$$
$$B(z_b) = 2^{-3/2}e^{-3K/2}(1+2e^{-K})^{-1/2}\,[2+3e^{-K}+(2-e^{-K})(1+2e^{-K})^{1/2}]$$

Let us now consider the low-temperature regime. In $G_b(z)$, we approximate Q_n^b by

$$Q_n^b = 4e^{-(n+1)2K}[1+O(n^2e^{-2K})]$$

This corresponds to a droplet of length n and height 1, with corrections due to excitations of energy factor e^{-2K} and entropy factor n^2. We thus get

$$G_b(z) = 4e^{-2K}\sum_{n\geqslant 2} z^ne^{-2nK}[1+O(n^2e^{-2nK})]$$
$$= 4z^2e^{-6K}\frac{1+O(e^{-2K}(1-ze^{-2K})^{-2})}{1-ze^{-2K}}$$

which we use to solve (3.4) at low temperature. We obtain $z_{ab} = A/B$, where

$$A = e^{-K''}+e^{-2K}+2e^{-2K''}-(e^{-K''}-e^{-2K})\{1+4e^{-2K''}(e^{-K''}-e^{-2K})^{-1}$$
$$+\,16e^{K''-8K}[1+O(e^{-2K}(1-z_{ab}e^{-2K})^{-2})(e^{-K''}-e^{-2K})^{-2}]\}^{1/2}$$
$$B = 2e^{-K''-2K}\{1+2e^{-K''}-4e^{2K''-6K}[1+O(e^{-2K}(1-z_{ab}e^{-2K})^{-2})]\}$$

We now restrict our attention to the case

$$2K-K'' \gg e^{-K} \tag{3.12}$$

which turns out be necessary to keep the error term small:

$$e^{-2K}(1-z_{ab}e^{-2K})^{-2} \ll 1$$

The formula for z_{ab} can then be simplified:

$$z_{ab} = e^{K''}\{1-2e^{-K''}-4e^{-6K+2K''}(e^{2K-K''}-1)^{-1}$$
$$+\,O(e^{-2K''}+e^{-2K-K''}(e^{2K-K''}-1)^{-3})\} \tag{3.13}$$

The results (3.11) near T_w and (3.13) near $T=0$ will be used and discussed in the next section.

4. RESULTS

Using the identity

$$e^{\beta\sigma_{AC}(0)} = z_{ab}, \qquad T < T_w$$

we thus get from (3.11) and (3.3), near T_w,

$$\beta\sigma_{AC}(0) = 2K - 2\log(1 + 2e^{-K}) - (e^{-K} + 2e^{-2K})^2 \times \left(\frac{m-1}{m}\right)^2 \frac{G_b(z_b)^2}{B(z_b)^2} + O(m-1)^3 \tag{4.1}$$

and from (3.13), near $T = 0$,

$$\beta\sigma_{AC}(0) = K'' - 2e^{-K''} - 4e^{-6K+2K''}(e^{2K-K''} - 1)^{-1} + O(e^{-2K''} + e^{-2K-K''}(e^{2K-K''} - 1)^{-3}) \tag{4.2}$$

It is clear from (3.5) that $m-1$ vanishes as $T_w - T$ and therefore the specific heat has a finite jump at T_w which is characteristic of a second-order transition. This can also be seen in the behavior of the contact angle θ_1: combining (4.1) and (2.14), we obtain for $T \uparrow T_w$

$$\begin{aligned}\theta_1 &= 2^{1/2} e^{-3K/2}(1 + 2^{-K})^{1/2} \frac{m-1}{m} \frac{G_b(z_b)}{B(z_b)} + O(\theta_1^2) \\ &= R(T_w - T) + O(T_w - T)^2\end{aligned} \tag{4.3}$$

where R is a positive constant. The line $\theta_1 = R(T_w - T)$ is reproduced in Fig. 5 (dotted line).

The behavior of the contact angle at low temperature is obtained using (4.2) and (2.14):

$$\begin{aligned}\tan\theta_1 = 1 &- e^{-K+K''/2} + e^{-K-K''/2} + 2e^{-7K+5K''/2}(e^{2K-K''} - 1)^{-1} \\ &- 2e^{-3K+K''/2}(e^{K-K''/2} - 1)^{-1} \\ &+ O(e^{-2K''} + e^{-2K-K''}(e^{2K-K''} - 1)^{-3})\end{aligned} \tag{4.4}$$

which is plotted in Fig. 5 (dashed line). Equation (4.4) becomes more illuminating if we consider

$$K'' = 2K - \delta \tag{4.5}$$

with

$$e^{-K} \ll \delta \ll 1$$

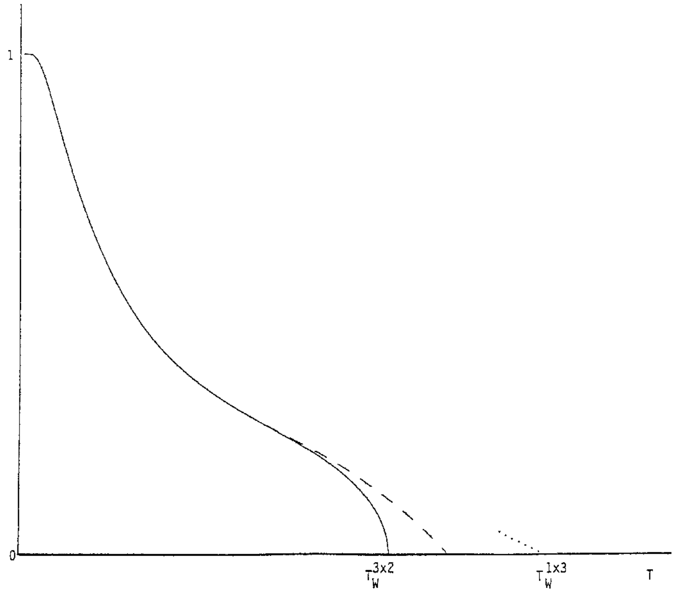

Fig. 5. Behavior of the contact angle θ_1 as a function of temperature T for $J=1$ and $J''=1.8$. The solid line represents the three-random-walk approximation [cf. (4.10)]. The dashed line represents the low-temperature expansion in the two-random-walk model [cf. (4.4)] and the dotted line corresponds to the expansion near T_w in the same model [cf. (4.3)].

so that (4.4) becomes

$$\theta_1 = \frac{\delta}{2} - \frac{\delta^2}{8} - 2e^{-2K}\delta^{-1} + O(e^{-4K}\delta^{-3} + \delta^3) \tag{4.6}$$

Equation (4.6) gives the variation of θ_1 from $T=0$, where $\theta_1 = \pi/4$, up to a temperature such that θ_1 is small, but much larger than e^{-K}. When $2K - K''$ is small, the wetting transition is in a low-temperature regime, and it makes sense to compare the expansions near $T=0$ and near T_w. It turns out, however, that the two ranges of valicity do not overlap. The expansion near T_w makes sense in the low-temperature regime if

$$K'' = 2K - \lambda e^{-K} + O(e^{-2K}) \tag{4.7}$$

We then get

$$\theta_1 = (\lambda - 2)\, e^{-K} + O(e^{-2K}) \tag{4.8}$$

For comparison, we shall now consider a simpler model where the interface with a meniscus is described by three independent interfaces which meet only at the endpoints of the meniscus. We can then compute $\sigma_{AC}(0)$ exactly at all temperatures from a single random walk model. For a restricted SOS model with $\beta J'' = K''$, we get

$$\beta\sigma_{AC}(0) = K'' - \log(1 + 2e^{-K''}) \tag{4.9}$$

From (2.14) we then obtain

$$\tan^2\theta_1 = 1 - 2e^{-K+K''/2}(1+2e^{-K''})^{-1/2} + e^{-2K+K''}(1+2e^{-K''})^{-1} - 4e^{-4K+K''}(1+2e^{-K''})^{-1} \tag{4.10}$$

which is shown in Fig. 5 (solid line). The wetting transition line is here given by

$$K'' - \log(1+2e^{-K''}) = 2K - 2\log(1+2e^{-K})$$

or

$$K'' = \log\frac{A + (A^2 + 8A)^{1/2}}{2} \tag{4.11}$$

with

$$A = e^{2K}(1+2e^{-K})^{-2}$$

This transition line is shown in Fig. 4. Near the wetting transition, the contact angle will behave according to

$$\theta_1 = A_3\left(\frac{T_w - T}{T_w}\right)^2 + O(T - T_w) \tag{4.12}$$

where the constant A_3 is defined by

$$A_3^2 = \frac{\left[\begin{array}{l}2K''e^{-K''}(1+2e^{-K''})^{-1} \\ \quad -4Ke^{-K}(1+2e^{-K})^{-1} + \log[(1+2e^{-K''})(1+2e^{-K})^{-2}]\end{array}\right]}{2 + e^{K} + \log(1+2^{-K}) - 2e^{-K}(1+\frac{1}{4}e^{2K})(1+2e^{-K})^{-1}}$$

which is to be evaluated at the wetting transition in this three-random-walk model. Formula (4.12) shows that, within this approximation, the wetting transition is of first order.

At low temperature, we obtain here, using (4.5),

$$\tan^2\theta_1 = 1 - 2e^{-\delta/2} + e^{-\delta} + e^{-K''}(2e^{-\delta/2} - 2e^{-\delta} - 4e^{-2\delta}) + O(e^{-\delta/2-2K''})$$

which becomes, in case $\delta = 2K - K''$ is small,

$$\theta_1 = \frac{\delta}{2} - \frac{\delta^2}{2} - 4e^{-2K}\delta^{-1} + 5e^{-2K} + O(\delta e^{-2K} + \delta^3) \tag{4.13}$$

Comparing with (4.6), we see that the three-random-walk model differs from the two-random-walk model at the order $e^{-2K}\delta^{-1}$.

5. MICROSCOPIC VALIDITY OF THE DOUBLE WULFF CONSTRUCTION AND OF THE HERRING RELATIONS

We first establish the shape of one large meniscus (Theorem 1 and Corollary) and then consider a "gas" of menisci embedded in an interface (Theorem 2), for which we show that the bulk of the total volume of the intruding phase is concentrated in one large meniscus.

Theorem 1. Let $h_1 \cdots h_N$, $h'_1 \cdots h'_N$ be random variables in $\mathbb{Z}$ distributed according to

$$\tilde{Z}_{V,N}^{-1} \exp\left[-\sum_{i=1}^{N} P_1(h_i - h_{i-1}) - \sum_{i=1}^{N} P_2(h'_i - h'_{i-1}) \right] \delta_{h_N, h'_N} \delta_{V, \sum_1^N (h_i - h'_i)} \tag{5.1}$$

where $h_0 = h'_0 = 0$, $P_1(x)$ and $P_2(x)$ satisfy the hypotheses of the Lemma (in Section 2), and N and $V = \lambda N^2$ are integers,

$$\delta_{x,y} = \begin{cases} 1 & \text{if } x = y \\ 0 & \text{otherwise} \end{cases}$$

and the partition function $\tilde{Z}_{V,N}$ normalizes the probability.

Let

$$t_1(c) = \frac{\sum_{x \in Z} x e^{-P_1(x) + cx}}{\sum_{x \in Z} e^{-P_1(x) + cx}} \tag{5.2}$$

$$I_1(c) = \frac{1}{2} \int_0^c c' t_1(c')\, dc' \tag{5.3}$$

and similarly for $t_2(c)$ and $I_2(c)$. Let c_λ be the solution of

$$I_1(c) + I_2(c) = \lambda c^2 \tag{5.4}$$

Then, for any sequence $N \to \infty$ with $V = \lambda N^2$ integer, the random variables $h_i - h_{i-1}$ and $h'_i - h'_{i-1}$ for $i = 1, \ldots, N$ are asymptotically distributed according to

$$\exp\left(- \sum_{1}^{N} \left\{ P_1(h_i - h_{i-1}) + P_2(h'_i - h'_{i-1}) + c_\lambda \left(1 - \frac{2i}{N}\right) [(h_i - h_{i-1}) - (h'_i - h'_{i-1})] \right\} \right) \tag{5.5}$$

If $\langle \cdot \rangle_N$ denotes expectation with respect to (5.1), we have

$$\langle h_i - h_{i-1} \rangle_N = t_1 \left(\left(1 - \frac{2i}{N}\right) c_\lambda \right) + O(N^{-1}) \tag{5.6}$$

$$\langle h_i \rangle_N = N \int_{(1-2i/N)\, c_\lambda}^{c_\lambda} t_1(c)\, dc + O(1)$$

$$\langle h'_i - h'_{i-1} \rangle_N = -t_2 \left(\left(1 - \frac{2i}{N}\right) c_\lambda \right) + O(N^{-1}) \tag{5.7}$$

$$\langle h'_i \rangle_N = -N \int_{(1-2i/N)\, c_\lambda}^{c_\lambda} t_2(c)\, dc + O(1)$$

$$\langle (h_i - h_{i-1})(h_j - h_{j-1}) \rangle_N - \langle h_i - h_{i-1} \rangle_N \langle h_j - h_{j-1} \rangle_N = O(N^{-1}) \qquad \forall i \neq j$$

$$\langle (h'_i - h'_{i-1})(h'_j - h'_{j-1}) \rangle_N - \langle h'_i - h'_{i-1} \rangle_N \langle h'_j - h'_{j-1} \rangle_N = O(N^{-1}) \qquad \forall i \neq j$$

$$\langle (h_i - h_{i-1})(h'_j - h'_{j-1}) \rangle_N - \langle h_i - h_{i-1} \rangle_N \langle h'_j - h'_{j-1} \rangle_N = O(N^{-1}) \qquad \forall i, j$$

$$\log \tilde{Z}_{V,N} = \sum_{i=1}^{N} \left\{ \log z_1 \left(\left(1 - \frac{2i}{N}\right) c_\lambda \right) + \log z_2 \left(\left(1 - \frac{2i}{N}\right) c_\lambda \right) \right\} + O(\log N) \tag{5.8}$$

with

$$z_1(c) = \sum_{x \in Z} e^{-P_1(x) + c(x - t_1(c))}$$

and similarly for $z_2(c)$.

Proof. The proof is essentially the same as for a drop on a wall.[7] We have two random walks which start together ($h_0 = h'_0 = 0$) and are subject to two global constraints: they meet after N steps ($h_N = h'_N$) and enclose a fixed area [$\sum (h_i - h'_i) = V$]. The Kronecker form of the constraints allows us to introduce Lagrange multipliers into the Boltzmann factor without changing the probability distribution. The conjugate fields can then be adjusted so that the constraints remain satisfied in average when the Kronecker δ's are removed. The corresponding decoupled measure is denoted $\langle \cdot \rangle_0 (c_\lambda^{(N)})$ and is just (5.5) except that c_λ is replaced by $c_\lambda^{(N)} \approx c_\lambda$ defined from Riemann sum approximations to $I_1(c)$ and $I_2(c)$. A suitably generalized version of the local central limit theorem then shows that reintroducing the Kronecker constraints induces negligible effects as $N \to \infty$, as stated in the theorem.

Corollary. Under the hypotheses of Theorem 1, suppose that the measure (5.1) is restricted to

$$h_i > h'_i, \qquad i = 1, N-1$$

and denote $\langle \cdot \rangle_{N, h > h'}$ and $Z_{V,N}$ the corresponding expectation values and partition function. Then the conclusions of Theorem 1 apply to $\langle \cdot \rangle_{N, h > h'}$ and $Z_{V,N}$, provided the error term $O(N^{-1})$, where present, is changed into

$$O(N^{-1}) + a \exp[-b \operatorname{Min}(i, N-i)]$$

for some fixed constants a and b.

Proof. As in Ref. 6.

Let us now denote

$$\tan \theta_1(x) = t_1((1-2x)\, c_\lambda)$$
$$\tan \theta_2(x) = t_2((1-2x)\, c_\lambda)$$

we then find, using (2.7),

$$\log z_1 \left(\left(1 - \frac{2i}{N} \right) c_\lambda \right) = - \frac{\beta \sigma_{AB}(\theta_1(i/n))}{\cos \theta_1(i/N)} \tag{5.9}$$

$$\log z_2 \left(\left(1 - \frac{2i}{N} \right) c_\lambda \right) = - \frac{\beta \sigma_{BC}(\theta_2(i/n))}{\cos \theta_2(i/N)} \tag{5.10}$$

and therefore, asymptotically, from (5.8) and its analogue in the corollary

$$\log Z_{V,N} = -N \int_0^1 \beta \sigma_{AB}(\theta_1(x)) \frac{dx}{\cos \theta_1(x)} - N \int_0^1 \beta \sigma_{BC}(\theta_2(x)) \frac{dx}{\cos \theta_2(x)} + O(\log N) \tag{5.11}$$

Equations (5.9) and (5.10) also yield

$$\frac{d}{d\tan\theta_1(x)}\,\frac{\beta\sigma_{AB}(\theta_1(x))}{\cos\theta_1(x)}=\frac{d}{d\tan\theta_2(x)}\,\frac{\beta\sigma_{AB}(\theta_2(x))}{\cos\theta_2(x)}=(1-2x)\,c_\lambda \quad (5.12)$$

which can also be written

$$\begin{aligned}&\sin\theta_1(x)\cdot\beta\sigma_{AB}(\theta_1(x))+\cos\theta_1(x)\cdot\beta\sigma'_{AB}(\theta_1(x))\\ &\quad=\sin\theta_2(x)\cdot\beta\sigma_{BC}(\theta_2(x))+\cos\theta_2(x)\cdot\beta\sigma'_{BC}(\theta_2(x))\\ &\quad=(1-2x)\,c_\lambda \qquad (5.13)\end{aligned}$$

Equation (5.12) or (5.13) shows that the $AB(h_0\cdots h_N)$ and $BC(h'_0\cdots h'_N)$ interfaces are given by Wulff constructions, with

$$\sum h_i=N^2\frac{I_1(c_\lambda)}{c_\lambda^2}$$

$$-\sum h'_i=N^2\frac{I_2(c_\lambda)}{c_\lambda^2}$$

It is remarkable that the same constant c_λ occurs for both interfaces, even if the two shapes are very different, as will be the case if $P_1(x)$ and $P_2(x)$ are very different. This is related to the second Herring relation (2.2), which is (5.13) taken at $x=0$ or 1, and which is thus established for the statistical model defined in Theorem 1 and the Corollary.

In order to complete our proof of the Wulff construction for a meniscus embedded in an interface, and of the corresponding first Herring relation, it is now necessary to show that within a "gas" of menisci subject to a global volume constraint, the bulk of the intruding phase will concentrate in one large meniscus. For simplicity of notation, we shall formulate our results for the restricted SOS model considered in the previous sections, as defined in (2.15)–(2.17), with the additional constraint

$$\sum_0^N (h_i-h'_i)=V \qquad (5.14)$$

The corresponding partition function will be denoted $\Xi_{V,N}$. Let us now describe configurations in terms of a gas of menisci: a meniscus of length l and volume v located at x is defined by the conditions

$$h_x=h'_x$$

$$h_i>h'_i, \qquad x<i<x+l$$

$$h_{x+l}=h'_{x+l}$$

$$\sum_x^{x+l}(h_i-h'_i)=v$$

Then

$$\Xi_{V,N}=\sum_{n\geqslant 1}\sum_{v_1\cdots v_n\geqslant 1}\delta_{\sum v_p,V}$$
$$\times\sum_{0\leqslant x_1<y_1\leqslant\cdots\leqslant x_n<y_n\leqslant N}\left\{\prod_1^n\left(Q^a_{x_p-y_{p-1}}Z_{v_p,y_p-x_p}\right)\right\}Q^a_{N-y_n}\qquad(5.15)$$

with $y_0=0$. We now call a meniscus "large" when its length l and volume v satisfy

$$\frac{v}{l}>(\log N)^{1+\varepsilon}\qquad(5.16)$$

where $\varepsilon>0$ is fixed. The following theorem shows that all menisci except one will be small.

Theorem 2. Let $h_1\cdots h_N$, $h'_1\cdots h'_N$ be distributed according to (2.15)–(2.17) and (5.14). Then for any sequence $N\to\infty$ with $V=\lambda N^2$ integer, we have

$$\log\Xi_{V,N}=\log\left(\sum_{v_1n_1}Z_{v_1n_1}\Xi^0_{V-v_1,N-n_1}\right)+O(\log N^{1+\varepsilon})\qquad(5.17)$$

where $\Xi^0_{V,N}$ is defined as $\Xi_{V,N}$ with the restriction that there should be no large meniscus.

Proof. As in ref. 7.

It is now simple to complete the proof of the validity of the double Wulff construction (Fig. 2b) and of the Herring relations for our statistical mechanical model. The sum over v_1 in (5.17) is restricted to

$$V-N(\log N)^{1+\varepsilon}<v_1<V$$

Z_{v_1,n_1} is essentially constant in this interval, whereas $\Xi^0_{V-V_1,N-n_1}$ has a Gaussian distribution around $V-v_1=cst(N-n_1)$ of width $(N-n_1)^{1/2}$. Summing over v_1 therefore gives

$$\log\Xi_{V,N}=\log\left(\sum_{n_1}Z_{v,n_1}Q_{N-n_1}\right)+O(\log N^{1+\varepsilon})\qquad(5.18)$$

where Q_N is defined like $\Xi_{V,N}$ without any volume condition. The sum over n_1 can now be analyzed as in the classical variational problem to obtain the first Herring relation (2.1).

ACKNOWLEDGMENTS

This work has benefitted from financial support as part of a CNRS–Communauté Française de Belgique exchange program. F.M. is an IRSIA Researcher.

REFERENCES

1. J. De Coninck, Ph. de Gottal, and F. Menu, *J. Stat. Phys.* **56**:23 (1989).
2. W. Selke and W. Pesch, *Z. Phys. B* **47**:335 (1982).
3. M. E. Fisher, *J. Stat. Phys.* **34**:667 (1984).
4. D. B. Abraham and P. M. Duxbury, *J. Phys. A* **19**:385 (1986).
5. F. Dunlop and J. Ruiz, *Ann. Inst. H. Poincaré* **48**:229 (1988).
6. C. Herring, in *Structure and Properties of Solid Surfaces*, R. Gomer and C. S. Smith, eds. (University of Chicago Press, Chicago, Illinois, 1953).
7. J. De Coninck, F. Dunlop, and V. Rivasseau, *Commun. Math. Phys.* **121**:401 (1989).
8. J. De Coninck and F. Dunlop, *J. Stat. Phys.* **47**:827 (1987).