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Low-temperature analysis of three-phase coexistence

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We study the properties of an isotropic lattice model by low-temperature expansion. In particular, the interface between ferromagnetic phases for the case when a third modulated phase is in thermodynamic equilibrium is considered. Throughout the three-phase coexistence region the interfacial tension between all three phases is very low and actually vanishes at zero temperature. This reflects the fact that the surface of the finite-temperature three-phase equilibria arises from a curve of zero-temperature multiphase points. We show that throughout the three-phase region and in the limit of low temperature, the modulated phase never wets the interface between the ferromagnetic phases.

I. INTRODUCTION

There has been considerable interest in the study of frustrated lattice models in attempts to describe diverse materials such a microemulsions,[1] magnetic structures,[2] and alloys.[3] The model that we have examined[4] is given by the Hamiltonian,

$$H=-\frac{J}{2}\sum_{n,n'}^{\mathrm{NN}}\sigma_n\sigma_{n'}-\frac{\gamma M}{2}\sum_{n,n'}^{\mathrm{DNN}}\sigma_n\sigma_{n'}-\frac{M}{2}\sum_{n,n'}^{\mathrm{LNNN}}\sigma_n\sigma_{n'}\ , \tag{1.1}$$

where NN, DNN, and LNNN label, respectively, nearest-neighbor, diagonal nearest neighbor, and linear next-nearest neighbor on a simple-cubic lattice. For this Hamiltonian there is a region on the phase diagram where the ferromagnetic phases and the period-6 modulated phase are in three-phase equilibrium. Across this region the surface tensions between the phases are all very low, a consequence of the fact that the surface tensions all vanish at zero temperature and $\delta=0$, where the parameter δ is defined by

$$\delta=J+(2+4\gamma)M\ . \tag{1.2}$$

The curve $\delta(J,M,\gamma)=0$ defines a curve of multiphase points, and the phase diagram for this region has already been examined using mean-field[4] and low-temperature[5] analysis, so it is now possible to study the interfacial properties in the region of three-phase coexistence. The freedom to choose parameters in the model (1.1) while remaining on the equilibrium surface leads one to hope that there might be a transition between the situation where the interface is nonwet to where it is wet by the modulated phase. Indications that this might be so come from an earlier mean-field calculation.[6] In this Brief Report we show that, in the limit of low temperature and for all parameters J, M, and γ satisfying $\delta=0$, the ferromagnetic phase's interface is dry. The transition, if it occurs, does so at temperatures higher than those for which our low-temperature expansion is valid.

II. LOW-TEMPERATURE ANALYSIS

We consider the case where one complete period of the $\langle 3\rangle$ phase is inserted between an $\langle\infty\rangle_+ : \langle\infty\rangle_-$ interface. For the interface to be wet means that the insertion of an arbitrary number of such periods is favored. In this section we will prove that the interface between the $\langle\infty\rangle_+$ and $\langle\infty\rangle_-$ phases [henceforth symbolized $(+-)$] across the three-phase equilibrium surface is not wet in the limit $T\to 0$. Thus we will show that along the line of bulk $\langle 3\rangle$-$\langle\infty\rangle$ phase equilibria

$$F_{+3-}(\delta_e)-F_{+-}(\delta_e)>0\ \text{ as } T\to 0\ , \tag{2.1}$$

where F_{+-} denotes the free energy of the system with one $+-$ interface, F_{+3-} denotes the free energy of the system with one cycle of the $\langle 3\rangle$ phase, and δ_e is the value of δ on the surface of $\langle 3\rangle$-$\langle\infty\rangle$ phase equilibria.

Our procedure will be to show that the lowest spin excitation that breaks the degeneracy between the $(+3-)$ and $(+-)$ interfaces has higher multiplicity in the $(+-)$ interface. We will then, by conventional low-temperature analysis methods, have established (2.1).

To implement the enumeration of spin excitations we will use a method of sectioning. The $(+-)$ and $(+3-)$ interface configurations are divided into the regions shown in Figs. 1(a) and 1(b), respectively. The free energies of the two systems may be written as

$$F_{+-}=F_\infty+4L^2E_{\pi\sigma}(\delta)+6L^2E_o(\delta)+\sum_{i=1}^{N}(F^{(i)}_{\pi\sigma}+F^{(i)}_{\pi\sigma\text{ to }\pi\sigma}+F^{(i)}_{\pi\sigma\text{ to out}}+F^{(i)}_{\text{out}})\ , \tag{2.2a}$$

$$F_{+3-}=F_\infty+4L^2E_{\pi\sigma}(\delta)+6L^2E_{\langle 3\rangle}(\delta)+\sum_{i=1}^{N}(F^{(i)}_{\pi\sigma}+F^{(i)}_{\pi\sigma\text{ to }3}+F^{(i)}_{\pi\sigma\text{ to out}}+F^{(i)}_{3^1})\ , \tag{2.2b}$$

where $E_{\pi\sigma}(\delta)$, $E_o(\delta)$, and $E_{\langle 3\rangle}(\delta)$ are the ground-state energies and are the only terms in which δ appears linearly. F_∞ is the total free energy of the bulk $\langle\infty\rangle$ phase for $(L-10)L^2$ sites of the system in which there is a total of L^3 sites. The $F^{(i)}_A$ are the ith spin-flip contributions associated with the region specified by the subscript A, and the regions labeled above, are as follows. The label $\pi\sigma$ to $\pi\sigma$ represents all excitations where at least one excitation is in each of the $\pi\sigma$ reigons. The label $\pi\sigma$ to out represents all excitations from the left (right) $\pi\sigma$ region out (o) to the oL and $\langle\infty\rangle_+$ (oR and $\langle\infty\rangle_-$) region in Fig. 1(a) and the $\langle\infty\rangle_+$ ($\langle\infty\rangle_-$) region in Fig. 1(b). In particular, these excitations do not cross the interface. The label $\pi\sigma$ to 3 represents all excitations with one term in the $\pi\sigma$ region and one in the $\langle 3^1\rangle$ reigon shown in Fig. 1(b). The label $\langle 3^1\rangle$ represents all excitations solely contained in the $\langle 3^1\rangle$ region of Fig. 1(b). Finally, the label out represents all excitations where at least one spin-flip is in the oL (oR) region, and the remaining are in either the oL (oR) or $\langle\infty\rangle_+$ ($\langle\infty\rangle_-$) regions.

Now, inspection of Eqs. (2.2a) and (2.2b) indicates that

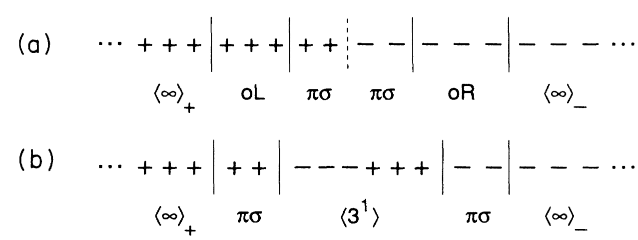

FIG. 1. Sectioned regions of the $(+-)$ interface configuration in (a) and the $(+3-)$ interface configuration in (b). Translational invariance in two directions allows only one direction to be shown.

F_∞, $4L^2E_{\pi\sigma}(\delta)$, $F^{(i)}_{\pi\sigma}$, and $F^{(i)}_{\pi\sigma\text{ to out}}$ cancel in the difference, Eq. (1), and hence need never be enumerated. In the final case of $F_{\pi\sigma\text{ to out}}$ [see Figs. 1(a) and 1(b)], excitations from $\pi\sigma$ to oL (oR or $\langle\infty\rangle_+$ ($\langle\infty\rangle_-$) in Fig. 1(a) are in one-to-one correspondence with excitations in Fig. 1(b) from $\pi\sigma$ to $\langle\infty\rangle_+$ ($\langle\infty\rangle_-$). Regions oL and oR in Fig. 1(a) were distinguished from $\langle\infty\rangle_+$ and $\langle\infty\rangle_-$ because they will be referred to separately later in this Brief Report.

However, to proceed further we must ensure that (2.1) is evaluated upon δ_e in order that all bulk $\langle 3\rangle$ and bulk $\langle\infty\rangle$ free-energy terms cancel. In order to separate these bulk excitations we may regroup some of the terms in (2.2) as

$$6L^2E_o(\delta)+\sum_{i=1}^{N}F^{(i)}_{\text{out}}=6L^2F_\infty\ , \tag{2.3a}$$

$$6L^2E_{\langle 3\rangle}(\delta)+\sum_{i=1}^{N}F^{(i)}_{\langle 3^1\rangle}=6L^2F_{\langle 3\rangle}-F_{\text{supp }3}\ , \tag{2.3b}$$

where we group in $F_{\text{supp }3}$ all correction terms that are needed to give equality. The important property of $F_{\text{supp }3}$ is that it contains only excitations that cross bands. Note that by way of definition of F_{out} no supplementary terms are needed in (2.3a). To see this we must show that F_{out} contains the same numbers of all connected and disconnected excitations as does six layers of bulk $\langle\infty\rangle$. In the case of the connected excitations we associate to every site of oL (likewise oR) the excitation attached to that site which has only its cross-layer bonds directed out towards the $\langle\infty\rangle$ reigon (to the left for oL and to the right for oR) and only in-layer bonds directed upwards or into the page in Fig. 1(a). This rule may be applied to all connected excitations that contribute to F_{out}. It is possible to show that the same correspondence procedure may be applied in bulk $\langle\infty\rangle$, and therefore yields the same multiplicity and excitation types in oL+oR as in $\langle\infty\rangle$. In the case of disconnected excitations, the only contributions to the free energy arise from excluded-volume terms. We observe that any such enumeration that is not accounted for due to the presence of the $\pi\sigma$ layers [see Fig. 1(a)] is compensated on the other side of the oL (likewise oR region bounding the $\langle\infty\rangle_+$ ($\langle\infty\rangle_-$) region. The important features in this argument are, first, that the extent of the interactions be limited so that they may only connect at most two layers, and second, that the $\pi\sigma$ regions encompass four layers. This means there are no overlapping effects between oL and oR, and hence a disconnected excitation with spins in both oL and oR regions contributes no excluded-volume terms to F_{out}.

Now, by substituting (2.3) into (2.2) and evaluating along $\delta=\delta_e$ we find

$$F_{+3}-F_{+-}=\sum_{i=1}^{N}(F^{(i)}_{\pi\sigma\text{ to }3}-F^{(i)}_{\text{supp }3}-F^{(i)}_{\pi\sigma\text{ to }\pi\sigma})\ . \tag{2.4}$$

Equation (2.4) is a convenient formula that may be used to compute the desired difference since it uniquely

TABLE I. All the excitations up to the three-spin-flip level needed to evaluate Eq. (2.4) are shown. Set A contains connected clusters and set B contains partially and fully disconnected excitations. IB and CB denote in-layer bonds and cross-layer bonds, respectively.

Type	Excitation energy	$\gamma=2$	$\frac{\text{Multiplicity}(+3-)-(+-)}{L^2}$
	Set A		
$\sigma\pi\pi$ 1NN IB, 1LNNN CB	$\frac{14j+28\gamma j+14\delta+28\gamma\delta}{1+2\gamma}$	$14j+14\delta$	-2
$\sigma\rho\pi$ 1NN IB, 1LNNN CB	$\frac{16j+28\gamma j+12\delta+28\gamma\delta}{1+2\gamma}$	$14.4j+13.6\delta$	4
$\sigma\rho\rho$ 1NN IB, 1LNNN CB	$\frac{18j+28\gamma j+10\delta+28\gamma\delta}{1+2\gamma}$	$14.8j+13.2\delta$	-2
	Set B		
$\sigma\pi\pi$ 1NN IB	$\frac{16j+28\gamma j+12\delta+28\delta\delta}{1+2\gamma}$	$14.4j+13.6\delta$	2
$\sigma\rho\pi$ 1NN IB	$\frac{18j+28\gamma j+10\delta+28\gamma\delta}{1+2\gamma}$	$14.8j+13.2\delta$	-6
$\sigma\rho\rho$ 1NN IB	$\frac{20j+28\gamma j+8\delta+28\gamma\delta}{1+2\gamma}$	$15.2+12.8\delta$	2
$\sigma\sigma\sigma$ 1DN CB	$\frac{12j+34\gamma j+12\delta+14\gamma\delta}{1+2\gamma}$	$16j+8\delta$	-52
$\sigma\sigma\sigma$ All disconnected	$\frac{12j+36\gamma j+12\delta+12\gamma\delta}{1+2\gamma}$	$16.8j+7.2\delta$	52

classifies all excitations into a small set of groups. The lowest-order excitations required for the evaluation of (2.4) are given in Table I. We observe that the connected excitations all span at least four layers.

Inspection of Table I shows that the lowest spin excitation (A1) has larger multiplicity in the $(+-)$ interface than in the $(+3-)$ interface, hence establishing its relative stability in the limit $T\rightarrow 0$. The dependence of the excitation energy in Table I reveals that this result holds for arbitrary γ.

Qualitatively, then, the analysis indicates that the two lowest excitations that govern the breaking of the degeneracy are both of the same shape and have the same multiplicity in their respective interfacial configurations. It is the replacement of a ρ spin in the $(+3-)$ configuration (using the notation in Ref. 5) with a π spin in the $(+-)$ configuration that makes the latter energetically more favorable. Furthermore, this degeneracy-breaking excitation only traverses two layers into both the $\langle\infty\rangle$ and period-6 wedge. This means that for any number l of period-6 cycles, the structure $(+3^l-)$ is less favorable than the $(+-)$ structure. This may be seen from the fact that the lowest-order degeneracy-breaking spin excitation always remains the one we have found above and involves only the two outermost half-cycles of the period-6 phase. We conclude, therefore, that in the low-temperature limit the $(+-)$ structure is neither wet, nor prewet by the period-6 phase.

It is also worth noting that previous studies[7] on related frustrated models indicate that similar phenomena may be present. Thus, for the axial next-nearest-neighbor interaction model it has been shown that the interface of the uniform phase is not wet by the modulated phases.

III. CONCLUSION

Despite the fact that all the interfacial tensions vanish in the zero-temperature limit, the $(+-)$ interface is not wet by the period-6 phase. The transition to wetting, if it occurs, must lie at higher temperatures than we have so far been able to examine. The multiphase point is, therefore, qualitatively distinct from a critical point, though in both cases all surface tensions vanish on approaching either point. It is emerging that the presence of this multiphase point in the present lattice model is an important part of the mechanism leading to ultralow interfacial tensions in amphiphilic systems (4,6). It is a mechanism that is quite independent of critical fluctuations and appears to be implicated in the observation that ultralow tensions are found along the Winsor III coexistence among oil, water, and microemulsion, but that the oil-water interface is not wet by microemulsion.[8] The physical origins of the effect are quite interesting. Thus the chemical potentials and interactions of the lattice model are adjusted so that the work required to insert an amphiphile into the amphiphilic film is vanishing. This is also presumed to be the prinicpal mechanism for the observation of ultralow tensions in amphiphilic systems. In a future analysis of the magnetic model, it would be worth attempting to carry out a Padé approximant analysis to see if a true continuous wetting transition can be observed at higher temperature.

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