Phenomenological theory of multiply reentrant solubility

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A phenomenological approach to the theory of complex phase diagrams in binary liquid mixtures is developed. The random-mixing Flory–Huggins free energy expression is modified by the generalization of local pairwise energies to the corresponding free energies which, for systems with specific interactions such as hydrogen bonds, are described in terms of multiple-level partition functions. The temperature-dependent effective interactions in recent lattice models for these systems appear as special cases of this more general result. While characteristic asymmetries of various interactional correlation functions evaluated in the coexisting phases are found to parallel those of the interactions themselves, the symmetry of the phase diagram is not affected by such interactions, in contrast to the results of decorated-lattice calculations. A heuristic explanation of this is given, supporting a recent suggestion that the description of interaction-driven asymmetric coexistence curves requires an enlarged space of statistical variables which includes density fluctuations.

I. INTRODUCTION

A wide variety of liquid mixtures[1] and polymer solutions exhibits involved coexistence-curve topologies as a consequence of intermolecular hydrogen bonding. The classic examples are lower critical solution points, which have been observed in numerous systems,[1] especially in recent studies of aqueous nonionic surfactant mixtures and other micellar solutions,[2-7] and in microemulsion systems. The simple microscopic mechanism[8] by which this interaction leads to these and other reentrant phenomena is well understood, yet existing theories[9-16] are not correspondingly simple, invoking complex lattice models[9-11] and spin Hamiltonians[12-16] to represent substitutional and molecular orientational degrees of freedom. Neither are they readily generalized to the wide range of systems exhibiting closed solubility loops and related transitions. It is thus of interest to investigate a formulation of the thermodynamics which is not tied to a particular representation of the degrees of freedom, but rather is *phenomenological*.

Previous theoretical work shows that the most important microscopic property is the existence of a *multiple-state* structure to the local interactions. In the simplest cases, there may only be two distinct modes of interaction, such as weak van der Waals forces and low entropy, but energetically favored hydrogen bonds, although a more complicated level structure describes multiple transitions in many systems.[14-16] Section II describes such a phenomenological theory, which uses this idea of multiple states in a straightforward generalization[17] of the random-mixing free energy function familiar from the theory of polymer solubility.[18,19] The simple replacement of the various pairwise *energies* with (phenomenological) *free energies*, representing averages over orientational degrees of freedom, reproduces all the qualitative results of the previous model calculations in a more physically and mathematically transparent way. Indeed, the previous models are seen to be special cases of the more general results obtained here. The main focus of this work is on a simple description of the microscopic mechanisms of the transitions, so that the prediction of classical critical behavior is not a serious shortcoming.

Virtually all of the coexistence curves of these mixtures lack the compositional symmetry of the Ising model, to whose universality class their critical points belong.[20] Size differences between the components certainly account for much of this, but it is equally clear that there is a fundamental *lack of component-exchange symmetry* with respect to the interactions, quite different from the spin-flip symmetry of the Ising ferromagnet in zero field. One of the intriguing issues is the role that such interactional asymmetry plays in that of the coexistence curves. Recently,[21,22] in the context of the spin models, it was concluded (i) that interactional asymmetry alone will not explain coexistence-curve asymmetry, and (ii) that such an explanation requires the incorporation of noncritical density fluctuations into the Hamiltonian. Even in the absence of these fluctuations, as in the present theory, there are characteristic asymmetries in the various microscopic correlations related to the specific interactions themselves, and these provide a detailed explanation of how the free energies of the coexisting phases achieve a balance. As shown in Secs. II and III, these correlation asymmetries appear with a very clear connection to the free-energy-level structure postulated. These results concerning the symmetry are in disagreement with decorated-lattice (DL) calculations[11(a)] for these systems, and a heuristic explanation for this discrepancy, along with a justification of conclusion (i), is proposed in Sec. IV. Finally, in Sec. V it is suggested that this phenomenological treatment of strongly temperature-dependent interactions has applications in the description of surfactant solutions, microemulsions, and certain polymeric liquid crystal systems.

II. ASYMMETRIC SPECIFIC INTERACTIONS IN A MEAN FIELD THEORY

A. Free energy

In the Flory–Huggins (FH) mean field approximation, the free energy is conveniently separated into contributions from the substitutional (mixing) degrees of freedom, and from the molecular interactions. For a mixture of N_p polymer molecules, each composed of M identical monomer

units, and N_s solvent molecules, this random-mixing free energy is[18,19]

$$F = Nk_B T \{(1 - \phi)\ln(1 - \phi) + (\phi /M)\ln(\phi /M)\}$$
$$+ dN \{(1 - \phi)^2 e_{ss} + \phi^2 e_{pp} + 2\phi (1 - \phi)e_{ps}\}, \quad (1)$$

where $\phi = MN_p/(MN_p + N_s)$ is the polymer volume fraction, $N = MN_p + N_s$, and d is one-half the coordination number.[23] The microscopic solvent–solvent, polymer–solvent, and polymer–polymer energies e_{ij} in Eq. (1) enter the expression for the free energy of mixing,

$$F_{mix} = Nk_B T$$
$$\times [(1 - \phi)\ln(1 - \phi) + (1/M)\phi \ln(\phi) + \chi\phi (1 - \phi)],(2)$$

only through the linear combination $w = e_{pp} + e_{ss} - 2e_{ps}$, in the dimensionless Flory parameter $\chi = - dw/k_B T$.

For systems with multiple-state interactions, it is not possible to specify uniquely the microscopic energies e_{ij}—only local *free energies* f_{ij} having meaning since the orientational degrees of freedom upon which the various energies depend are in thermal equilibrium. We make the phenomenological assumption that the totality of relative orientational states may be grouped into levels, each with a characteristic energy and "degeneracy." If the interactions can be grouped into two classes, e.g., van der Waals-like and hydrogen bonds, these local free energies are described by two-level partition functions Z_{ij}, with $f_{ij} = - k_B T \ln(Z_{ij})$, and

$$Z_{ij} = \omega_{ij}^0 \exp[- e_{ij}^0/k_B T] + \omega_{ij}^* \exp[- e_{ij}^*/k_B T], \quad (3)$$

where ω_{ij}^0 and ω_{ij}^* are orientational phase space factors associated, respectively, with the nonbonding and bonding states, with energies e_{ij}^0 and e_{ij}^*. Clearly, the energy and entropy of formation of this specific interaction are $e_{ij}^* - e_{ij}^0$, and $k_B \ln(\omega_{ij}^*/\omega_{ij}^0)$,[15] respectively. In the description of lower critical solution points the most important two-level system, and the one considered previously,[17] is that for polymer–solvent interactions, since the one-phase region below the LCST is characterized by, and indeed stabilized through significant polymer–solvent hydrogen bonding. Generalizing all the energies to free energies yields the reduced free energy per particle $f = - (1/N)F/k_B T$:

$$f = - \{(1 - \phi)\ln(1 - \phi) + (\phi /M)\ln(\phi /M)\}$$
$$+ d \{(1 - \phi)^2\ln(Z_{ss}) + \phi^2 \ln(Z_{pp}) + 2\phi (1 - \phi)\ln(Z_{ps})\}, \quad (4)$$

and the reduced free energy of mixing

$$f_{mix} = - \{(1 - \phi)\ln(1 - \phi) + (1/M)\phi \ln(\phi)\} - \chi_{eff}\phi (1 - \phi), \quad (5)$$

where,

$$\chi_{eff} = dK_{eff} = d \ln\{Z_{ss}Z_{pp}/[Z_{ps}]^2\}. \quad (6)$$

The parameter K_{eff} is now the generalization of the dimensionless energy $- w/k_B T$ of the original theory, and it arises from a thermal average over the *noncritical*[24] orientational degrees of freedom. From the general structure of the partition functions Z_{ij}, it is clear that the temperature dependence of K_{eff} may be quite complicated, especially for systems with more than two interaction modes.[14]

Note that, independent of the complexity of the local

free energies, and independent of any asymmetry between polymer–polymer and solvent–solvent interactions, the free energy of mixing, Eq. (15) is *symmetric* under the exchange $\phi \rightarrow 1 - \phi$ when $M = 1$. In this theory, then, interactional asymmetry does not produce coexistence-curve asymmetry. In addition, for $M > 1$, the deviation of the diameter from $\phi = 1/2$ is solely a consequence of this size difference. These points are discussed further in Sec. IV.

B. Connection with the spin models

In the model of Walker and Vause (WV),[12–16] which is in the same spirit as the earlier work of Barker and Fock,[9] and Wheeler and Andersen,[10,11] substitutional degrees of freedom are represented by Ising variables $s = \pm 1$ (A,B), as in the usual model of a binary mixture,[25] and q-state Potts[26] spins $\sigma = 1,2,...,q$ represent a discretization of orientational phase space. The form of the coupling (see below) between the Potts spins captures, for $q > 1$, the essence of the hydrogen bond, its low degeneracy. For the simplest systems showing closed solubility loops, the appropriate reduced Hamiltonian is[12]

$$-\beta H = \sum_{\langle ij \rangle} [K_1(1 - \delta_{s_i s_j})\delta_{\sigma_i \sigma_j} + K_2(1 - \delta_{s_i s_j})(1 - \delta_{\sigma_i \sigma_j})], \quad (7)$$

where $\beta = 1/k_B T$, the sum is over nearest neighbors on a cubic lattice, δ is the Kronecker delta, and the reduced energy parameters K_1 and K_2 establish the following energy levels for nearest-neighbor pairs:

(i) K_1, the AB hydrogen bonding level, with degeneracy $2q$,

(ii) K_2, the AB van der Waals energy, with a considerably higher degeneracy of $2q(q - 1)$, and,

(iii) zero, the like–molecule energy level, independent of the orientational correlations of the AA or BB pairs, thus having a high degeneracy of $2q^2$.

In comparing this model to experimental systems, the proper interpretation[15] of the parameter q is that the entropy of formation of the AB hydrogen bond is $\Delta S = - k_B \ln(q - 1)$.

This Hamiltonian has been studied with two approximation schemes, real-space renormalization-group (RG) theory[27] and a high-temperature series expansion[12(b),14–16,21,22] which, to leading order, maps the system onto the Ising model with a temperature-dependent nearest-neighbor coupling. This latter transformation is equivalent to the RG results in its qualitative predictions concerning the solubility transitions and the microscopic correlations (see below), and quite useful in matching theory to experiment. The general form of this "single-bond" approximation is illustrated in Fig. 1. A bond Hamiltonian H_{12} coupling Ising spins s_1 and s_2, and dependent on other fluctuating spin degrees of freedom σ_1 and σ_2 (such as orientations), is mapped onto that of a simple Ising model by an exact trace over those noncritical variables, written as
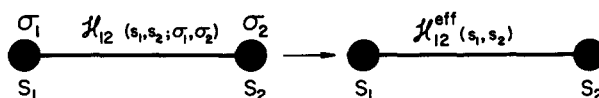

FIG. 1. Schematic illustration of the single-bond approximation which maps a multiple-variable model onto the Ising model.

$$Z(s_1,s_2) \equiv \sum_{\{\sigma_1,\sigma_2\}} \exp[-\beta H_{12}(s_1,s_2;\sigma_1,\sigma_2)]$$

$$= \exp[-\beta H_{12}^{\text{eff}}(s_1,s_2)], \qquad (8)$$

thus defining the conditional partition functions $Z(s_1,s_2)$. For the AB-symmetric Hamiltonian in Eq. (7), $Z(+,+) = Z(-,-)$, but the inclusion of interactional asymmetries makes them distinct. The effective bond Hamiltonian for the symmetric case is

$$-\beta H_{12}^{\text{eff}} = K_{\text{eff}}(1 - \delta_{s_1,s_2}) + K_0, \qquad (9)$$

where K_{eff} is the Ising model coupling, and K_0 is a zero-spin coupling. Solving Eqs. (8) and (9) for K_{eff}, and transforming to the standard form of the Ising Hamiltonian, with an interaction $K_I s_i s_j$, one finds

$$K_I = (1/4)\ln\{Z(+,+)Z(-,-)/[Z(+,-)]^2\}. \quad (10)$$

This is precisely Eq. (6) of the phenomenological theory, just transcribed into the magnetic "language". The spin Hamiltonians thus involve a particular set of the more general configuration-counting "rules" embodied in Eq. (3) and its multiple-state analogs. More importantly, the formal equivalence of these results demonstrates that, for most purposes, the particular geometric interpretation envisioned in constructing the bonding rules is irrelevant; the resultant free energy level structure is the central object.

Equation (10) is also the form of the effective coupling between nearest-neighbor sites of the primary lattice in a decorated-lattice calculation.[10,11] However, the "dedecoration transformation" in such calculations involves traces over the entire set[28] of statistical variables of the particles on the secondary lattice, and not just on the non-Ising degrees of freedom, which are, of course, absent from the primary lattice sites. The implication of the existence of these *inequivalent* sites in the study of asymmetric coexistence curves has been noted in the literature,[29] and is further discussed in Sec. IV.

In addition, unlike the present mean field theory, none of the spin models is capable of being generalized to polymer solutions, except by changing composition variables at the end of the calculation,[30] a procedure which neglects all of the entropic effects from particle-size asymmetry.

C. Interactional correlations

The various interactional correlations which reveal[14,16,21] the mechanisms behind reentrant transitions driven by hydrogen bonding may be calculated from appropriate derivatives of the free energy. In the WV model, it is straightforward to see that the ensemble averages conjugate to K_1 and K_2 in Eq. (7) are[14,16]

$$\partial \hat{f}/\partial K_1 = \langle(1 - \delta_{s_i s_j})\delta_{\sigma_i \sigma_j}\rangle$$

—the fractional hydrogen bonding among unlike-molecule neighbors, and

$$\partial \hat{f}/\partial K_2 = \langle(1 - \delta_{s_i s_j})(1 - \delta_{\sigma_i \sigma_j})\rangle$$

—the fractional nonbonding among unlike-molecule neighbors,

where $\hat{f} = f/d$ is the reduced free energy per bond. With the introduction of symmetry-breaking fields one may further calculate the separate contributions to correlations due to AA and BB pairs.[21,22]

In the mean field approximation, these same thermodynamic derivatives may be calculated, and although there is no explicit conjugate spin correlation, they clearly have precisely the same meaning as in the lattice theory: The derivative of the reduced free energy per bond with respect to any particular energy parameter is the fraction of bonds correlated through that interaction. From Eq. (3), the general form of such derivatives is

$$(G_{ij}^{\alpha})_{\pm} \equiv (\partial \hat{f}/\partial K_{ij}^{\alpha})_{\pm}$$

$$= C_{ij}^{\alpha} \times \begin{cases} [\phi^2]_{\pm} & i=j=p \\ [(1-\phi)^2]_{\pm} & i=j=s, \\ [2\phi(1-\phi)]_{\pm} & i \neq j \end{cases} \quad (11)$$

where

$$C_{ij}^{\alpha} = \omega_{ij}^{\alpha}\exp(K_{ij}^{\alpha})/Z_{ij}. \qquad (12)$$

The $K_{ij}^{\alpha} = -e_{ij}^{\alpha}/k_B T$ are dimensionless interaction parameters of the form as those in the WV theory, where $\alpha = *,0$ represents the two possible interactions, bonding or nonbonding. Subscripts $+(-)$ refer to the polymer-(solvent-) rich phases, and the compositions $\phi_{\pm}$ are determined from the standard common-tangent construction[18,19] at a value of the effective parameter χ corresponding to Eq. (5). Thus, the fractional "occupation" of any level of the interaction hierarchies is simply the usual Boltzmann-factor-times-degeneracy expression C_{ij}^{α}: Each of the various interactions occurs to an extent dictated by a simple equilibrium rule, and complex multiple phase separations in these systems arise from competition between the various association equilibria. This result appears in previous work, although perhaps in a somewhat less transparent way.[31]

Inasmuch as the functions C_{ij}^{α} are smooth, the singular properties of the difference between the values of a given interactional correlation in the coexisting phases are governed by the quantity $(\phi_+^2 - \phi_-^2)$ which, near a critical point, varies like t^{β} ($t = |T - T_c|/T_c$), where β is the exponent characterizing the order parameter variation. In contrast, the average value will have a singular term proportional to the internal energy of the system,[22] and will vary as $t^{1-\alpha}$, α being the specific heat exponent. Of course, in this mean field theory, $\beta = 1/2$ and $\alpha = 0$.

Since the free energy Eq. [(4)] is already decomposed into separate terms arising from the substitutional entropy and from the specific interactions, we may easily compute the contribution to the total entropy due to each of the two-level interactions. As with the correlations above, one finds that these contributions $(S_{ij})_{\pm}$ are (per bond)

$$(S_{ij})_{\pm} = L_{ij} \times \begin{cases} [\phi^2]_{\pm} & i=j=p \\ [(1-\phi)^2]_{\pm} & i=j=s, \\ [2\phi(1-\phi)]_{\pm} & i \neq j \end{cases} \quad (13)$$

where

$$L_{ij} = \ln(Z_{ij}) - Z_{ij}^{-1}\{K_{ij}^0 \omega_{ij}^0 \exp(K_{ij}^0) + K_{ij}^* \omega_{ij}^* \exp(K_{ij}^*)\}. \qquad (14)$$
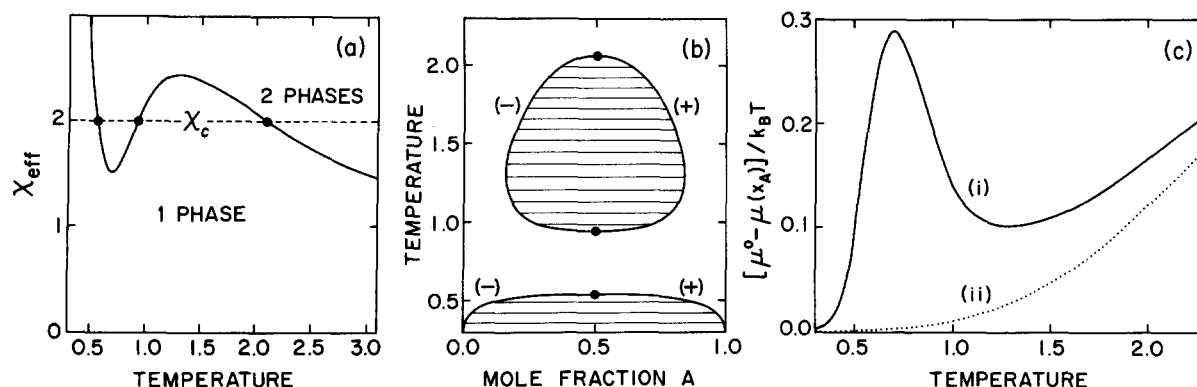
FIG. 2. Phenomenological description of a binary mixture with three critical solution points. The temperature dependence to the effective mixing parameter [Eq. (6)] shown in (a) arises from the parameters in Table I, and yields the temperature–composition phase diagram in (b). The temperature scale here and in Figs. 3–5 is in units of e_{AB}^0/k_B, and critical points are indicated by solid dots. The labeling of the two branches of the coexistence curve corresponds to that used in Figs. 4 and 5(c). The chemical potential shift is shown as line (i) in (c), contrasted with that for a "simple" system with only one UCST (ii).

III. MICROSCOPIC DESCRIPTIONS OF COMPLEX PHASE DIAGRAMS

In the following, two examples of complex phase diagrams are analyzed, with particular emphasis on the effects of interactional asymmetry. First, systems with no size-induced phase diagram asymmetry $(M = 1)$ are studied to elucidate clearly the essential physics. There then follows a brief discussion of the $M > 1$ case.

A. A symmetric phase diagram

In many aqueous mixtures showing LCSTs, such as those with the pyridines,[32–34] there is, in addition to strong AB hydrogen bonding, significant hydrogen bonding between water molecules, but little between the organic molecules. For sufficiently strong like-molecule bonding, it is possible[10–15] for a further phase separation to occur below the LCST, yielding a total of three CSTs.

Shown in Figs. 2(a) and 2(b) are the temperature dependence of χ_{eff} and the phase diagram for such a mixture, at the critical composition, described by the parameters in Table I. Temperature is measured in units of e_{AB}^0/k_B. The phase separation at the highest CST is due to the relatively favorable nondirectional interactions for AA and BB pairs. In general, the logarithm of the degeneracy ratio between the nonbonding and bonding level sets the scale for the temperature ratio between this UCST and the onset of bonding correlations.[12–14,16] When the loops are small, though, these temperatures move closer together, as is seen in the average interactional correlations $(1/2)[(G_{ij}^\alpha)_+ + (G_{ij}^\alpha)_-]$ shown in Figs. 3(a) and 3(b). Since the BB bonding is stronger than that

of AA pairs, its conjugate correlation is the larger of the two, and the BB nonbonding correlation is consequently smaller. The phase space factors ω_{AA}^* and ω_{BB}^* are smaller than ω_{AB}^*, so the LCST, driven by AB bonding, occurs at a distinctly different temperature than the lower UCST, driven by AA and BB bonding. The like-molecule bonding correlations in each of the coexisting phases are shown in Figs. 4(a) and 4(b), and we see that there is no component-exchange symmetry

FIG. 3. Average interactional correlations in the two phases for the system shown in Fig. 2.

TABLE I. Energy and entropy parameters for the system studied in Sec. II A, with $M = 1$.

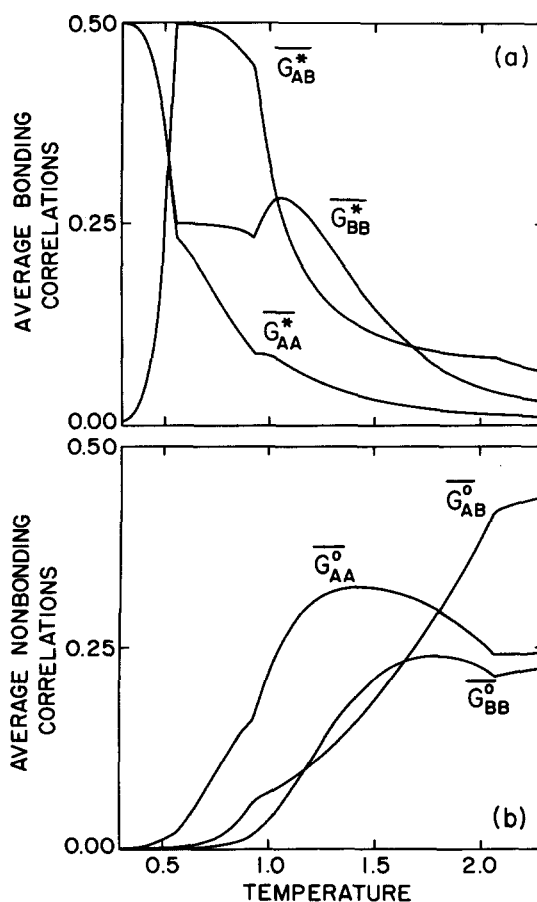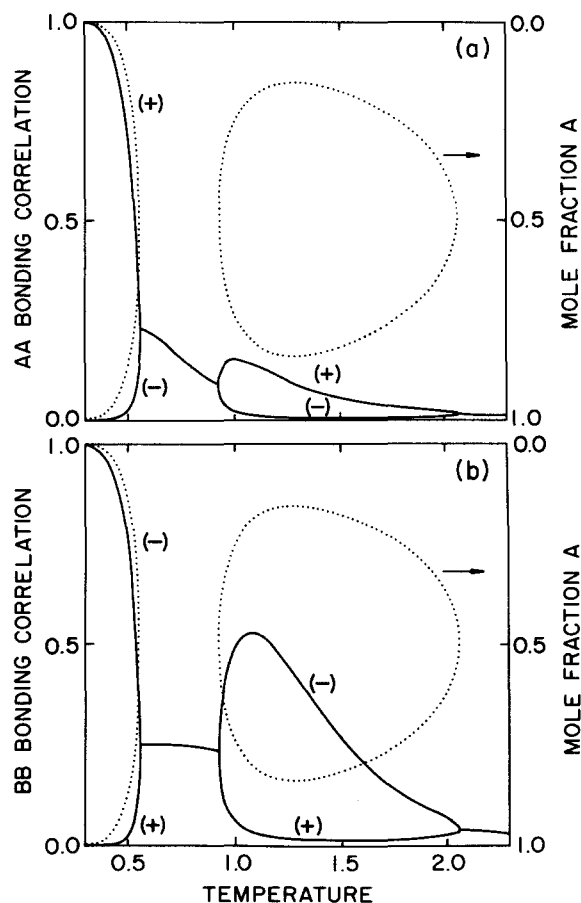| i	j	ω_{ij}^0	ω_{ij}^*	e_{ij}^0/e_{AB}^0	e_{ij}^*/e_{AB}^0
A	A	200	1	0.15	−4.2
B	B	200	1	0.15	−7.2
A	B	200	2	1	−5.15

FIG. 4. Bonding correlation functions in the coexisting phases. The labels (+) and (−) refer to the coexistence curve branches in Fig. 2.

in that, for instance, the AA correlation in the A-rich phase differs from the BB correlation in the B-rich phase. In the case that $M = 1$, though, the AB correlations are the same in the two phases, and have the values shown in Fig. 3. The separate contributions to the total entropy per bond of the system, computed using Eqs. (13) and (14), are shown in Fig. 5. The nonmonotonicity of the mixing entropy in Fig. 5(a) is compensated by the rapidly decreasing total orientational entropy, which is decomposed into its various contributions in Fig. 5(b). As we would expect, the temperature at which a particular bonding correlation begins to set in also marks the start of a rapid decrease in the orientational entropy associated with that interaction. Figure 5(c) shows that the orientational entropy, and hence the total entropy, is larger in the (+) branch, balancing against the lower energy and entropy of the (−) branch, which is more highly correlated through hydrogen bonds. The basic mechanism for a mixing free energy balance between the phases is this tradeoff of orientational energy and entropy.[21,22]

Finally, returning to Fig. 2(c), we see that the temperature dependence of the chemical potential shift $\mu(x_A) - \mu(1)$ of component A contrasts sharply with that for the Ising-like system with a simple UCST, shown as a dotted line. While the chemical potential shifts of A and B have more complicated temperature dependences than those of the simple system, their difference is exactly zero at coexistence, just as the Ising model transition occurs in zero external magnetic field.
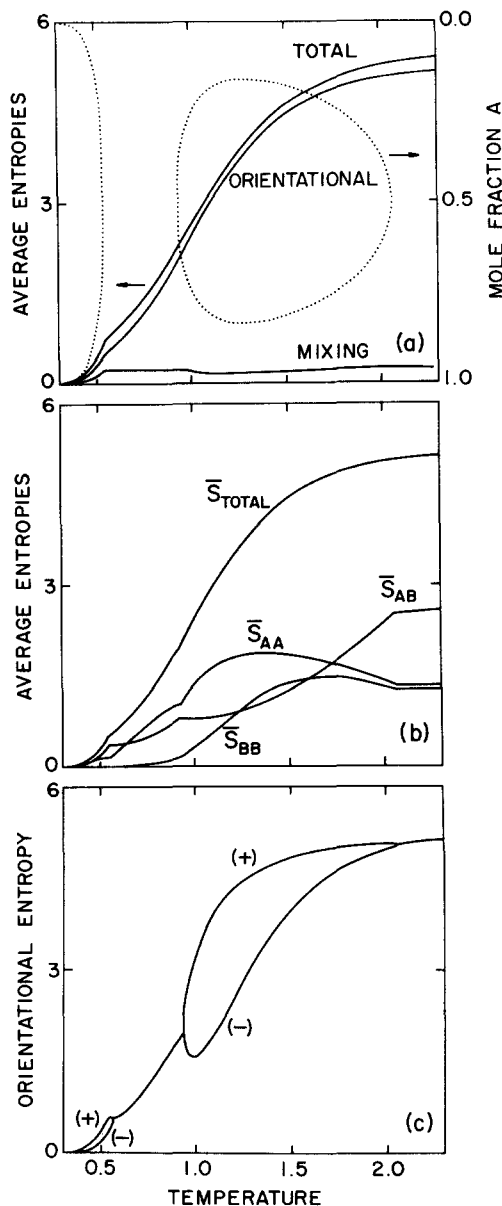

FIG. 5. Contributions to the entropy per bond. The average total, orientational, and mixing entropies are shown in (a); the separate contributions to the orientational entropy are in (b). Panel (c) displays the orientational entropy in each of the two phases.

B. An asymmetric phase diagram

The second system studied in this section is that of a moderate sized polymer $(M = 10)$ dissolved in a polar solvent, as is typical of the nonionic surfactant mixtures. The phase diagram which results from the parameters in Table II is shown in Fig. 6. Here, the temperature is in units of e^0_{ps}/k_B. Although the coexistence curve is no longer symmetric

TABLE II. Energy and entropy parameters for the system studied in Sec. II B, with $M = 10$.

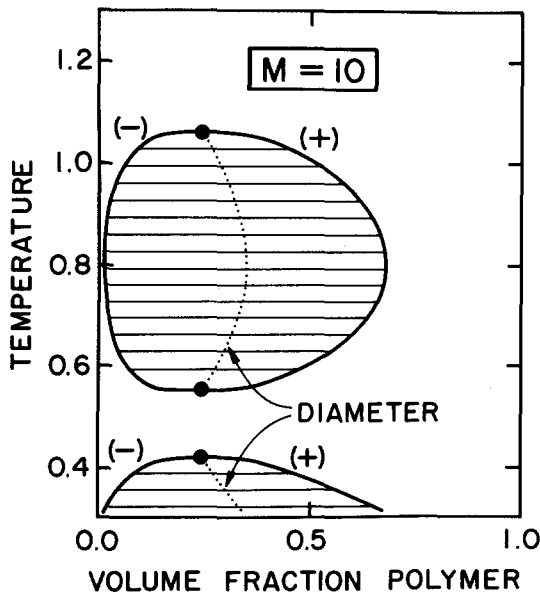| i	j	ω^0_{ij}	ω^*_{ij}	e^0_{ij}/e^0_{ps}	e^*_{ij}/e^0_{ps}
p	p	100	1	0.9	− 2.7
s	s	100	1	0.9	− 4.317
p	s	100	1	1	− 3.45

FIG. 6. Phase diagram for a hydrogen bonding polymer ($M = 10$) in a polar solvent. The model parameters are listed in Table II. Temperature is in units of e^0_{ps}/k_B.

about volume fraction one-half, there is a residual symmetry in the theory in that all of the critical points (which occur at $\chi_{eff} = \chi_c = (1 + N^{1/2})^2/2N$) are at the same critical composition $\phi_c = 1/(1 + N^{1/2})$. Indeed, in many solutions with
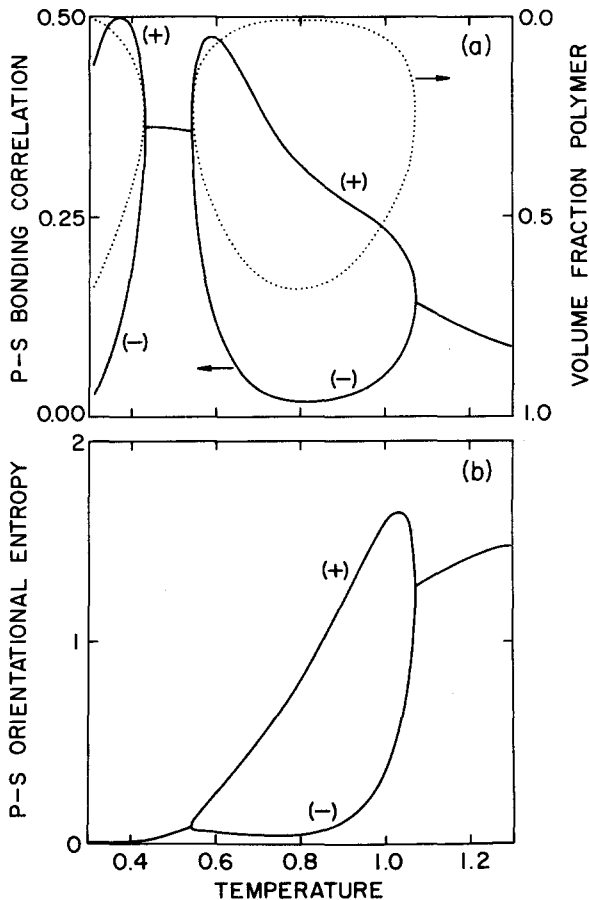

FIG. 7. Polymer–solvent bonding correlations and entropy contributions in the two phases for the system in Fig. 6. In (b), the (+) and (−) curves at the lowest temperatures are indistinguishable at the scale of the graph.

closed-loop phase diagrams, the upper and lower critical compositions are roughly equal, with the diameter showing the characteristic curvature which emerges from the present calculation.

The qualitative features of the various correlation functions and contributions to the entropy are similar to those of the symmetric phase diagram in the previous section. Of course, the unlike-molecule correlations now differ in the two phases [Fig. 7(a)] because of the asymmetric distribution of polymer and solvent between them. Again, the differences in polymer–polymer and solvent–solvent interactional characteristics lead to one phase having more orientational entropy than the other, and less (favorable) interaction energy. Shown in Fig. 7(b) is the orientational entropy per bond in the two phases due to the polymer–solvent interactions.

The size asymmetry also accentuates the extent to which a given set of monomer–solvent interactions leads to immiscibility. Thus, for a larger polymer than the one studied here, the phase diagram would consist of a single two-phase region with only an upper critical solution temperature and a pinched-in coexistence curve at roughly the temperature of the lower UCST in Fig. 6.

IV. THE ROLE OF SPECIFIC INTERACTIONS IN COEXISTENCE-CURVE ASYMMETRY

The failure of interactional asymmetries alone to change the symmetry of the coexistence curve may be understood through the following heuristic argument, which is supported by detailed calculations.[21,22]

It is perhaps simplest to discuss this issue in the context of magnetic systems, which have an intrinsic symmetry. Consider[35] a "complex" magnet (CM), with degrees of freedom beyond those accounted for by the Ising model, a "simple" magnet (SM). It is often possible to account for these extra variables by mapping the CM approximately (or occasionally exactly) onto the SM, but with an effective temperature (T_{eff}) and field (H_{eff}) which are functions of the temperature (T) and field (H) of the complex system, and also of the physical parameters which describe its "complexity." This is exactly what was done with molecular orientations in arriving at Eqs. (6) and (10), and is the essence of the decorated-lattice approach. Denoting the free energy of the SM by $F_s(T,H)$ and that of the CM by $F_c(T,H)$, we are then assuming it is possible to write

$$F_c(T,H) = F_s[T_{eff}(T,H),H_{eff}(T,H)] + G(T,H), \quad (15)$$

where G is a smooth function analogous to the zero-spin coupling K_0 in Eq. (9), and the effective fields T_{eff}, H_{eff} are assumed to be free of singularities. The phase transition in the simple system occurs at zero field, and the condition $H_{eff} = 0$ then determines the value of the "bare" field H in the two-phase region of the complex magnet.[36] Along this curve, $H_{crit}(T)$, the entropies of the two phases (+ , −) of the complex system are

$$S_c(T,H_{crit})_\pm = S_s(T_{eff})(\partial T_{eff}/\partial T)_c$$
$$- (\partial G/\partial T)_c \pm M_s(T_{eff})(\partial H_{eff}/\partial T)_c, \quad (16)$$

where

$$M_s(T_{eff}) = -\partial F_s(T_{eff},0^+)/\partial H_{eff}$$

is the spontaneous magnetization of the simple system, evaluated at its effective temperature, in the limit $H_{eff} \to 0^+$, and similarly for the reference entropy $S_s(T_{eff})$. The subscripts on the derivatives indicate that they are evaluated along $H_{crit}(T)$. Since the entropy of the SM is continuous at $H_{eff} = 0$, as is G by hypothesis, the difference in entropy across the magnetization curve of the CM is

$$\Delta S_c(T,H_{crit}) = S_c(T,H \to H_{crit}{}^+) - S_c(T,H \to H_{crit}{}^-)$$

$$= \Delta M_s(T_{eff})(\partial H_{eff}/\partial T)_c, \qquad (17)$$

where ΔM_s is the order parameter jump of the SM. Thus, the criterion for an entropy difference between the phases is a temperature-dependent effective field. The field-like energy asymmetries of the system studied on Sec. III A are responsible for the difference in both the total entropy in the two phases, and the separate contributions from the pairwise interactions shown in Fig. 5.

Similarly, the order parameter jump of the CM, at the field H_{crit}, is

$$\Delta M_c(T,H_{crit}) = M_c(T,H \to H_{crit}{}^+) - M_c(T,H \to H_{crit}{}^-)$$

$$= \Delta M_s(T_{eff})(\partial H_{eff}/\partial H)_c, \qquad (18)$$

proportional to that of the simple magnet, although its temperature dependence can be quite different, as in the case of reentrant transitions. The *average* magnetization has a more complicated structure,

$$\bar{M}_c(T,H_{crit})$$
$$= 1/2\{M_c[T,H \to H_{crit}{}^+] + M_c[T,H \to H_{crit}{}^-]\}$$
$$= -(\partial G/\partial H)_c + S_s(T_{eff})(\partial T_{eff}/\partial H)_c, \qquad (19)$$

showing that the criterion for a nonzero average magnetization, and hence a shifted coexistence-curve diameter, is a field-dependent effective temperature.[37,38] Yet, the effective "temperature" in the present theory, Eq. (6), has no dependence on the chemical potentials, hence the symmetry of the "simple" coexistence curve is preserved in averaging over the orientational degrees of freedom (in the case $M = 1$). This independence is not simply a consequence of the mean field level of the approximation, for it appears in calculations which explicitly account for fluctuations.[21,22]

A more microscopic argument that the orientational degrees of freedom, as considered here, do not mix the thermodynamic fields so as to give asymmetry is as follows: In the standard correspondence between the Ising model and a lattice model of a simple binary mixture, there are two important circumstances involving component asymmetry in which the latter can be mapped exactly onto the former. In the first, the mixture can be described by the usual microscopic energies e_{ij}, but $e_{AA} \neq e_{BB}$. This contrasts with the zero field Ising model, which has the same energy for up–up and down–down nearest neighbor spins. It is straightforward to show[19] that this inequality acts simply to redefine the values of the component chemical potentials by additive constants, and does not affect any thermodynamic properties. A second instance in which one recovers the Ising model with a shifted field is when one of the species has some degree of freedom which gives it an extra overall degeneracy. Again, the only significant effect of this asymmetry is, in the magnetic language, to shift the zero of the reduced field

$-H/k_B T$ by $(1/2)\ln(\omega)$ where ω is the extra degeneracy.[22] This shift also does not alter the symmetry of the coexistence curve.

This preservation of the symmetry remains valid if, in either or both of these two cases, the microscopic dissimilarities are given an arbitrary temperature dependence: The only result is that the derivative $(\partial H_{eff}/\partial T)_c$ in Eq. (17) will be nonzero, leading to an entropy asymmetry between the phases. We believe that the orientational degrees of freedom studied herein have done nothing more than introduce such a temperature dependence to the energy and degeneracy splittings between like-molecule pairs, where the origin of the dependence is the multiple-level structure of the local free energies.[21,22]

This significance of a field-dependent interaction suggests why decorated-lattice calculations with asymmetric nearest-neighbor interactions have produced coexistence-curve asymmetry. If the bare field (chemical potential difference) is the only odd interaction in the theory then the symmetry is, of course, not broken.[28] However, interactional asymmetries conditional upon *non-Ising* degrees of freedom introduce in addition the field-like terms described above. Thus, because the partial partition functions involve a statistical trace over the Ising variables on the secondary sites, in addition to their orientational degrees of freedom, there appears more than one field-like term, and the decimation step explicitly creates a dependence of the effective interaction on the bare field.[22] Stated another way, asymmetric coexistence curves appear to be due to the way in which a DL projects a system with *four* types of particles (A and B molecules on both primary and secondary sites) onto the Ising model. In real-space renormalization-group calculations for these systems,[22] which also involve statistical traces over the Ising variables in their decimation steps, the two-component nature of the system is preserved since all sites have the same set of spin variables.

The necessity of including density fluctuations in a theory of phase diagram asymmetry can be seen even at the level of the van der Waals equation of state of a binary mixture.[39] In the infinite-pressure limit of that model, the free energy of mixing of equal-sized particles is symmetric around composition one-half, independent of the symmetry of the like-particle attractive interactions. Only when the pressure is finite, and hence density fluctuations are allowed, do energetic asymmetries shift the coexistence curve.

In the usual mixture–magnet correspondence, the lattice is taken to be completely full, which is analogous to the above close-packed limit of the van der Waals model. As shown in detail elsewhere,[21,22] the finiteness of the pressure may be incorporated into the description of binary mixtures by embedding the complex hierarchy of pairwise energy levels described in this paper in a larger space of statistical variables which includes lattice vacancies controlled by an appropriate chemical potential. This approach is quite different from that of the decorated-lattice calculations, in which the structure of the lattice (i.e., two inequivalent sublattices with different coordination numbers) appears to mimic the effects of density fluctuations. In this sense, the DL has a *quenched* extra "degree of freedom", whereas the

vacancies are in thermodynamic equilibrium, and thus aptly described as *annealed*.

V. DISCUSSION

The notion of considering local free energies described in terms of multiple-level partition functions, as a generalization of simple energies, finds application in a variety of systems. In fact, many quite distinct "reentrant" phenomena can be viewed as essentially the same manifestation of this basic free energy structure.

For those nonionic surfactant systems which do not form micelles, such as the shorter members of the polyoxyethylene series, the approach in Sec. III B is directly applicable. In micellar solutions and microemulsions, showing lower consolute points, for which a theory of the micelle structure may be developed, the interactions of the polar head groups of the amphiphiles with the aqueous component can be represented by a multiple-level hierarchy.[40] Recent theoretical studies of the nonionic surfactant systems have been unable to describe the existence of both upper and lower critical solution temperatures in a unified way.[41]

Kahlweit and collaborators[5–7] have studied in great detail the phase equilibrium properties of aqueous solutions of nonionic surfactants and a third, nonpolar species. Their basic conclusion is that the properties of the regions of three-phase coexistence can be understood as arising from the confluence of the upper miscibility gap of the binary surfactant + water mixture with the lower phase separation of the aqueous + nonpolar system. The present theory, generalized to three components, explicitly accounts for the strongly temperature-dependent surfactant–water interactions and the entropic effects due to molecular size asymmetry.

Finally, very recent experimental work[42] by Subramanian, Wittebort, and Dupré highlights the important role that hydrogen bonding has on a variety of thermodynamic and molecular properties. They investigated the effect that the conformational (helix–coil) transition of poly-γ-benzyl-L-glutamate (PBLG) has on its nematic ordering.[43–46] In certain hydrogen-bonding solvents, PBLG shows an inverted helix–coil transition,[43] which is, in many respects, thermodynamically equivalent to a lower critical solution point in a binary liquid mixture.[47] At sufficiently high concentrations, the conformational transitions intersect a region of two-phase coexistence which has the topology of a closed-loop phase diagram, and within the coexistence curve nematic ordering occurs. The same temperature-dependent interactions which drive the reentrant solubility transition are clearly responsible for the reentrant conformational transitions, and may be described with the present methods.

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