A generalization of Widom's model of microemulsions

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We construct a generalization of Widom's model of microemulsions which permits the contact of polar and apolar material. This is necessary to explain the behavior of certain short chain amphiphilic systems. The same interactions have previously been proposed by Robledo, but the partition function which he derived from these interactions and discussed in detail in his paper (a partition function of a spin 1 Ising system) does not quite represent these interactions. We arrive at a spin 3/2 Ising model with nearest neighbor interactions. Robledo's spin 1 form is recovered as an approximation whose range of validity is discussed. We particularly investigate the limit towards Widom's model, the progression of Winsor microemulsion, and the question of retrograde solubility in the binary water–amphiphile subsystem, which has been advocated by Robledo.

I. INTRODUCTION

Widom[1,2] has introduced a lattice model of microemulsions in which the links of a simple cubic lattice are occupied by water, oil, or amphiphile "molecules." The endpoints of these link-molecules are assigned to be either of type A (water or polar head of the amphiphile) or of type B (oil or hydrocarbon chain of the amphiphile) as shown in Fig. 1(a). Only A or B ends are allowed to meet at each lattice site [Figs. 1(b), 1(c)]. This makes his construction equivalent to an Ising model. To account for the formation of microemulsions with its typical three-phase coexistence and the associated low interfacial tension, one has to introduce next nearest neighbor interactions representing mean[2] or Gaussian[3] curvature energies of the surfactant film.

Widom[2] has calculated some properties of his model in a generalized mean-field approximation using only the mean curvature energy plus contact energies between amphiphile molecules. The resulting picture of phase equilibria and interfacial tensions is quite promising and one may hope that the model does indeed describe some features of microemulsions.

It is, however, obvious that the infinite repulsions between the unlike A and B ends impose constraints which are often not met in real systems. Although the infinite repulsion is quite appropriate if A and B represent water and a strongly hydrophobic oil, the three other possible A–B encounters (water–hydrocarbon amphiphile tail, oil–polar amphiphile head, hydrocarbon tail–polar head of the amphiphile) may have much weaker repulsions. This is, for example, witnessed by the monomer or oligomer solution of short chain amphiphiles in pure water or oil.[4] Despite the absence of micellar aggregation at the binary composition boundaries, such systems may form proper microemulsions.[5]

Consequently, in order to account for the variation of microemulsions with the chemical nature of its components, it may be important to soften the infinite AB repulsions and to lift the energetic degeneracy of the four possible AB encounters. As Robledo[6] has pointed out, such a generalization will also permit the study of the evolution of microemulsions from conventional solution behavior.

In the work of Wheeler and Widom,[7] which forms the basis of Widom's models, it has already been noticed that such softened repulsions may be incorporated using an Ising model on a decorated lattice. An explicit formulation has been given by Huckaby, Kowalski and Shinmi.[8] If these models are restricted to nearest neighbor interactions, only three energies ϵ_{AA}, ϵ_{AB}, ϵ_{BB} are possible and no distinction can be made as to whether A refers to the polar head of the amphiphile or to water and whether B refers to oil or the hydrocarbon tail of the amphiphile. To differentiate the various AB (as well as AA or BB) energies from each other, four-spin interactions have to be introduced.

Robledo[6] has proposed another generalization of Widom's model which allows for arbitrary values of all the possible pair interactions between water (A), oil (B), amphiphile polar head (a) and hydrocarbon tail (b). His formulation allows one to incorporate Widom's curvature energies[2] using nearest neighbor interactions only. The price which has to be paid for these simple interactions is an enlargement of the spin space. It requires more than the two local states of the spin 1/2 Ising model.

Unfortunately, Robledo's claim that Widom's model and its generalization is equivalent to a spin 1 Ising model is wrong. As we shall show in the sequel, the equivalence holds for the spin 3/2 model only. Robledo's spin 1 formulation may then be recovered as an approximation.

II. THE SPIN 3/2 ISING MODEL

In order to account for the four different types of molecular constituents in a ternary water–oil–amphiphile solu-

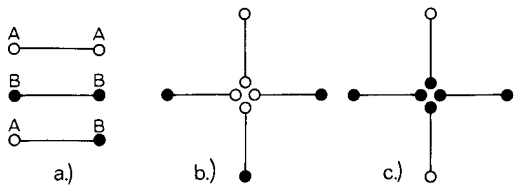

FIG. 1. (a) The three link molecules AA (water), BB (oil), and AB (amphiphile), (b) A endpoints, (c) B endpoints meeting at a lattice site.

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tion, Robledo introduces the link-molecules AA for water, BB for oil and ab for the amphiphile, a representing its polar head and b its apolar hydrocarbon tail [Fig. 2(a)]. All possible combinations of A, B, a, b ends are allowed to meet at the lattice sites. Each pair of links which are joined at a right angle gives rise to an energy ϵ_{RS} where $R, S \in \{A, B, a, b\}$ label the two molecular ends which meet at the central site [Fig. 2(b)]. For $R,S = a,a$ or b,b this construction includes Widom's mean curvature energies.[2] We shall slightly generalize this scheme to include also Widom's contact interactions, assigning the energies δ_{RS} ($R,S \in \{A, B, a,b\}$) to the encounter of the species R and S at the central site of a straight pair of links [Fig. 2(b)].

Setting up the partition function, Robledo has tried to sum directly over the two possible orientations of each amphiphile molecule. In doing so he apparently commits an error and his partition function [his Eq. (5)] ignores the coupling between the amphiphile orientations. In order to account for that, we are forced to leave the summation undone. Then the four possible occupations on each link of the simple cubic lattice may be parametrized by a spin 3/2 variable. For our purposes it will be convenient to use a mixed spin 1–spin 1/2 representation which represents a standard way of writing spin 3/2 models.[9] Introducing separate spin variables for the occupational and orientational degree of freedom, we set $s_i(\mathbf{x}) = 0, +1, -1$ for amphiphile, water, oil on the link which emerges from the site $\mathbf{x}$ along one of the three positive lattice vectors $\mathbf{a}_i$ ($i = 1,2,3$). If $s_i(\mathbf{x}) = 0$, a further spin 1/2 variable specifies the orientation of the amphiphile: $\sigma_i(\mathbf{x}) = +1$ or -1 if the a end or the b end of the amphiphile is at the site $\mathbf{x}$ (Fig. 3).

For a compact notation and easier calculations it is a convenient standard procedure[9,10] to introduce the projectors onto the spin states:

$$P_i^0(\mathbf{x}) = 1 - s_i^2(\mathbf{x}), \quad P_i^{\pm}(\mathbf{x}) = \tfrac{1}{2} s_i(\mathbf{x})[s_i(\mathbf{x}) \pm 1],$$
$$Q_i^{\pm}(\mathbf{x}) = \tfrac{1}{2}[1 \pm \sigma_i(\mathbf{x})], \tag{1}$$

which assume the values 0 or 1 for the four exclusive link occupations. They evidently obey the relations

$$P_i^0(\mathbf{x}) + P_i^+(\mathbf{x}) + P_i^-(\mathbf{x}) = 1,$$
$$[P_i^0(\mathbf{x})]^2 = P_i^0(\mathbf{x}),$$
$$[P_i^{\pm}(\mathbf{x})]^2 = P_i^{\pm}(\mathbf{x}),$$
$$P_i^{\pm}(\mathbf{x}) P_i^0(\mathbf{x}) = P_i^+(\mathbf{x}) P_i^-(\mathbf{x}) = 0,$$
$$Q_i^+(\mathbf{x}) + Q_i^-(\mathbf{x}) = 1, \quad [Q_i^{\pm}(\mathbf{x})]^2 = Q_i^{\pm}(\mathbf{x}),$$
$$Q_i^+(\mathbf{x}) Q_i^-(\mathbf{x}) = 0. \tag{2}$$

In terms of these variables, the partition function is

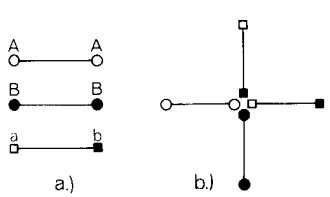

FIG. 2. (a) The three molecules in Robledo's model. (b) Four molecules meeting at a site (in two dimensions) producing the energy $\epsilon_{AB} + \epsilon_{Ab} + \epsilon_{Ba} + \epsilon_{ab} + \delta_{Aa} + \delta_{Bb}$.

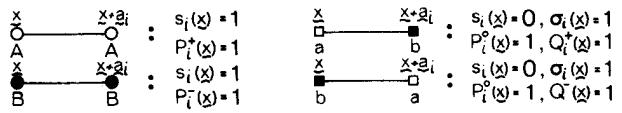

FIG. 3. The four possible link occupations and the associated spin and projector values.

$$Z = \left[\prod_{\mathbf{x},i} \sum_{s_i(\mathbf{x})=0,\pm 1} \sum_{\sigma_i(\mathbf{x})=\pm 1}\right] \exp\left\{-\frac{E}{kT} + \mu \sum_{\mathbf{x},i} P_i^0(\mathbf{x}) + \nu \sum_{\mathbf{x},i} [P_i^+(\mathbf{x}) - P_i^-(\mathbf{x})]\right\}. \tag{3}$$

Here E is the energy which will be specified subsequently. μ and ν are chemical potentials which control the amphiphile concentration (μ) and the water-to-oil ratio (ν). Notice that the $Q_i^{\pm}(\mathbf{x})$ do not enter in the chemical potential terms as in general there will be no external field which allows manipulation of the overall amphiphile orientation. In Eq. (3) we have counted each water and oil occupation twice, allowing these molecules to have the same orientational degrees of freedom as the amphiphile. If one prefers to count each water or oil molecule only once, one may insert a factor $P_i^0(\mathbf{x}) + \frac{1}{2}P_i^+(\mathbf{x}) + \frac{1}{2}P_i^-(\mathbf{x})$ for each link into Eq. (3). Due to Eq. (2) this merely introduces a shift in the chemical potential $\mu \to \mu - \ln 2$ and an overall constant factor for Z which has no consequences for the properties of the model.

For the purpose of writing down the interaction energy E, it is convenient to introduce also projectors P, Q for links which emerge from a site $\mathbf{x}$ along one of the three negative lattice vectors $-\mathbf{a}_i$. The following definitions will facilitate the notation:

$$s_{-i}(\mathbf{x}) \equiv s_i(\mathbf{x} - \mathbf{a}_i), P_{-i}^{\pm}(\mathbf{x}) = P_i^{\pm}(\mathbf{x} - \mathbf{a}_i),$$
$$P_{-i}^0(\mathbf{x}) = P_i^0(\mathbf{x} - \mathbf{a}_i),$$
$$\sigma_{-i}(\mathbf{x}) \equiv -\sigma_i(\mathbf{x} - \mathbf{a}_i), \quad Q_i^{\pm}(\mathbf{x}) = Q_i^{\mp}(\mathbf{x} - \mathbf{a}_i). \tag{4}$$

With this convention Fig. 3 is also valid if one replaces $i \to -i$ along with $\mathbf{a}_i \to -\mathbf{a}_i$.

The energy may be expressed as a sum over the contributions from the lattice sites. At each site, 12 pairs of bent links and three pairs of straight links contribute to the energy

$$\frac{E}{kt} = \sum_{\mathbf{x},\mu \neq \nu} \{\tfrac{1}{2}\beta_{AA} P_\mu^+ P_\nu^+ + \tfrac{1}{2}\beta_{BB} P_\mu^- P_\nu^- + \beta_{AB} P_\mu^+ P_\nu^- + P_\mu^0(\beta_{Aa} Q_\mu^+ P_\nu^+ + \beta_{Bb} Q_\mu^- P_\nu^- + \beta_{Ab} Q_\mu^- P_\nu^+ + \beta_{Ba} Q_\mu^+ P_\nu^-) + P_\mu^0 P_\nu^0 (\tfrac{1}{2}\beta_{aa} Q_\mu^+ Q_\nu^+ + \tfrac{1}{2}\beta_{bb} Q_\mu^- Q_\nu^- + \beta_{ab} Q_\mu^+ Q_\nu^-)\}(\mathbf{x}). \tag{5}$$

The indices μ,ν run over the values $\pm i$ and all P,Q should be read as $P(\mathbf{x}), Q(\mathbf{x})$. The factors 1/2 in front of the diagonal β_{RR} account for the fact that these terms are included twice in the summation over $\mu \neq \nu$. As we want to allow for different energies of bent and straight pairs of links, we identify

$$\beta_{RS} = \begin{cases} \epsilon_{RS}/kT, & \mu \neq -\nu \\ \delta_{RS}/kT, & \mu = -\nu \end{cases}, \quad R,S \in \{A,B,a,b\}. \tag{6}$$

Notice that although Eqs. (3) and (5) define a nearest neighbor spin 3/2 model, the model is unconventional in two

respects: As the spins are defined on the links of a simple cubic lattice, an unusual nearest neighbor structure results. Moreover, if $\delta_{RS} \neq \epsilon_{RS}$ in Eq. (6) the interactions have a directional dependence.

The infnite repulsions of polar–apolar species in Widom's model correspond to the limit

$$\beta_{AB} = \beta_{Ab} = \beta_{Ba} = \beta_{ab} = \beta \to \infty \tag{7}$$

and a particularly simple condition which reproduces his mean curvature and contact energies is

$$\beta_{AA} = \beta_{BB} = \beta_{Aa} = \beta_{Bb} = 0,$$
$$\beta_{aa} = K(1+\lambda)/kT, \quad \beta_{bb} = K(1-\lambda)/kT \tag{8}$$

with K and λ being Widom's rigidity and spontaneous curvature parameters.[2] As we will show in the next section, Eq. (8) is not a necessary condition to recover Widom's model in the limit (7). For the general case, K and λ will be given in Eq. (14).

III. THE LIMIT OF WIDOM'S SPIN 1/2 MODEL

It is useful to see how our partition function (3) reduces to the spin 1/2 form of Widom's model in the limit (7). We rewrite the energy (5) as

$$E = E_1 + E_2,$$

$$E_1/kT = \beta \sum_{\mathbf{x},\mu \neq \nu} \{P_\mu^+ P_\nu^- + P_\mu^0 (Q_\mu^- P_\nu^+ + Q_\mu^+ P_\nu^-) + P_\mu^0 P_\nu^0 Q_\mu^+ Q_\nu^-\}(\mathbf{x})$$

$$\frac{E_2}{kT} = \sum_{\mathbf{x},\mu \neq \nu} \{\tfrac{1}{2}\beta_{AA} P_\mu^+ P_\nu^+ + \tfrac{1}{2}\beta_{BB} P_\mu P_\nu^- + P_\mu^0 (\beta_{Aa} Q_\mu^+ P_\nu^+ + \beta_{Bb} Q_\mu^- P_\nu^-) + P_\mu^0 P_\nu^0 (\tfrac{1}{2}\beta_{aa} Q_\mu^+ Q_\nu^+ + \tfrac{1}{2}\beta_{bb} Q_\mu^- Q_\nu^-)\}(\mathbf{x}). \tag{9}$$

In the limit $\beta \to \infty$, the occupations of E_1 are forbidden and one has

$$\lim_{\beta\to\infty} e^{-E_1/kT} = \prod_{\mathbf{x},\mu<\nu} F_{\mu\nu}(\mathbf{x}),$$
$$F_{\mu\nu}(\mathbf{x}) = A_\mu^+(\mathbf{x}) A_\nu^+(\mathbf{x}) + A_\mu^-(\mathbf{x}) A_\nu^-(\mathbf{x}),$$

with

$$A_\mu^\pm(\mathbf{x}) = P_\mu^\pm(\mathbf{x}) + P_\mu^0(\mathbf{x}) Q_\mu^\pm(\mathbf{x}).$$

As the $A_\mu^\pm(\mathbf{x})$ are projectors $\{A_\mu^+(\mathbf{x}) A_\mu^-(\mathbf{x}) = 0$, $[\mathbf{A}_\mu^\pm(\mathbf{x})]^2 = \mathbf{A}_\mu^\pm(\mathbf{x})\}$, one has

$$\prod_{\mu<\nu} F_{\mu\nu}(\mathbf{x}) = \prod_\mu A_\mu^+(\mathbf{x}) + \prod_\mu A_\mu^-(\mathbf{x})$$
$$= \sum_{s(\mathbf{x})=\pm 1} \left\{\frac{1+s(\mathbf{x})}{2} \prod_\mu A_\mu^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2} \prod_\mu A_\mu^-(\mathbf{x})\right\}$$
$$= \sum_{s(\mathbf{x})=\pm 1} \prod_\mu \left\{\frac{1+s(\mathbf{x})}{2} A_\mu^+(\mathbf{x}) \times \frac{1-s(\mathbf{x})}{2} A_\mu^-(\mathbf{x})\right\}.$$

Having introduced the spin 1/2 variables $s(\mathbf{x})$, the partition function (3) reads

$$Z_{\beta\to\infty} = \left[\prod_{\mathbf{x}} \sum_{s(\mathbf{x})=\pm 1}\right]\left[\prod_{\mathbf{x},i} \sum_{s_i(\mathbf{x})=0,\pm 1} \sum_{\sigma_i(\mathbf{x})=\pm 1}\right] \times e^{-E_2/kT + \mu \sum_{\mathbf{x},i} P_i^0(\mathbf{x}) + \nu \sum_{\mathbf{x},i} [P_i^+(\mathbf{x}) - P_i^-(\mathbf{x})]} \times \prod_{\mathbf{x},\mu} \left\{\frac{1+s(\mathbf{x})}{2} A_\mu^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2} A_\mu^-(\mathbf{x})\right\}. \tag{10}$$

As we want to perform the summation over the spin 3/2 variables $s_i(\mathbf{x})$, $\sigma_i(\mathbf{x})$, we rewrite the last factor as

$$\prod_{\mathbf{x},\mu} \left\{\frac{1+s(\mathbf{x})}{2} A_\mu^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2} A_\mu^-(\mathbf{x})\right\} = \prod_{\mathbf{x},i} \left\{\frac{1+s(\mathbf{x})}{2} A_i^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2} A_i^-(\mathbf{x})\right\} \times \prod_{\mathbf{x},i} \left\{\frac{1+s(\mathbf{x})}{2} A_{-i}^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2} A_{-i}^-(\mathbf{x})\right\}.$$

With the aid of Eq. (4) and the shift $\mathbf{x} \to \mathbf{x} + \mathbf{a}_i$, this becomes

$$\prod_{\mathbf{x},i} \left\{\frac{1+s(\mathbf{x})}{2}[P_i^+(\mathbf{x}) + P_i^0(\mathbf{x}) Q_i^+(\mathbf{x})] + \frac{1-s(\mathbf{x})}{2}[P_i^-(\mathbf{x}) + P_i^0(\mathbf{x}) Q_i^-(\mathbf{x})]\right\} \times \left\{\frac{1+s(\mathbf{x}+\mathbf{a}_i)}{2}[P_i^+(\mathbf{x}) + P_i^0(\mathbf{x}) Q_i^-(\mathbf{x})] + \frac{1-s(\mathbf{x}+\mathbf{a}_i)}{2}[P_i^-(\mathbf{x}) + P_i^0(\mathbf{x}) Q_i^+(\mathbf{x})]\right\}$$
$$= \prod_{\mathbf{x},i} \left\{\frac{1+s(\mathbf{x})}{2}\frac{1+s(\mathbf{x}+\mathbf{a}_i)}{2} P_i^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2}\frac{1-s(\mathbf{x}+\mathbf{a}_i)}{2} P_i^-(\mathbf{x}) + \frac{1+s(\mathbf{x})}{2}\frac{1-s(\mathbf{x}+\mathbf{a}_i)}{2} P_i^0(\mathbf{x}) Q_i^+(\mathbf{x}) + \frac{1-s(\mathbf{x})}{2}\frac{1+s(\mathbf{x}+\mathbf{a}_i)}{2} P_i^0(\mathbf{x}) Q_i^-(\mathbf{x})\right\}. \tag{11}$$

The projectors P, Q in the chemical potentials and in the energy E_2 in Eq. (10) may now be identified as

$$P_i^\pm(\mathbf{x}) = \frac{1 \pm s(\mathbf{x})}{2}\frac{1 \pm s(\mathbf{x}+\mathbf{a}_i)}{2},$$
$$P_i^0(\mathbf{x}) Q_i^\pm(\mathbf{x}) = \frac{1 \pm s(\mathbf{x})}{2}\frac{1 \mp s(\mathbf{x}+\mathbf{a}_i)}{2},$$
$$P_i^0(x) = \frac{1 - s(x) s(x+a_i)}{2}, \tag{12}$$

and the summation over the spin 3/2 variables $s_i(\mathbf{x})$, $\sigma_i(\mathbf{x})$ may be performed, as they occur only in the factorized form [Eq. (11)] in the partition function [Eq. (10)]. The result is

$$Z_{\beta\to\infty} = \left[\prod_{\mathbf{x}} \sum_{s(\mathbf{x})=\pm 1}\right] \exp\left\{-E_2/kT + \frac{\mu}{2}\sum_{\mathbf{x},i}[1 - s(\mathbf{x}) s(\mathbf{x}+\mathbf{a}_i)] + 3\nu \sum_{\mathbf{x}} s(\mathbf{x})\right\}, \tag{13}$$

with E_2 [Eq. (9)] expressed in terms of the spin 1/2 Ising variables $s(\mathbf{x})$ using Eq. (12).

Employing Eq. (8), it is trivial to verify that this is indeed the partition function of Widom's model. To express Widom's interaction parameters K, λ in terms of the β_{RS} in the general case, one may consider a single pair of bent links which contributes to E_2 in Eq. (9). With Eq. (12), this contribution may be expressed in terms of the spin 1/2 Ising variables which reside on the sites of the lattice. As the contributions which are linear in s or which couple nearest neighbors $s(\mathbf{x})s(\mathbf{x}+\mathbf{a}_i)$ may be absorbed in the chemical potential terms of Eq. (13), only the quadratic s terms which couple next to nearest neighbors and the terms cubic in s are relevant for the interaction. Comparing with Widom's work[2] or with the special case defined in Eq. (8), one obtains that Widom's K and λ parameters are given by

$$\frac{K(1+\lambda)}{kT} = \beta_{aa} - 2\beta_{Aa} + \beta_{AA},$$
$$\frac{K(1-\lambda)}{kT} = \beta_{bb} - 2\beta_{Bb} + \beta_{BB}. \tag{14}$$

IV. THE LIMIT OF ROBLEDO'S SPIN 1 MODEL

Robledo's spin 1 formulation[6] may be obtained by an approximate summation over the amphiphile orientations. For this purpose we split the energy in Eq. (5) into the first three Q-independent terms which we call E_0 and rewrite the Boltzmann factors of the Q-dependent energy part E_1 as

$$e^{-E_1/kT} = \prod_{\mathbf{x}} \prod_{\mu<\nu} [1 + G_{\mu\nu}(\mathbf{x})],$$

$$\begin{aligned} G_{\mu\nu}(\mathbf{x}) = {} & P_\mu^0 \{K_{Aa} Q_\mu^+ P_\nu^+ + K_{Bb} Q_\mu^- P_\nu^- \\ & + K_{Ab} Q_\mu^- P_\nu^+ + K_{Ba} Q_\mu^+ P_\nu^- \} \\ & + P_\mu^0 P_\nu^0 \{\tfrac{1}{2} K_{aa} Q_\mu^+ Q_\nu^+ + \tfrac{1}{2} K_{bb} Q_\mu^- Q_\nu^- \\ & + K_{ab} Q_\mu^+ Q_\nu^- \} + (\mu \leftrightarrow \nu). \end{aligned} \tag{15}$$

Here again all projectors P,Q should be read as $P(\mathbf{x})$, $Q(\mathbf{x})$ and the K_{RS} are defined as

$$K_{RS} = e^{-\beta_{RS}} - 1; \quad R,S \in \{A,B,a,b\}. \tag{16}$$

It is easy to verify that this does indeed properly reproduce the Boltzmann weights of the various configurations.

Rewriting the partition function (3) as

$$\begin{aligned} Z = {} & \left[\prod_{\mathbf{x},i} \sum_{s_i(\mathbf{x})=0,\pm 1}\right] \exp\Big\{ -E_0/kT + \mu \sum_{\mathbf{x},i} P_i^0(\mathbf{x}) \\ & + \nu \sum_{\mathbf{x},i} [P_i^+(\mathbf{x}) - P_i^-(\mathbf{x})] \Big\} \tilde{Z}[P], \end{aligned} \tag{17}$$

$$\tilde{Z}(P) = \left[\prod_{\mathbf{x},i} \sum_{\sigma_i(\mathbf{x})=\pm 1}\right] \prod_{\mathbf{x},\mu<\nu} [1 + G_{\mu\nu}(\mathbf{x})], \tag{18}$$

we may expand the products over $1+G$ and organize the terms by the number of involved link pairs. Keeping only single pairs, we approximate

$$\prod_{\mathbf{x},\mu<\nu} [1 + G_{\mu\nu}(\mathbf{x})] \to 1 + \sum_{\mathbf{x},\mu<\nu} G_{\mu\nu}(\mathbf{x}). \tag{19}$$

The summation over $\sigma_i(x)$ may now be performed easily in this lowest order approximation. Extracting an overall factor 2^{3N}, where N is the total number of lattice sites, this amounts to replacing the $Q_\mu^\pm(\mathbf{x})$ in Eq. (15) by 1/2. Denoting this new G by $\bar{G}$, we approximate in a second step

$$\begin{aligned} \tilde{Z}_0[P] &= \left[\prod_{\mathbf{x},i} \sum_{\sigma_i(\mathbf{x})=\pm 1}\right] \left[1 + \sum_{\mathbf{x},\mu<\nu} G_{\mu\nu}(\mathbf{x})\right] \\ &= 2^{3N} \left[1 + \sum_{\mathbf{x},\mu<\nu} \bar{G}_{\mu\nu}(\mathbf{x})\right] \\ &\to 2^{3N} \prod_{\mathbf{x},\mu<\nu} [1 + \bar{G}_{\mu\nu}(\mathbf{x})]. \end{aligned} \tag{20}$$

This procedure is well known from the conventional high-temperature expansions of spin models. Both approximation steps together amount to the summation over all disconnected link pairs on the lattice. Inserting the approximate $\tilde{Z}^{(0)}$ into Eq. (17) we may again rewrite the $(1+\bar{G})$ factors as an energy in the exponent of the Boltzmann factor with the result

$$\begin{aligned} Z^{(0)} = {} & 2^{3N} \left[\prod_{\mathbf{x},i} \sum_{s_i(\mathbf{x})=0,\pm 1}\right] \exp\Big\{\mu \sum_{\mathbf{x},i} P_i^0(\mathbf{x}) \\ & + \nu \sum_{\mathbf{x},i} [P_i^+(\mathbf{x}) - P_i^-(\mathbf{x})] - \bar{E}/kT \Big\}. \end{aligned} \tag{21}$$

The new energy is

$$\begin{aligned} \frac{\bar{E}}{kT} = \sum_{\mathbf{x},\mu\neq\nu} \{ & \tfrac{1}{2}\beta_{AA} P_\mu^+ P_\nu^+ + \tfrac{1}{2}\beta_{BB} P_\mu^- P_\nu^- + \beta_{AB} P_\mu^+ P_\nu^- \\ & + K_+ P_\mu^+ P_\nu^0 + K_- P_\mu^- P_\nu^0 + \tfrac{1}{2} K_0 P_\mu^0 P_\nu^0 \}(\mathbf{x}), \end{aligned} \tag{22}$$

where we have

$$\begin{aligned} K_+ &= -\ln\{(e^{-\beta_{Aa}} + e^{-\beta_{Ab}})/2\}, \\ K_- &= -\ln\{(e^{-\beta_{Bb}} + e^{-\beta_{Ba}})/2\}, \\ K_0 &= -\ln\{(e^{-\beta_{aa}} + e^{-\beta_{bb}} + 2e^{-\beta_{ab}})/4\}. \end{aligned} \tag{23}$$

This expression does indeed reproduce Robledo's result if one uses $\delta_{RS} = 0$ in Eq. (6).

Using $P_i^+(\mathbf{x}) + P_i^-(\mathbf{x}) + P_i^0(\mathbf{x}) = 1$, the energy may be rewritten in a form which employs P^+P^-, P^+P^0, P^-P^0 interactions only. This allows us to read off directly the behavior at the binary boundaries. Absorbing linear terms $\sim \Sigma_{\mathbf{x},i}[P_i^+(\mathbf{x}) - P_i^-(\mathbf{x})]$, $\sim \Sigma_{\mathbf{x},i} P_i^0(\mathbf{x})$ in the chemical potentials and dropping an irrelevant constant, one obtains

$$\frac{\bar{E}}{kT} = \sum_{\mathbf{x},\mu\neq\nu} \{ a P_\mu^+ P_\nu^0 + b P_\mu^- P_\nu^0 + c P_\mu^+ P_\nu^- \}(\mathbf{x}) \tag{24}$$

with

$$\begin{aligned} a &= K_+ - \tfrac{1}{2}K_0 - \tfrac{1}{2}\beta_{AA}, \\ b &= K_- - \tfrac{1}{2}K_0 - \tfrac{1}{2}\beta_{BB}, \\ c &= \beta_{AB} - \tfrac{1}{2}(\beta_{AA} + \beta_{BB}). \end{aligned} \tag{25}$$

As Robledo has noticed, the temperature dependence of the a,b couplings may give rise to an unconventional solution behavior on the binary oil–amphiphile or water–amphiphile boundaries. The latter, in particular, may develop an upper miscibility gap which has been advocated by Kahlweit[5] as a prerequisite for the formation of three-phase equilibria in nonionic amphiphile–water–oil mixtures.

Indeed, the model presented here, shares some features with standard lattice models of binary mixtures which describe retrograde solubility: Based on an idea by Hirschfelder, Stevenson, and Eyring[11] from 1937, the interactions among the components of the mixture have an orientational dependence which reflects special binding directions of the molecules. As the temperature is raised, the attraction is washed out by thermal fluctuations and a phase separation may occur. This effect becomes apparent in the temperature dependence of the isotropic interaction energies which remain after the extra orientational degrees of freedom have been summed over. Whereas this summation may be performed exactly in the decorated lattice model of Wheeler and Andersen,[12] it can only be done approximately in the model of Walker, Vause, and Goldstein.[13] They use very successfully the lowest order of the high temperature expansion which is identical to the steps leading from Eq. (15) to Eq. (21).

It must be noticed, however, that this does not imply the same approximation to work well also in the present model. In fact, it was found that a large number q of possible orientations had to be introduced in the lattice theories of retrograde solubility to explain the experimental widths of upper coexistence curves[11–13]: typically $q = 500$[12] or $q = 5000$.[11,13] Consequently, one should expect that the two possible amphiphile directions which are included in Robledo's approximation ($q = 2$), give much too narrow coexistence curves. [We also do not agree with Robledo's claim that the coexistence curves may be asymmetrical, in the binary composition space, e.g., for the binary water–amphiphile boundary, Eqs. (21) and (24) always give a critical point at $\langle P^+ \rangle = \langle P^- \rangle = \frac{1}{2}$. Robledo's claim of asymmetrical critical points results from a misinterpretation of the activity.] The number q of accessible orientations plays yet another important role. The expansion parameters of the approximation [Eqs. (15)–(25)] and its corrections are the K_{RS} of Eq. (16) divided by q. Small values of K_{RS}/q are not only needed to obtain a quantitatively good approximation but are also a prerequisite of its qualitative validity: High-temperature expansions have, in general, a finite radius of convergence and above some critical coupling (here the K_{RS}/q), the expansion breaks down and approximate forms like Eqs. (21)–(23) become useless.

Whether this happens in the present model depends on the physically relevant ranges of the parameters β_{RS}. A reliable answer to this question requires quite elaborate calculations but some qualifications can be given more easily. Working out the σ dependence in Eq. (15), one verifies that only the following linear combinations of the K_{RS} enter into the expansion parameters

$$
\begin{aligned}
&K_{Aa} - K_{Ab} = e^{-\beta_{Aa}} - e^{-\beta_{Ab}},\\
&K_{Bb} - K_{Ba} = e^{-\beta_{Bb}} - e^{-\beta_{Ba}},\\
&K_{aa} + K_{bb} - 2K_{ab} = e^{-\beta_{aa}} + e^{-\beta_{bb}} - 2e^{-\beta_{ab}},\\
&K_{aa} - K_{bb} = e^{-\beta_{aa}} - e^{-\beta_{bb}}.
\end{aligned}
\tag{26}
$$

Indeed, if these combinations vanish, the a and b ends of the amphiphile act identically, the energy [Eq. (5)] of the spin 3/2 model no longer depends on $Q^{\pm}$ and the summation over σ in the partition function (3) becomes trivial. The first three expressions in Eq. (26) acquire maximal values in the limit (7) of Widom's model (at fixed β_{Aa}, β_{Bb}, β_{aa}, and β_{bb}). Therefore, it is reasonable to check the validity of Robledo's approximation in this simplifying limit. Then the water–amphiphile, oil–amphiphile, and water–oil couplings in Eq. (25) reduce to

$$
\begin{aligned}
&a = \beta_{Aa} - \tfrac{1}{2}(\beta_{AA} + \beta_{aa}) + \tfrac{1}{2}\ln(1 + e^{(\beta_{aa} - \beta_{bb})}),\\
&b = \beta_{Bb} - \tfrac{1}{2}(\beta_{BB} + \beta_{bb}) + \tfrac{1}{2}\ln(1 + e^{-(\beta_{aa} - \beta_{bb})}),\\
&c \to \infty.
\end{aligned}
\tag{27}
$$

Notice that in this limit the spin 1 partition function specified by Eqs. (21) and (24) cannot be reduced to the spin 1/2 form of Widom's model. This should come as no surprise, as the amphiphile orientation does not occur any more in the spin 1 partition function [Eq. (21)], whereas it plays an essential role in the setup of Widom's model.

For this reason it remains nontrivial to judge the quality of Robledo's approximation even in this limit. We will return to this question in the next section where we focus on the binary amphiphile–water and amphiphile–oil boundaries, trying to gain some further insight into the role of retrograde solubility in these models.

V. THE WIDOM MODEL AT THE BINARY BOUNDARIES AND RETROGRADE SOLUBILITY

Let us first investigate how the binary miscibility gaps of the water–amphiphile and the oil–amphiphile systems arise in Widom's model: In the absence of either oil (BB) or water (AA), the amphiphile (AB) can only occur in the form of elementary "micelles" which consist of six amphiphile links joined together at a common site. Each micelle produces a fixed intramicellar energy which arises from the contact of amphiphile links at its central site. Then the total intramicellar energy is proportional to the number of micelles, or equivalently to the amphiphile concentration and may therefore be absorbed in its chemical potential. The remaining intermicellar energies are due to the contact of micelles, giving rise to $K(1 + \lambda)$ or $K(1 - \lambda)$ contributions for the water–amphiphile or oil–amphiphile solutions (Fig. 4). Depending on the sign and magnitude of λ (assuming $K > 0$), these intermicellar interactions are either purely attractive or purely repulsive. So in Widom's model, these two binary subsystems are both equivalent to a hard core gas of micelles with either attractive or repulsive short-range interactions. Only lower miscribility gaps will occur, unless K or λ are themselves appropriate functions of the temperature.

λ fixes the spontaneous curvature of the amphiphile interface and plays the role of the Bancroft parameter in Widom's model.[2] For the Winsor I microemulsions at lower temperatures, λ has to be positive, favoring oil-in-water curvatures. As the temperature is raised through the Winsor III region of three-phase equilibria, λ has to decrease to become negative, favoring the water-in-oil curvatures of the Winsor II microemulsions at higher temperatures. (This scheme refers to systems with nonionic amphiphiles. For ionic amphi-

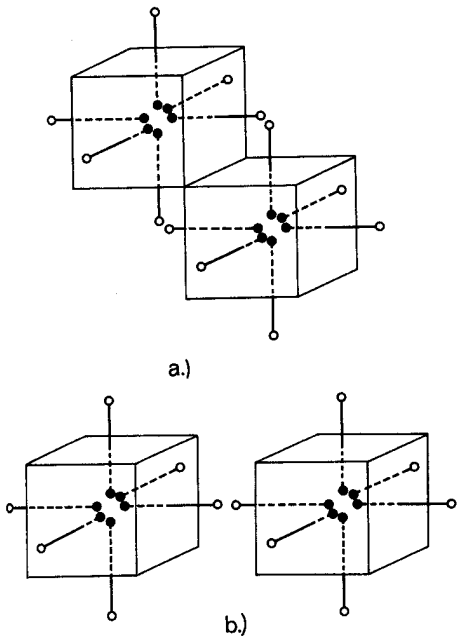

FIG. 4. Contacts of two micelles in the water–amphiphile system which contribute (a) $2K(1+\lambda)$, (b) $K(1+\lambda)$ to the intermicellar energy.

philes, salinity replaces the role of temperature.) Then with λ being a monotonically decreasing function of T, the repulsive contact energies $K(1+\lambda)$ of micelles in the water–amphiphile system also go down as the temperature is raised, giving way to an attraction for $\lambda < -1$ which will eventually lead to a phase separation if $-\lambda$ becomes sufficiently large. The same picture applies to the binary oil–amphiphile system with the reverse temperature dependence, leading to regular solution behavior in agreement with experimental results.[5]

Let us now discuss the implications of this scenario for the spin 3/2 model and Robledo's spin 1 form:

In the last section we have argued that Robledo's approximation should become worst in Widom's limit [Eq. (7)]. Using Eq. (14) to rephrase the contact energies of water–amphiphile (a) and of oil–amphiphile (b) [see Eq. (25)] in terms of Widom's parameters K and λ, we have

$$a = -\frac{K(1+\lambda)}{kT} + \frac{1}{2}\ln(1+e^{+(\beta_{aa}-\beta_{bb})}),$$
$$b = -\frac{K(1-\lambda)}{kT} + \frac{1}{2}\ln(1+e^{-(\beta_{aa}-\beta_{bb})}). \qquad (28)$$

At the binary water–amphiphile boundary the absence of oil implies $P_\mu^-(\mathbf{x}) = 0$, $P_\mu^+(\mathbf{x}) + P_\mu^0(\mathbf{x}) = 1$. Absorbing a linear term $\sim \Sigma_{\mathbf{x},i} P_i^0(\mathbf{x})$ in the chemical potential and dropping an irrelevant constant, the energy (24) reduces to

$$\frac{E_{WA}}{kT} = -2a \sum_{\mathbf{x},\mu<\nu} P_\mu^0(\mathbf{x}) P_\nu^0(\mathbf{x}). \qquad (29)$$

Similarly, at the oil–amphiphile boundary, Eq. (24) reduces to

$$\frac{E_a}{kT} = -2b \sum_{\mathbf{x},\mu<\nu} P_\mu^0(\mathbf{x}) P_\nu^0(\mathbf{x}). \qquad (30)$$

Thus for $\beta_{aa} = \beta_{bb}$, this produces the same amphiphile contact energies as Widom's model. Of course, the association into micelles is absent in Robledo's approximation. This is evident from the fact that this approximation reduces to simple Ising models at the binary boundaries which can exhibit only a single nonuniform phase, the long-ranged antiferromagnet. Still, the overall phase behavior at the binary boundaries is the same. Although this does not imply that this also holds for the full ternary composition space, the result suggests that Robledo's approximation reproduces the macroscopic phase behavior all the way from the monofunctional amphiphile [vanishing expansion parameters in Eq. (26)] to the extremely difunctional amphiphiles of Widom's limit (7), provided $\beta_{aa} - \beta_{bb}$ is "small" enough.

However, this also implies that the unconventional temperature dependence of the couplings in Eqs. (23) and (25) drops out in Widom's limit. Indeed this property arose from the (approximate) summation over the amphiphile orientation, a degree of freedom which is absent in Widom's model as there the orientation of the amphiphile is completely fixed by its local neighbors. The variation of λ, or more generally of $K(1\pm\lambda)$, which is needed in Widom's model to obtain retrograde solubility and the progression of the Winsor phases, implies by Eq. (14) that also some of the β_{RS} have to have a more complicated temperature dependence than the simple $1/T$ behavior of Eq. (6). Thus the ϵ_{RS}, δ_{RS} cannot be interpreted as elementary interaction energies but have to be phenomenological functions of T.

As the above results only apply to the limit (7) of Widom's model, one could try to maintain the idea that retrograde solubility and the progression of Winsor phases arises naturally in the spin 3/2 model or Robledo's approximate spin 1 form by adopting the following point of view.

Widom's model may be unphysical as it completely neglects any orientational degree of freedom of the amphiphile molecules and a more realistic description should be obtained if one drops the limit (7) and uses finite values of all β_{RS}. Then the summation over the amphiphile orientations will produce approximately Robledo's spin 1 model [Eqs. (21) and (24)] with its temperature dependent coupling, Eqs. (23) and (25).

Such an approach does, however, pose several problems which would have to be resolved: As we have argued in the last section, the two orientational options for the amphiphile molecules are likely to produce too narrow coexistence curves in the water–amphiphile system. If this is true, one would have to generalize the model to incorporate a larger number of possible orientations. Furthermore, if one increases the repulsion between polar and apolar groups, moving in the direction indicated by Widom's limit (7), the feasibility to obtain retrograde solution behavior is weakened (raising the cloud point temperature and/or narrowing the coexistence curve) and at the same time, the tendency of the amphiphile to aggregate into micelles in oil or water is increased. But this connection between micellar aggregation and retrograde solubility is not present in real systems and one would have to show that this interrelation disappears with a proper choice of the interaction energies [Eq. (6)]. Finally, one should notice that if the Hirschfelder–Stevenson–Eyring[11] mechanism is the origin of the retrograde be-

havior in aqueous amphiphile solutions (which is by no means ascertained) it is unlikely that the amphiphile orientation is the main cause of this phenomenon: In the original proposal[11] and in the detailed models and their applications to real systems,[12–14] the hydrogen bonds of the water molecules are the important orientational degrees of freedom. This readily explains why oil–amphiphile systems exhibit only regular solution behavior. Of course, the same difference between aqueous and organic amphiphile solutions may be obtained by proper choices for the interaction energies [Eq. (6)] in the spin 3/2 model but it seems to be rather artificial to attribute the retrograde solubility to the amphiphile orientation alone.

VII. CONCLUSION

We have seen that if we want to permit the contact between polar and apolar material, Widom's Ising-like model generalizes into a spin 3/2 Ising-like model. This seems to have all necessary ingredients to discuss formation of realistic microemulsions that involved shorter chain amphiphile molecules.

The spin 1 form of Robledo, who had originally proposed a related generalization, has been exposed as an approximation. In the limit of very weak amphiphiles it becomes exact and one obtains the regular ternary solution model. In the opposite extreme of infinite repulsions between polar and apolar species, the spin 3/2 model turns into Widom's model. In this case the spin 1 approximation fails to describe the micellar aggregation but still reproduces the macroscopic phase behavior, at least at the binary water–amphiphile and oil–amphiphile boundaries. This led us to conjecture that the spin 1 form is a good approximation for the macroscopic properties for all relevant couplings.

In Widom's model the progression through the Winsor phases of nonionic amphiphile–oil–water systems implies retrograde solubility behavior at the binary water–amphiphile boundary and normal solubility behavior at the oil–amphiphile boundary, in agreement with experimental results. This behavior has to be introduced by an appropriate phenomenological choice for the temperature dependence of the couplings. In the spin 3/2 model, such a temperature dependence may, in principle, be generated intrinsically through the orientational degrees of freedom of the amphiphile. This becomes apparent in Robledo's spin 1 approximation. However, both in the limit of Widom's model as well as in the regular solution limit, this property is lost. Moreover, as the available number of amphiphile orientations is very small and the role of water is completely neglected it is hard to imagine that the model can properly account for retrograde solubility behavior and the Winsor phase progression without introducing the appropriate temperature dependence explicitly into the interaction energies.

In this work we have not yet presented any applications. Some preliminary studies, however, encourage us to expect that the model will describe the known phase diagrams[5,15] as well as the recently measured correlation functions[16] of microemulsions, using as an input only the temperature-, pressure-, and salinity-dependent strengths of the hydrophilic and hydrophobic parts of the amphiphiles. This will be helpful in determining the necessary properties of tensides which make the three-phase regime as large as possible and place it into the desired position in the multidimensional phase diagram.

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