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LETTER TO THE EDITOR

Description of phases in a film-thickening transition

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Abstract. Several criteria are discussed for a phase transition from partial to complete wetting in binary mixtures and their analogues. These criteria are based on order parameters and mechanical stability. A further geometrical description of the phase transition is given.

Recently the phenomenon of surface film thickening, which was proposed by Cahn (1977) on phenomenological grounds, has been revealed in an exactly solvable statistical-mechanical model of a phase transition in a binary mixture (Abraham 1980). This model is based on a lattice gas and thus has a magnetic analogue for domain walls. The typical picture is that we have a mixture of two components a and b which separates at low enough temperatures into an a-rich phase and a b-rich one, denoted A and B respectively. Let the bulk phase be pure A and suppose that one face, which we shall call the wall, wets component b differentially. Then we have a low-temperature structure with a thin surface phase $C_<$ separating the wall from the bulk phase A. At a definite temperature, depending on the strength of the differential wetting, we have a transition to a new structure with a thin phase $C_>$ separating the wall from phase B; this film of B is of infinite thickness in principle and is followed by the bulk phase A. We expect the A–B interface to be unaffected by the boundary. The situation described above is also called a transition from partial to complete wetting. It may be characterised at a bulk level by the phenomenological Young equation (Cahn 1977, Antonov 1907, Rowlinson and Widom 1982)

$$\sigma_{AB} \cos \theta = \sigma_{Aw} - \sigma_{Bw} \tag{1}$$

where θ is the contact angle, σ_{AB} is the A–B surface tension and σ_{iw} with $i = A, B$ is the wall tension. The mechanical origin of (1) is quite obvious, but it needs rigorous justification since at the point of film thickening, characterised by $\theta = 0$, bulk thermodynamic concepts of surface tension and contact angle may well not apply (Jamieson 1982).

In this letter we report that the exact phase transition condition in the planar model of Abraham (1980) is precisely of the form (1) by evaluating the two wall tensions, not both previously known. This phase transition condition was originally obtained from the density profile; no information was obtained either about the geometry of the phases $C_<$ and $C_>$ or whether the wetting film B is composed of small or large droplets.

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Several authors (Burkhardt 1981, Chalker 1981, Chui and Weeks 1981, Hilhorst and van Leeuwen 1981, Vallade and Lajzierowicz 1981) showed that the planar film-thickening transition could be modelled by an Onsager–Temperley string (Temperley 1952). Here the bulk phase A is bounded on the wall side by a surface with no re-entrants which is specified uniquely by its distance y_i from the wall at each point i of a rectangular grid which represents the wall. The energy of a configuration is given by

$$E=2\tau\sum|y_i-y_{i+1}| \tag{2}$$

with y_i real, non-negative. The canonical probability of a configuration is

$$p_\Lambda\{y\}=Z_\Lambda^{-1}\exp(-E)\prod_{i=1}^{N}(1+a\delta(y_i)). \tag{3}$$

Equations (2) and (3) can be obtained as the isotropic limit of the Ising model (Temperley 1952). But for phenomena on the scale of the correlation length, a suitable choice of τ in (2) and (3) reproduces exactly the results for the isotropic planar Ising model (Abraham and Reed 1974, 1976, Abraham and Smith 1982).

Equation (3) is evidently associated with a Markov process. This fact is now used to elucidate the structure of bubbles by appealing to the theory of recurrent events. This structure changes dramatically on passing through the phase transition.

Let

$$P_x=P\{y_{x+1}=0|y_1=0\} \tag{4}$$

and define a generating function by

$$G(z)=\sum_1^\infty P_xz^x. \tag{5}$$

On the other hand, let Q_x be the probability that the first return to $y=0$ occurs after x steps and let

$$H(z)=\sum_1^\infty Q_xz^x. \tag{6}$$

It follows that

$$H(z)=G(z)/(1+G(z)). \tag{7}$$

Two cases are distinguished by the limiting behaviour of $H(z)$ as $z\to1$.

(I) $\lim H(z)=1$. By the Borel–Cantelli lemmas (Feller 1971) the event $\{y_x=0\}$ occurs for infinitely many x. The mean length between two neighbouring returns is $H'(1)$; this is the mean droplet size.

(II) $\lim H(z)<1$: with probability one $\{y_x=0\}$ occurs only finitely many times: we have a finite number of macroscopic drops at the wall.

An order parameter can be defined by

$$\rho=\lim_{N\to\infty}\frac{1}{N}\sum_1^N\delta(x_i). \tag{8}$$

This should vanish in case II, but be non-zero in case I.

We also consider the case of a finite channel with $0\leq y_i\leq L$ for all i and attraction at each edge. The growth of the recurrence interval with L can be studied.

All our results come from the eigenvalue problem associated with transfer kernels

$$\lambda\phi(x)=\int_0^\infty e^{-2\tau|x-y|}\phi(y)\,dy+a\,e^{-2\tau|x|}\phi(0) \tag{9}$$

and

$$\lambda\phi_L(x)=\int_0^L e^{-2\tau|x-y|}\phi_L(y)\,dy+a\,e^{-2\tau x}\phi_L(0)+b\,e^{-2\tau(L-x)}\phi_L(L). \tag{10}$$

The technique of solution is to convert (9) and (10) to Schrödinger equations with appropriate boundary conditions using the identity

$$(\partial^2/\partial x^2-4\tau^2)\,e^{-2\tau|x-y|}=-4\tau\delta(x-y). \tag{11}$$

The results for (9) depend on $\tau-\tau_c(a)$ where $\tau_c(a)=1/2a$: when $\tau>\tau_c(a)$ there is a unique maximum eigenvalue

$$\lambda_m=4a^2\tau/(4a\tau-1) \tag{12}$$

with eigenvector

$$\phi_m(x)=2K_m\exp(-K_m x) \tag{13}$$

and

$$K_m=(2a\tau-1)/a. \tag{14}$$

It can be shown that

$$G(z)=[z/(1-z)]C+A(z) \tag{15}$$

where $C=2(\tau-\tau_c(a))/(2\tau-\tau_c(a))$, $A(1)<\infty$ and $A'(1)<\infty$. Thus $H(1)=1$ and

$$H'(1)=1+\tau_c(a)/2(\tau-\tau_c(a)) \tag{16}$$

and we have case I. The order parameter is $\rho=4K_m^2$. When $\tau<\tau_c(a)$, (9) has a continuous spectrum and a simple calculation shows that $G(1)<\infty$, so that case II obtains: the drops at the wall are macroscopic and finite in number and the order parameter vanishes (as $1/N$ as $N\to\infty$).

We now point out an adhesion phenomenon for the channel of finite width L. Let $Z_L(a)$ denote the partition function with $a=b$. We define an incremental free energy per unit length of channel by

$$f^\times(L)=-\lim N^{-1}\log(Z_L(a)/Z_\infty(a)) \tag{17}$$

and we can show that for $L/a\gg1$

$$f^\times(L)=\begin{cases}\sim-(2a\tau-1)a/(4a\tau-1)L & \text{for } \tau>\tau_c/a,\\ 0 & \text{for } \tau<\tau_c(a).\end{cases} \tag{18}$$

Thus below the roughening transition there is long-ranged *attraction* between the edges of the channel. For $\tau>\tau_c(a)$ one might anticipate an entropic *repulsion* of the channel walls, but this is not so.

We now turn to a discussion of the Cahn detachment criterion. The partition function for a finite planar Ising lattice wrapped on a cylinder with fields h_1 and h_2 applied at opposite ends is

$$Z(h_1,h_2)=Z_+ +\mathrm{sgn}(h_1h_2)Z_- \tag{19}$$

where

$$Z_{\pm} = \prod_{\omega \in S_M \pm} \pm[e^{N\gamma(\omega)} A_1(\omega) A_2(\omega) + e^{-N\gamma(\omega)} B_1(\omega) B_2(\omega)] \tag{20}$$

with

$$A_j(\omega) = e^K(\cosh 2h_j^* - \sinh 2h_j^* \cos\omega)\cos(\delta^*(\omega)/2)\, e^{-K} \sinh 2h_j^* \sin\omega \sin(\delta^*(\omega)/2), \tag{21}$$

$$B_j(\omega) = e^K(\cosh 2h_j^* - \sinh 2h_j^* \cos\omega)\sin(\delta^*(\omega)/2) - e^{-K} \sinh 2h_j^* \sin\omega \cos(\delta^*(\omega)/2). \tag{22}$$

The variable x^* is defined by

$$\exp(2x^*) = \coth x. \tag{23}$$

The functions $\gamma(\omega)$ and $\delta^*(\omega)$, originally defined by Onsager (1944), are given by

$$\cosh \gamma(\omega) = \cosh 2K \cosh 2K^* - \cos\omega \tag{24}$$

with $\gamma \geqslant (0)$, and

$$\sin \delta^*(\omega) = \sinh 2K^* \sin\omega / \sinh \gamma(\omega) \tag{25}$$

with $\delta^*(\pi) = 0$. The products are taken over the sets

$$S_M^{\pm} = \{\omega \in [0, \pi], \exp iM\omega = \mp 1\}. \tag{26}$$

These results generalise those of Au-Yang and Fisher (1975) which are restricted by $\operatorname{sgn} h_1 h_2 = +1$.

Suppose $h_2 \to \infty$, but that $h_1 = \pm aK$ with $0 < a < 1$. The incremental free energy for the 'plus' phase with surface field aK is (McCoy and Wu 1967)

$$f_{++}(a, \tau) = (4\pi)^{-1} \int_0^{2\pi} d\omega \log A_2(\omega). \tag{27}$$

When the surface field is $-aK$ there is an additional term

$$f_{+-}(a, \tau) = f_{++}(a, \tau) - v(a). \tag{28}$$

Let

$$w = e^{2K}(\cosh 2K - \cosh 2aK)/\sinh 2K \tag{29}$$

when $w > 1$; then $v(a)$ is given by

$$\cosh v(a) = \cosh 2(K - K^*) + 1 - (w + 1/w)/2. \tag{30}$$

The point $w = 1$ defines the transition temperature $T_R(a)$. For $w < 1$, or equivalently $T > T_R(a)$, we have

$$v(a) = 2(K - K^*). \tag{31}$$

This is the usual Onsager surface tension (Onsager 1944, Fisher and Ferdinand 1967) between pure phases. Returning to (28), for $T < T_R(a)$ we have $v(a) < 2(K - K^*) = \tau_{AB}$ with equality at $T = T_R(a)$, confirming the Young rule phenomenology alluded to above. It should be pointed out that this picture is not entirely felicitous on a lattice outside the scaling region because a contact angle cannot be defined in an obvious way. But Pandit *et al* (1982) have shown that the same criterion can be obtained from the Wulf construction (Wulf 1901, Herring 1951); this construction does not have a rigorous basis in general.

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