Exact solution of an intrinsic interface profile

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An exactly solvable model describing phase separation in a planar lattice gas has been shown to confirm aspects of Weeks's phenomenological columnar model. Here an *intrinsic* interface structure is defined and computed precisely. The conclusions support Widom's original scaling ideas and also some aspects of the work of Jasnow and Rudnick.

Recently it has been realized that the interface between coexisting fluid phases probably has a diffuse character[1] which is adequately modeled on a suitable length scale by capillary wave theory.[2] This theory replaces discrete molecular structure by a continuum; the interface between phases is represented by a surface without overhangs characterized energetically by a surface tension. The surface is treated by a linearization so that the essential statistical mechanics is the equipartition theorem.

Such a theory may be derived from first principles at a molecular level for the planar Ising lattice gas[3] using a suitable length scaling, to be discussed below, which smooths all events on a scale of the correlation length. Capillary wave theory assumes the interchange from bulk liquid to gas to be abrupt on crossing the surface; this is undoubtedly true on the length scale alluded to above but cannot be precisely true at a molecular level. Indeed, it is tempting to assume that there is an intrinsic, or local, structure varying on the scale of the bulk correlation length carried by a capillary wave. The purpose of this Communication is to show how a recent, exactly solvable model[4] can give such a structure. This model is related to the columnar model of Weeks.[5]

Referring to Fig. 1, we place solid-on-solid (SOS) restrictions on the lines $x=0$, N_1, and N_1+N_2+1. Then the long contour crosses these lines exactly once each, giving two adjacent strips of the type considered in Ref. 4. Capillary wave theory may be characterized by the probability $P_{\text{cap}}(y \mid N_1,N_2)$ which is conditioned by the intersection at $y=0$ on $x=0$ and N_1+N_2+1; it is given by

$$P_{\text{cap}}(y \mid N_1,N_2)=\text{const}\exp\{-[(N_1^2+y^2)^{1/2}\tau(\theta_1)+(N_2^2+y^2)^{1/2}\tau(\theta_2)]\} , \quad (1)$$

where $\tau(\theta)$ is the angle-dependent surface tension.[5] The exact distribution for y is

$$P(y \mid N_1,N_2)=\text{const}Z^{+-}(y \mid N_1)Z^{+-}(y \mid N_2) , \quad (2)$$

where $Z^{+-}(y \mid N)$ is the partition function for a strip width N with extensive factors absorbed in the normalizing constant.

Let the magnetization (or density) profile be defined by

$$m(y \mid N_1,N_2)=m^*[P(y'>y \mid N_1,N_2)-P(y'<y \mid N_1,N_2)] . \quad (3)$$

Then both (1) and (2) give the limiting theorem of[3] exactly

$$\lim_{N\to\infty} m(\alpha N^{1/2} \mid N(1-\beta),N(1+\beta))=m^*\text{sgn}\alpha\Phi[b\mid\alpha\mid/(1-\beta^2)^{1/2}] , \quad (4)$$

where m^* is the usual spontaneous magnetization[6] and the scale factor in the Gaussian function $\Phi(x)$ is

$$b=[\tau(0)+\tau^{(2)}(0)]^{1/2} \quad (5)$$

as discussed in Ref. 7. It should be noted that (1) contains the leading terms of (2) in a development for large N; this is the interface thermodynamic term.[8] Equation (1) is a more precise formulation of capillary wave theory which can have a scaling limit

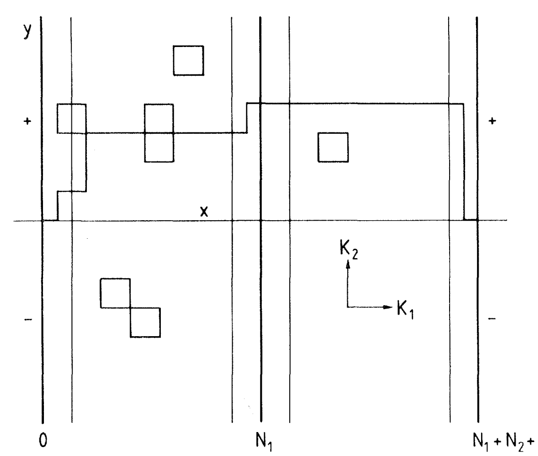

FIG. 1. The vertical lines on which the solid-on-solid restriction is made are $x=0$, N, and N_1+N_2+1. A typical low-temperature expansion contour on the dual lattice is shown. The orientation of bond weights is as indicated.

as we shall see.

Many definitions of intrinsic structure might be tried.[9]

Here we define $P_{\rm int}(y \mid N_1,N_2)$ by

$$P(y \mid N_1,N_2) = \sum_{y_0} P_{\rm int}(y - y_0 \mid N_1,N_2)\, P_{\rm cap}(y_0 \mid N_1,N_2) \ . \tag{6}$$

There is an obvious analog with Ornstein-Zernike theory[10]: One would like $P(y \mid N_1,N_2)$ to have a well-defined nontrivial limit as $N_1,N_2 \to \infty$ containing a length scale related to the correlation length. Here we consider the simplest case $N_2 \to \infty$, $N_1 = N$. Using a convolution theorem, (7) becomes

$$\hat{P}_{\rm int}(\omega \mid N) = \hat{P}(\omega \mid N)/\hat{P}_{\rm cap}(\omega \mid N) \ , \tag{7}$$

where $\hat{f}(\omega \mid N)$ is a function whose Fourier series is $f(y \mid N)$. Now from Ref. 11,

$$\hat{P}_{\rm cap}(\omega \mid N) = \exp\{-N[\gamma(\omega) - \gamma(0)]\} \ , \tag{8}$$

whereas

$$\hat{P}(\omega \mid N) = e^{N\gamma(0)}/A_N(\omega) \tag{9}$$

with

$$A_N(\omega) = \cosh N\gamma(\omega) + \sinh N\gamma(\omega) \cos\delta^*(\omega) \ , \tag{10}$$

where

$$\cosh\gamma(\omega) = \cosh 2K_1^* \cosh 2K_2 - \sinh 2K_1^* \sinh 2K_2 \cos\omega \tag{11}$$

and

$$e^{i\delta^*(\omega)} = \left[\frac{(e^{i\omega}-A)(e^{i\omega}-B^{-1})}{(e^{i\omega}-A^{-1})(e^{i\omega}-B)}\right]^{1/2} \left[\frac{B}{A}\right]^{1/2} , \tag{12}$$

with $A = \coth K_2 \coth K_1^*$, $B = \coth K_2 \tanh K_1^*$. Here K_1 and K_2 are interactions scaled by kT and $\exp(-2K_1^*) = \tanh K_1$. The low-temperature region is characterized by $0 < B < 1$. The branches taken in (12) and (13) are $\gamma(\omega) > 0$ for real ω and $\exp i\delta^*(\pi) = 1$. To develop $P_{\rm int}(y \mid N)$ we examine the singularities of $A_N(\omega)$ in the complex plane. There are poles at zeros of $A_N(\omega)$, which are simple, in the complex plane, given by

$$t^N = \pm \left[\frac{(t-\alpha)(t-\beta)}{(t-\alpha^{-1})(t-\beta^{-1})}\right]^{1/2} \frac{1}{(\alpha\beta)^{1/2}} \ , \tag{13}$$

where $t = \exp\gamma$; α and β are A and B with K_1 and K_2 interchanged. The associated locations in the ω plane are found from (12). There is also a branch-cut structure coming from the factor $(1 + \cos\delta^*)$ from $A_N(\omega)$ and (13). The picture is shown in Fig. 2. The limit as $N \to \infty$ is just

$$P_{\rm int}(y \mid \infty) = \frac{1}{\pi} \int_{-\pi}^{\pi} d\omega\, e^{i\omega y}/[1 + \cos\delta^*(\omega)] \ . \tag{14}$$

Thus as $y \to \infty$ we have

$$P_{\rm int}(y \mid \infty) \sim e^{-v_0 y}/y^{3/2} \ , \tag{15}$$

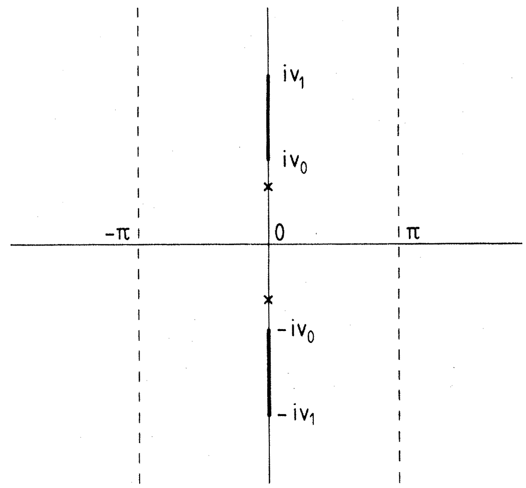

FIG. 2. The singularity structure of $\hat{P}_{\rm int}(\omega \mid N)$ which has period 2π. There is a cut from $v_0 = 2(K_1 - K_2^*)$ to $v_1 = 2(K_1 + K_2^*)$ with simple poles embedded in it, and a mirror image in the lower half-plane. There are also simple poles indicated by × coming from the two pure real solutions of (13).

where $v_0 = 2(K_1 - K_2^*)$; v_0 is the inverse correlation length in the y direction.

Equation (13) also governs the distribution of wave numbers in the planar Ising-model transfer matrix with free edges,[12] or its dual which is the hard-edged case.[13] The result (15) is characteristic of a half-planar Ornstein-Zernike problem.[14]

On the other hand, it should be noted that the simple pole in Fig. 2 gives a one-dimensional Ornstein-Zernike decay, but the residue vanishes as $N \to \infty$. The occurrence of the length scale v_0^{-1} in (15) confirms one aspect of Widom scaling theory.[15] Equation (7) and its development are reminiscent of the ideas of Jasnow and Rudnick.[16]

The limit $N_1 = N_2 = N \to \infty$ recaptures Eq. (22) of Ref. 4, which is the lowest-order dispersion approximation to the *exact* profile of a finite strip, which can be obtained exactly in terms of a Fredholm problem; this is considerably less explicit than the calculation here.

Finally by taking the solid-on-solid (SOS) limit overall it is clear that a capillary wave can carry an intrinsic structure with the SOS correlation length as scale and reproduce the exact SOS profile.

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