Sublattice-ordered phases in a lattice model for a micellar solution

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We describe the mean-field global phase diagram for a Widom-type lattice mixture of bifunctional molecules ab and AA with general finite interactions. Our results follow from the known features of the phase diagrams along the symmetric sections of Griffiths's three-component (spin-1) model when both uniform and sublattice-ordered states are considered. The properties of the mixture are analogous to those of a binary alloy with one magnetic component. We find first- and second-order transitions between uniform fluid states and five different types of ordered phases.

I. INTRODUCTION

The study of the microstructure and the consequent phase behavior of amphiphile solutions is a topic of considerable current interest.[1] The reasons are varied. These systems offer useful models for cell membranes in biological systems. They are also of technological importance because of their solubilization properties. They also present singular phase diagrams that combine isotropic micellar solutions with lyotropic liquid-crystalline phases of different geometrical packings.[1] The challenge of their physical understanding rests on the derivation of their macroscopic behavior from molecular models that adequately represent the nature of the amphiphile in a solvent (or solvents) environment.

In 1968 Wheeler and Widom[2] introduced a lattice of bifunctional molecules AA (○—○), BB (●—●), and AB (○—●) that abstracted some features of a ternary system composed of two immiscible solvents and an amphiphile. The molecules are confined to the bonds of a regular lattice filling every bond with one, and one only molecule, allowing only same-letter molecular ends to meet at a given lattice site. This restriction makes the model mixture equivalent to the nearest-neighbor spin-$\frac{1}{2}$ Ising model in the same lattice. The basic character of each constituent is specified by means of infinite repulsions or no attractions between molecular ends. Because in all the configurations consistent with the filling rule an amphiphile molecule AB is never found pointing the "wrong" end towards either solvent, the phases of the model have a "permanent" microstructure in the sense that a perfectly oriented film of AB molecules separates AA from BB molecules. Temperature does not affect the phase diagram, and the only relevant thermodynamic fields are chemical potential differences.

In the binary mixture $AA + AB$ limit of this model only two phases are possible—an AA-rich isotropic micellar solution where all AB molecules are grouped into units resembling "empty" micelles (each with an aggregation number equal to the lattice coordination number),

and an AB-rich long-range sublattice-ordered phase where the micelles form a closed-packed pattern. Their associated phase boundary corresponds to an order-disorder transition in a lattice gas at the critical packing fraction where the absence of BB bonds implies nearest-neighbor exclusion of B sites, or equivalently, to that occurring in an antiferromagnet in the limit of an infinitely large coupling as the applied magnetic field passes through a critical value.

Recently, the model of Wheeler and Widom has been reconsidered through a variety of generalizations[3-7] in an attempt to test its potentialities as a more realistic representation for amphiphile systems. An important type of generalization to the original model is that in which finite molecular end-end interactions are allowed;[5-7] and therefore, in them, the microstructure referred to above is affected by temperature. Exact results[5] have been obtained for the case when the molecular ends A and B of the amphiphile AB are considered identical to those of the solvents AA and BB. However, with only three kinds of end-end interactions, denoted by ε_{AA}, ε_{AB}, and ε_{BB} ($\varepsilon_{ij} > 0$ for repulsions), different conformations for a film of oriented AB molecules that separates a given number of AA and BB molecules all have the same energy.[3,6] Surfactant-film bending energies are assumed[1,3] to be responsible for many characteristic features of amphiphile-solution phase diagrams, such as the three-phase states in water-surfactant-oil mixtures in these multicomponent fluids. Thus, as would be expected, with the exception of a temperature dependence of the phase transitions, the phase diagram of the generalized model is similar to that of the original one.

A different generalization of the original Wheeler-Widom model to finite interactions but one which allows for nonvanishing-film bending energies has been recently proposed.[6,7] In this version the nature of the molecular ends of the amphiphile, denoted by ab (□—■), differ from that of the ends of the solvents. This differentiation makes the mixture no longer equivalent to a spin-$\frac{1}{2}$ Ising system and has a strong effect on phase behavior.[6,7] The

formulation of the Ising spin system equivalent to the mixture model has been provided;[7] the properties of the $AA+ab+BB$ mixture are represented now by a spin-$\frac{3}{2}$ model with staggered fields, and those of the $AA+ab$ binary case by a related spin-1 system. This model has also been recently studied by other authors.[8]

Here we present the global phase behavior of the binary $AA+ab$ mixture under mean-field approximation when two interpenetrating sublattices are considered. We take advantage of the opportunity that knowledge of the global phase diagram of the Furman-Dattagupta-Griffiths (FDG) three-component model[9] (when both uniform and sublattice-ordered phases are considered) presents to add to the phase behavior given in Ref. 7. In two preceding articles,[10,11] referred to here as I and II, we presented, respectively, the FDG global phase diagram mentioned above and the transcription of its so-called symmetrical sections to the language of a binary alloy with one magnetic component. Because the mean-field properties of the $AA+ab$ micellar solution model are also given by the same symmetrical sections, we employ the physically transparent example of the magnetic alloy to interpret our results. We also make repeated use of the notation for multiple phase coexistence and associated critical states developed in I and employed in II.

II. THE SPIN-1 SYSTEM EQUIVALENT TO THE MICELLAR SOLUTION MODEL

With the two species AA and ab there are six kinds of end-to-end encounters between pairs of molecules, the values of which are denoted by ε_{AA}, ε_{Aa}, ε_{Ab}, ε_{aa}, ε_{ab}, and ε_{bb}. In Ref. 7, a construction is described for an Ising spin-1 model with nearest-neighbor interactions which is equivalent to the model micellar solution. Specific features in this construction are the following: (i) Only those pairs of molecules placed along contiguous bonds at right angles have nonzero interaction energies. (ii) The Ising spins are located at the bonds (or secondary sites) of the lattice. (iii) The primary and secondary lattices are divided into two sublattices each, P and Q for primary, and o and x for secondary sites. [See Fig. 1(a).] (iv) The values $S=0$, 1, and -1 are assigned to the spins according to the molecular occupations shown in Fig. 1(b). $S=0$ indicates occupation by AA, and $S=\pm1$ specifies orientations of ab. The orientation assignments appear reversed in sublattices o and x to ensure that configurations for pairs of nearest-neighbor spins, irrespective of their positions, make uniquely defined contributions to the total energy. (v) The energy values for each configuration of nearest-neighbor spin pairs are given in Table I, where the two columns refer to the fact that molecular ends meet at sites of type P or Q. With the above-mentioned considerations the AA-ab lattice mixture is equivalent[7] to the Ising system with a spin-1 Hamiltonian

$$\mathcal{H}=q^{-1}\left[-J\sum_{\langle ij\rangle}S_iS_j-K\sum_{\langle ij\rangle}S_i^2S_j^2\right.$$
$$\left.-C\sum_{\langle ij\rangle}(S_i^2S_j+S_iS_j^2)\right]-H\Sigma_iS_i+\Delta\Sigma_iS_i^2 \ ,$$
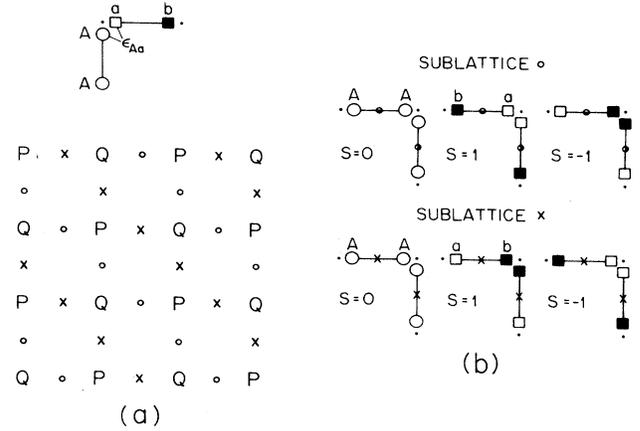
(1)

FIG. 1. (a) Sublattice arrangement for primary (P and Q) and secondary (o and x) sites. (b) Spin value assignation of molecular orientations in the two sublattices o and x.

with fields given by

$$J=\tfrac{1}{2}\varepsilon_{ab}-\tfrac{1}{4}(\varepsilon_{aa}+\varepsilon_{bb}) \ ,$$

(2a)

$$K=\varepsilon_{Aa}+\varepsilon_{Ab}-\varepsilon_{AA}-\tfrac{1}{4}(\varepsilon_{aa}+\varepsilon_{bb}+2\varepsilon_{ab}) \ ,$$

(2b)

$$\pm C=\tfrac{1}{2}(\varepsilon_{Aa}-\varepsilon_{Ab})-\tfrac{1}{4}(\varepsilon_{aa}-\varepsilon_{bb}) \ ,$$

(2c)

$$H=0 \ ,$$

(2d)

and

$$\Delta=\tfrac{1}{2}(\varepsilon_{Ab}-\varepsilon_{AA})+\tfrac{1}{2}(\varepsilon_{Aa}-\varepsilon_{AA})-\mu \ ,$$

(2e)

where $\mu=\mu_{ab}-\mu_{AA}$ is the chemical potential difference between the two species. The sign in front of C is positive if the pair of spin belongs to a primary site of type P, and is negative otherwise, i.e., C is a staggered field. Also the total magnetic field H acting on any spin vanishes.

As shown in Ref. 7, within mean-field approximation, the staggered quality of C drops out when uniform phases in the spin-1 model are considered. As we shall see shortly, this also occurs for some of its sublattice-ordered nonuniform phases within the same approximation. The sublattice subdivision for which this happens is that studied in I and II, i.e., when the secondary lattice is divided into two interwoven sublattices, α and β, such that nearest-neighbor pairs of sites fall each on one sublattice. Therefore, we can make use of the phase diagrams of I and II to learn about the mean-field phase behavior of the

TABLE I. Spin-spin interaction energies.

Encounters at sites P			Encounters at sites Q		
S_i	S_j	ε_{ij}	S_i	S_j	ε_{ij}
0	0	ε_{AA}	0	0	ε_{AA}
1	0	ε_{Aa}	1	0	ε_{Ab}
-1	0	ε_{Ab}	-1	0	ε_{Aa}
1	1	ε_{aa}	1	1	ε_{bb}
1	-1	ε_{ab}	1	-1	ε_{ab}
-1	-1	ε_{bb}	-1	-1	ε_{aa}

micellar solution model. It is convenient then to recall[7] the form of the equivalences in Eqs. (2a)–(2e) in the language of the ternary mixture of three components x, y, and z. Its five (FDG) relevant fields, three interaction energy parameters a, b, and c, and two chemical potential differences v_1, and v_2, are related to the bifunctional molecular interaction parameters and chemical potential differences by[7]

$$a_P = \varepsilon_{Ab} - \tfrac{1}{2}(\varepsilon_{AA} + \varepsilon_{bb}) = b_Q \, , \tag{3a}$$

$$b_P = \varepsilon_{Aa} - \tfrac{1}{2}(\varepsilon_{AA} + \varepsilon_{aa}) = a_Q \, , \tag{3b}$$

$$c_P = \varepsilon_{ab} - \tfrac{1}{2}(\varepsilon_{aa} + \varepsilon_{bb}) = c_Q \, , \tag{3c}$$

and

$$v_1 = v_2 = \mu + \tfrac{1}{4}(2\varepsilon_{AA} - \varepsilon_{bb} - \varepsilon_{aa}) \, , \tag{3d}$$

where the subindexes refer to nearest-neighbor pairs of particles associated with primary sites of type P and Q, respectively. In this language, x and y represent the two possible orientations of the amphiphile ab and z represents the solvent AA.

If x^α, y^α, and z^α, and x^β, y^β, and z^β represent the mole fractions of the three species for each sublattice in an ordered phase of the spin-1 model of Eq. (1), the grand potential per secondary site ω in the mean-field approximation is

$$2\omega = kT(x^\alpha \ln x^\alpha + y^\alpha \ln y^\alpha + z^\alpha \ln z^\alpha + x^\beta \ln x^\beta + y^\beta \ln y^\beta + z^\beta \ln z^\beta) + \tfrac{1}{2}[a_P(y^\alpha z^\beta + z^\alpha y^\beta) + b_P(x^\alpha z^\beta + z^\alpha x^\beta)$$

$$+ c_P(x^\alpha y^\beta + y^\alpha x^\beta)] + \tfrac{1}{2}[a_Q(y^\alpha z^\beta + z^\alpha y^\beta) + b_Q(x^\alpha z^\beta + z^\alpha x^\beta) + c_Q(x^\alpha y^\beta + y^\alpha x^\beta)] - v_1(x^\alpha + x^\beta) - v_2(y^\alpha + y^\beta) \, , \tag{4}$$

or

$$2\omega = kT(x^\alpha \ln x^\alpha + y^\alpha \ln y^\alpha + z^\alpha \ln z^\alpha + x^\beta \ln x^\beta + y^\beta \ln y^\beta + z^\beta \ln z^\beta)$$

$$+ \bar{a}(y^\alpha z^\beta + z^\alpha y^\beta + x^\alpha z^\beta + z^\alpha x^\beta) + \bar{c}(x^\alpha y^\beta + y^\alpha x^\beta) - \bar{\mu}(x^\alpha + x^\beta + y^\alpha + y^\beta) \, , \tag{5}$$

where

$$\bar{a} = \bar{b} \equiv \tfrac{1}{2}(a_P + b_P) = \tfrac{1}{2}(J + K) = \tfrac{1}{2}(\varepsilon_{Aa} + \varepsilon_{Ab} - \varepsilon_{AA}) - \tfrac{1}{4}(\varepsilon_{aa} + \varepsilon_{bb}) \, , \tag{6a}$$

$$\bar{c} \equiv c_P = 2J = \varepsilon_{ab} - \tfrac{1}{4}(\varepsilon_{aa} + \varepsilon_{bb}) \, , \tag{6b}$$

and

$$\bar{\mu} \equiv v_1 = v_2 = \tfrac{1}{2}(J + K - 2\Delta) = \mu + \tfrac{1}{4}(2\varepsilon_{AA} - \varepsilon_{aa} - \varepsilon_{bb}) \, . \tag{6c}$$

Thus, the phase behavior of the model micellar solution in this approximation is given by the symmetrical sections of the FDG three-component model under the additional restriction $v_1 = v_2$.

III. SYSTEM PHASE DIAGRAMS

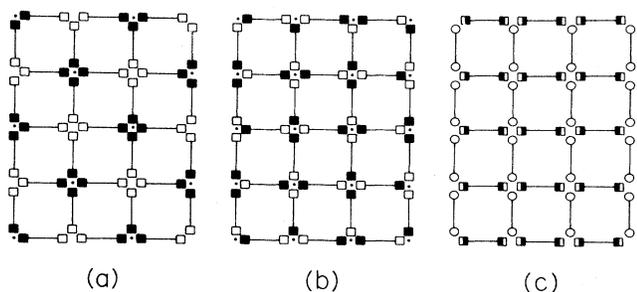In view of II it is also convenient to think of the two ab orientations as the up and down spin values of a magnetic

(a)   (b)   (c)

FIG. 2. Ordered sublattice arrangements of bifunctional molecules. (a) Close-packed ab molecules in the O_1 phase. (b) Closed-packed ab molecules in the O_2 phase. (c) Sublattice segregation of AA and ab molecules in the O_3 phase. The half-filled squares indicate no preference in the ab orientations. Superpositions of O_1 and O_2 on O_3 produce, respectively, representations of the O_4 and O_5 phases.

species and of the solvent AA as a nonmagnetic alloy diluent. In this way we can classify the different types of system phase diagrams for the mixture according to whether they are "ferromagnetic" or "antiferromagnetic," as well as to whether they are of the "segregating" or of the "ordering" kinds. All we require for this transcription is to (i) identify the end-end interaction parameter expressions that correspond to the magnetic coupling and to the heat of mixing of the alloy image; and (ii) translate the structure of each alloy phase into the corresponding structure for the $AA + ab$ mixture according to the identifications shown in Fig. 1(b). (Note, for example, that a uniform spin-1 phase does not necessarily transform into a uniform phase of the $AA + ab$ mixture.) [See Fig. 2(a)]. With these instruments the global phase diagram for the micellar soluton can be readily obtained from that of the magnetic alloy in zero field described in II.

To accomplish point (i) we first recall from II that the magnetic coupling in the alloy model is given by the FDG energy parameter c, which according to Eq. 6(b) is, in mixture language, a "heat of mixing" of the two molecular ends of the pure amphiphile substance. "Ferromagnetic" behavior corresponds to same-letter ends meeting at primary sites, where the ab molecules acquire the long-range aggregated arrangement shown in Fig. 2(a), and denoted by O_1 in subsequent figures. "Antifer-

romagnetic" behavior corresponds to the alternating-letter ends arrangement at primary sites shown in Fig. 2(b), and denoted by O_2 in the following figures. We refer to mixtures with $c > 0$ as type I mixtures and those with $c < 0$ as mixtures of type II.

In the preceding paper, II, the heat of mixing of the magnetic alloy is given by the spin-1 energy-parameter expression $\Lambda = 4\bar{a} - \bar{c}$, which of combined with Eqs. (6a) and 6(b), becomes

$$\Lambda = 2(\varepsilon_{Aa} + \varepsilon_{Ab}) - 2\varepsilon_{AA} - \tfrac{1}{2}(\varepsilon_{aa} + \varepsilon_{bb} + 2\varepsilon_{ab}) . \quad (7)$$

And if we define molecular interaction energy parameters ε_{WW}, ε_{SS}, and ε_{WS} as

$$\varepsilon_{WW} = \varepsilon_{AA} , \quad (8a)$$

$$\varepsilon_{WS} = \tfrac{1}{2}(\varepsilon_{Aa} + \varepsilon_{Ab}) , \quad (8b)$$

and

$$\varepsilon_{SS} = \tfrac{1}{4}(\varepsilon_{aa} + \varepsilon_{bb} + 2\varepsilon_{ab}) , \quad (8c)$$

where the subindexes W and S denote the solvent ("water") and the amphiphile ("surfactant") species, respectively. Equation (7) becomes

$$\Lambda = 4[\varepsilon_{WS} - \tfrac{1}{2}(\varepsilon_{WW} + \varepsilon_{SS})] , \quad (9)$$

so that the purely chemical heat of mixing of the magnetic alloy corresponds to the average, or molecular, heat of mixing of the micellar solution. We refer to mixtures with $\Lambda > 0$ as segregating, and to mixtures with $\Lambda < 0$ as ordering.

Segregation of paramagnetic phases in the model alloy described in II corresponds to phase separation of uniform phases (denoted by the letter U in the phase diagrams) that differ only in their content of the species AA and ab. Segregation of ferromagnetic or antiferromagnetic phases occurring for some alloy systems in II corresponds here to phase separation of ordered phases of type O_1 or of type O_2, respectively. Paramagnetic ordered phases in the model alloy [twofold degenerate states (AA) in the notation of I] correspond to ordered phases in the mixture in which one sublattice is preferentially occupied by AA and the other by ab molecules. In the latter sublattice the two amphiphile orientations are equally probable. A representation of this phase is shown in Fig. 2(c), which we denote by O_3. Finally, the ordered ferromag-
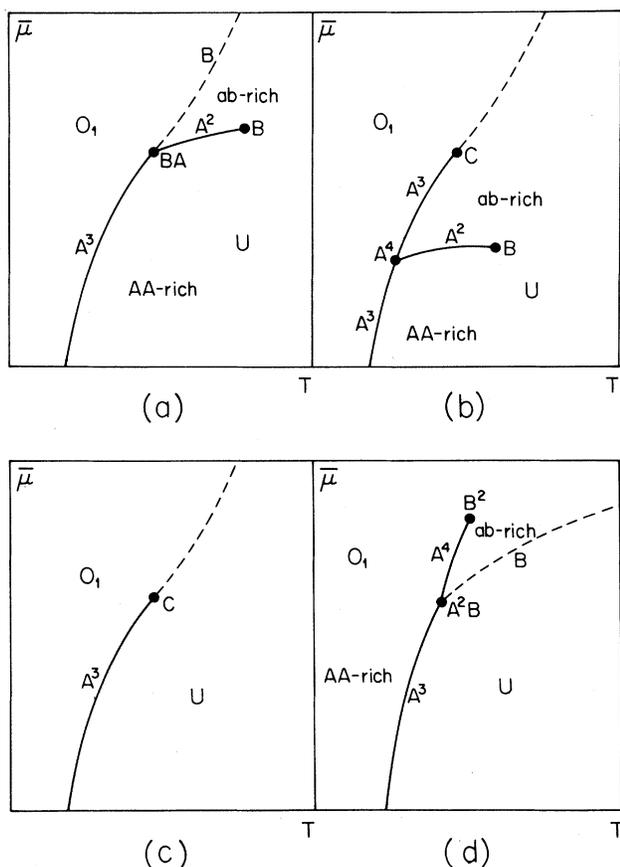

FIG. 3. Phase diagrams in $(\bar{\mu}, T)$ space for $AA + ab$ mixtures of type I that correspond to different locations on the symmetrical section of the P triangle. Unbroken and dashed lines represent, respectively, first- and second-order transitions.
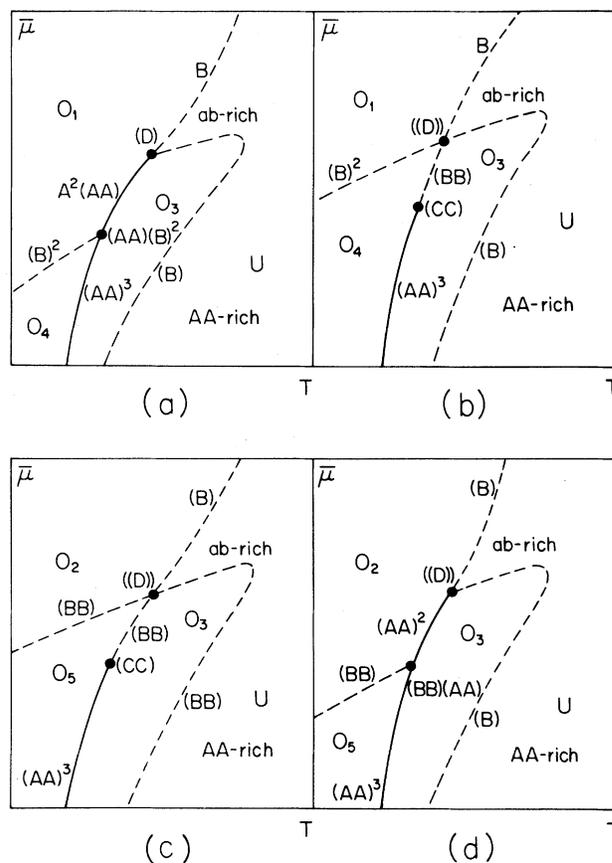

FIG. 4. Phase diagrams in $(\bar{\mu}, T)$ space for $AA + ab$ mixtures. In (a) and in (b) they are of type I and show the two different kinds of ordering systems for the symmetrical section of the R triangle. In (c) and (d) they are of type II and show the two kinds of ordering systems, analogous to (a) and (b), found along the symmetrical section of the S triangle.
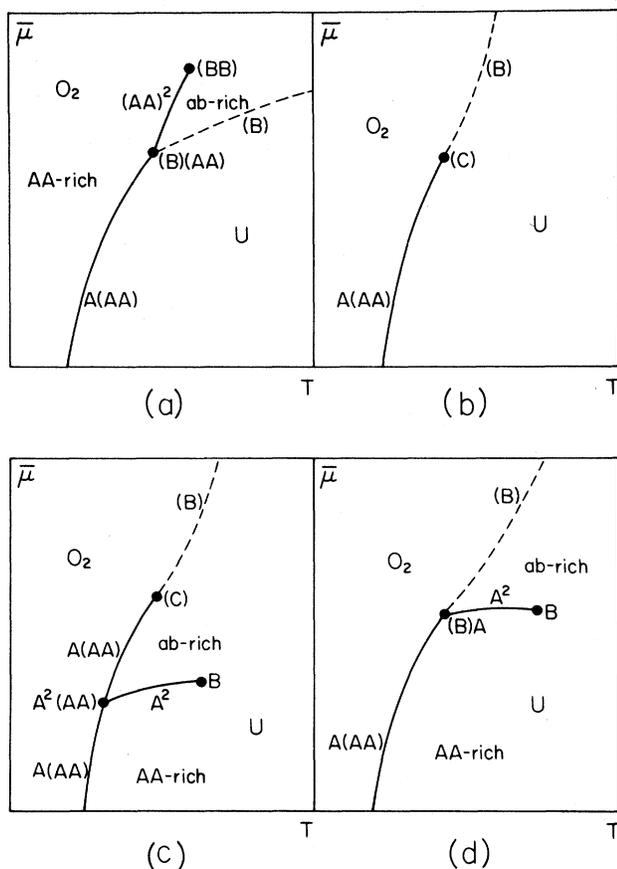
FIG. 5. Phase diagrams in $(\bar{\mu}, T)$ space for $AA + ab$ mixtures of type II analogous to those shown in Fig. 3 that correspond to different locations on the symmetrical sections of the S and Q triangles.

netic and ordered antiferromagnetic phases in II $[(AA)^2$ states in the notation of I] correspond here to ordered phases in the mixture in which one sublattice is preferentially occupied by AA and the other by ab molecules. The two amphiphile orientations are not equally probable in either sublattice and they follow in one case the pattern of the O_1 phase and in the other that of the O_2 phase. Representations for these phases, denoted by O_4 and O_5, respectively, can be obtained by superposing Figs. 2(a) and 2(b) on Fig. 2(c).

A detailed description of all the types of system phase diagrams for the model mixture would become a repetition of that given in II. We only present here the corresponding phase diagrams in the space of temperature T and chemical potential difference $\bar{\mu}$ between the two species. These are shown in Figs. 3–5 where we have employed the notation of I and II to mark the special points where multiple-phase coexistence and high-order critical points of the FDG model occur. The reader may savor examining them together with Fig. 3 of II, which shows

the relevant section of the FDG global phase diagram for the micellar solution model projected on the (T, c) plane.

IV. SUMMARY AND DISCUSSION

We have obtained, under both mean-field approximation and the consideration only of a particular type of nonuniformity, implied by a simple lattice subdivision, a rich family of phase diagrams for the $AA + ab$ model. Simplified in this manner, the overall behavior of the model can be understood in terms of a binary alloy with one magnetic component. There are two types of amphiphiles ab which correspond to "ferromagnet" and "antiferromagnet" and are distinguished by the sign of

$$c = \varepsilon_{ab} - \tfrac{1}{2}(\varepsilon_{aa} + \varepsilon_{bb}) .$$

The solvent amphiphile mixture $AA + ab$ can in turn be "segregating" or "ordering." Amongst the phase behavior found, there is phase separation of uniform phases associated with only one (upper) critical point. When this occurs a single type of ordered phase appears when the mixture is rich in ab (Figs. 3 and 5). On the other hand, ordering solutions exhibit three different sublattice-ordered phases.

The phase diagrams described are not necessarily correct for the unapproximated $AA + ab$ model. Even within the mean field, the phase behavior found is not complete. We have not probed into the interesting feature of the model mixture that is the staggered quality of the spin-1 field C. It is likely that some important physical properties of a micellar solution may be represented by the changing sign of C, since this arises from the orientational degrees of freedom of the amphiphile ab. The sublattice subdivision that we considered here has the effect of removing (within the mean field) this property in the equivalent spin-1 model. Other sublattice arrangements preserve the alternating nature C and may lead to the identification of additional phases (and phase transition lines), some of which may resemble (more closely than the phases described here) real uniform micellar-aggregated and nonuniform liquid-crystalline phases.

The exercise that we have illustrated here for the binary $AA + ab$ mixture can be extended to the ternary mixture $AA + ab + BB$. This case can be described in the language of a ternary alloy of one magnetic component and two different nonmagnetic diluents. The increased (but simple to account for) complexity in phase behavior may correlate with that of real microemulsions. The less ambitious objective of generalizing the original Wheeler-Widom model in order to enrich its phase behavior has been accomplished.

ACKNOWLEDGMENTS

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