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Capillary Waves and Surface Tension: An Exactly Solvable Model

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An exactly solvable model of an interface between coexisting phases in a modified planar lattice gas, or its magnetic equivalent, is described. The results reconcile the apparent conflict between intrinsic structure and capillary fluctuation theory. There are anomalously long-ranged correlations in the interface.

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Despite considerable effort, there still remains a fundamental controversy in attempts to describe in statistical-mechanical terms the phenomenon of phase separation and its associated surface tension. Recently Weeks[1] has indicated a resolution in a general phenomenological theory founded upon reasonable, but not necessarily mutually compatible, assumptions. This Letter describes an exact calculation for a planar classical lattice gas which, by making a single assumption in its interpretation, supports Weeks's point of view. This assumption is that a restriction of ensemble used is irrelevant.

Current theories of phase separation may be categorized as follows:

(A) Capillary waves.—Consider the surface of separation in d dimensions as a $(d-1)$-dimensional membrane with side L acted upon by a surface tension τ. In the regime of linearized fluctuations application of equipartition at temperature T gives, for the rms displacement w of the membrane,

$$w \propto \begin{cases} (L/\tau)^{1/2}, & d=2 \quad (1) \\ a_0 \ln(L/\tau a_0), & d=3, \quad (2) \end{cases}$$

where τ is the surface tension in units of kT. In computing the result for $d=3$ a mode wavelength cutoff is required, giving a_0 in (2) an atomic dimension. These results are contained in the theory of Buff, Lovett, and Stillinger[2]; the surface is assumed to provide an *abrupt* boundary between liquid and vapor *bulk* phases; this is inconsistent. Equation (1) is not even correct for very low temperatures, where τ is large, as is shown in (13) below.

(B) Free-energy density theories.—The existence of an intrinsic density profile $\rho(z)$ is assumed from the outset. The equilibrium free energy F, according to van der Waals[3] and Cahn and Hilliard,[4] is written as an Euler problem,

$$F = \min_{\rho} \int_{-\infty}^{\infty} f(\rho(z))dz, \qquad (3)$$

such that $\rho(-\infty)=\rho_l$ and $\rho(\infty)=\rho_g$, ρ_l and ρ_g being the liquid and gas densities, respectively. The origin $z=0$ is chosen so that

$$\int_{-\infty}^{\infty} dz\, z\, d\rho/dz = 0. \qquad (4)$$

The *Ansatz* for $f(\rho)$ (Refs. 3 and 4) was refined by Fisk and Widom[5] to render it consistent with scaling; then $\rho(z)$ varies on a scale determined by the correlation length ξ. Were approach A true, the only solution of (3) and (4) would be trivial: $\rho = \frac{1}{2}(\rho_l + \rho_g)$. A theory of type B was obtained from first principles by Triezenberg and Zwanzig,[6] but with the *ab initio* assumption that $\rho(z)$ is nontrivial.

(C) Rigorous calculations.—This discussion will be restricted to $d=2$ since the general results for $d=3$ are only valid at low temperatures. Consider a lattice $\Lambda=\{(i_1,i_2): -N\leq i_1\leq N, -M \leq i_2\leq M\}$ with a spin $\sigma((i_1,i_2))=\pm 1$ at each point. Take boundary conditions, which we shall label $B^{+-}(0,2N+1)$, defined by $\sigma((N,i_2))=\sigma((-N,i_2))=1$ for $0\leq i_2\leq M$, $\sigma((N,i_2))=\sigma((-N,i_2))=-1$ for $-M \leq i_2<0$, and $\sigma((i_1,M))=-\sigma((i_1,-M))=1$ for $-N \leq i_1\leq N$. There is a configurational energy

$$E_\Lambda(\{\sigma\})=\sum J(x-y)\sigma(x)\sigma(y), \tag{5}$$

where $J((0,1))=J_2$, $J((1,0))=J_1$, $J(l)=J(-l)$, and $J(l)=0$ if $|l|>1$, and where x and y are points of Λ; $J_i>0$ are ferromagnetic couplings. The probability of such a configuration is

$$p_\Lambda^{+-}(\{\sigma\})=(Z_\Lambda^{+-})^{-1}\exp(-\beta E_\Lambda\{\sigma\}), \tag{6}$$

where $\beta=1/kT$, T being the absolute temperature. Hereafter we shall put $K=\beta J$. The surface tension is defined by[7]

$$\tau=\lim_{N\to\infty}(2N+1)^{-1}\lim_{M\to\infty}\ln(Z_\Lambda^{++}/Z_\Lambda^{+-}), \tag{7}$$

where Z_Λ^{++} is the partition function with all boundary spins up. The profile for a finite-width strip is

$$F(p,N)=\lim_{M\to\infty}\langle\sigma((0,p))\rangle_\Lambda^{+-}, \tag{8}$$

where $\langle\cdots\rangle_\Lambda^{+-}$ denotes average with respect to (6). The results are[7,8]

$$\tau=\begin{cases} 2K_2+\ln\tanh K_1, & T\leq T_c \\ 0, & T>T_c, \end{cases} \tag{9}$$

where T_c is the critical temperature which solves $\sinh 2K_1 \sinh 2K_2=1$, and

$$\lim_{N\to\infty}F(\alpha N^\delta,N) =\begin{cases} 0, & 0\leq\delta<\frac{1}{2} \\ m^*\operatorname{sgn}\alpha, & \delta>\frac{1}{2} \\ m^*(\operatorname{sgn}\alpha)\Phi(|\alpha|b), & \delta=\frac{1}{2}, \end{cases} \tag{10}$$

with

$$b=(\sinh\tau/\sinh 2K_1{}^*\sinh 2K_2)^{1/2}, \tag{11}$$

where

$$\Phi(x)=(2/\sqrt{\pi})\int_0^x e^{-u^2}du. \tag{12}$$

(m^* is the usual Ising spontaneous magnetization.) The second moment of the profile given by (11) and (12) is

$$w^2=(N/\sinh\tau), \tag{13}$$

which has the same length dependence as (1), in agreement with theory A, but a *different* τ dependence. For reasonable macroscopic values, the width would be quite unobservable with the naked eye, but the forms (11), (12), and (13) are totally at variance with theory B. On the other hand, (9) accords with Widom's scaling ideas[9]: $2t=1/\xi$, where ξ is the correlation length of a pure phase.[10]

(D) Widom[11] proposed that there is an intrinsic structure with a length scale ξ, to be treated by theory B, in the vicinity of a wandering surface of phase separation. This point of view is refined by Week's theory.[1] Suppose phase separation is occurring along the z direction. Then the system is broken up into d-dimensional hyperstrips *with sides of length* ξ. Making reasonable assumptions, a phenomenological statistical mechanical treatment shows that the heights z_i of the Gibbs dividing surfaces in each column are distributed as

$$P(\{z\})=Z^{-1}\exp[-\tfrac{1}{8}\tau\sum_{i,\delta}(z_i-z_{i+\delta})^2], \tag{14}$$

where i indexes a slab with neighbors $(i+\delta)$. The *internal* degrees of freedom of every slab have thus been integrated out. An essential assumption of the theory is that the fluctuations in height within each slab are finite away from the critical point; were this not so the exercise would be quite pointless. We now describe an exact calculation along the lines of (C) and (D).

Recalling the boundary condition $B^{+-}(0,2N+1)$ in (C), define $B^{+-}(y,2N+1)$ exactly as before but with $\sigma((-N,i_2))=-1$ for $i_2<y$ and 1 for $i_2\geq y$. Then by sliding p strips $B^{+-}(y_j,2N+1)$ together, such that they share common edges, and such that $\sum_1^p y_j=0$, we obtain a single strip $B^{+-}(0, 2N(2P+1))$ with an interface restricted to pass through the given points y_j, $j=-b,\ldots,p-1$ for $x_j=(2j+1)N$. There is an additional restriction best clarified with use of the usual low-temperature expansions; each vertical line $l_j=[(2j+1)N, y]$ is crossed by one and only one contour segment; each such segment is connected to $(-pN,0)$ and $(pN,0)$ via the "long contour" of $B^{+-}(0,2N(2p+1)+1)$. Equivalently, no closed contour is allowed to straddle any line l_j. The methods of Ref. 8 lead to

$$Z(B^{+-}(y,2N+1))/Z(B^{++}(2N+1))=\Phi(y,N), \tag{15}$$

where $B^{++}(2N+1)$ implies that all boundary spins are up, with

$$\Phi(y,N)=\tfrac{1}{2}\pi\int_{-\pi}^{\pi}d\omega\, e^{iy\omega}/\{\cosh[2N\gamma(\omega)]+\sinh[2N\gamma(\omega)]\cos\delta^*(\omega)\},\qquad(16)$$

where

$$\cosh\gamma(\omega)=\cosh 2K_1^*\cosh 2K_2-\sinh 2K_1^*\sinh 2K_2\cos\omega\qquad(17)$$

and

$$e^{i\delta^*(\omega)}=[(e^{i\omega}-A)(Be^{i\omega}-1)/(Ae^{i\omega}-1)(e^{i\omega}-B)]^{1/2},\qquad(18)$$

with $A=\exp 2K_1\coth K_2$ and $B=\exp 2K_1\tanh K_2$ and $\delta^*(0)=0$. Equation (16) is exact for all N. The probability of a configuration of heights z_j, $j=1,\ \ldots,\ p$ is

$$P(z_{-p},\ldots,z_{p-1})=\tilde{Z}^{-1}\prod_{-p}^{p}\Phi(z_j-z_{j-1},N),\qquad(19)$$

with $z_{-p-1}=z_p=0$. The factorization here is a trivial consequence of the restriction of the low-temperature expansion. Provided the strips are not less wide than ξ this restriction is unlikely to matter much. The asymptotics of (16) are as follows: For $y\ll N\sim\xi$,

$$\Phi(y,N)\sim(\pi\sinh\tau/N)^{1/2}\exp-N[\tau+(y^2\sinh\tau)/2N^2],\qquad(20)$$

which recaptures Weeks's form (14), with the usual flat interface contribution for $y=0$. For $y\gg N\sim\xi$, $\Phi(y,N)\sim\exp[-|y|/\xi]$ is obtained by deforming towards the branch-cut structure in (17) and (18). Notice that the limit $J_2\to\infty$ in (16) leads back to the SOS results.

The surface tension should be evaluated by summing directly within the integral representation of the product of Φ's, rather than taking (20). This gives a surface tension

$$\tau'=\lim_{p\to\infty}[2N(2p+1)]^{-1}\ln\{\tfrac{1}{2}\pi\int_{-\pi}^{\pi}d\omega\,[\cosh 2N\gamma(\omega)+\sinh 2N\gamma(\omega)\cos\delta^*(\omega)]^{-(2p+1)}\}.\qquad(21)$$

Provided $N\sinh\tau>(\sinh 2K_1^*)^2$, to ensure rather crudely that there is a unique turning point for Laplace's method, we get $\tau'=\tau$; simply summing products of terms like (20) gives spurious terms in the surface tension. The leading term in the dispersion expansion for the profile within a strip can be analyzed when $(2N+1)\gamma(0)=\text{const}$. If r is the distance from the midheight in the strip, then, for $r\gg N$,

$$\langle\sigma((0,r))\rangle\sim\operatorname{sgn}(p)m^*[1-e^{-2|r|/\xi}(N/r)^{-2}r^{-1}J(K)],\qquad(22)$$

where $J(K)$ is some function. This is to be constrasted with (10), (11), and (12). For the characteristic function defined by $G(\theta,p)=\langle\exp i\,\theta z_0\rangle$ we get

$$\lim_{p\to\infty}G(\theta p^{-1/2},p)=\exp(-N\theta^2/2b^2),\qquad(23)$$

which leads back to the results (10) and (11) for the unrestricted ensemble. The conditional probability that $|z_j|\le\xi$, given that $z_0=0$, is given as $p\to\infty$ and for Nj large by [recall (12)]

$$P(j)=\Phi[b/4\tau(Nj)^{1/2}].\qquad(24)$$

Recalling the definition of ξ and (22), (24) obviously relates to the wandering of the support of the intrinsic structure in different strips. As $j\to\infty$, (24) decays as $1/\sqrt{j}$; such long-range correlations were first suggested by Wertheim[12] in an approximate theory, the assumptions of which are not consistent with our exact results.

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Note added.—The original treatment of Gallavotti,[13] which provided the first rigorous evidence of interface wandering in planar models, has been developed[14] to give a precise definition *at sufficiently low temperature* of local structure. Further in their discussion these authors proposed dividing the system into strips having width roughly ξ. They suggested that the magnetization profile within a strip conditioned by the entry and exit point of the phase separation region should vary on a scale of ξ. This is precisely what we show, for all $T<T_c$, in (22) for first order in dispersion. In another publication (22) will be fortified with precise error estimates to see whether it is compatible with a van der

Waals–Fisk–Widom profile.

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