Comments

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Comment on "Surfaces and interfaces of lattice models: Mean-field theory as an area-preserving map"

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Using the continuum theory derived from the lattice mean-field theory, Pandit and Wortis [Phys. Rev. B **25**, 3226 (1982)] encountered an unphysical phase boundary in the surface phase diagrams. This problem is solved taking into account boundary minima for the surface excess free-energy functional.

Pandit and Wortis studied surface phase transitions such as wetting, prewetting, and layering using lattice mean-field theory for a one-dimensional inhomogeneous magnetic system and the corresponding continuum theory.[1]

This continuum theory seems to be troubled by a paradox. Namely, consider the surface excess free-energy functional[1,2]

$$\gamma[m]=\int_1^\infty dx\left[\frac{J}{2}\left(\frac{dm}{dx}\right)^2+T\int_0^{m(x)}dy\tanh^{-1}y-dJm^2(x)-Hm(x)\right]+\frac{J}{2}m_1^2-h_1m_1 \tag{1}$$

of the order-parameter profile $m(x)$ for $x\geq 1$. J is the nearest-neighbor exchange coupling, T is the temperature, and H is a bulk field. The free surface at $x=1$ modifies the field and exchange coupling in the surface layer $m(x=1)=m_1$. h_1 is the surface field and we suppose there is no surface-coupling enhancement. We shall consider henceforth a three-dimensional system ($d=3$), with a boundary condition in the bulk

$$m(x)\rightarrow -m_b \text{ as } x\rightarrow +\infty, \tag{2}$$

where $-m_b$ is the bulk gas order parameter (in the lattice-gas language). In order to get the equilibrium order-parameter profile, one minimizes this functional with respect to the variational parameters $\{m(x)\}$,

$$\frac{\delta\gamma[m]}{\delta m(x)}=0. \tag{3}$$

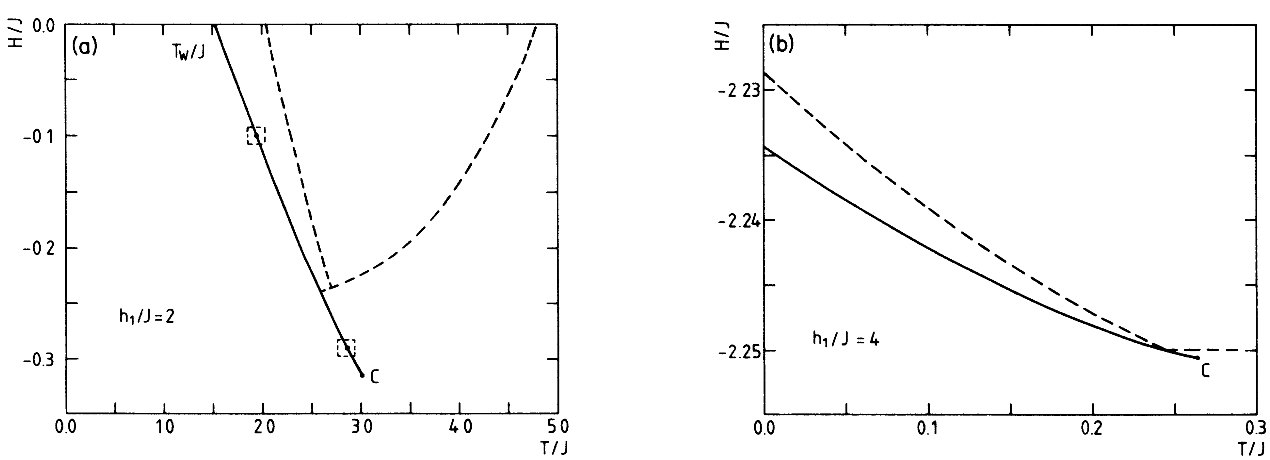

FIG. 1. Surface phase diagrams for the continuum description of wetting and prewetting. The full line is the first-order prewetting line ending at a critical point C. The dashed line represents the phase boundary Pandit and Wortis obtained (Fig. 9 in Ref. 1). (a) $h_1/J=2$; the two marked points correspond to the situations of Figs. 2 and 3. (b) $h_1/J=4$.

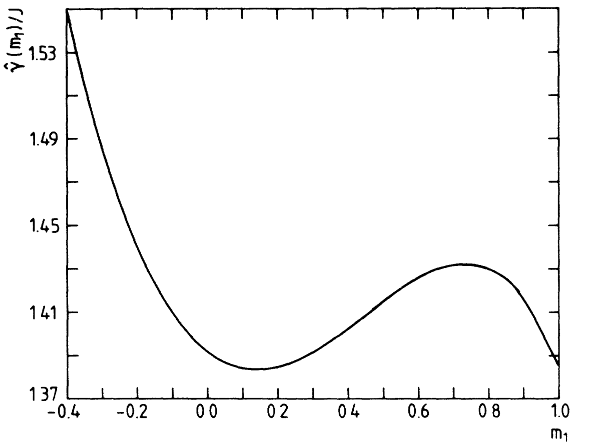

FIG. 2. Surface excess free energy as a function of the order parameter at the surface m_1. The second minimum is a boundary minimum; $h_1/J=2$, $H/J=-0.1$, and $T/J=1.941$.

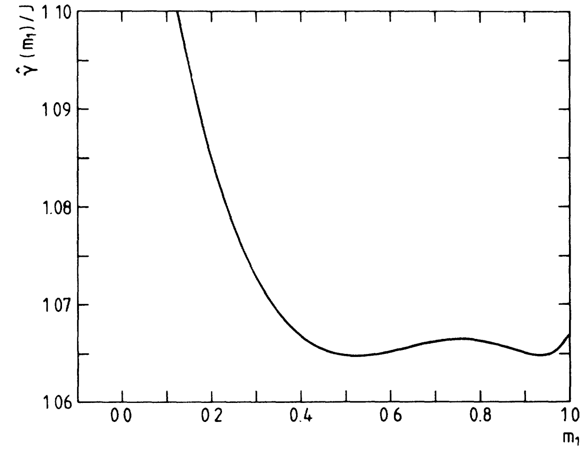

FIG. 3. Surface excess free energy as a function of the order parameter at the surface m_1. This picture corresponds to a first-order prewetting phase transition between a thin-wetting-layer solution and a thick-wetting-layer solution; $h_1/J=2$, $H/J=-0.29$, and $T/J=2.85$.

This leads to the following bulk equation:

$$H+J\frac{d^2m}{dx^2}+2dJm(x)=T\tanh^{-1}m\,. \tag{4}$$

We denote by $\tilde{m}(x)$ the solutions of (4) and (2). We define $\hat{\gamma}(m_1)=\gamma[\tilde{m}]$ as the (multivalued) free-energy *function* of the surface order parameter. Now we must look for the minimum of $\hat{\gamma}(m_1)$ in the interval $-1\leq m_1\leq 1$. This is usually done by requiring

$$\frac{d\hat{\gamma}(m_1)}{dm_1}=0\,, \tag{5}$$

which leads to the surface equation

$$h_1+J\frac{dm}{dx}\bigg|_{x=1}-Jm_1=0\,. \tag{6}$$

If one derives the phase portraits using these equations, a region (in the T-H plane) develops at sufficiently large h_1 where the boundary condition (6) cannot be satisfied.[1] As a consequence, an "elbow" appears in the first-order prewetting line, which is unphysical.

This problem can be solved when we remember that the aim is to find the minimum of the surface energy $\hat{\gamma}(m_1)$. If (6) has no solution this only means that we do not have minima or maxima in the domain $-1<m_1<1$. But a *boundary minimum* at the end points $m_1=-1$ or $m_1=+1$ also leads to an equilibrium order-parameter profile, although it is not a solution of (6).[3] Minima and maxima of a real valued differentiable function f whose domain is $[a,b]$, are (a) at the end points a and b or (b) at points for which the derivative is 0. So, writing down the condition (5) is not sufficient to find all relative minima and maxima.

When we include these boundary minima for the surface excess free-energy functional, the elbow in the phase diagram disappears and we get the surface phase diagrams shown in Fig. 1. There is a first-order wetting phase transition at $H=0$ and $T=T_W$. This first-order behavior extends to nonzero H, the prewetting phase transition, and finally terminates at a "prewetting critical point" C. In the region where no boundary minima turn up, our phase boundary exhibits no differences compared to the one Pandit and Wortis obtained. The phase boundary features a third-order singularity (a discontinuity in the third derivative of H/J with respect to T/J along the phase boundary) at the point where the minimum of the free energy corresponding to a thick-wetting-layer solution becomes a boundary minimum (for example, this point is situated for $h_1/J=2$ at $H/J=-0.240$, $T/J=2.576$).

When you raise the temperature at a constant bulk field, the surface excess free energy, as a function of the order parameter at the surface m_1, displays an evolution. The minimum free-energy principle results in a competition between a thin-wetting-layer solution (minimum at small m_1) and a thick-wetting layer solution (minimum at large m_1). Raising the temperature causes a discontinuous jump from the thin-layer solution towards the thick-layer solution. In Fig. 2, the thick-layer solution is a boundary minimum, whereas in Fig. 3 it is not. The points, corresponding to these two figures, are shown in the surface phase diagram [Fig. 1(a)].

Finally, this problem does not appear in the discrete theory, which is much closer to the original Ising model and becomes exact at $T=0$.

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[1]R. Pandit and M. Wortis, Phys. Rev. B **25**, 3226 (1982).
[2]R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).
[3]G. Langie and J. O. Indekeu, Phys. Rev. B **40**, 417 (1989).