Surface-film thickening: An exactly solvable model

D. B. Abraham and E. R. Smith*
Department of Theoretical Chemistry, Oxford OX1 3TG, England
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A model is proposed, and solved exactly in two dimensions, for film thickening at a boundary in a binary mixture.

In this Communication we consider a model of an interface between coexistent thermodynamic phases near a surface of the system. Our model originates from the lattice gas with a pairwise attractive potential and thus can describe liquid vapor, binary alloys, and mixtures as well as the usual uniaxial ferromagnetic properties.[1] Suppose that the state of the system is such that phases A and B coexist, but that the bulk is entirely in phase A. Now suppose that the surface wets phase B differentially and that this phenomenon is represented by a differential surface fugacity $\hat{z}$. It is known[2] for the planar lattice gas with nearest-neighbor interactions that, according to the magnitude of $\hat{z}$, we have a phase transition at temperature $T=T_0(\hat{z})$ between a low-temperature region characterized by a surface phase $C_<$ of microscopic extent in equilibrium with the bulk A phase. For $T_c > T > T_0(\hat{z})$ there is a surface phase $C_>$, then a bulk phase of type B having infinite extent followed by the bulk A phase. This is an example of the surface-wetting phenomenon of Cahn.[3] The length scale in both $C_>$ and $C_<$ as we go to the scaling region is the bulk correlation length.

If, on the other hand, the surface differentially wets phase A, then we have a surface phase of type $C_>$ and *no included layer* of B phase. This is in accord with the theory of Au Yang, de Gennes, and Fisher.[4]

A natural question raised by the above concerns the vicinity of the coexistence region. Suppose the bulk fugacity favors phase A. Is there ever a bulk included B phase? We now discuss a simple extension of the solid-on-solid or Onsager-Temperley version of the above model.[5]

Let phases A and B be separated by a region which we represent by a thread with no overhangs (see Fig. 1).

There is a Boltzmann factor $\exp(-2\sum K \times |y_j - y_{j+1}|)$ describing the stiffness of the line. This is the SOS model. In our model there is an extra factor $\exp(-2H\sum|y_i|)$ which weighs the inclusion of a B layer by the bulk fugacity. (Reference 2 refers to the case $H=0$.) When the y_j are assigned *continuous* positive values we can introduce a transfer kernel acting parallel to the surface whose spectrum can be determined exactly: We take the nonsymmetrical form of the eigenvalue equation

$$\int_0^\infty \exp(-2K|x-y|)e^{-2Hy}\phi(y)\,dy = \lambda\phi(x) \quad . \tag{1}$$

We note that the integral operator is Hilbert-Schmidt whenever $H>0$, whereas, when $H=0$, it has a continuum spectrum on [0,1]. Thus we expect substantial mathematical differences from Refs. 5 and 6. Using the fact that the $\exp(-2K|x-y|)$ is the Green's function for the differential operator

$$-\frac{1}{4K}\left(\frac{d^2}{dx^2}-4K^2\right) ,$$

(1) can be written in the Schrödinger form[6]

$$\lambda\left(\frac{d^2\phi}{dx^2}-4K^2\phi\right) = -4K\,e^{-2H|x|}\phi(x) \quad , \tag{2}$$

with the boundary condition

$$2K\phi(0) = \phi^{(1)}(0) \quad . \tag{3}$$

Define $\alpha = 2K/H$ and $\nu = 1/\sqrt{\lambda K}$. Then the solution of (2) and (3) is

$$\phi_j(x) = A_j J_\alpha(\alpha\nu_j e^{-Hx}) \quad , \tag{4}$$

where the ν_j solve

$$J_{\alpha-1}(\alpha\nu_j) = 0 \quad . \tag{5}$$

with ordering $\nu_0 < \nu_1 < \cdots$. With $\alpha > 0$, all solutions are real. The correct normalization for (4) [recall (1)

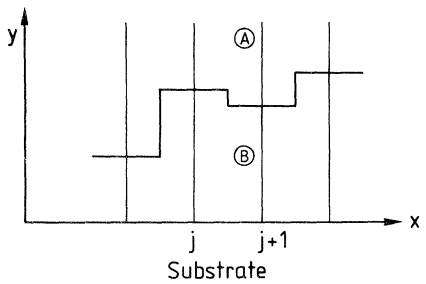

FIG. 1. Geometrical arrangement showing typical contour separating components in solid-on-solid version.

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is not in self-adjoint form] is

$$A_j = \sqrt{2H}\,/J_\alpha(\alpha\nu_j) \quad . \tag{6}$$

Equations (4), (5), and (6) can be established by perusal of Watson's work.[7] Evidently eigenvalues have a homogeneous representation $\lambda_j = 1/K\nu_j^2$ with $\nu_j = f_j(\alpha)$.

The distribution of matter near the surface is given by the function

$$F(y) = \int_y^\infty dx\, e^{-2Hx}[\phi_0(x)]^2 \quad . \tag{7}$$

Define $u = e^{-Hy}$; then

$$F(y) = u^2\{[1-(\nu_0 u)^{-2}][J_\alpha(\alpha\nu_0 u)]^2 + [J_\alpha^{(1)}(\alpha\nu_0 u)]^2\}/[J_\alpha(\alpha\nu)]^2 \quad . \tag{8}$$

Equations (5) and (8) may be analyzed for $H \to 0$ using the uniform asymptotic expansions of Ref. 8. It turns out that, to leading order in α, (5) gives $\nu_j = 1 + \gamma_j \alpha_j^{-2/3}$, where γ_j solves $\mathrm{Ai}(-\gamma_j) = 0$, $\gamma_j < \gamma_{j+1}$ for $j \geq 0$. The γ_j are real positive. The function Ai is of Airy type; there is an equivalent fractional Bessel form

$$J_{1/3}(t_j) + J_{-1/3}(t_j) = 0 \quad , \tag{9}$$

with

$$t_j = 2\gamma_j^{3/2}/3 \quad . \tag{10}$$

Returning to (8), the Bessel functions can be expressed in terms of $\mathrm{Ai}(u-\gamma_0)$, where $u = 2Kx\alpha^{-1/3}$. The leading term in α tends to zero as $u \to \infty$. Length scales other than $\alpha^{1/3}$ are insignificant. Another way to anticipate this new length scale is to expand the exponential in (2) to order H and then to scale the variable x as above: (2) becomes an Airy equation directly. The conclusion to be drawn here is that when $H > 0$ the absorbed phase is neither of infinite width, nor does it scale like $1/H$ as might have been expected on naive grounds; rather, it grows as $H \to 0$ on a length scale $K^{-2/3}H^{-1/3}$. There is no evidence for a sharp Cahn transition except at $H = 0$ (Ref. 3).

The model described above is slightly inconsistent since there is nothing *prima facie* to stop the surface film detaching and disintegrating. Equation (1) can be extended to include a contact potential $\beta\delta(x)$ creating a "sticky" hard wall, which gives

$$\int_0^\infty \exp(-2K|x-y|)\,e^{-2Hy}\phi(y)\,dy + \beta e^{-2K|x|}\phi(0) = \lambda\phi(x) \tag{11}$$

in place of (1). This gives the same Schrödinger equation as (2) but with the modified boundary conditions

$$\phi^{(1)}(0) = 2K(1-2\beta\lambda^{-1})\phi(0) \quad . \tag{12}$$

The eigenvectors are again of form (4) but with the eigenvalue condition (5) replaced by

$$J_{\alpha-1}(\alpha\nu) = 2K\beta\nu J_\alpha(\alpha\nu) \quad , \tag{13}$$

which is equivalent to the equation

$$(2H\beta)^{-1} = \nu^2 \sum_0^\infty 1/(\nu_n^2 - \nu^2) \quad , \tag{14}$$

with ν_n the solutions of (5): (14) may be investigated graphically. There is a pure point spectrum. As $H\beta$ decreases, the minimal ν satisfying (14) increases from 0 towards ν_0; there is always a bound state in λ outside $[0, 1/K]$ for $H > 0$. On the other hand, when $H = 0$ there is a critical value of β satisfying

$$\beta_c = 1/2K \quad . \tag{15}$$

Given K, for $\beta < \beta_c$ there is no bound state, whereas for $\beta > \beta_c$ there is; this is the roughening transition as in Refs. 2 and 6. Again, the scaling region can be investigated as $H \to 0$. Taking $2\beta K = 1 + \zeta\alpha^{1/3}$ and $\nu^2 = 1 + 2\gamma(\zeta)\alpha^{-2/3}$, it turns out that $\gamma(\zeta)$ is smooth, strictly positive, but has a minimum at $\zeta = 0$.

There is thus no Cahn transition except at $H = 0$; rather, the surface phase can be made arbitrarily thick, in particular, of macroscopic dimensions, by taking H small enough. Thus for $H > 0$, the Burton-Cabrera-Frank argument holds[9]: There is no surface phase transition since the surface is one dimensional.

We have carried out a Monte Carlo simulation of the underlying lattice gas model using a procedure tested against an exact solution.[2,10] This is consistent with the length scale $\alpha^{1/3}K^{-1}$, provided K is not too small.

Scaling Theory. Equation (1) can be modified to obtain a scaling theory for the critical region which gives the known profile structure for the two-dimensional Ising model when $H = 0$ (Ref. 11) and the correct surface tension.[12] Scaling the lengths by ξ_0, where $\xi_0 = 1\ (K - \frac{1}{2}\ln\coth K)$ [note that the correlation length is actually $\xi_0/2$ (Ref. 13) showing a breakdown of Ornstein-Zernike theory], (1) becomes

$$\int_0^\infty \exp(-\sqrt{2}|x-y|)\exp[-2g(h)hy]\,\Phi(y)\,dy = \lambda\Phi(x) \tag{16}$$

Here h is the scaling field $\sim H[(T_c - T)/T_c]^{-15/8}$ and the magnetization $m(H,T)$ has been put in the form $m^* g(h)$ (Ref. 14), where $m^* = [(T_c - T)/T_c]^{1/8}$ is the spontaneous magnetization.[15] In this way we get a correction to the Au Yang–de Gennes-Fisher critical film theory; this absorbed film, already of thickness the correlation length ξ_0, should diverge even faster

in width, as $\xi_0 h^{-1/3}$ as $h \to 0^+$.

Note. the correlation length along the direction of the interface is given by $\xi_{\parallel}^{-1} = \ln(\lambda_0/\lambda_1)$, where λ_0 and λ_1 are the maximal and next-to-maximal eigenvalues of (1), provided $H \neq 0$. The asymptotic behavior of this as $\alpha \to 0$ is thus $\xi_{\parallel}^{-1} \sim 2(\gamma_1 - \gamma_0)\alpha^{-2/3}$. This type of behavior, as well as the transverse correlation length reported, has been seen in an approximate renormalization-group calculation.[17]

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*On leave from Department of Mathematics, University of Melbourne, Parkville, Victoria 3052, Australia.

[1]C. N. Yang and T. D. Lee, Phys. Rev. 88, 404 (1952).

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

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

[4]M. E. Fisher and P-G. de Gennes, C. R. Acad. Sci. Ser. B 287, 207 (1978); H. Au Yang and M. E. Fisher, Phys. Rev. B 21, 3956 (1980); M. E. Fisher and H. Au Yang, Physica (Utrecht) 101A, 255 (1980); P-G. de Gennes, C. R. Acad. Sci. 292, 701 (1981); see also Ref. 2 above.

[5]L. Onsager (unpublished); H. N. V. Temperley, Proc. Cambridge Philos. Soc. 48, 693 (1952).

[6]T. W. Burckhardt, J. Phys. A 14, L63 (1981); J. T. Chalker, J. Phys. A (in press); S. T. Chui and J. D. Weeks, Phys. Rev. B 23, 2438 (1981); Hilhorst and J. M. J. van Leeuwen (unpublished).

[7]G. N. Watson, *Theory of Bessel Functions,* 2nd ed. (Cambridge University, Cambridge, 1941).

[8]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, 1968), 7th printing.

[9]W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London, Ser. A 243, 299 (1951).

[10]D. B. Abraham and E. R. Smith, J. Phys. A 14, 2059 (1981); and (unpublished).

[11]D. B. Abraham and P. Reed, Phys. Rev. Lett. 33, 377 (1974); Commun. Math. Phys. 49, 35 (1976); D. B. Abraham and M. E. Issigoni, J. Phys. A 13, L89 (1980).

[12]L. Onsager, Phys. Rev. 65, 117 (1944); M. E. Fisher and A. E. Ferdinand, Phys. Rev. Lett. 19, 169 (1967); D. B. Abraham, G. Gallavotti, and A. Martin-Löf, Physica (Utrecht) 65, 73 (1973).

[13]T. T. Wu, Phys. Rev. 149, 380 (1966).

[14]D. B. Abraham, Phys. Lett. 61A, 271 (1977).

[15]C. N. Yang, Phys. Rev. 85, 808 (1952).

[16]R. B. Stinchcombe (unpublished).