Interfacial Phase Transitions of Microemulsions

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In this paper we study the interfaces between phases in a phenomenological model of a microemulsion that is in equilibrium simultaneously with an oil-rich and a water-rich phase. The tensions and chemical-composition profiles of the interfaces are calculated. We ask whether the oil–water, oil–microemulsion and microemulsion–water tensions σ_{ow}, σ_{om} and σ_{mw} are related by $\sigma_{ow} < \sigma_{om} + \sigma_{mw}$ or by $\sigma_{ow} = \sigma_{om} + \sigma_{mw}$. In the former case the microemulsion phase does not wet the oil–water interface, whereas in the latter it does. We find separate ranges of values of the model's parameters in which each possibility is realized, while the microemulsion is a middle phase related symmetrically to the oil and water phases. When a parameter that breaks that symmetry is varied and a critical endpoint of the three-phase equilibrium is approached, an originally non-wet oil–water interface becomes wet (while an originally wet interface remains wet). The transition is of first order, accompanied by a change in interfacial structure. A microscopic lattice model of such three-phase equilibria is also described. In its context we raise (but do not fully answer) the same questions that we treated in the earlier phenomenological model.

It has been reported[1–3] that when a middle-phase microemulsion is in equilibrium simultaneously with an oil-rich upper phase and a water-rich lower phase the tension σ_{ow} of the oil–water interface is less than the sum of the tensions σ_{om} and σ_{mw} of the oil–microemulsion and microemulsion–water interfaces:

$$\sigma_{ow} < \sigma_{om} + \sigma_{mw}. \tag{1}$$

This implies that the microemulsion does not perfectly wet (spread at) the oil–water interface; rather, the three phases meet with non-zero contact angles.[4] This has been verified by direct visual observation.[2,5] When the microemulsion is related symmetrically to the other two phases, $\sigma_{om} = \sigma_{mw}$; so when, as is sometimes found,[1,3] σ_{ow} is equal to the larger of those two, in that symmetrical equilibrium the three tensions σ_{ow}, σ_{om} and σ_{mw} would have a common value and the three contact angles would all be 120°.

From Cahn's theory of wetting[6] it follows that close enough to either critical endpoint (the critical point of the equilibrium between the middle-phase microemulsion and either the upper or lower phase, in the presence of the other) the microemulsion should spread at the interface between the other two phases. Thus, at some three-phase state between the symmetrical one, in which $\sigma_{om} = \sigma_{mw}$ and in which the microemulsion does not wet the oil–water interface, and either critical endpoint, in which it does, there should be a transition between incomplete and complete wetting. This was remarked by Chatenay *et al.*[5] Such a transition would entail a discontinuous change in structure of the oil–water interface. In the non-wet regime that interface presumably consists of a microscopically thin, concentrated layer of oriented surfactant (perhaps even a monolayer),[1–3] while in

the wetting regime it would consist of a thick layer of the bulk microemulsion phase. The predicted transition has been seen in some of these microemulsion phase equilibria,[7a] but not in others.[7b]

The connection between these three-phase equilibria and those in mixtures with smaller amphiphiles, such as the mixture benzene–water–ethanol–ammonium sulphate, has been emphasized.[8] In that and analogous mixtures it was found[9] that $\sigma_{ow} = \sigma_{om} + \sigma_{mw}$ in all the three-phase states between the two critical endpoints, including the symmetrical equilibrium in which $\sigma_{om} = \sigma_{mw}$, so that the middle phase always spreads at the interface between the top and bottom phases. Thus, the existence of a range of non-wetting states is not universal. In a progression of systems with increasingly large surfactants one should see a change from those in which the oil–water interface is always wet by the middle phase to those in which it is wet near the critical endpoints but not everywhere between, *i.e.* a change from systems whose oil–water interfaces do not, to those whose oil–water interfaces do, undergo the wetting transition. This is also noted by Telo da Gama and Thurtell[10] in their paper at this Symposium.

To test and illustrate these ideas we calculate the tensions and structures (composition profiles) of the interfaces in the three-phase equilibria that occur in a model microemulsion.[11] The model is an adaptation of the earlier ones of Talmon and Prager[12-14] and of de Gennes *et al.*[15, 16]

In the next section we recall how the model is defined and we construct a free-energy functional from which the interfacial tensions and composition profiles may be calculated. We then outline the calculation and give the results. We find that there is indeed a range of values of the model's parameters for which, in the symmetrical three-phase equilibrium, the oil–water interface is wet by the microemulsion phase, and a range in which it is not; when it is not, a transition to wetting then occurs when the symmetry is broken and either of the critical endpoints is approached.

Finally we describe, as an alternative to the phenomenological model, a lattice model equivalent to an Ising model with second-neighbour and three-spin interactions. Its phase equilibria are like those of microemulsions, with ultralow interfacial tensions, but its possible interfacial phase transitions have not yet been studied.

Phenomenological Model

We picture an oil–water–surfactant solution as divided into cubic cells of edge length ξ, the fraction ϕ of them oil-filled and the fraction $1 - \phi$ water-filled, with surfactant molecules of number density ρ confined to the microscopic interface between oil-filled and water-filled cells (the surfactant film). The model is defined[11] by the free-energy density $F(\phi, \rho, \xi)$:

$$F(\phi, \rho, \xi) = \begin{cases} [\phi \ln \phi + (1 - \phi) \ln (1 - \phi)] \, kT/\xi^3 + 6\sigma_0 \phi(1 - \phi)/\xi \\ \quad + \rho kT \ln [\xi \rho a^2 / \phi(1 - \phi)] + D\rho[1 - \Lambda(2\phi - 1)\xi]/2\xi^2, & (\xi > a) \\ \infty, & (\xi < a) \end{cases} \quad (2)$$

where a is a fixed microscopic length (a few Å), σ_0 is the oil–water interaction energy per unit area of contact between oil- and water-filled cells (*ca.* 50 dyn cm^{-1}) and D and Λ are two parameters in the curvature free energy of the surfactant film: the dimensionless $D/a^2kT \lesssim 1$ for a flexible film or > 1 for a stiff film,[15] and the curvature-bias parameter Λa (favouring oil-in-water or water-in-oil curvature, according to its sign[16]) is tunable (by varying salinity, for example) between *ca.* -2 and $+2$.

For given ϕ and ρ (and fixed kT, a, σ_0, D and Λ) the equilibrium ξ is that which minimizes the $F(\phi, \rho, \xi)$ in eqn (2). The minimum may occur either at $\xi = a+$, with

$\partial F/\partial \xi > 0$ there, or at some $\xi = \xi_1(\phi, \rho) > a$ at which $\partial F/\partial \xi = 0$. The system's equilibrium free-energy density Φ at any ϕ, ρ is the smaller of $F(\phi, \rho, a+)$ and $F[\phi, \rho, \xi_1(\phi, \rho)]$:

$$\Phi(\phi, \rho) = \min \{F(\phi, \rho, a+), F[\phi, \rho, \xi_1(\phi, \rho)]\}. \tag{3}$$

The free-energy surface $\Phi(\phi, \rho)$ is thus a composite, with a seam in which the separate surfaces $F(\phi, \rho, a+)$ and $F[\phi, \rho, \xi_1(\phi, \rho)]$ intersect. The projection of that seam onto the ϕ, ρ plane defines the crossover locus:

$$F[\phi, \rho, \xi_1(\phi, \rho)] = F(\phi, \rho, a+) \quad \text{(crossover)}. \tag{4}$$

The equilibrium phases are found by the tangent-plane construction applied to the surface $\Phi = \Phi(\phi, \rho)$. Three-phase equilibrium arises from triple tangency. Two of the points of tangency are found to lie in the $F(\phi, \rho, a+)$ sheet of the $\Phi(\phi, \rho)$ surface and one in the $F[\phi, \rho, \xi_1(\phi, \rho)]$ sheet.[11] The former are the oil- and water-rich phases, which we shall call α and γ, respectively; in them $\xi = a$. The latter is the microemulsion phase, which we call β; in it $\xi = \xi_1(\phi, \rho) > a$.

Let ω represent any stable phase, with ϕ_ω, ρ_ω its coordinates in the ϕ, ρ plane. Suppose the plane tangent to the $\Phi(\phi, \rho)$ surface at ϕ_ω, ρ_ω has the equation $\Phi = L_\omega(\phi, \rho)$ with L_ω a linear function of its arguments. The height $\bar{U}_\omega(\phi, \rho)$ of the $\Phi(\phi, \rho)$ surface above this plane is, from eqn (3),

$$\bar{U}_\omega(\phi, \rho) = F[\phi, \rho, \bar{\xi}(\phi, \rho)] - L_\omega(\phi, \rho) \tag{5}$$

where $\bar{\xi}(\phi, \rho)$ means $a+$ on that side of the crossover locus where $F(\phi, \rho, a+) < F[\phi, \rho, \xi_1(\phi, \rho)]$ and it means $\xi_1(\phi, \rho)$ on the other side. If ψ is any phase in equilibrium with ω the respective tangent planes are the same, $L_\omega(\phi, \rho) \equiv L_\phi(\phi, \rho)$, so $\bar{U}_\omega(\phi, \rho) \equiv U_\psi(\phi, \rho)$. Then $\bar{U}_\omega(\phi, \rho) = 0$ when ϕ, ρ are the coordinates ϕ_ω, ρ_ω or when they are the coordinates ϕ_ψ, ρ_ψ of any other phase ψ that may be in equilibrium with ω; while $\bar{U}_\omega(\phi, \rho) > 0$ at all other ϕ, ρ.

We now define a related function $U_\omega(\phi, \rho, \xi)$ of the three variables ϕ, ρ and ξ:

$$U_\omega(\phi, \rho, \xi) = F(\phi, \rho, \xi) - L_\omega(\phi, \rho). \tag{6}$$

By definition, the $\bar{U}_\omega$ in eqn (5) and the U_ω in eqn (6) are connected by

$$\bar{U}_\omega(\phi, \rho) = U_\omega[\phi, \rho, \bar{\xi}(\phi, \rho)]. \tag{7}$$

If a phase ψ is in equilibrium with ω then $U_\omega \equiv U_\psi$. This $U_\omega(\phi, \rho, \xi)$ vanishes at $\phi_\omega, \rho_\omega, \xi_\omega$, the coordinates of phase ω in the three-dimensional ϕ, ρ, ξ space, and at the ϕ, ρ, ξ that are the coordinates of any other phase in equilibrium with ω, while $U_\omega(\phi, \rho, \xi) > 0$ elsewhere. We see this as follows.

First, ξ_ω is either $a+$ or $\xi_1(\phi_\omega, \rho_\omega)$, according to which sheet of the composite $\Phi(\phi, \rho)$ surface the phase ω lies in; *i.e.* $\xi_\omega = \bar{\xi}(\phi_\omega, \rho_\omega)$. Thus, by eqn (7), $U_\omega(\phi_\omega, \rho_\omega, \xi_\omega) = \bar{U}_\omega(\phi_\omega, \rho_\omega)$, which we know to be 0; similarly $U_\omega(\phi_\psi, \rho_\psi, \xi_\psi) = 0$ for any phase ψ in equilibrium with ω, since then $U_\omega \equiv U_\psi$. Secondly, since $\bar{\xi}(\phi, \rho)$ is the ξ that minimizes $F(\phi, \rho, \xi)$, we have $U_\omega(\phi, \rho, \xi) \geqslant \bar{U}_\omega(\phi, \rho)$, from eqn (5) and (6). Therefore, since $\bar{U}_\omega(\phi, \rho) > 0$ when ϕ, ρ are not the coordinates of the phase ω or of any phase in equilibrium with ω, it follows that $U_\omega(\phi, \rho, \xi) > 0$, too, everywhere in the three-dimensional ϕ, ρ, ξ space other than at such phases.

Thus the three-dimensional hypersurface $U = U_\omega(\phi, \rho, \xi)$ in the U, ϕ, ρ, ξ space generally lies above the hyperplane $U = 0$, but touches it at the points ϕ, ρ, ξ that are the coordinates of the phase ω or of any phase in equilibrium with ω. The surface is singular at the hyperplane $\xi = a$, with $U_\omega(\phi, \rho, \xi)$ finite for $\xi > a$ and infinite for $\xi < a$, by eqn (2) and (6). The surface is otherwise analytic in ϕ, ρ, ξ for all $1 > \phi > 0$, $\rho > 0$, $\xi > a$. This is unlike the original surface $U = \bar{U}_\omega(\phi, \rho)$ in the three-dimensional U, ϕ, ρ space, which has a seam in it, of which eqn (4) is the projection in the ϕ, ρ plane.

In the ϕ and ρ directions the plane $U = 0$ is tangent to the U_ω surface where it touches it; *i.e.* $\partial U_\omega/\partial\phi = 0$ and $\partial U_\omega/\partial\rho = 0$ at such points; and also in the ξ direction, when such a point is a β (microemulsion) phase, in which $\xi = \xi_1(\phi_\beta, \rho_\beta) > a$, because $\partial F(\phi, \rho, \xi)/\partial\xi = 0$ at $\xi = \xi_1(\phi, \rho)$, so $\partial U_\omega/\partial\xi = 0$ then, too. However, when the point of contact is at an α or γ phase, where $\xi = a+$, the contact is not a tangency in the ξ direction; instead, $\partial U_\omega/\partial\xi > 0$ at such a point. Except for this circumstance, which we shall have to keep in mind in the calculations that follow, the contacts of the hypersurface $U = U_\omega(\phi, \rho, \xi)$ with the hyperplane $U = 0$ are tangencies, just as, earlier, the contacts of the surface $U = \bar{U}_\omega(\phi, \rho)$ with the plane $U = 0$ in the three-dimensional U, ϕ, ρ space were tangencies.

In this model the structure of the interface between two coexisting phases is given by the profiles $\phi(z)$, $\rho(z)$ and $\xi(z)$, which show how ϕ, ρ and ξ vary as functions of the distance z in the direction perpendicular to the plane of the interface. If the two phases are α and β, say, at $z = -\infty$ and $z = +\infty$, respectively, then $\phi(-\infty) = \phi_\alpha$, $\rho(-\infty) = \rho_\alpha$, $\xi(+\infty) = \xi_\beta$ etc. The equations $\phi = \phi(z)$, $\rho = \rho(z)$ and $\xi = \xi(z)$ are the parametric equations of a trajectory on the hypersurface $U = U_\alpha(\phi, \rho, \xi)$ or in the three-dimensional ϕ, ρ, ξ space. This trajectory connects the points $\phi_\alpha, \rho_\alpha, \xi_\alpha$ and $\phi_\beta, \rho_\beta, \xi_\beta$ and describes how ϕ, ρ and ξ vary with each other through the interface.

We calculate the composition profiles and tensions of the interfaces from mean-field theory in the square-gradient approximation.[17] We adopt as the free-energy functional σ,

$$\sigma = \int_{-\infty}^{\infty} \{U[y_1(z), y_2(z), y_3(z)] + \tfrac{1}{2} \sum_{i,j=1}^{3} m_{ij}[dy_i(z)/dz][dy_j(z)/dz]\}\,dz \tag{8}$$

where y_1, y_2 and y_3 are ϕ, ρ and ξ, respectively; where we shall later choose and fix the coefficients $m_{ij}(= m_{ji})$; and where (in principle) the function U is the $U_\omega(\phi, \rho, \xi)$ [$\equiv U_\psi(\phi, \rho, \xi)$] defined by eqn (6), with ω and ψ the two bulk phases whose interface we are studying. In practice, as explained in the next section, we approximate $U_\omega(\phi, \rho, \xi)$ by a simpler function that retains the most important features of U_ω but allows much of the calculation to be done analytically; and we use $\ln(\xi/a)$ in place of ξ. In our applications of eqn (8) the phases ω and ψ are any two of α, β and γ, where, following our earlier notation, α and γ are the oil- and water-rich phases and β the microemulsion in three-phase equilibrium.

The conditions that the $y_i(z)$ minimize the σ in eqn (8) are

$$\partial U/\partial y_i = \tfrac{1}{2} \sum_{j=1}^{3} (m_{ij} + m_{ji})\,d^2y_j/dz^2 \quad (i = 1, 2, 3). \tag{9}$$

These are the equations we solve to obtain the $y_i(z)$. The minimum σ in question is the equilibrium surface tension, obtained from eqn (8) once the $y_i(z)$ are known.

Method of Calculation

In the immediate neighbourhood of each equilibrium phase ω the hypersurface $U_\omega(\phi, \rho, \xi)$ is parabolic in the ϕ and ρ directions, and also in the ξ direction when ω is a β phase, but is linear in the ξ direction when ω is an α or γ phase (previous section). Thus [now calling U_ω simply U, as in eqn (8)], near the β phase U is of the form

$$U(\phi, \rho, \xi) \approx A(\phi - \phi_\beta)^2 + B(\rho - \rho_\beta)^2 + C(\phi - \phi_\beta)(\rho - \rho_\beta)$$
$$+ D(\xi - \xi_\beta)^2 + E(\phi - \phi_\beta)(\xi - \xi_\beta) + F(\rho - \rho_\beta)(\xi - \xi_\beta) \tag{10}$$

while near the α phase it is of the form

$$U(\phi, \rho, \xi) \approx A'(\phi - \phi_\alpha)^2 + B'(\rho - \rho_\alpha)^2 + C'(\phi - \phi_\alpha)(\rho - \rho_\alpha) + D'(\xi - a) \tag{11}$$

and similarly near the γ phase. The coefficients A, B etc. are the appropriate second derivatives (or, in the case of D', a first derivative) of U with respect to ϕ, ρ and ξ, evaluated at the location ϕ_ω, ρ_ω, ξ_ω ($\omega = \alpha, \beta$, or γ) of the phase in question. The function U is as given by eqn (2) and (6). The equilibrium α, β and γ phases are accurately located numerically by the triple-tangent construction.[11]

In a related problem of two-phase equilibrium in which U is parabolic near each equilibrium phase, it was found that U could be successfully replaced by a composite of the two paraboloids that fit it at the separate phases.[18] With y a general point in the density or composition space, with the two phases at y_α and y_β, and with $P_\alpha(y)$ and $P_\beta(y)$ the respective quadratic functions of y that match $U(y)$ through and including its second derivatives, at y_α and y_β, this scheme[18] replaces $U(y)$ at each point y by min $[P_\alpha(y), P_\beta(y)]$. The first derivatives of this composite, approximate $U(y)$ are discontinuous at the seam in which the two paraboloids intersect, whereas the original $U(y)$ was analytic. Since U in this example now deviates from 0 quadratically as y departs from y_α or y_β, the solutions of the trajectory equations (9) are exponential in z; on each sheet the physically relevant solutions $y(z) - y_\alpha$ etc. are linear combinations of terms of the form $\exp(-|z|/\zeta)$. The full solution for the physically relevant $y(z)$ is a composite consisting of a solution on the α paraboloid for $z \leqslant z_0$ (for some z_0, which we may call 0 if we wish) and of one on the β paraboloid for $z \geqslant z_0$. The separate α and β solutions are chosen from the respective families of such solutions so as to make the several $y_i(z_0)$ and their first derivatives $y_i'(z_0)$ continuous at z_0, with $y(z_0)$ one of the points of the seam in the composite U surface. The second derivatives y_i'' are discontinuous there; that is an artifact of the approximation.

We now adapt that scheme to the present problem of three-phase equilibrium. The truncated expansion (10) defines a paraboloid in the four-dimensional U, ϕ, ρ, ξ space at the β phase, while the truncated expansion (11), and its analogue for the γ phase, define surfaces that are parabolic in the ϕ and ρ directions and linear in the ξ direction, at the α and γ phases. We replace U at each point by that one of these three surfaces which lies lowest there. The resulting approximate, composite U surface has two seams, one where the α and β surfaces intersect and one where the β and γ surfaces do. [We observed numerically that these seams, projected onto the ϕ, ρ plane, are very close to the crossover locus (4) associated with the original Φ surface.]

On the β sheet the physically relevant solutions $\phi(z) - \phi_\beta$, $\rho(z) - \rho_\beta$ and $\xi(z) - \xi_\beta$ are again linear combinations of exponentials of $-|z|$. On the α and γ sheets the decay of $\phi(z)$ and $\rho(z)$ to their values ϕ_α, ρ_α or ϕ_γ, ρ_γ in the bulk phases is again exponential, but not that of $\xi(z)$ to its bulk-phase value a. Instead, the decay is parabolic and the value $\xi = a$ is achieved at a finite z. This is equally true of the exact trajectories that would be obtained from the original U surface. It happens because $\partial U/\partial \xi > 0$ at the α and γ phases (previous section). A schematic $\xi(z)$ profile for an $\alpha\beta$ interface is shown in fig. 1.

The trajectories $\phi(z)$ etc., for the $\alpha\beta$ or $\beta\gamma$ interface cross only one seam of the approximate U surface, that between the α and β or β and γ sheets. The solutions are then constructed so as to yield $y_i(z)$ and $y_i'(z)$ that are continuous across the seam, as described above and as in the original application of the method.[18] The trajectories for the $\alpha\gamma$ interface cross both seams, and we enforce continuity of $y_i(z)$ and $y_i'(z)$ at both crossing points. For the non-wet $\alpha\gamma$ interface, which does not consist of a layer of β phase and for which the trajectory, therefore, in going from α to γ, does not go *via* β, the matching is done numerically rather than analytically; it requires, in particular, the numerical determination of the (finite) distance Δz between the two points z at which the crossing of the seams occurs.

For simplicity we have presented the story to this point as though ϕ, ρ and ξ were the basic variables, but in our actual calculations we used $\ln(\xi/a)$ in place of ξ as the third coordinate: in eqn (8), $y_3 = \ln(\xi/a)$; in eqn (10) the expansion is in powers of
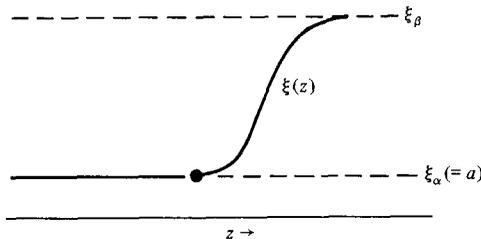
Fig. 1. Variation of ξ through the $\alpha\beta$ interface (schematic). The ξ profile achieves its value a in the α phase at a finite z, in the neighbourhood of which $\xi(z)$ is parabolic. It approaches its value ξ_β in the β phase asymptotically, but exponentially rapidly, as $z \to \infty$.

$\ln (\xi/a) - \ln (\xi_\beta/a) = \ln (\xi/\xi_\beta)$; and in eqn (11) the expansion is in powers of $\ln (\xi/a)$. We found that by choosing $m_{ij} = 0$ for $i \neq j$, *i.e.* by assuming the diagonal form

$$m_\phi(\mathrm{d}\phi/\mathrm{d}z)^2 + m_\rho(\mathrm{d}\rho/\mathrm{d}z)^2 + m_\xi(\mathrm{d} \ln \xi/\mathrm{d}z)^2 \tag{12}$$

for the gradient sum in eqn (8), we still had enough flexibility, through freedom of choice of the coefficients m_ϕ, m_ρ and m_ξ, to produce and explore a wide range of possible behaviour of the profiles and interfacial tensions. We then, for simplicity, adopted the diagonal form (12) in most of our calculations, including all those whose results we report in the next section.

Except for the necessity of finding Δz, the distance between the two seam-crossing points for the non-wet $\alpha\gamma$ interface, numerically, the solutions of eqn (9) for the profiles are obtained analytically. The coordinates ϕ, ρ, and $\ln (\xi/a)$ are rescaled by dividing them by the square-roots of m_ϕ, m_ρ and m_ξ, respectively. Then, in particular, the decay lengths ζ in the terms of the form $\exp(-|z|/\zeta)$ are found from the eigenvalues of the resulting matrix of coefficients of the rescaled quadratic terms in eqn (10) and (11). Going beyond expression (12) to include non-diagonal terms $(\mathrm{d}y_i/\mathrm{d}z)(\mathrm{d}y_j/\mathrm{d}z)$ in the gradient sum in eqn (8) requires only the simultaneous diagonalization of the gradient sum and of the matrix of quadratic terms in eqn (10) or (11). We did that in a few instances and found the cross-terms to have no qualitative effect on the profiles or tensions.

Results

Our results are shown in fig. 2–8. All those we present are with the values $D/a^2kT = 3$ and $\sigma_0 a^2/kT = 7/6$ of the two parameters D and σ_0 (in dimensionless form) that occur in the free-energy density in eqn (2). This value of $\sigma_0 a^2/kT$ is the same as that adopted in an earlier study;[11] the value of D/a^2kT is less than that used earlier,[11] but is probably more realistic.[15] We consider various values of the asymmetry parameter Λ. The remaining parameters of significance are the dimensionless forms am_ϕ/kT, m_ρ/a^5kT and am_ξ/kT of the coefficients in expression (12).

We observed numerically that whether in the symmetrical three-phase equilibrium ($\Lambda = 0$) the middle-phase microemulsion does nor does not completely wet the oil–water interface depends only on the ratios of the coefficients in expression (12), not their separate values. We show in fig. 2, for the fixed values of D/a^2kT and $\sigma_0 a^2/kT$ quoted above, the wetting and non-wetting regions of the m_ξ/m_ϕ, m_ρ/a^6m_ϕ parameter plane. The incomplete-wetting region expands as the curvature-energy parameter D/a^2kT increases. In fig. 2 this region is enclosed within the region of wetting; the boundary between regions extends to very small, but still positive, m_ρ/a^6m_ϕ. In the narrow area between the boundary and the vertical axis as well as in most of the plane below the non-wetting
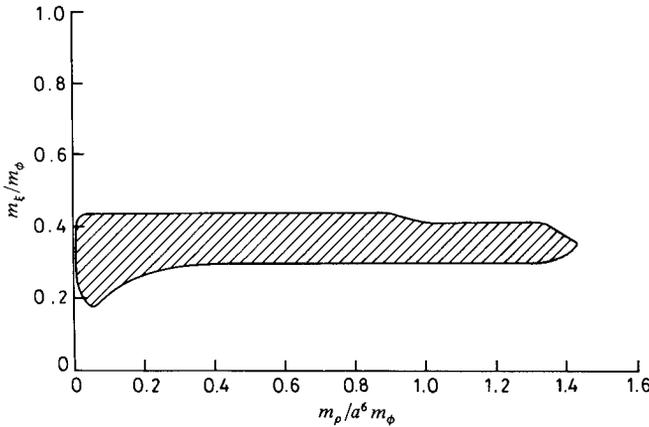
Fig. 2. Region of the $m_\xi/m_\phi, m_\rho/a^6m_\phi$ plane (shaded) within which the $\alpha\gamma$ interface is not wet by the β phase in the symmetrical three-phase equilibrium ($\Lambda = 0$).
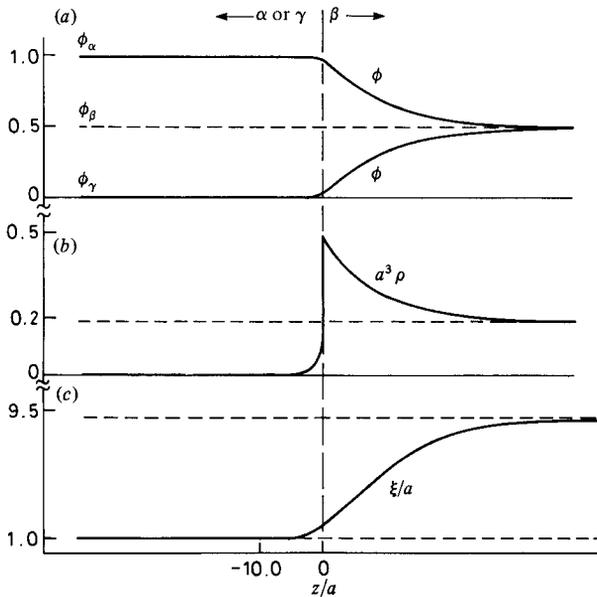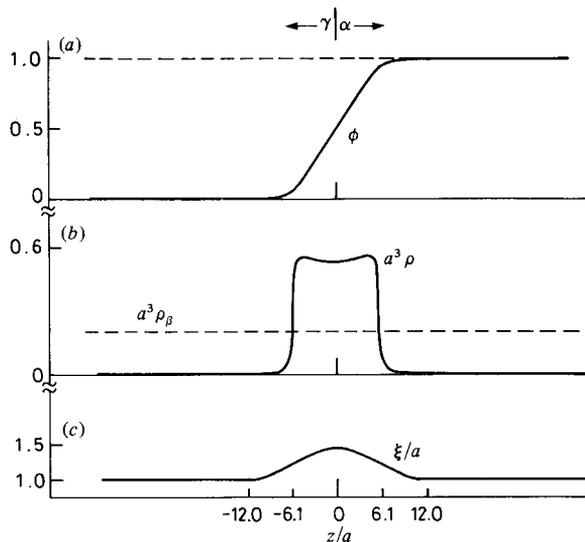

Fig. 3. Profiles of the $\alpha\beta$ and $\beta\gamma$ interfaces in the symmetrical three-phase equilibrium. (a) $\phi(z)$, (b) $a^3\rho(z)$ and (c) $\xi(z)/a$; $\xi/a \equiv 1$ for $z/a \leqslant -10.0$. The crossing point is at $z/a = 0$.

region (small m_ξ/m_ϕ) there is a physical solution for Δz (previous section), so a stable, non-wet $\alpha\gamma$ interface exists there, although it is less stable than the interface that is wet by the β phase. Above the non-wetting region (higher m_ξ/m_ϕ) there is no physical solution Δz, so no stable, non-wet $\alpha\gamma$ interface exists there.

The rest of the results we present are for the aforementioned D/a^2kT and $\sigma_0 a^2/kT$, and for the fixed values $am_\phi/kT = 10$, $m_\rho/a^5kT = 1/10$ and $am_\xi/kT = 3.5$ of these parameters. These imply $m_\xi/m_\phi = 0.35$ and $m_\rho/a^6m_\phi = 0.01$, which lies just within the

Fig. 4. Profiles of the $\alpha\gamma$ interface in the symmetrical three-phase equilibrium. (a) $\phi(z)$, (b) $a^3\rho(z)$ and (c) $\xi(z)/a$; $\xi/a \equiv 1$ for $|z/a| \geqslant 12.0$. The crossing points are at $z/a = \pm 6.1$.

region in which the middle-phase microemulsion (at $\Lambda = 0$) does not spread at the oil–water interface (fig. 2). It is perhaps because this is so close to the boundary that we are able subsequently, as Λ increases, to locate the transition to wetting at an easily attainable proximity to the critical endpoint.

In fig. 3 we show the composition profiles of the $\alpha\beta$ and $\beta\gamma$ interfaces in the symmetrical equilibrium ($\Lambda = 0$). Note the slow decay to the bulk-phase values in the β phase. The ultimate decay is exponential,[19] but the microemulsion has a great osmotic compressibility,[11] implying large composition fluctuations and large fluctuations also[20] in ξ, and hence a long decay length ζ in $\exp(-|z|/\zeta)$. As the critical endpoint is approached with increasing Λ, the osmotic compressibility of the β phase, the fluctuations of ϕ, ρ and ξ in that phase[11,20] and the decay length ζ will be even greater. Note in fig. 3(b) that there is a concentration of surfactant at the interface greater even than that in the bulk microemulsion phase. Note in fig. 3(c) that in the α and γ phases the value $\xi = a$ is achieved at finite z (cf. fig. 1). We have arbitrarily taken the crossing point, where in our method of calculation the trajectory that represents the variations of ϕ, ρ and ξ crosses from one sheet of the (approximate) U surface to the other, to be at $z = 0$. The profiles have discontinuous second derivatives there, but these are not visible in the figure. The first derivatives are finite and continuous there. That $\rho(z)$ in fig. 3(b) appears sharply peaked is only because of the small scale of the figure; its slope is finite, and its maximum is rounded and occurs at slightly positive z.

In fig. 4 we show the structure of the oil–water ($\alpha\gamma$) interface in this symmetrical three-phase equilibrium. We note in fig. 4(b) the concentration of surfactant in the interface with a slight dip in the middle, so that it has local maxima reminiscent of those in the $\alpha\beta$ and $\beta\gamma$ interfaces seen in fig. 3(b). We recall that with these values of the parameters the $\alpha\gamma$ interface is not wet by β. The interface is nevertheless broad, of width *ca.* $12a$. It is interesting that ξ increases slightly in the interface from its bulk-phase value a [fig. 4(c)], although it does not become nearly as great as in the bulk β phase [fig. 3(c)].
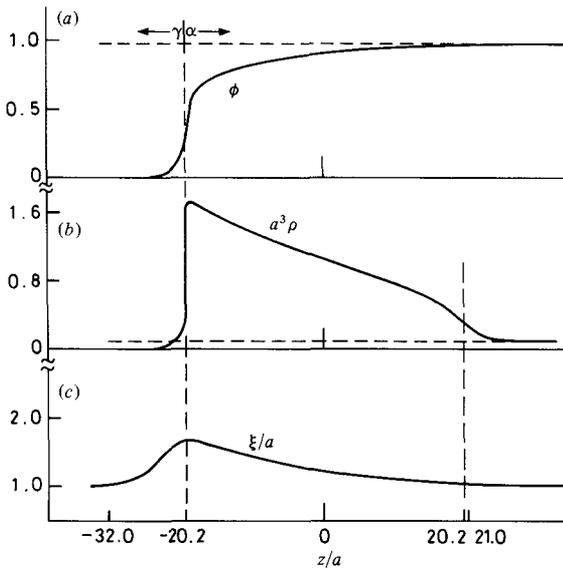
At these values of D/a^2kT and $\sigma_0 a^2/kT$ the $\alpha\beta$ critical endpoint is at $\Lambda a \approx 1.1$. In
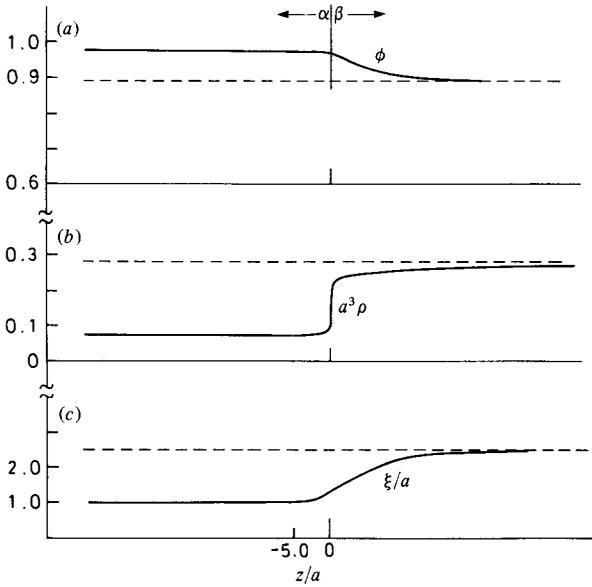
Fig. 5. Profiles of the $\alpha\beta$ interface when $\Lambda a = 0.75$. (a) $\phi(z)$, (b) $a^3\rho(z)$ and (c) $\xi(z)/a$; $\xi/a \equiv 1$ for $z/a \leqslant -5.0$. The crossing point is at $z/a = 0$.
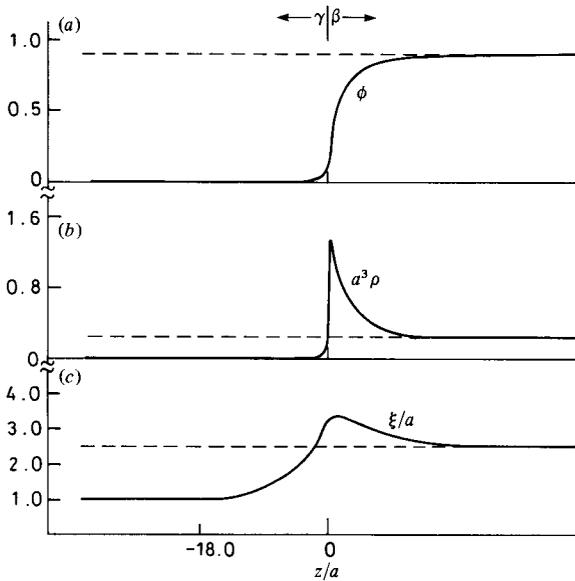
Fig. 6. Profiles of the $\beta\gamma$ interface when $\Lambda a = 0.75$. (a) $\phi(z)$, (b) $a^3\rho(z)$ and (c) $\xi(z)/a$; $\xi/a \equiv 1$ for $z/a \leqslant -18.0$. The crossing point is at $z/a = 0$.

Fig. 7. Profiles of the $\alpha\gamma$ interface when $\Lambda a = 0.75$. (*a*) $\phi(z)$, (*b*) $a^3\rho(z)$ and (*c*) $\xi(z)/a$; $\xi/a \equiv 1$ for $z/a \leqslant -32.0$ and $z/a \geqslant 21.0$. The crossing points are at $z/a = \pm 20.2$.

fig. 5, 6 and 7 we show the profiles of the $\alpha\beta$, $\beta\gamma$ and $\alpha\gamma$ interfaces, respectively, at $\Lambda a = 0.75$ (which, it will transpire, is still below that of the wetting transition). Now [fig. 5(*b*) and (*c*)] there is no longer a maximum in $\rho(z)$ or in $\xi(z)$ in the $\alpha\beta$ interface, which is the one that is becoming critical, although there is still a sharp maximum in $\rho(z)$ and a maximum in $\xi(z)$ in the $\beta\gamma$ interface [fig. 6(*b*) and (*c*)]. Note that ξ in the bulk β phase is less than before [fig. 3(*c*)]; although the fluctuations in ξ in that phase diverge at the critical point,[20] the mean value itself decreases to a there.[11] In fig. 7 we have chosen $z = 0$ to be half way between the two crossing points. The interface is now very broad, mainly because of the great distance between crossing points; *i.e.* the part of the (approximate) U surface that arises from the β phase is now very extensive. Thus, although at this Λ the $\alpha\gamma$ interface is not yet perfectly wet by β, the β phase has already a considerable influence on its structure.

Fig. 8 shows the sum $\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ of the tensions of the $\alpha\beta$ and $\beta\gamma$ interfaces, and the tension $\sigma_{\alpha\gamma}$ of the (stable or metastable) non-wet $\alpha\gamma$ interface, as functions of Λ. These cross at $\Lambda a \approx 0.86$. That is the wetting transition; at smaller Λ the $\alpha\gamma$ interface is not wet by the β phase, at greater Λ it is, and it then remains wet to the critical endpoint at $\Lambda a \approx 1.1$. As D/a^2kT increases, the ratio of Λ at the wetting-transition point to Λ at the critical point approaches 1. Somewhere between the wetting and critical points (a little past $\Lambda a = 0.9$ for the value of D/a^2kT we have been assuming here) there ceases to be a physical solution (*i.e.* there is no longer even a metastable structure) for a non-wet $\alpha\gamma$ interface.

In fig. 8 we see that $\sigma_{\alpha\gamma}$ in the symmetrical equilibrium ($\Lambda = 0$) is $10^{-3}\,kT/a^2$, *i.e. ca.* 10^{-3} times the tension of an oil–water interface in the absence of surfactant, which is realistic for microemulsions. That $\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ has a minimum at $\Lambda = 0$ and is greatest at the critical endpoints is also as in experiment (although here the increase is unrealistically great).

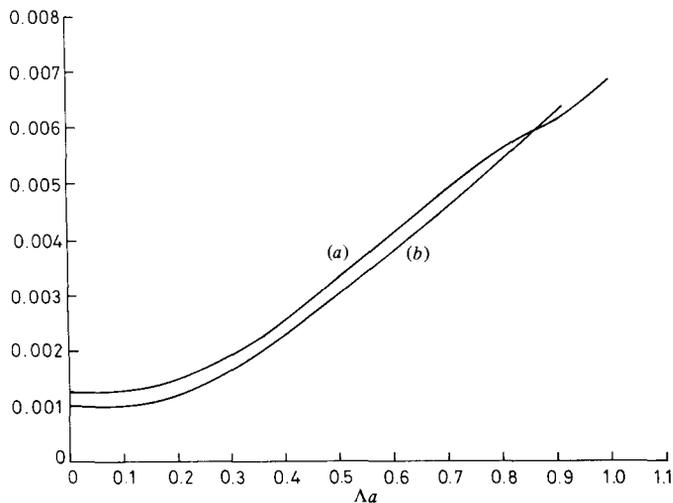When at this D/a^2kT and $\sigma_0 a^2/kT$ the point m_ξ/m_ϕ, $m_\rho/a^6 m_\phi$ lies outside the shaded

Fig. 8. (a) $(\sigma_{\alpha\beta}+\sigma_{\beta\gamma})a^2/kT$, and (b) $\sigma_{\alpha\gamma}a^2/kT$ for the non-wet $\alpha\gamma$ interface, as functions of Λa.

region of fig. 2, so that in the symmetrical equilibrium at $\Lambda = 0$ the $\alpha\gamma$ interface is wet by β, it remains so, we have found, for all Λ up to the critical endpoint.

Lattice Model

As an alternative to the phenomenological model we have been discussing we shall here describe a lattice model with prescribed intermolecular interactions,[21] for which one may hope ultimately to answer the same questions about the interfacial tensions. Wheeler has proposed a related model.[22] The one we describe here is a generalization of an earlier one,[23, 24] in which three species of molecules, AA, BB and an amphiphilic species AB, are confined to the bonds of a lattice, subject to the conditions that every bond be occupied once but once only, and that only the like ends (all A ends or all B ends) of molecules may meet at the same lattice site.

That model is equivalent to the spin-$\frac{1}{2}$ Ising model with nearest-neighbour interactions, and so can have only a two-phase equilibrium with a critical solution point (or, at high concentrations of AB, an ordered phase analogous to an antiferromagnet, but that is irrelevant here). The critical and near-critical phases have large amounts of 'oil' (AA) and 'water' (BB) in the same phase, but only by virtue of also having a comparably high concentration of amphiphile (AB); the interfacial tension is then vanishing or low, but only by virtue of the system's being at or close to a critical point. Thus, these critical or near-critical phases are not usefully thought of as microemulsions, in which oil and water would be solubilized by much lower concentrations of amphiphile and in which the interfacial tensions would be low (*ca.* a thousand times lower than in the absence of surfactant) even when, judged by their compositions, the phases are far from a critical point. Also, by having at most two phases coexisting, the earlier model cannot describe a middle-phase microemulsion in equilibrium simultaneously with an oil-rich and a water-rich phase, which is one of the signatures of microemulsion phase equilibria.

It is the curvature energy of the surfactant film in the phenomenological model that allows it to have such a three-phase equilibrium.[11] In the earlier lattice model[23, 24] there is also an identifiable surfactant film; it may be thought of as the intricately folded, self-intersecting structure made up of squares each of which is the perpendicular bisector of the bond on which an AB molecule lies. By the conditions of the model this surfactant

Table 1. Equivalences between the lattice micro-
emulsion model and the Ising model for a
simple-cubic lattice

lattice microemulsion model	Ising model
$\frac{1}{2}kT \ln [(z_{AA} z_{BB})^{\frac{1}{2}}/z_{AB}] + \frac{5}{2}Q$	J
$kT \ln (z_{BB}/z_{AA})^{\frac{3}{2}} + \frac{15}{4}\lambda Q$	H
$-\frac{1}{4}Q$	M
$-\frac{1}{4}\lambda Q$	L

film forms the microscopic interface between AA-filled and BB-filled regions. In that
model there is no energy associated with the folding of the film; different allowable
configurations of the AA, BB and AB molecules yield different film conformations, but
all are of the same energy.

We are thus led to postulate an additional interaction giving an energy of film folding.[21]
This may be taken to be an energy of interaction of pairs of amphiphiles AB when their
A ends or B ends meet at the same lattice site. If that energy is the same for both A ends
and B ends we have the symmetrical case, as when $\Lambda = 0$ in the phenomenological model.
If it is different, there is a curvature bias: AA-in-BB curvature is different in energy from
BB-in-AA curvature, as when $\Lambda \neq 0$ in the phenomenological model.

Extended in this way, the model is equivalent to a spin-$\frac{1}{2}$ Ising model with next-
nearest-neighbour and three-spin interactions.[21] In this context 'next-nearest-neighbour'
means separated by two lattice steps, whatever that metrical distance might be. The
equivalences for a simple-cubic lattice are summarized in table 1. In the microemulsion
model z_{AA}, z_{BB} and z_{AB} are the thermodynamic activities of the three species, $(1-\lambda) Q$
is the energy when the A ends of two AB meet at the same site, and $(1 + \lambda) Q$ is the energy
when the B ends of two AB meet. The parameters Q and λ are analogous to D/a^2 and
Λa, respectively, in the phenomenological model. In the equivalent Ising model $-J$ and
$+J$ are the respective energies of interaction of neighbouring parallel and antiparallel
spins; $\pm 2M$ are the corresponding energies of interaction when the spins are separated
by a diagonal of one of the square faces of any of the cubic cells of the lattice; $\pm M$
are the energies when the interacting spins are separated by two lattice steps in the same
direction; $\pm L$ are the three-spin interaction energies of connected triples of spins, $-L$
when the number of 'up' spins in the triple is odd, $+L$ when it is even; and H is the
external magnetic field (multiplied by the magnetic moment, as is conventional, so that
it has the dimensions of an energy), favouring 'up' spins when it is positive.

This isotropic Ising model is equivalent,[25] in the mean-field approximation, to the
anisotropic, or axial, next-nearest-neighbour Ising model (the 'ANNNI' model).[26] Even
in the symmetrical case, where $H = L = 0$ ($z_{BB} = z_{AA}$ and $\lambda = 0$ in the microemulsion
model; table 1), it has multiphase equilibria.[26] In particular, there is a curve in the
$J/kT, M/kT$ plane along which two ferromagnetic phases and a 'modulated' phase
coexist. These play the roles, respectively, of the oil- and water-rich phases, α and γ, and
the microemulsion phase, β, in surfactant solutions. There are structural periodicities in
the modulated phase, but these are complex and of mean periods that vary quasi-
continuously with the thermodynamic state.[26] The periodicities are due to the lattice
structure, with which they are mostly commensurate. It is readily believable that were
the same physical mechanisms at work in a continuum model, this phase, in some parts
of the thermodynamic plane at least, would be a disordered, bicontinuous micro-
emulsion. There is also a disordered paramagnetic phase, which in the equivalent solution
model is the oil–water–surfactant solution that one has with a sufficiently high concen-
tration of surfactant even when there is no film-curvature energy ($Q = 0$); however,
that, as we remarked earlier, is not a microemulsion.

As we see from table 1, for the simple-cubic lattice the states in which $J+10M = 0$ in the Ising model are those in which $z_{AB} = (z_{AA} z_{BB})^{\frac{1}{2}}$ in the equivalent solution model. In the symmetrical case $z_{AA} = z_{BB}$, $\lambda = 0$ (or $H = L = 0$ in Ising-model language), the work required to insert an AB molecule at fixed total number of AA, BB and AB molecules, and thus to increase the area of the microscopic surfactant film by that of one elemental square, is $kT \ln [z_{AB}/(z_{AA} z_{BB})^{\frac{1}{2}}]$. This vanishes on the locus $z_{AB} = (z_{AA} z_{BB})^{\frac{1}{2}}$ (or $J+10M = 0$). However, this locus, for the symmetrical case in mean-field approximation, is that of vanishing tension of the macroscopic interface between the bulk α and γ (or ferromagnetic) phases. Those phases are only metastable at that locus just because of the vanishing tension of their interface; the stable phase there is one of the periodic phases (the one called $\langle 3 \rangle$ by Fisher and Selke,[26] which has a wavelength of six lattice spacings).

The tensions of the interfaces between stable phases (the $\alpha\gamma$ interface, for example, where the ferromagnetic phases are stable), influenced by the proximity of those states of vanishing tension, are all low, as in real surfactant solutions. Fisher and Selke[26] give the tension of the interface between the ferromagnetic phases and that of the interface between either of those and the $\langle 3 \rangle$ phase, at low temperatures (still in the symmetrical case $H = L = 0$). In an extension of that work, Fisher and Liu[27] studied what in solution-model language we would call $\sigma_{\alpha\gamma} - (\sigma_{\alpha\beta} + \sigma_{\beta\gamma})$, if we take the $\langle 3 \rangle$ phase now to play the role of β. (Here, by $\sigma_{\alpha\gamma}$ we mean the tension of the non-wet $\alpha\gamma$ interface.) The $\langle 3 \rangle$ phase is not the modulated phase we spoke of before, but it is produced by the same mechanism, and for our present purposes we may take it, too, to be analogous to a microemulsion. Translated into our present language, the result of Fisher and Selke for the simple-cubic lattice,

with
$$w = \exp [-2(J+3M)/kT], \quad x = \exp [-2(J+8M)/kT] \qquad (13)$$

and with a the lattice spacing, is

$$\sigma_{\alpha\gamma} \sim 2\sigma_{\alpha\beta} = 2\sigma_{\beta\gamma} \sim w^4 x(1-x)^2 kT/a^2. \qquad (14)$$

We are near $J+10M = 0$, and we may suppose for a microemulsion that[15] $Q \approx kT$; i.e. from table 1, that $M \approx -\frac{1}{4}kT$. Thus, to see what the typical values of these tensions are we may take $M = -\frac{1}{4}kT$ and $J = (5/2) kT$ in eqn (13), and so estimate $\sigma_{\alpha\gamma} \sim 2\sigma_{\alpha\beta} = 2\sigma_{\beta\gamma} \approx 1 \times 10^{-7} kT/a^2$ from eqn (14). These tensions are ultralow, as in real microemulsion phase equilibria. Fisher and Liu[27] found no difference between $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ to a high order in w, so it is still not known whether β wets the equilibrium $\alpha\gamma$ interface.

This shows promise of being a useful model of microemulsion phase equilibria. It is not yet known whether or when it will have the kinds of interfacial phase transitions we saw in the phenomenological model, but we may hope that further analysis of the model will answer that question.

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