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An Exactly Solved Model with a Wetting Transition

D. B. Abraham[1,2] **and E. R. Smith**[1,3]

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A model of a binary mixture, showing a wetting transition, is examined. No prewetting phenomena are found. The scaling functions are obtained for the film thickness and for the correlation lengths.

KEY WORDS: Wetting transition; exact solution; random walk; S.O.S. model.

1. INTRODUCTION

Consider a thermodynamic system at equilibrium in phase A, which is precisely at coexistence with a second phase B. If the phase B is sufficiently attracted by the wall of the container enclosing the bulk phase A, then a phase transition from partial to complete wetting may be observed under appropriate conditions.[1] In the completely wet state, a film of bulk phase B is inserted at the wall; it is separated from the bulk phase A by an $A|B$ interface which behaves independently of what is happening at the wall and has an incremental free energy τ_{AB} per unit area. On the other hand, under partially wet conditions, there is a contact angle θ at the wall, as shown in Fig. 1. Following Cahn[2,3], this should satisfy the Young–Dupré equation

$$\tau_{AW} - \tau_{BW} = \tau_{AB} \cos \theta \tag{1.1}$$

for mechanical equilibrium, where τ_{iW} is the incremental free energy per unit area for contact between phase $i = A, B$ and the wall.

Suppose that

$$\tau_{AW} - \tau_{BW} > \tau_{AB} \tag{1.2}$$

[1] Department of Mathematics, University of Melbourne, Parkville, Victoria 3052, Australia.

[2] Permanent address: Department of Theoretical Chemistry, Oxford University, 1 South Parks Road, Oxford, OX1 3TG, United Kingdom.

[3] Permanent address: Department of Mathematics, Latrobe University, Melbourne, Australia.

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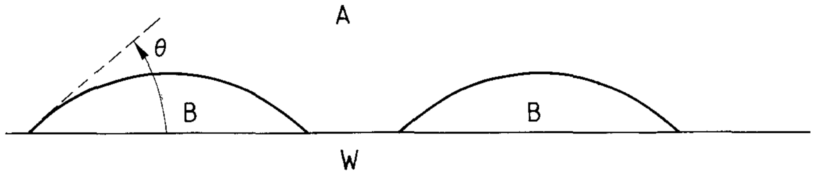

Fig. 1. Sketch of two droplets of phase B against a wall in equilibrium with a bulk phase A, to illustrate contact angle θ.

Then (1.1) has no solution for real θ and complete wetting should obtain.

The statement that $\tau_{AB} \to 0$ as $T \to T_c^-$ together with continuity implies that (1.2) will always be satisfied near the critical point is not strictly valid, since $\tau_{AW} - \tau_{BW}$ might well vanish faster.

A more subtle criticism is that (1.2) refers to τ_{BW} in a situation where a BW interface is thermodynamically unstable, so that it really begs the question.[4] Further, referring to Fig. 1, if the bubbles at the wall in the partially wet regime are not significantly bigger than or commensurate with the bulk correlation length, then the thermodynamic concept of surface tension could hardly be expected to apply.

It should be clear then that this simple scenario, its intuitive appeal notwithstanding, requires further investigation.

A two-dimensional lattice gas model has been constructed,[5,6] however, which is exactly solvable and which shows a phase transition of the type predicted by the Cahn argument.[2] This model is only solvable with existing techniques at coexistence of the bulk phases. The purpose of the present paper is to describe in detail results reported[7] for a simplified model which is again exactly solvable and which works away from coexistence. By virtue of its simplicity, it also allows a more detailed examination of the geometry of the phases.

Let us assume at the outset that the phase transition is associated with fluctuations of the interface on a scale much longer than the correlation length. By a thought-renormalization to this length scale, the intrinsic fluctuations of the pure phases are made to disappear; the fluctuations of the $A \mid B$ interface are controlled by a surface tension rather than a "bare" or microscopic coupling. The idea is to construct a probabilistic model for these fluctuations which is simple enough to solve. This is unlike the usual approach through a "molecular" Hamiltonian, but it is remarkably useful as the reader can find in recent work of Fisher and Huse[8,9] where a wide range of problems are analyzed.

II. MODELS

Consider a two-dimensional square lattice with a spin $\sigma(\mathbf{i}) = \pm 1$ at each lattice site $\mathbf{i} = (i_1, i_2)$ with $-M \leqslant i_2 \leqslant M$. The spins are coupled by the Ising Hamiltonian

$$\mathscr{H} = \mathscr{H}(\Lambda) + \mathscr{H}(\partial\Lambda) \tag{2.1}$$

where $\mathscr{H}(\Lambda)$ is the usual bulk term given by

$$\beta\mathscr{H}(\Lambda) = -\sum_{j=-M}^{M} \left\{ \sum_{i=1}^{N-1} K_1 \sigma(i, j)\, \sigma(i+1, j) + K_2 \sigma(i, j)\, \sigma(i, j+1) + h \sum_{i=2}^{N-1} \sigma(i, j) \right\} \tag{2.2}$$

with cyclic conditions in the (0, 1) direction, where K_1 and K_2 are strictly positive couplings scaled by $\beta = 1/kT$ in the customary notation for the canonical ensemble and h is the bulk field which is zero at coexistence [10].

The extra term in (2.1) acts on the surface

$$\beta\mathscr{H}(\partial\Lambda) = -\sum_{i=-M}^{M} \{h(i)\, \sigma(1, i) + h'(i)\, \sigma(N, i)\} \tag{2.3}$$

As is well-known, the planar Ising model has yet to be solved with $h \neq 0$ (bulk field). The selection of bulk phase, however, can be achieved by choice of *boundary* fields,[11] which can be handled within the fermion framework. Suppose, in lattice gas language, the presence of a molecule A corresponds to $\sigma = +1$. Then the limiting process $h'(i) \to \infty$, $h(i) = 0$ say, $M \to \infty$, followed by $N \to \infty$ prepares the system in the bulk phase A.

On the line $(0, j)$ the choice of field $h(i) = aJ_1$ with $a > 0$ favors $\sigma(0, j) = -1$ or phase B. If $a > 1$, common sense suggests that there would be an $A \mid B$ interface essentially "at infinity" to minimize the free energy and no singularity other than the critical point. This is confirmed by an exact result,[5] which also gives a phase transition for $0 < a < 1$. Suppose we calculate

$$m(x) = \lim \langle \sigma(x, 0) \rangle \tag{2.4}$$

where $\langle\ \rangle$ is the canonical expectation value and lim denotes the A phase selection procedure alluded to above with $h(i) = -aJ_1$, $0 < a < 1$ (and, of course, $h = 0$). Let $T_c(2)$ be the critical temperature. Then there exists a wetting temperature $T_W(a) < T_c(2)$ such that

$$\lim_{x \to \infty} m(x) = m^* \operatorname{sgn}[T_W(a) - T] \tag{2.5}$$

Thus for $T_W(a) > T$, there is a B film of infinite thickness at the surface. As $T \to T_W(a)-$ a new divergent length scale for $m(x)$ emerges, denoted by $\xi^x(a, T)$ where

$$\xi^x(a, T) \sim (T_W(a) - T)^{-1} \tag{2.6}$$

Thermodynamically, this transition manifests a jump in the specific heat at $T_W(a)$. Further details may be found elsewhere.[5,12]

The surface field term acting on $\{(i, j)\}$ can be replaced by a column of perturbed bonds to "ghost" spins $\sigma(0, j)$, $-M \geqslant j \leqslant M$ with interaction

$$\sum_{j=-M}^{M} \{-aJ_1 \sigma(0, j)\, \sigma(i, j) + h'' \sigma(0, j)\} \tag{2.7}$$

and $h'' \to -\infty$, fixing $\sigma(0, j) = -1$ for all j. In this case it is useful to think of a low-temperature series expansion: any configuration of spins on the extended lattice is equivalent to a set of contours on the dual lattice

$$\Lambda^* = \Lambda - (\tfrac{1}{2}, \tfrac{1}{2}) \tag{2.8}$$

This set of contours separates antiparallel pairs of spins and only configurations with 0, 2, or 4 contour lines meeting at each and every vertex of Λ^* are allowed in the A-phase selection limit. With probability one there is a *single* long contour running round the cylinder in the (0, 1) direction in this limit. The effect of the surface term (2.7) is to pin the contour elements at the surface, without any distinction between long and short contours.

If we take the S.O.S. (solid-on-solid) limit,[13] $K_1 \to \infty$, then any line $\{(i, j);\ i \geqslant 0, j \text{ fixed}\}$ is crossed by one and only one contour element; this can only be the long contour, which now has no overhangs. There is a unique intercept $x_j + \frac{1}{2}$, x_j some nonnegative integer on each horizontal line $y = j$, j integral. This construct is also referred to as the Onsager–Temperley string.

For a cylinder of circumference $(2M + 1)$, $-M \leqslant j \leqslant M$, we arrive at the probability measure

$$P\{x_{-M},..., x_M\} = \frac{1}{Z_M} \exp\left\{-2K \sum_{j=-M}^{M} |x_j - x_{j+1}|\right\} \tag{2.9}$$

If the S.O.S. limit be taken on the surface term by the replacement $K_0 = aK_1$ and then setting $K_0 = K_1 - b$ and taking the limit $K_1 \to \infty$, there is a surface term

$$\prod_{j=-M}^{M} \{1 + (e^{2b} - 1)\, \delta(x_j, 0)\} \tag{2.10}$$

Finally, departure from coexistence is allowed by including a term

$$\prod_{j=-M}^{M} \exp(-2hx_j) \tag{2.11}$$

where

$$h = m(h_b, T)\, h_b \tag{2.12}$$

Here h_b is the uniform applied field which induces a bulk magnetization $m(h_b, T)$.

We now discuss how to relate the parameter K in (2.9) to K_1 and K_2 by considering phase separation in a strip.

Consider a planar Ising spin lattice of length $2L+1$ in the (1, 0) direction in units of lattice spacing. Let it be divided into $2N$ identical slabs. Then, as a guess, the S.O.S. weight becomes, on integrating out small fluctuations

$$W = e^{-2L\tau_{\rm h}} \sum_{j=-N+1}^{N} e^{-2K|y_j - y_{j-1}|} \tag{2.13}$$

where the y_j are continuous real variables with $-\infty < y_j < \infty$ but $y - N = y_N = 0$. The $\tau_{\rm h}$ is a "horizontal" surface tension and K is a coupling constant to be determined. Let τ be the incremental free energy of such a string. Then Fourier analysis shows that

$$\tau = \delta\tau_{\rm h} - \delta \lim_{N\to\infty} \frac{1}{2N} \log\left\{\frac{1}{4\pi}\int_{-\infty}^{\infty} d\omega \left(\frac{4K}{4K^2+\omega^2}\right) 2N\right\} \tag{2.14}$$

with

$$\delta = \lim \frac{N}{L} \tag{2.15}$$

the length-scale factor. Elementary asymptotics give

$$\tau = \delta\tau_{\rm h} + \delta \log K \tag{2.16}$$

Now τ is known exactly for the planar Ising model[14]

$$\tau = 2(K_1 - K_2^*) \tag{2.17}$$

for an interface with normal (1, 0).

The parameters are fixed completely by the interface profile result. Consider the magnetization $m_M(x, 0)$ defined by an Ising strip lattice with vertices (i, j) having $-M \leqslant j \leqslant M$, $-\infty < i < \infty$. Then[15]

$$\lim_{M \to \infty} m_M(\alpha M^\delta, 0) = m^* \operatorname{sgn}(\alpha) \qquad \Phi(b\,|\alpha|) \tag{2.18}$$

with

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \tag{2.19}$$

and

$$b^2 = \sinh \tau (\sinh 2K_2^* \sinh 2K_1)^{-1} \tag{2.20}$$

The magnetization is obtained from the S.O.S. model by

$$m_M(x, 0) = m^* P\{x_0 \leqslant x\} - m^* P\{x_0 > x\} \tag{2.21}$$

where $P\{x_0 \leqslant x\}$ is calculated using the normalized equation (2.13) which evidently will not contain τ_h. A result like (2.18) is obtained with

$$b = K\sqrt{2} \tag{2.22}$$

With (2.20) this then gives

$$K^2 = \frac{\delta \sinh \tau}{2 \sinh 2K_2^* \sinh 2K_1} \tag{2.23}$$

On physical grounds, we expect to have $\delta = 1/\xi$ in the critical region. Since[16]

$$2\xi\tau = 1 \tag{2.24}$$

this means

$$K^2 = \frac{1}{2\xi} \sinh\left(\frac{1}{2\xi}\right)\left\{1 + 0\left(\frac{1}{\xi}\right)\right\} \tag{2.25}$$

using the results that $K_1^* = K^2$ defines the critical point and that $\xi \sim A(K_2 - K_1^*)^{-1}$. Thus, as $\xi \to \infty$, $K \to 1/2\xi$, giving the natural scaling of the x_i by ξ which is expected from standard critical point theory.

Motivated by fluctuation theory and the remarks of Fisher, Fisher, and Weeks,[17] the reader might prefer a Gaussian form in (2.9) and (2.13) where K is chosen to take into account angle-dependent surface tension.[18]

This certainly gives (2.18) and (2.20) correctly, but does not lead to an exactly solvable wetting problem. All models $\exp\{-2K|x_j - x_{j-1}|^p\}$ with $p \geqslant 1$ are considered to be in the same universality class.[19] Further, for two dimensions it does not seem to matter if the x_j are continuous or discrete. This is certainly not true for three dimensions, where Fröhlich and Spencer[20] have shown that the free S.O.S. model for coexisting phases has a phase transition of roughening type at finite, nonzero temperature when the x_j are integral.

In the next section we use transfer kernel ideas to compute the partition function $Z_N(x)$ for a domain wall on Λ^* pinned at $(0, 0)$ and (x, N). This gives the probability density $p_N(x, 0)$ that an S.O.S. wall from $(0, -N)$ to $(0, N)$ passes through $(x, 0)$ as

$$p_N(x, 0) = \frac{Z_N(x)^2}{Z_{2N}(0)} e^{-2hx}[1 + a\delta(x)] \tag{2.26}$$

The mathematical analysis is somewhat complicated, so we have given a summary of the results in Section 7.

3. THE TRANSFER MATRIX

By using customary transfer matrix ideas we have

$$Z_N(x_0) = [\delta_{x_0}, (T_1 T_2 T_3)^{N-1} T_1 \delta_0] \tag{3.1}$$

where

$$(T_1 f)(x) = \int_0^\infty e^{-2K|x-y|} f(y)\, dy \tag{3.2}$$

$$(T_2 f)(x) = e^{-2hx} f(x) \qquad x \geqslant 0 \tag{3.3}$$

and

$$(T_3 f)(x) = f(x) + af(0)\, \delta(x) \tag{3.4}$$

provided $f(0)$ exists. The function δ_x is defined by

$$\int_0^\infty g(x)\, \delta x_0(x)\, dx = g(x_0) \tag{3.5}$$

for all $x_0 \geqslant 0$.

The operator T_1 is bounded on $L^2(R_+)$ and is self-adjoint there, with continuous spectrum on $[0, 1/K]$. Thus we can construct $T_1^{1/2}$, which is again bounded and self-adjoint (in fact, real symmetric) and thereby introduce a self-adjoint operator

$$\hat{T} = T_1^{1/2} T_2 T_3 T_1^{1/2} \tag{3.6}$$

with

$$\hat{T}(x, y) = \int_0^\infty dz\, T_1^{1/2}(x, z)\, e^{-2hz} T_1^{1/2}(z, y) + a T_1^{1/2}(x, 0)\, T_1^{1/2}(0, z) \tag{3.7}$$

Evidentally $\hat{T}$ is bounded; moreover, whenever $a \geqslant 0$, $(\hat{T}f, f) \geqslant 0$ for all $f \in L^2(R_+)$. Thus the spectrum is nonnegative. For $h > 0$ (strictly), $\hat{T}$ is also Hilbert–Schmidt; it therefore has a complete set of eigenfunctions $\hat{\psi}_n$ with eigenvalues λ_m such that

$$\sum_{n=0}^{\infty} \lambda_n^2 < \infty \tag{3.8}$$

It follows that (3.1) can be written as

$$Z_N(x) = \sum_{n=0}^{\infty} (T_1^{1/2} \hat{\psi}_n)(0) (T_1^{1/2} \hat{\psi}_n)(x)\, \lambda_n^{N-1} \tag{3.9}$$

with convergence assured by (3.8) for $N \geqslant 3$.

It turns out that $T_1^{1/2}$, while being readily constructed in principle, is not a particularly convenient object. It is easier to proceed with the unsymmetrized eigenvalue problem

$$T_1 T_2 T_3 \psi_m = \lambda_m \psi_m \tag{3.10}$$

The eigenvectors ψ_m are associated with those of $\hat{T}$ by

$$\psi_m = T_1^{1/2} \hat{\psi}_n \tag{3.11}$$

Returning to (3.4), it is clear that (3.10) must work in a subspace of $L^2(R_+)$; we choose $C^{(2)}(R_+)$ which is dense in $L^2(R_+)$ and in which $\psi_n(0)$ is always defined, giving

$$\int_0^\infty e^{-2K|x-y|} e^{-2hy} \psi_n(y)\, dy + a e^{-2Kx} \psi_n(0) = \lambda_n \psi_n(x) \tag{3.12}$$

The differentiability enables us to convert (3.12) to a Schrödinger equation by using the Green's function identity

$$\left(\frac{\partial^2}{\partial x^2} - 4K^2 \right) e^{-2K|x-y|} = -4K\delta(x-y) \tag{3.13}$$

which gives

$$\lambda_n \frac{d^2\psi_n}{dx^2} = (4K^2\lambda_n - 4Ke^{-2hx})\,\psi_n \tag{3.14}$$

with the boundary condition

$$\lambda_n[\psi_n^{(1)}(0) - 2K\psi_n(0)] = -4Ka\psi_n(0) \tag{3.15}$$

The substitutions

$$u = \alpha v e^{-hx} \tag{3.16}$$

and

$$\alpha = 2K/h \qquad v^2 = 1/\lambda K \tag{3.17}$$

transform (3.14) to

$$\frac{d^2G}{dx^2} + \frac{1}{u}\frac{dG}{du} + \left(1 - \frac{\alpha^2}{u^2}\right) G = 0 \tag{3.18}$$

which is Bessel's equation[21-23] with solutions

$$G(u) = AJ_\alpha(u) + BJ_{-\alpha}(u) \tag{3.19}$$

From (3.16) we see that the large x behavior is controlled by small u. The standard power series for $J_\alpha(z)$ shows that to place ψ_n in $L^2(R_+)$ we must have $B = 0$. The boundary condition (3.15) reduces to

$$J_{\alpha-1}(\alpha v) = 2Kav J_\alpha(\alpha v) \tag{3.20}$$

Thus for $a = 0$ the eigenvalue problem reduces to the location of zeros of $J_{\alpha-1}(z)$; these are pure real and simple for $\alpha > 0$.[23] The main features of the solution of (2.19) can then be obtained from the Mittag-Leffler expansion (see Ref. 23, p. 61, eq. 7.9.3) of $J_\alpha(\alpha v)/J_{\alpha-1}(\alpha N)$ in terms of the $\hat{v}_j(\alpha)$ defined by

$$J_{\alpha-1}[\alpha\hat{v}_j(\alpha)] = 0 \tag{3.21}$$

ordered by

$$0 < \hat{v}_j(\alpha) < \hat{v}_{j+1}(\alpha) \tag{3.22}$$

giving

$$\frac{\alpha}{4Ka} = v^2 \sum_{j=1}^{\infty} [\hat{v}_j(\alpha)^2 - v^2]^{-1} \tag{3.23}$$

First, we check that (3.23) only has solutions for v^2 pure real. Denote the right-hand side of (3.23) by $F(v, \alpha)$; then

$$\frac{\partial F}{\partial v} = 2v \sum_{j=1}^{\infty} \frac{\hat{v}_j(\alpha)^2}{[\hat{v}_j(\alpha)^2 - v^2]^2} \tag{3.24}$$

which implies $F(v, \alpha)$ is monotone increasing on $(0, \infty)$ except for infinite negative jump discontinuities whenever $v_j = \hat{v}_j(\alpha)$. From its definition it is clear that

$$F[v_j(\alpha), \alpha] = 0 \tag{3.25}$$

where

$$v_{j+1}(\alpha) > v_j(\alpha) > 0$$

and

$$J_\alpha[\alpha v_j(\alpha)] = 0 \tag{3.26}$$

Thus a simple fixed point argument shows that for $a > 0$ there is a solution of (3.20) in $[0, \hat{v}_1(\alpha)]$ and one in each interval $[v_j(\alpha), \hat{v}_{j+1}(\alpha)]$ for $j \geqslant 1$. For $a < 0$, on the other hand, there is a solution in each interval $[\hat{v}_j(\alpha), v_j(\alpha)]$ for all $j \geqslant 1$. In addition, returning to (3.23), we find a single solution with $v^2 < 0$. This corresponds to a value $\lambda < 0$ from (3.17), but this is not excluded by positivity, which was only proved for $a \geqslant 0$.

In this paper we are particularly interested in the behavior near coexistence which obtains for large α. The asymptotic behavior of (3.20) can be investigated by writing it as

$$2Kav - (1/v) = J_\alpha^{(1)}(\alpha v)/J_\alpha(\alpha v) \tag{3.27}$$

using the recurrence relations (see Ref. 22, p. 361, eq. 9.1.27) and then applying Olver's results (see Ref. 22, pp. 368–9) to obtain

$$1 - 2Kav^2 = \left(\frac{1 - v^2}{\xi}\right)^{1/2} \left[\frac{\mathrm{Ai}'(\alpha^{2/3}\xi)}{\alpha^{1/3}\mathrm{Ai}(\alpha^{2/3}\xi)} + \frac{1}{\alpha} + 0(\alpha^{-5/3})\right] \tag{3.28}$$

where $\mathrm{Ai}(x)$ is the Airy function (see Ref. 22, Chap. 10, p. 446 et seq.) and ξ is given by the real solution of

$$(-\xi)^{3/2} = \frac{2}{3}\int_1^v dt(t^2 - 1)^{1/2}\, t \tag{3.29}$$

for $v > 1$ and by

$$\xi^{3/2} = \frac{3}{2}\int_v^1 dt\, \frac{(1 - t^2)^{1/2}}{t} \tag{3.30}$$

for $v < 1$.

First, we look at the solution for $v \varepsilon [0, \hat{v}_1(\alpha)]$. By (3.30), $\xi > 0$ and the asymptotic expansion of the Airy functions gives

$$2Kav^2 - 1 = \sqrt{1 - v^2}\,[1 + 0(1/\alpha)] \tag{3.31}$$

In the limit $\alpha \to \infty$, (3.28) for $v \in (0, 1)$ becomes

$$\frac{1}{2Ka} = 1 - \sqrt{1 - v^2} \tag{3.32}$$

which only has a real solution for $a > a_c$, where the critical binding is given by

$$a_c = \frac{1}{2K} \tag{3.33}$$

That this solution is approached in a stable way as $\alpha \to \infty$ may be checked by a Newton–Raphson method on (3.28) and (3.30); we cannot rely on (3.31) since the $0(1/\alpha)$ term is ξ-dependent.

The sticking phenomenon is reminiscent of the spherical model.[24]

We now investigate the solutions for $v > \hat{v}_1(\alpha)$ in the large α region. From (3.28) it is clear that the solutions v interlace the zeros of $\mathrm{Ai}(\alpha^{2/3}\xi)$ with v and ξ associated by (3.29). With the solution

$$\mathrm{Ai}(a_s) = 0 \tag{3.34}$$

it is known (see Ref. 22, Chap. 10, p. 446 et seq.) that for integral $s \geqslant 1$

$$a_s = f[(3\pi/8)(4s - 1)] \tag{3.35}$$

where

$$f(z) \sim z^{2/3}[1 + 0(1/z^2)] \tag{3.36}$$

Returning to (3.28) and (3.29), it is clear that the behavior of solutions depends qualitatively on whether $\xi \sim 0$ or whether $\xi \ll 0$

Region A: *solutions* v_j, $j \ll \alpha$. We have $v_j \gtrsim 1$, and the solutions interlace

$$v_j' = 1 + 2^{-1}[(3\pi/\alpha)(j - \tfrac{1}{4})]^{2/3} \tag{3.37}$$

Region B: $j \gg \alpha$. We have $v_j \gg 1$ and the solutions interlace

$$v_j'' \sim (j - \tfrac{1}{4})\,\pi/\alpha \tag{3.38}$$

In going from region A to B the spacing of the v_j broadens. The interlacing estimate can be refined by applying the Newton–Raphson method, iterating from the zeros of $\mathrm{Ai}'(\alpha^{2/3}\xi)$ in (3.28).

The foregoing analysis shows that $\alpha \to \infty$ and $a \to a_c \pm$ is a critical region for the qualitative behavior of the spectrum of the transfer operator. We now extract scaling variables from (3.28) and (3.29) or (3.30)

Let the solutions of (3.28) be

$$v \sim 1 - \alpha^{-2/3}\gamma \tag{3.39}$$

as $\alpha \to \infty$. Then we should introduce the scaling variable $\tilde{a}$ by the limiting procedure $a \to a_c$, $\alpha \to \infty$ such that

$$\tilde{a} = s - \lim\left(\frac{a - a_c}{a_c}\alpha^{1/3}\right) \tag{3.40}$$

exists. This gives

$$\frac{2^{1/3}\mathrm{Ai}^{(1)}(2^{1/3}\gamma)}{\mathrm{Ai}(2^{1/3}\gamma)} = -\tilde{a} + \frac{2a}{a_c}\alpha^{-1/3}\gamma + a^{-2/3} + 0(\alpha^{-4/3}) \tag{3.41}$$

Equation (3.41) shows corrections to scaling on the equation

$$2^{1/3}\mathrm{Ai}'(2^{1/3}\gamma) = -\tilde{a}\mathrm{Ai}(2^{1/3}\gamma) \tag{3.42}$$

the solutions of which are illustrated in Fig. 2. Notice, as $\tilde{a} \to \infty$ we have the limiting behavior

$$2\gamma \sim \tilde{a}^2 - 1/\tilde{a} \tag{3.43}$$

which agrees with (3.32). As a mathematical curiosity, (3.42) is equivalent to the Ricatti equation

$$d\tilde{a}/d\gamma = -2\gamma + \tilde{a}^2 \tag{3.44}$$

We now examine the eigenfunctions of (3.10). The eigenfunctions $\hat{\psi}_n$of $\hat{T}$ are a complete orthonormal set for $L^2(R_+)$. Using (3.11), the correct orthonormalization for the ψ_m is

$$(\psi_m, T_2 T_3 \psi_m) = \Lambda_m \delta nm \tag{3.45}$$

which gives

$$\int_0^\infty e^{-2hx}\, dx\, \psi_m^*(x)\, \psi_m(x) + a\psi_m^*(0)\, \psi_m(0) = \Lambda_m \delta nm \tag{3.46}$$

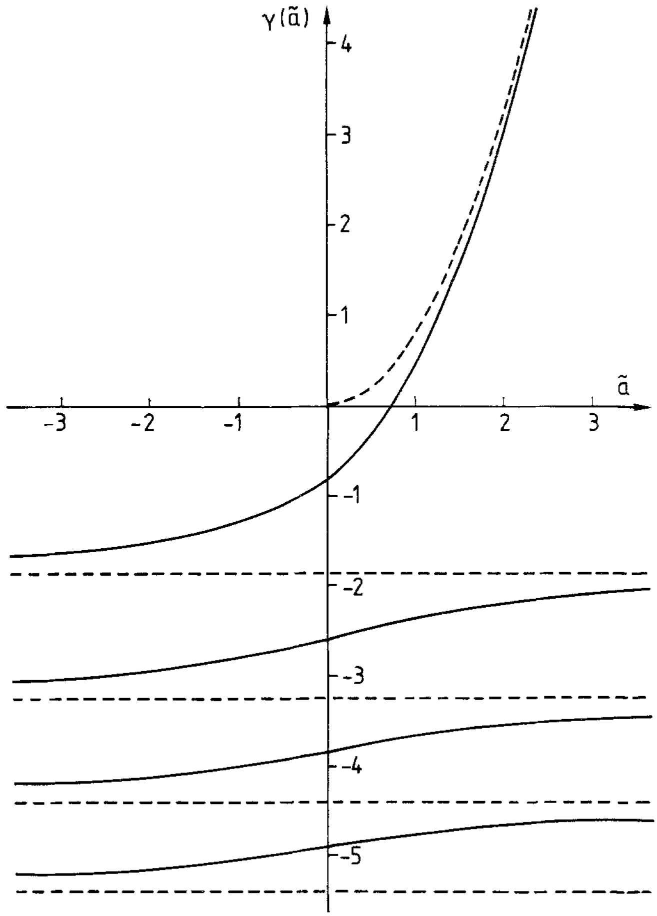

Fig. 2. Graph of eigenvalues γ_k vs $\tilde{a}$.

Taking (3.19) with $B=0$, (3.16) and the substitution $t=\exp(-hx)$ gives

$$\frac{1}{h}\int_0^1 t\,dt\,J_\alpha(\alpha v_n t)\,J_\alpha(\alpha v_m t)+aJ_\alpha(\alpha v_n)\,J_\alpha(\alpha v_m)=(KA_n^2 v_n^2)^{-1}\,\delta_{nm} \tag{3.47}$$

where the normalized eigenfunctions are

$$\psi_n(x)=A_n J_\alpha(\alpha v_n e^{-hx}) \tag{3.48}$$

These integrals are standard (see Ref. 21, Chaps, 12, 13); with (3.20) they confirm orthonormality and give

$$A_n^2 K v_n^2 [J_\alpha(\alpha v_n)]^2 [1-(2a/a_c)+(a/a_c)^2\,v_n^2+(2a/\alpha a_c)]=2h \tag{3.49}$$

First consider the case $a > a_c$ and $h \to 0$. We have

$$\psi_1(x)/\phi_1(0) \sim \exp\{\alpha^{2/3}[\xi(x) - \xi(0)]\}$$

from the asymptotic form of the Bessel functions, where

$$[\xi(x)]^{3/2} = \frac{3}{2}\int_{ve^{-hx}}^{1} dt\, \frac{\sqrt{1-t^2}}{t} \tag{3.50}$$

Hence, holding x fixed gives

$$\lim_{h \to 0} \frac{\psi_1(x)}{\psi_1(0)} = \exp(-2K\sqrt{1-v_0^2}\,x) \tag{3.51}$$

with v_0 given by (3.32). On the line $h = 0$, (3.51) establishes a length scale ξ defined by

$$\xi^{-1} = 2K\sqrt{1-v_0^2} \tag{3.52}$$

with the critical behavior

$$\xi = a[1 - (a/a_c)]^{-1} \tag{3.53}$$

along the line $h = 0$.

If (3.12) were solved with $h = 0$ at the outset, there would be a continuous spectrum on $[0, 1/K]$ with "eigenvectors"[25]

$$\phi(x, w) = (A(\omega)/\pi)^{1/2} \sin[\omega x - \theta(\omega)] \tag{3.54}$$

where

$$\tan\theta(\omega) = \omega/[(4K^2 + \omega^2)\, a - 2K] \tag{3.55}$$

and

$$A(\omega) = 4K/(4K^2 + \omega^2) \tag{3.56}$$

In the above, $\omega > 0$, when and only when $a > a_c$, an isolated eigenvalue, is found above the continuum described exactly by (3.51) and (3.52).

Evidentally, as $h \to 0+$, any point $v > 1$ must be a limit point of solutions of the basic eigenvalue equation (3.20).

4. INCREMENTAL WALL-FREE ENERGY

We define the incremental wall-free energy by $f^x(a, h, K)$ where

$$-\beta\delta f^x(a, h, K) = \tau_h + \lim_{N \to \infty} \frac{1}{N} \log Z_N(0) \tag{4.1}$$

with δ given by (2.15) and τ_h by (2.16, 17, and 23). The first term on the right comes from the horizontal bonds, which are now given a coupling K in the S.O.S. case. The partition function $Z_N(0)$ is from (3.1). We proceed here with $Z_N(x)$. When $h > 0$, the eigenfunctions ψ_n of $T_1 T_2 T_3$ are complete in $L^2(R_+)$; this is the Fourier–Dini analogue of Fourier series convergence (see Ref. 21, Chap. 18). Thus we can expand $T_1 \delta_0$ in the ψ_n which satisfy (3.46) and obtain

$$T_1 \delta_0 = \sum_{k=0}^{\infty} \psi_k \lambda_k^{-1} (\psi_k, T_2 T_3 T_1 \delta_0) \tag{4.2}$$

and then

$$Z_N(x) = \sum_{k=0}^{\infty} \psi_k(x)\, \lambda_n^{N-2} [\psi_k, (T_2 T_3 T_1)\, \delta_0] \tag{4.3}$$

By using the substitution $t = e^{-hx}$, the scalar product in (4.3) becomes

$$\begin{aligned}(\psi_k, T_2 T_3 T_1 \delta_0) &= A_k \left[\frac{1}{h} \int_0^1 t^{1+\alpha}\, dt\, J_\alpha(\alpha v_k t) + a J_\alpha(\alpha v_k) \right] \\ &= 2 A_k (a_c / v_k^2)\, J_\alpha(\alpha v_k)\end{aligned} \tag{4.4}$$

by using standard integrals (see Ref. 21, Chaps. 12, 13) and (3.20). Thus we have

$$Z_N(x) = \sum_{k=0}^{\infty} A_k^2 J_\alpha(\alpha v_k e^{-hx})\, J_\alpha(\alpha v_k)\, \lambda_k^{N-1} \tag{4.5}$$

and can readily prove that

$$-\beta f^x(a, h, K) = \tau(0) + (2/\delta) \log v_0 \tag{4.6}$$

valid for $h > 0$. When $h = 0$ and $a > a_c$ we get (4.6) again, but for $a < a_c$ the term $(2/\delta) \log v_0$ is missing. This part is a simple manipulation of a continuous spectrum.

By inspection of (3.20), the minimal solution v_0 (and, indeed, any other) is real-analytic in h and a. On $h = 0$, $a - a_c > 0$, we have

$$v_0^2 = 1 - [(a_c/a) - 1]^2 \tag{4.7}$$

from (3.32). Thus $\beta f^x(a, 0, K)$ has a jump in its second K partial derivative at $K_c = 1/2a$. The first two terms on the right of (4.6) are the incremental free energy of an S.O.S. string with $h = 0$ and no binding or additional geometrical constraint.

Using (3.39) and (3.42) we can go to the scaling region

$$s-\lim \alpha^{2/3}[-\beta f^{x}(a, h, K)-\tau(0)]=v_0(\tilde{a}) \tag{4.8}$$

with $\tilde{a}$ given by (3.40) and v_0 on the maximal branch of (3.42).

5. FILM THICKNESS

The probability density that the S.O.S. walk from $(0, -N_1)$ to $(0, N_2)$ passes through $(x, 0)$ with $x>0$ is given by

$$p[(x, 0) \mid N_1, N_2)]=Z_{N_1}(x)\, Z_{N_2}(x)\, e^{-2hx/Z}N_1+N_2^{(0)} \tag{5.1}$$

for $h>0$. The mean width of the interface may be defined by

$$\bar{x}=\int_0^\infty x\,dx \lim_{N_1,N_2\to\infty} p[(x, 0) \mid N_1, N_2] \tag{5.2}$$

Using (4.5) and (3.49) gives

$$\bar{x}=\frac{2h}{1-(2a/a_c)+(av_0/a_c)^2+(2a/\alpha a_c)}[J_\alpha(\alpha v_0)]^{-2} \times \int_0^\infty xe^{2hx}\,dx[J_\alpha(\alpha v_0 e^{-hx})]^2 \tag{5.3}$$

This has a simple scaling limit. Inserting (3.39) and (3.40) and rescaling the integration variable gives

$$s-\lim \alpha^{-1/3}\bar{x}=[2^{2/3}K\,\mathrm{Ai}^2(2^{1/3}\gamma_0)(\tilde{a}^2-2\gamma_0)]^{-1}\times\int_0^\infty u\,du\,\mathrm{Ai}^2(2^{1/3}\gamma_0+u) \tag{5.4}$$

This integral can be carried out by noting the identities

$$(d/dx)\{x^2\,\mathrm{Ai}^2(x)-x[\mathrm{Ai}'(x)]^2+\mathrm{Ai}(x)\,\mathrm{Ai}'(x)\}=3x\,\mathrm{Ai}^2(x) \tag{5.5}$$

and

$$(d/dx)\{x\,\mathrm{Ai}^2(x)-[\mathrm{Ai}'(x)]^2\}=\mathrm{Ai}^2(x) \tag{5.6}$$

Use of the eigenvalue equation (3.42) then gives

$$s-\lim \alpha^{-1/3}\bar{x}=\frac{1}{3K}\left\{\frac{\tilde{a}}{2(\tilde{a}^2-2\gamma_0)}-\gamma_0\right\} \tag{5.7}$$

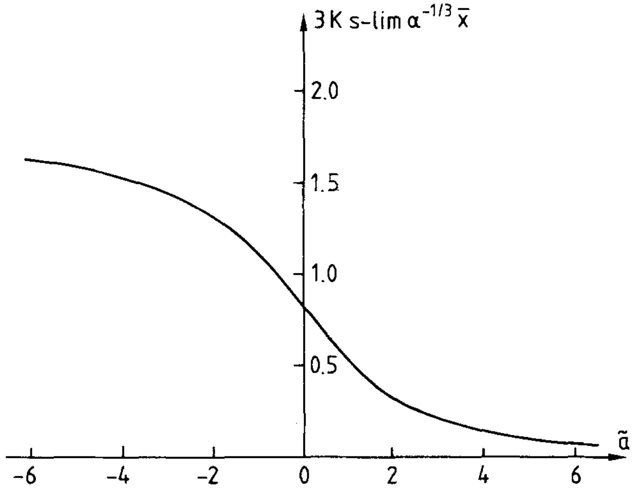

Fig. 3. Graph of scaled mean film thickness $\bar{x}$ vs. $\tilde{a}$.

As $\tilde{a} \to \infty$, a careful analysis shows that the right-hand side of (5.7) vanishes. Indeed in that limit $\bar{x}$ has the finite value

$$\bar{x} \to a_c/4(a - a_c) \tag{5.8}$$

The scaled film thickness $s - \lim 3K\alpha^{-1/3}\bar{x}$ is represented graphically in Fig. 3.

6. CORRELATION LENGTHS AND DROPLET SHAPE

Examination of $Z_N(x)$ suggests that the scaling idea be applied to the variable N as well as to x. Let us define

$$t = s - \lim \alpha^{-2/3} N \tag{6.1}$$

and

$$u = 2K\, s - \lim \alpha^{-1/3} x \tag{6.2}$$

We then have existence of

$$F(u, t) = s - \lim Z_{\alpha^{2/3} t}(\alpha^{1/3} u/2K) \tag{6.3}$$

with

$$F(u, t) = \sum_{k=0}^{\infty} \frac{K^{-Ne^{2t\gamma_k}}}{\tilde{a}^2 - 2\gamma_k} \frac{\mathrm{Ai}[2^{1/3}(u + \gamma_k)]}{\mathrm{Ai}(2^{1/3}\gamma_k)} \tag{6.4}$$

It follows that

$$\frac{\partial^2 F}{\partial u^2} - 2uF = \frac{\partial F}{\partial t} \tag{6.5}$$

With the boundary conditions

$$F(u, 0) = \lim_{\varepsilon \to 0} \delta(u + \varepsilon) \tag{6.6}$$

and

$$F(0, t) = \sum_{k=0}^{\infty} \frac{K^{-N} e^{2t\gamma_k}}{\tilde{a}^2 - 2\gamma_k} \tag{6.7}$$

This is a Euclidean Schrödinger equation, showing the underlying diffusive character of the problem.

This also permits analysis of the statistics of a point (x, y) on the S.O.S. string, given that the string passes through $(0, 0)$. Consider

$$\lim_{N_2 \to \infty} p[(x, 0) \mid y, N_2] = p(x \mid y)$$

where

$$p(x \mid y) = \sum_{k=0}^{\infty} A_k^2 \left(\frac{\lambda_k}{\lambda_0}\right) y - 1 \frac{J_\alpha(\alpha v_0 e^{-hx}) J_\alpha(\alpha v_k e^{-hx}) J_\alpha(\alpha v_k)}{\lambda_0 J_\alpha(\alpha v_0)} \tag{6.8}$$

Passing to the scaling limit

$$\tilde{y} = s - \lim \alpha^{-2/3} y \tag{6.9}$$

$$\tilde{x} = 2K s - \lim \alpha^{-1/3} x \tag{6.10}$$

gives

$$p(\tilde{x} \mid \tilde{y}) = 2 \sum_{k=0}^{\infty} \frac{e^{2\tilde{y}(\gamma_k - \gamma_0)}}{\tilde{a}^2 - 2\gamma_k} \frac{\mathrm{Ai}[2^{1/3}(\tilde{x} + \gamma_k)] \, \mathrm{Ai}[2^{1/3}(\gamma_0 + \tilde{x})]}{\mathrm{Ai}(2^{1/3}\gamma_k) \, \mathrm{Ai}(2^{1/3}\gamma_0)} \tag{6.11}$$

The conditional expectation of $\tilde{x}$ is then

$$E(\tilde{x} \mid \tilde{y}) = \sum_{k=0}^{\infty} \frac{e^{\tilde{y}(\gamma_k - \gamma_0)}}{\tilde{a}^2 - 2\gamma_k} \frac{1}{\mathrm{Ai}(2^{1/3}\gamma_k) \, \mathrm{Ai}(2^{1/3}\gamma_0)}$$
$$\times \int_0^\infty x \, dx \, \mathrm{Ai}[2^{1/3}(x + \gamma_0)] \, \mathrm{Ai}[2^{1/3}(x + \gamma_k)] \tag{6.12}$$

Use of the collection of Airy function integrals in the appendix gives

$$E(\tilde{x} \mid \tilde{y}) = \sum_{k=1}^{\infty} \frac{e^{2\tilde{y}(\gamma_k - \gamma_0)}}{\tilde{a}^2 - 2\gamma_k} \frac{\gamma_0 + \gamma_k - \tilde{a}^2}{(\gamma_0 + \gamma_k)^2} + \frac{1}{3}\left[\frac{\tilde{a}}{\tilde{a}^2 - 2\gamma_0} - 2\gamma_0\right] \tag{6.13}$$

Thus the limiting value $E(\tilde{x} \mid \infty)$ is approached from below on a length scale of $1/(\gamma_0 - \gamma_1)$. This defines a correlation length parallel to the wall by

$$s - \lim \xi_{\parallel}(a, h)\, \alpha^{-2/3} = 1/(\gamma_0 - \gamma_1) \tag{6.14}$$

where the right-hand side is given as a function of $\tilde{a}$ by appropriate solutions of (3.42).

In view of the Young–Dupré equation mentioned in the introduction, it would be very interesting to obtain the contact angle. One might be tempted to try the scaling limit definition

$$\tan \tilde{\theta} = \lim_{\tilde{y} \to 0} E(\tilde{x} \mid \tilde{y})/\tilde{y} \tag{6.15}$$

It follows from (6.13) that

$$\tan \tilde{\theta} = 2 \sum_{k=1}^{\infty} \frac{1}{\gamma_0 - \gamma_k} \frac{\tilde{a}^2 - \gamma_0 - \gamma_k}{\tilde{a}^2 - 2\gamma_k} \tag{6.16}$$

Since $\gamma_k \sim -k^{2/3}$ (as $k \to \infty$), this series diverges.

Bearing in mind (6.9) and (6.10), a more reasonable definition is in terms of the unscaled lengths

$$\tan \theta = \lim_{y \to 0} [E(x \mid y)/y] \tag{6.17}$$

analyzed asymptotically for α large.

7. SUMMARY

In this paper we have shown that the partial to complete wetting transition of two phases at coexistence can be described by a string model which extends to the region near coexistence.

Returning to definitions (2.9)–(2.11), there is a critical value of a, denoted a_c, $a_c = 1/2K$, and a scaling variable

$$\tilde{a} = s - \lim_{\substack{h \to 0 \\ a \to a_c}} \left(\frac{2K}{h}\right)^{1/3} \frac{a - a_c}{a_c} \tag{7.1}$$

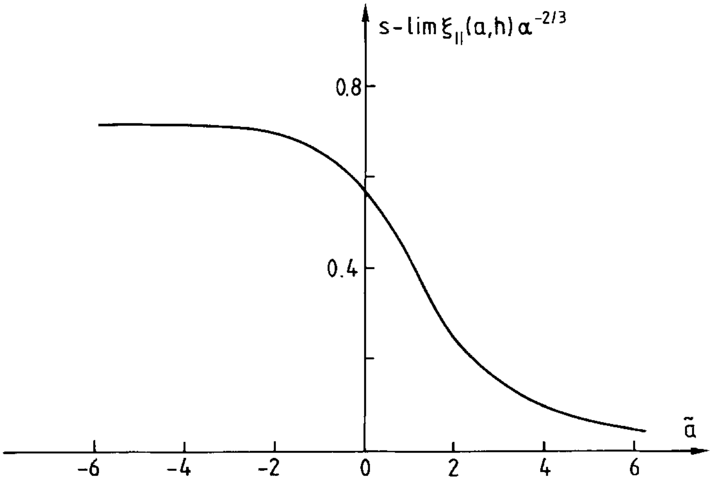

Fig. 4. Graph of scaled correlation length $\xi_{\parallel}$ parallel to the surface vs. $\tilde{a}$.

so that

$$\tilde{a} \sim h^{-1/3}(T_0 - T) \tag{7.2}$$

loosely speaking.

The incremental free energy has the scaling behavior

$$-\beta f^{x} \sim \tau(0) + \alpha^{-2/3}\gamma_0(\tilde{a}) \tag{7.3}$$

which is represented graphically by the uppermost branch in Fig. 2. The film thickness is

$$\bar{x} \sim \alpha^{1/3} \frac{1}{3K}\left[\frac{\tilde{a}}{2(\tilde{a}^2 - 2\gamma_0)} - \gamma_0\right] \tag{7.4}$$

which is shown in Fig. 3.

Our final result is a correlation length $\xi_{\parallel}$ parallel to the surface:

$$\xi_{\parallel}(a, h) \sim \alpha^{2/3}/[\gamma_0(\tilde{a}) - \gamma_1(\tilde{a})] \tag{7.5}$$

which is plotted in Fig. 4.

APPENDIX

We consider Airy function integrals of the form

$$I(a, b; p) = \int_0^\infty x^p \operatorname{Ai}(x+a) \operatorname{Ai}(x+b)\, dx \tag{A1}$$

for p an integer $\geqslant 0$. For $a \neq b$, if we differentiate (A1) twice with respect to a, use the differential equation for $\mathrm{Ai}(x+a)$, and rearrange the result, we obtain

$$I(a, b; p+1) = (\partial^2/\partial a^2)\, I(a, b; p) - aI(a, b; p) \qquad a \neq b \qquad p \geqslant 0 \tag{A2}$$

a useful recurrence relation. If we consider now

$$I(a, b; 0) = \int_0^\infty \mathrm{Ai}(x+a)\,\mathrm{Ai}(x+b)\,dx \tag{A3}$$

for $a \neq b$, we may write it as

$$I(a, b; 0) = \frac{1}{a-b} \int_0^\infty [\mathrm{Ai}''(x+a)\,\mathrm{Ai}(x+b) - \mathrm{Ai}(x+a)\,\mathrm{Ai}''(x+bl]\,dx \tag{A4}$$

by using the differential equation for $\mathrm{Ai}(x)$ in (A3). Integration by parts then gives

$$I(a, b; 0) = [1/(a-b)][\mathrm{Ai}'(b)\,\mathrm{Ai}(a) + \mathrm{Ai}(b)\,\mathrm{Ai}'(a)] \tag{A5}$$

The recurrence relation (A2) then gives, in particular

$$\begin{aligned} I(a, b; 1) = {} & [-2/(a-b)^3][\mathrm{Ai}'(b)\,\mathrm{Ai}(a) - \mathrm{Ai}'(a)\,\mathrm{Ai}(b)] \\ & + [1/(a-b)^2][(a+b)\,\mathrm{Ai}(a)\,\mathrm{Ai}(b) - 2\mathrm{Ai}'(a)\,\mathrm{Ai}'(b)] \end{aligned} \tag{A6}$$

Establishing recurrences for $I(a, a; p)$ is not so simple. We set $J(a; p) = I(a, a; p)$ and

$$K(a; p) = \int_0^\infty x^p \mathrm{A}i^2(x)\,dx \tag{A7}$$

so that

$$J(a; p) = \sum_{l=0}^{p} \frac{p!}{l!(p-l)!} (-a)^l K(a; p-l) \tag{A8}$$

Now a generalization of (5.5) gives the identity

$$\begin{aligned} & (d/dx)[x^{p+1}\mathrm{Ai}^2(x) - x^p[\mathrm{Ai}'(x)]^2 + px^{p-1}\mathrm{Ai}(x)\,\mathrm{Ai}'(x)] \\ & \quad = (2p+1)\,x^p\mathrm{Ai}^2(x) + p(p-1)\,x^{p-2}\mathrm{Ai}(x)\,\mathrm{Ai}'(x) \end{aligned} \tag{A9}$$

This gives, for $p \geqslant 3$

$$\begin{aligned} K(a; p) = {} & \frac{1}{2p+1} \{a^p[\mathrm{Ai}'(a)]^2 - a^{p+1}\mathrm{Ai}^2(a) - pa^{p-1}\mathrm{Ai}(a)\,\mathrm{Ai}'(a)\} \\ & + \frac{p(p-1)(\phi-2)}{2(2p+1)} K(a; p-3) \end{aligned} \tag{A10}$$

To start this recurrence scheme for $J(a;\, p)$ we may then use (from 5.6)

$$K(a;0) = [\mathrm{Ai}'(a)]^2 - a\mathrm{Ai}^2(a) \qquad \text{(A11)}$$

and (from 5.5)

$$K(a;\,1) = \tfrac{1}{3}\{a[\mathrm{Ai}'(a)]^2 - a^2\mathrm{Ai}^2(a) - \mathrm{Ai}(a)\,\mathrm{Ai}'(a)\} \qquad \text{(A12)}$$

and (from A9 with $p = 2$)

$$K(a;\,2) = \tfrac{1}{5}\{a^2[\mathrm{Ai}'(a)]^2 - a^3\mathrm{Ai}^2(a) - 2a\mathrm{Ai}(a)\,\mathrm{Ai}'(a) + \mathrm{Ai}^2(a)\} \qquad \text{(A13)}$$

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