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Spin Ising transcription of a lattice model of micellar solutions

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It is pointed out that the spin-1 Hamiltonian

$$\mathcal{H}=-J\sum_{\langle ij\rangle}S_iS_j-K\sum_{\langle ij\rangle}S_i^2S_j^2-C\sum_{\langle ij\rangle}(S_i^2S_j+S_iS_j^2)+\Delta\sum_i S_i^2$$

with staggered field C represents the Widom-type lattice mixture of bifunctional molecules ab and AA with finite interactions. The structure of the mean-field phase behavior of the model micellar solution is provided partially by that of the symmetrical section of Griffiths's three-component model.

I. INTRODUCTION

In 1968 Wheeler and Widom[1] introduced a lattice model of bifunctional molecules AA (○—○), BB (●—●), and AB (○—●) that abstracts some features of a ternary system composed of two immiscible solvents and an amphiphile. The molecules are confined to the bonds of a (simple cubic) lattice filling every bond with one, and only one, 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. More recently, Widom[2] has generalized this model with the introduction of next-nearest neighbor and three-spin interactions and, as a consequence, amphiphile AB structures exhibit nonvanishing bending energies.[2] The additional interactions generate phase diagrams and interfacial properties which concord with some features of real microemulsions.[2]

Also recently, a different generalization of the original model has been proposed,[3] only now, instead of further interactions, finite molecular end-end interactions are allowed. The amphiphile molecule is now denoted by ab (□—■) to help distinguish between end-end encounters originating from different kinds of molecules (A-a as different from A-A, etc.) This differentiation allows for nonvanishing amphiphile-film bending energies while considering only end-end interactions. As discussed in Ref. 3, the model properties are obtainable in terms of simple Ising systems with spins located at the bonds (or secondary sites) of the lattice if the (nearest-neighbor) couplings are given a specific temperature dependence. A spin-1 system describes the ternary mixture while spin-$\frac{1}{2}$ systems apply to the associated binary mixtures. Closed solubility loops, liquid-crystalline-like phases, microemulsionlike phase progressions, and other features common to amphiphile systems are reproduced through the study of such mappings.[3]

Following the publication of Ref. 3 the author discovered that the establishment of the equivalence between the partition functions involved a neglect of orientational correlations. Therefore, the range of application of that mapping is reduced to either small differences between certain end-end interaction energies where a molecule of amphiphile is involved or to high temperatures. An appropriate reformulation that takes into account this circumstance has been provided.[4] Here we consider the definition of the spin Ising system that authentically represents the lattice mixture for all possible values of its parameters. Details are given for the binary case $AA+ab$ only, which, as shown below, corresponds now to a spin-1 system. The properties of the three-component $AA+ab+BB$ mixture would be represented now by a spin-$\frac{3}{2}$ system, and its formulation is a straightforward extension to the one given here.[5]

II. FORMULATION OF THE SPIN MODEL

With the two species AA and ab there are six kinds of end-to-end encounters between pairs of molecules. Only those placed along bonds at right angles have nonzero interaction energies, the values of which are denoted by ε_{AA}, ε_{Aa}, ε_{Ab}, ε_{aa}, ε_{ab}, and ε_{bb} ($\varepsilon_{ij}>0$ for repulsions). See Fig. 1. Consider now the subdivision shown in Fig. 2(a) of the primary and secondary lattices each into two sublattices. The sublattices, P and Q, for the primary lattice are interwoven and those, ○ and ×, for the secondary lattice form layers. The values $S=0$, 1, and -1 are assigned to the spins located at the secondary sites according to the molecular occupations shown in Fig. 2(b). $S=0$ indicates occupation by AA and $S=\pm1$ specifies orientations of ab. The orientation assignments for $S=\pm1$ appear reversed in the sublattices ○ and ×.[6] This reversal ensures that the configurations of every pair of nearest-neighbor spins have each a uniquely defined contribution to the total configurational energy. These contributions are listed in Table I, where the two different columns refer to the fact that end-end encounters and nearest-neighbor pairs of spins fall into one of the two sets, according to whether they occur at,

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}

or are placed next to, a primary site of type P or Q. The equivalence between mixture and magnet can be established by comparison of their respective Boltzmann factors. For an end-to-end encounter this is

$$\exp\{-(kTq)^{-1}[\varepsilon_{ij}-\mu(S_i^2+S_j^2)]\} ,$$

where ε_{ij} $(i,j=0,\pm 1)$ takes the values ε_{AA}, ε_{Aa}, ε_{Ab}, ε_{aa}, ε_{ab}, and ε_{bb} according to Table I, $\mu=\mu_{ab}-\mu_{AA}$ is the chemical potential difference between the two species, and q is the coordination number of the secondary lattice. For nearest-neighbor pairs of spins the Boltzmann factor[7] is

$$F\exp\{-(kTq)^{-1}[-JS_iS_j-KS_i^2S_j^2-C(S_i^2S_j+S_iS_j^2) -H(S_i+S_j)+\Delta(S_i^2+S_j^2)]\} ,$$

where F is a constant, J and K are dipolar and quadrupolar exchange couplings, while H is a magnetic field and Δ a crystal-field splitting. The term C is normally absent in magnetic systems but it is needed in the description of multicomponent lattice gases.[7-9] The equality of the Boltzmann factors leads [within the particular choice of $F=\exp(-\varepsilon_{AA}/kTq)$] to the identifications

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

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

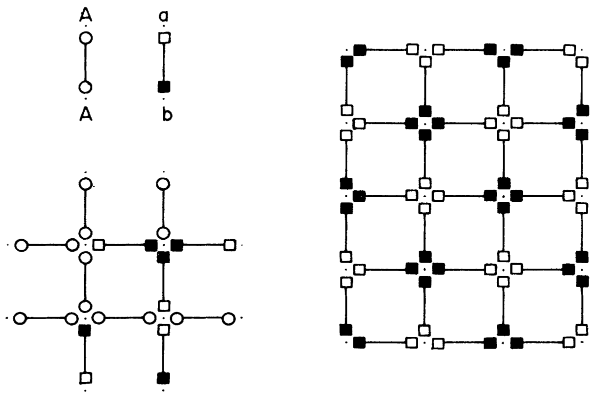
$$\pm C=\tfrac{1}{2}(\varepsilon_{Aa}-\varepsilon_{Ab})-\tfrac{1}{4}(\varepsilon_{aa}-\varepsilon_{bb}) , \tag{1c}$$

$$H=0 , \tag{1d}$$

and

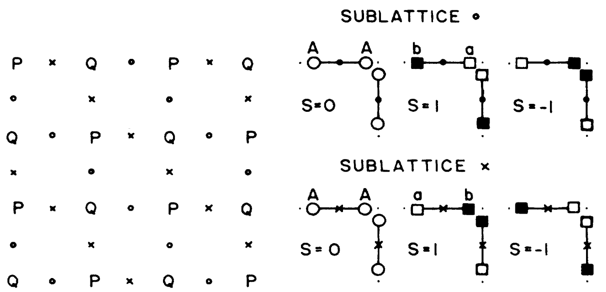
$$\Delta=\tfrac{1}{2}(\varepsilon_{Ab}-\varepsilon_{AA})+\tfrac{1}{2}(\varepsilon_{Aa}-\varepsilon_{AA})-\mu , \tag{1e}$$

where the sign in front of C is positive if the pair of spins belongs to a primary site of type P and is negative otherwise. Thus the spin-1 model obtained differs from the usual[7-9] in that the field C is not uniform but alternates in sign throughout the lattice. Also, the total magnetic field H acting on any spin S_i vanishes because the contribution H_{ij} to H from a pair of spins S_i,S_j is $H_{ij}=\pm\frac{1}{2}q^{-1}(\varepsilon_{Ab}-\varepsilon_{Aa})$, where again a positive sign is given to type P pairs and negative otherwise, and thus $H=\sum_{\langle ij\rangle}H_{ij}=0$. It is convenient to express the above equivalences also in the language of a ternary mixture or alloy consisting of the three components x, y, and z on the same lattice where the spins are located. Its five relevant fields, three interaction energy parameters a, b, and c, and two chemical potential differences, μ_{x-z} and μ_{y-z}, are related[7] to the spin-1 fields through



(a) (b)

FIG. 1. (a) Bifunctional molecules AA and ab on the bonds of the primary lattice. The secondary lattice is formed by the bond midpoints. (b) Ordered sublattice arrangement of close-packed ab molecules.



(a) (b)

FIG. 2. (a) Sublattice arrangement for primary (P and Q) and secondary (○ and ×) sites. (b) Spin value assignation of molecular orientations in the two sublattices ○ and ×.

$$a=\tfrac{1}{2}(J+K-2C)\ , \tag{2a}$$

$$b=\tfrac{1}{2}(J+K+2C)\ , \tag{2b}$$

$$c=2J\ , \tag{2c}$$

$$\mu_{x-z}=b-(\Delta-H)=\tfrac{1}{2}(J+K+2C-2\Delta+2H)\ , \tag{2d}$$

and

$$\mu_{y-z}=a-(\Delta+H)=\tfrac{1}{2}(J+K-2C-2\Delta-2H)\ . \tag{2e}$$

In terms of these we obtain

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

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

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

$$(\mu_{x-z})_P=\mu+\tfrac{1}{2}(\varepsilon_{AA}-\varepsilon_{aa})=(\mu_{y-z})_Q\ , \tag{3d}$$

and

$$(\mu_{y-z})_P=\mu+\tfrac{1}{2}(\varepsilon_{AA}-\varepsilon_{bb})=(\mu_{x-z})_Q\ , \tag{3e}$$

where the subindexes refer to nearest-neighbor pairs of particles associated to primary sites of types P and Q. In this language x and y represent the two possible orientations of the amphiphile ab and z the solvent AA. There is only one independent chemical potential difference and therefore, as would be expected, overall amphiphile orientation cannot be modified by an external field. The staggered property of the equivalent spin-1 system requires the interchange of the interaction parameters a and b and chemical potential differences μ_{x-z} and μ_{y-z} whenever the type of a nearest-neighbor pair of molecules changes from P to Q.

III. SOME MEAN-FIELD PROPERTIES

The properties in mean-field approximation of the $ab+AA$ model mixture can be obtained from those of the usual spin-1 model with uniform fields also in the same approximation. To see this, consider the uniform states of the staggered spin-1 model. If x, y, and z represent the mole fractions of the corresponding three components, constant throughout the lattice, the grand potential per bond (or secondary site) ω in the mean-field approximation is

$$\begin{aligned}\omega=kT[x\ln x+y\ln y+z\ln z]&\\ +\tfrac{1}{2}[ayz+bxz+cxy-\mu_{x-z}x-\mu_{y-z}y]&\\ +\tfrac{1}{2}[byz+axz+cxy-\mu_{y-z}x-\mu_{x-z}y]&\ ,\end{aligned} \tag{4}$$

or

$$\begin{aligned}\omega=kT[x\ln x+y\ln y+z\ln z]&\\ +\bar{a}(yz+xz)+\bar{c}xy-\bar{\mu}(x+y)&\ ,\end{aligned} \tag{5}$$

where

$$\begin{aligned}\bar{a}=\tfrac{1}{2}(a+b)=\tfrac{1}{2}(J+K)=\tfrac{1}{2}(\varepsilon_{Aa}+\varepsilon_{Ab}-\varepsilon_{AA})&\\ -\tfrac{1}{4}(\varepsilon_{aa}+\varepsilon_{bb})&\ ,\end{aligned} \tag{6a}$$

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

and

$$\begin{aligned}\bar{\mu}\equiv\bar{\mu}_{x-z}=\bar{\mu}_{y-z}=\tfrac{1}{2}(\mu_{x-z}+\mu_{y-z})=\tfrac{1}{2}(J+K-2\Delta)&\\ =\mu+\tfrac{1}{2}(2\varepsilon_{AA}-\varepsilon_{bb}-\varepsilon_{aa})&\ .\end{aligned} \tag{6c}$$

Thus, the phase behavior of the model micellar solution in this approximation is given by that of the so-called symmetrical section ($\bar{a}=\bar{b}$) (Ref. 7) of Griffiths' three-component model under the additional restriction that $\bar{\mu}_{x-z}=\bar{\mu}_{y-z}$. The symmetrical section of interest cuts through four "energy" triangles,[7] $\bar{a}>0$, $\bar{b}>0$, $\bar{c}>0$; $\bar{a}>0$, $\bar{b}>0$, $\bar{c}<0$; $\bar{a}<0$, $\bar{b}<0$, $\bar{c}>0$; and $\bar{a}<0$, $\bar{b}<0$, $\bar{c}<0$. Of these, the "principal" energy triangle $\bar{a}>0$, $\bar{b}>0$, $\bar{c}>0$, is the richest in multiphase equilibria among uniform phases in the spin-1 language (some of which, as we see below are not uniform in the bifunctional molecule mixture language). As one changes the magnitudes (and signs) of the interaction parameters $\bar{a}$, $\bar{b}$, and $\bar{c}$, these kinds of phase equilibria gradually simplify and finally lead to only one-phase states in the central region of the energy triangle with $\bar{a}<0$, $\bar{b}<0$, $\bar{c}<0$.[7] In Fig. 3 we show the symmetrical section in the principal energy triangle projected on the $(T,\bar{c})$ plane. Only the main features of the section, which happen to appear precisely when $\bar{\mu}_{x-z}=\bar{\mu}_{y-z}$ are marked in the figure. We follow a similar notation for phase coexistence and critical boundaries as in Ref. 7. Thus, α^2 represents two coexisting phases and β denotes an ordinary critical point where the two phases coalesce. Likewise, three-phase

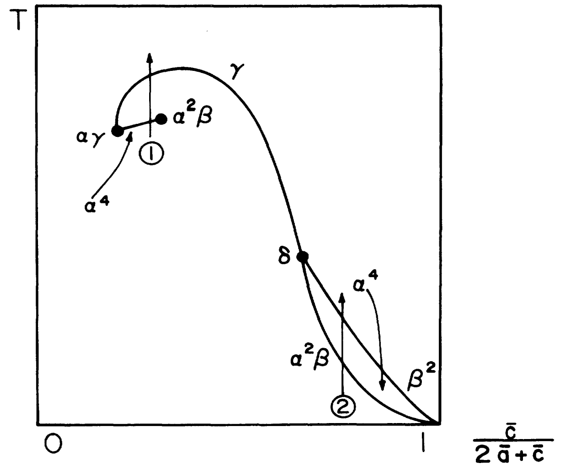


FIG. 3. Projection of the symmetrical section of the full phase diagram on the $(T,\bar{c}/(2\bar{a}+\bar{c}))$ plane. This figure is essentially Fig. 8 in Ref. 6. The notation for phase coexistence and critical boundaries is explained in the text. The arrows labeled 1 and 2 indicate the paths that yield the phase progressions shown in Figs. 4 and 5, respectively.

states α^3 terminate at a critical end point $\alpha\beta$ or at a tricritical point γ. Four-phase states α^4 may appear bounded by critical points coexisting with two phases $\alpha^2\beta$, by a double critical point β^2, by a tricritical end point $\alpha\gamma$, or by a fourth-order critical point δ.

The symmetrical section in the principal energy triangle contains two different regions of four-phase coexistence. The first region appears close to the center of the triangle and forms part of the so-called shield region that extends out of the symmetrical section.[7] The α^4 points of this type that lie on the symmetrical section form a line bounded by $\alpha^2\beta$ and $\alpha\gamma$ points. The $\alpha\gamma$ point is in turn the end of a line of symmetrical tricritical points γ, that extends at higher temperatures over the α^4 points and spans an interval of $\bar{c}$ values. At the large $\bar{c}$ end of this interval the line terminates at a fourth-order point δ, and, as shown in Fig. 3, this is also the common end of two loci of β^2 and $\alpha^2\beta$ points, the boundaries of the second set of α^4 points. The symmetrical sections in the other three energy triangles exhibit only α^2 and β points. (There are two exceptions, the merging of two γ points from outside the symmetrical section in the $\bar{a}>0$, $\bar{b}>0$, $\bar{c}<0$ triangle and a γ point at the boundary $\bar{c}=0$ between the $\bar{a}<0$, $\bar{b}<0$, $\bar{c}>0$ and the $\bar{a}<0$, $\bar{b}<0$, $\bar{c}<0$ triangles.) Figures 4 and 5 show two different phase diagram sequences obtained when the temperature is incremented in mixtures with values of $\bar{c}$ such that each displays one type of four-phase coexistence. The trajectories followed in $(T,\bar{c})$ space are shown by the arrows labeled 1 and 2 in Fig. 3.

The condition $\bar{\mu}=\bar{\mu}_{x-z}=\bar{\mu}_{y-z}$ selects from these phase diagrams only the states with compositions $(x,y,z)=(x+\delta, x-\delta, 1-2x)$. In the $ab+AA$ mixture language these states are either uniform phases ($\delta=0$) or nonuniform "aggregated" phases ($\delta\neq0$), where the ab molecules acquire the sublattice arrangement shown in Fig. 1(b). In Figs. 6(a) and 6(b) we show the phase boundaries in $(\bar{\mu},T)$ space for the two kinds of mixtures, respectively, together with the location of the α^4, $\alpha^2\beta$, β^2, and γ points. Because phases differing only in the sign of δ indicate only degeneracy of the same sublattice ordering, α^3 and α^4 points appear forming simple first-order lines bounded by the higher-order γ or β^2 critical points. If, in a system represented by Fig. 6(a), $\bar{c}$ is decreased in value the γ point approaches the location of the α^4 state, and both eventually coalesce at an $\alpha\gamma$ point. For smaller values of $\bar{c}$ the first-order line between sublattice order and an isotropic AA-rich solution terminates at an $\alpha\beta$ point. When $\bar{c}=0$ this point occurs at $T=0$. The mixtures in the $\bar{a}>0$, $\bar{b}>0$, $\bar{c}<0$ triangle exhibit only phase separation of isotropic liquids differing only in solvent content, and thus their phase diagrams consist of a single α^2 line bounded by a β point. On the other hand, in Fig. 6(b) if $\bar{c}$ is incremented in value, or alternatively $\bar{a}$ is decremented, the α^4 line becomes shorter in extent and the $\alpha^2\beta$ point moves to lower temperatures. When the system enters the $\bar{a}<0$, $\bar{b}<0$, $\bar{c}>0$ triangle only the second order points β that separate sublattice order and isotropic solution remain.

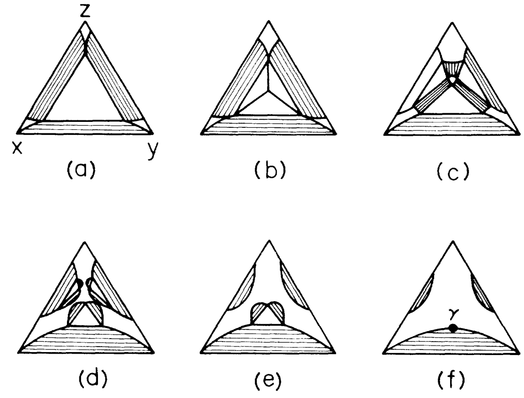


FIG. 4. Phase diagrams obtained when the temperature is increased, (a)–(f), in a mixture with interaction parameter $\bar{c}/(2\bar{a}+\bar{c})$ indicated by the label 1 in Fig. 3.

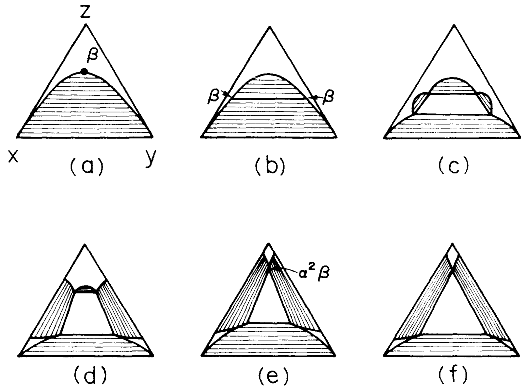


FIG. 5. Phase diagrams obtained when the temperature is increased, (a)–(f), in a mixture with interaction parameter $\bar{c}/(2\bar{a}+\bar{c})$ indicated by the label 2 in Fig. 3.

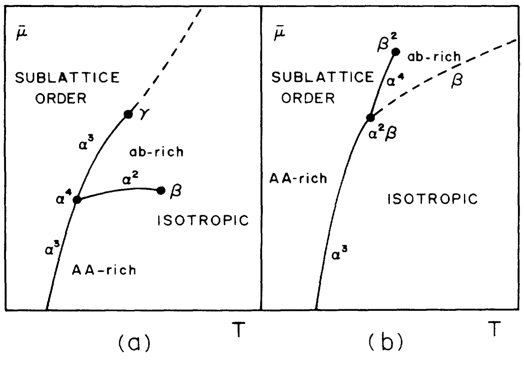


FIG. 6. (a) Phase diagram in the $(\bar{\mu},T)$ for the $ab+AA$ mixture that corresponds to the system described in Fig. 4. Solid and dashed lines represent first- and second-order boundaries, respectively. (b) The same as (a) but for the system described in Fig. 5.

Additional phase equilibrium properties of the model mixture may be obtained (also within mean-field) through the consideration of the nonuniform states of the staggered spin-1 model. However, the analysis of the model's capability in describing amphiphile aggregation in uniform (isotropic) solutions, such as occurrence of a critical micellar concentration, would probably require the study of the staggered spin-1 model beyond the mean-field approximation.

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