

the adparticles. This is also one of the basic assumptions of the BET theory, which is a natural extension of the Langmuir isotherm for the description of the thermodynamics of multilayer adsorption. This model is, however, inconsistent in so far as it neglects attractive interactions between adsorbed particles within the same layer. As a consequence the isotherms on energetically uniform surfaces at low enough temperatures become steplike, indicating layer-by-layer growth instead of partial population of the $(n + 1)$ th layer before the n th layer is completed as predicted by the BET model. Such a situation is, however, approached above the temperature characterizing the "roughening transition", the effect of which merges multilayer adsorption with the theory of crystal growth as developed first by Burton, Cabrera and Frank.

If the binding energies between adsorbate and surface become comparable to those between the surface atoms themselves, the substrate may no longer be regarded as an array of fixed lattice points. Instead the surface atoms may be displaced from their original positions via first-order phase transitions. Oscillations in the rate of a catalytic reaction associated with temporal and spatial self-organization of the surface structure represent a striking example of periodic nonequilibrium phase transitions of this kind. These phenomena belong in the general area of "synergetics", which is of great actual importance in many different fields.⁴⁴

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Phase Transitions in Surfactant Solutions and in Their Interfaces

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A surfactant solution may separate into three coexisting phases of which the middle one is a microemulsion. That phase may or may not wet the interface between the top (oil-rich) and bottom (water-rich) phases. The distinction may be an important one in distinguishing microemulsions from less structured solutions of smaller amphiphiles. There is both experimental and theoretical evidence for a transition from nonwetting to wetting as the critical end points of the phase separation are approached. A theoretical model of microemulsions that is described is consistent both with the ultralow tensions of the interfaces and with the nonwetting of the oil-water interface by the microemulsion. The model is consistent also with the earlier picture of that interface as consisting of a monolayer of amphiphile.

Oil-water-surfactant solutions sometimes separate into three coexisting liquid phases: a top phase α that is nearly pure oil, a bottom phase γ that is nearly pure water, and a middle-phase microemulsion β in which most of the amphiphilic surfactant is concentrated and which contains large amounts of both oil and water.

The tensions of the interfaces between pairs of these phases are $\sigma_{\alpha\beta}$, $\sigma_{\beta\gamma}$, and $\sigma_{\alpha\gamma}$. We ask whether these are related by

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \quad (1)$$

When they are, β is said to wet the interface between α and γ , and the $\alpha\gamma$ interface, in its equilibrium structure, consists of a macroscopically thick layer of β phase.¹ The composition profiles of the interfaces are then as in Figure 1, in which x is some composition variable that has the values x_α, x_β , and x_γ in the bulk phases and z is the vertical distance (depth). Between x_α and x_β the profile is that of the $\alpha\beta$ interface; between x_β and x_γ it is that of the $\beta\gamma$ interface. The full profile, between x_α and x_γ , is that of the $\alpha\gamma$ interface; where x goes through the value x_β characteristic of the bulk β phase this profile has a step in it of indeterminate, macroscopic height, which is the layer of β that constitutes the $\alpha\gamma$ interface when (1) holds.

Relation 1 among the tensions, and the composition profiles of Figure 1, is implied by the van der Waals or mean-field theory of interfaces based on a single order

parameter (composition variable).² In Figure 2 we see how, in such a theory,^{3,4} the tensions vary between the two critical end points that bound the three-phase region and how they extend into the two-phase regions beyond the critical end points. What is plotted are the logarithms of the tensions, as has become conventional in the representation of the interfacial tensions in microemulsion phase equilibria.

The $\alpha\beta$ critical end point is a critical point (consolute point) of the $\alpha\beta$ phase equilibrium in which the critical $\alpha\beta$ phase is in coexistence with a γ phase, which remains distinct, and similarly for the $\beta\gamma$ critical end point. The α and β phases become identical at the $\alpha\beta$ critical end point, so it marks one boundary of the three-phase region, and $\sigma_{\alpha\beta}$ vanishes there, so $\log \sigma_{\alpha\beta} \rightarrow -\infty$, as seen in the figure. The $\beta\gamma$ critical end point marks the other boundary of the three-phase region, and there $\log \sigma_{\beta\gamma} \rightarrow -\infty$. By varying S —called that because in practice S is often the salinity of the aqueous component of the mixture—we may traverse the three-phase region between the two critical end points and even go into the two-phase regions beyond them.

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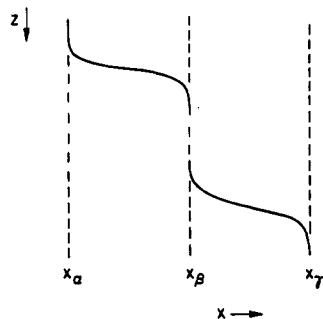


Figure 1. Composition profiles of the $\alpha\beta$, $\beta\gamma$, and $\alpha\gamma$ interfaces. x is a composition variable with values x_α , x_β , and x_γ in the bulk α , β , and γ phases; z is distance perpendicular to the interfaces.

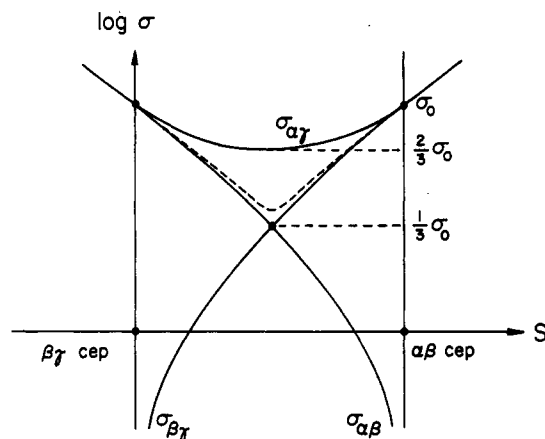


Figure 2. Surface tensions as functions of salinity in the three-phase region between the two critical end points and extended into the adjoining two-phase regions.

In the simplest version of this theory,⁵ which is intended to hold only when the two critical end points are not too far apart (i.e., near the tricritical point of the three-phase equilibrium), α and γ play symmetrical roles, so that, for example, $\sigma_{\alpha\beta}$ at the $\beta\gamma$ critical end point and $\sigma_{\beta\gamma}$ at the $\alpha\beta$ critical end point have a common value, called σ_0 in Figure 2. The theory then requires that in the middle of the three-phase region, where the β phase is symmetrically related to α and γ and where $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$, the common value of these two tensions be $\sigma_0/3$, as shown in the figure. This is the " $1/3$ rule". Because this theory entails eq 1, in this symmetrical equilibrium in the middle of the three-phase region $\sigma_{\alpha\gamma} = 2\sigma_0/3$, as also shown in the figure, while at the critical endpoints $\sigma_{\alpha\gamma} = \sigma_0$.

The qualitative features of Figure 2 and relation 1 among the tensions (Antonow's rule) have been confirmed in solutions with small nonionic amphiphiles (ethanol, propanol, butanol).^{5,6} However, the symmetry of the figure, which is required by the theory when the two critical end points are close to each other, is not (or has not yet been) confirmed by experiment.⁷ Such an asymmetry is found in the mixture toluene + brine (salinity S) + n -butanol + sodium dodecyl sulfate,^{8,9} for which $\sigma_{\alpha\beta}$ at the $\beta\gamma$ critical end point is found to be 0.011₅ dyn/cm while $\sigma_{\beta\gamma}$ at the $\alpha\beta$ critical end point is 0.017 dyn/cm, at 20 °C.

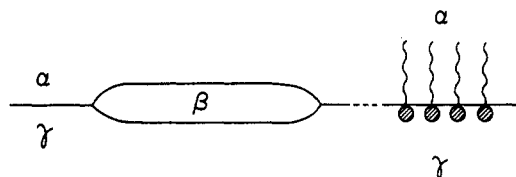


Figure 3. Schematic of a lens of β not spreading at the $\alpha\gamma$ interface, the latter being imagined to consist of a monolayer of oriented amphiphile between the bulk oil and water phases.

It is not known if this asymmetry is another example of a persistent one,⁷ which violates theory, or means merely that the system is not close enough to its tricritical point to be in the asymptotic regime in which the theory requires symmetry. In spite of the asymmetry in this case, the $1/3$ rule is well satisfied on the average: $1/3$ of the average of 0.011₅ and 0.017 dyn/cm is 0.0047₅ dyn/cm, while from the measurements at intermediate salinities,^{8,9} the common value of $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$, where the two curves in a plot like that in Figure 2 cross in the middle of the three-phase region, is 0.0047 dyn/cm.

Although the behavior of $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ in this and similar systems is in at least rough accord with the theory that is summarized in Figure 2, that of the tension $\sigma_{\alpha\gamma}$ of the oil-water interface is not. Apparently eq 1 does not hold in microemulsion phase equilibria in which the surfactant molecules are large. Instead, $\sigma_{\alpha\gamma}$ is nearly equal to the larger of $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ (instead of to their sum)⁸⁻¹¹ and so follows what is shown as the dashed curve in Figure 2 instead of the solid curve. This implies that the middle-phase microemulsion does not wet (spread at) the oil-water interface; it rests on that interface as a thin lens, as shown schematically in Figure 3. This has been seen by eye.¹¹⁻¹³

The failure of eq 1 in these microemulsion phase equilibria is in contrast to what was found in the analogous three-phase equilibria with smaller, nonionic amphiphiles.^{5,6} It may be a fundamental distinction between these two kinds of three-phase equilibria in solutions of oil + water + amphiphile, which are otherwise, as emphasized by Kahlweit¹⁴ and by Knickerbocker et al.,¹⁵ closely analogous. Traditionally, microemulsions are thought of as composed of large oil-coherent and water-coherent regions, micellar or bicontinuous, separated by a film of oriented surfactant molecules; the film is then treated as an autonomous structure of vanishing or very low tension and a favored curvature.¹⁶ The traditional view of oil-water mixtures with smaller amphiphiles is less specifically structural; it is assumed implicitly that there is not one dominant structure but a whole range of important structures with rapid fluctuations among them in space and time. In the progression from solutions with small amphiphiles to microemulsions there may be a continuous evolution of structure with the gradual emergence of a dominant one, so that the two kinds of oil-water-amphiphile solutions come to be qualitatively different. We may be seeing that difference reflected in the

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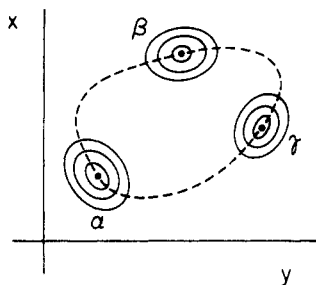


Figure 4. Two independent composition variables x and y varying through the interfaces between bulk α , β , and γ phases. The variations in x and y follow the dashed-line curves. The full-line contours are those of constant free-energy density, which has three equally deep minima at the three bulk phases.

wetting vs. nonwetting of the oil-water interface by the middle phase.

When the β phase does not spread at the $\alpha\gamma$ interface, the structure of the latter is not that of a macroscopically thick layer of β . What then is it? The usual view⁸⁻¹¹ is that the oil-water interface then consists of a monolayer of oriented amphiphile, as indicated schematically in Figure 3. We shall find some support for that view below, in a model microemulsion.

We expect from general principles¹⁷ a transition from nonwetting to wetting of the $\alpha\gamma$ interface by β as either of the two critical end points that bound the three-phase region is approached. Such a transition has been seen in experiment,¹³ and we shall see other examples of it in theoretical models, below.

We remarked that the wetting of the $\alpha\gamma$ interface by β was inevitable in any theory based on a single order parameter; so to accommodate nonwetting in the theory we must consider the possible independent variation of two or more order parameters through the interfaces. In Figure 4 we see schematically² the possible variation of two such composition variables, x and y . The contours are those of constant free-energy density, which has three equally deep minima at the compositions x, y of the coexisting α , β , and γ phases. The dashed curve is the trajectory that shows how x and y vary together in going from one bulk phase to another. We see alternative paths from α to γ , one via β and one not. When that which goes via β has the lower integrated free energy, the $\alpha\gamma$ interface is wet by β and in its equilibrium structure consists of a layer of bulk β (Figure 1), and eq 1 then holds. When the other, more direct, path from α to γ gives the interface of lower free energy, β does not wet the $\alpha\gamma$ interface, which now does not resemble bulk β in its structure, and $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$. The transition between wetting and nonwetting, at which there is a discontinuous change in structure of the $\alpha\gamma$ interface, occurs when the alternatives are of equal free energy.

Some of these questions have been addressed¹⁸ in the context of a phenomenological microemulsion model¹⁹ that evolved from earlier ones of Talmon and Prager²⁰ and of de Gennes et al.^{16,21} The model is illustrated in Figure 5. Cells of edge length ξ are filled at random with oil or water, while the surfactant molecules are confined to the microscopic interfaces between oil- and water-filled cells.

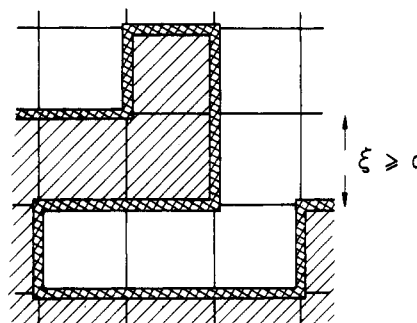


Figure 5. Phenomenological microemulsion model, with cells of size $\xi \geq a$ filled randomly with oil (unshaded) or water (shaded) and with amphiphile confined to the microscopic interface (cross-hatched) between oil-filled and water-filled cells.

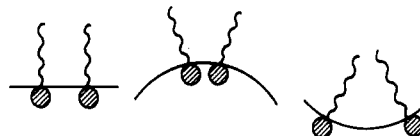


Figure 6. Planar and curved portions of the surfactant film. Amphiphiles lie parallel at the planar portions, but their polar heads are forced together and their hydrocarbon tails apart, or vice versa, where the film is curved.

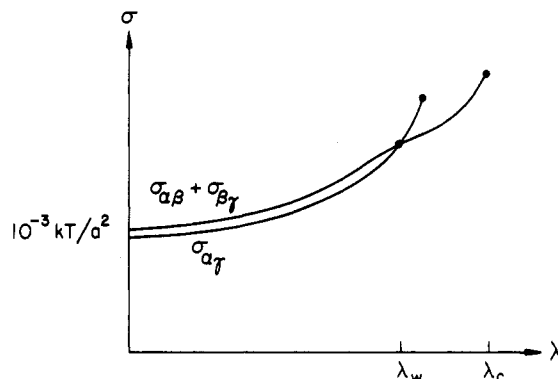


Figure 7. Surface tension in the phenomenological microemulsion model as a function of the curvature-bias parameter λ . The wetting-nonwetting transition occurs at λ_w , the critical endpoint at λ_c .

There is a cost in free energy for the microscopic interface to bend away from planarity, and a dimensionless parameter λ that measures the bias in this curvature free energy: the extent to which this free energy depends on whether water or oil is on the inside of the bend. This is in imitation of the presumed curvature free energy of the surfactant film in real microemulsions, arising from the interaction between the polar heads and between the hydrocarbon tails of neighboring surfactant molecules,^{16,20,21} as shown schematically in Figure 6.

The cell size ξ is a variational parameter in the full free-energy density but is bounded below by a fixed length a of molecular size. Without such a lower limit imposed on ξ the system's free energy would decrease without bound as ξ decreased all the way to $\xi = 0$, because the entropy of mixing would then increase without bound. The model imposes a lower limit on ξ , hence an upper limit on the entropy of mixing, in the same way that nature does: by insisting that the mixing not occur on a scale smaller than the molecules.

The calculated interfacial tensions for this model¹⁸ are shown schematically in Figure 7. The curvature-bias parameter λ is analogous to S (which is often the salinity) in Figure 2. The value $\lambda = 0$ corresponds to the S about which Figure 2 is symmetric; there the microemulsion

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phase β is symmetrically related to the oil-rich phase α and the water-rich phase γ . At $\lambda = 0$ in the present model, then, the curvature free energy is independent of the sense of the curvature: for the same amount of bending, the free energies of the second and third configurations in Figure 6 are equally far above that of the first. As λ departs from 0 a bias sets in, which favors one sense of curvature over the other. At the same time, phase β comes to be unsymmetrically related to α and γ , and as λ grows, positively or negatively, the $\alpha\beta$ or $\beta\gamma$ critical end point is approached. Figure 7 may be thought of as the $\lambda > 0$ half of a diagram, the $\lambda < 0$ half of which is just its mirror image.

Figure 7 shows $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ at $\lambda = 0$, i.e., for the symmetric phase equilibrium, which is in the middle of the three-phase region. That is so with particular, although realistic, choices of values of the other parameters in the model. The surface free energies $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ are nearly equal, so when one or the other is smaller it is only slightly smaller; i.e., in this model the difference in free energy between wetting and nonwetting is slight. The model, then, allows either, just as both are realizable in experiment, and it is the nonwetting alternative at $\lambda = 0$ that is seen in Figure 7.

We note in the figure that the equilibrium tension of the $\alpha\gamma$ interface, which is always that given by the lower of the two curves, is minimal at $\lambda = 0$ and increases as λ increases. That, together with its mirror image for $\lambda < 0$, is as in Figure 2.

We also see from Figure 7 that the tensions are of the order of $10^{-3}kT/a^2$. The natural unit of surface tension in the model is kT/a^2 ; any tension much greater or much less than this is very high or very low in an absolute sense. We see, then, that in this model the tensions are very low, as they are in real microemulsion phase equilibria.

Where the two curves in Figure 7 cross, at $\lambda = \lambda_w$, is the wetting-nonwetting transition. That is in accord with the principle mentioned earlier, according to which the microemulsion phase will come to wet the oil-water interface close to the critical end points even if it does not already do so in the middle of the three-phase region. For $\lambda > \lambda_w$, the $\alpha\gamma$ interface contains, in its equilibrium structure, a layer of bulk β , and its tension is $\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$. The nonwet $\alpha\gamma$ interface, the tension of which is what is called $\sigma_{\alpha\gamma}$ in Figure 7, is the stable structure for $\lambda < \lambda_w$ but becomes a metastable structure, of higher free energy than that of the wet interface, for $\lambda > \lambda_w$. The extension to $\lambda > \lambda_w$ of the $\sigma_{\alpha\gamma}$ curve in Figure 7 gives the tension of that metastable interface. That extension, as shown in the figure, comes to an end some way before the critical end point at $\lambda = \lambda_c$. It ends when, in Figure 4, there ceases to exist any direct path from α to γ that is even a local minimum-free-energy structure. From there on, the only path from α to γ is the indirect one, via β . That happens when, in Figure 4, the β phase is too nearly intermediate between α and γ , so that the β minimum in the free-energy density occurs too close to the line between the α and γ minima.

The model just described^{18,19} is phenomenological, based on a prescribed free-energy density that is a function of chemical composition but not based on a Hamiltonian. Now we shall look at a related lattice model²² that is based on prescribed intermolecular interactions.

We imagine three species of molecules, O-O (oil), ●-● (water), and O-● (amphiphile). These lie along the bonds of a lattice in such a way that only the like ends (only O ends or only ● ends) of molecules may come together at any lattice site; see Figure 8. We introduce also a bending

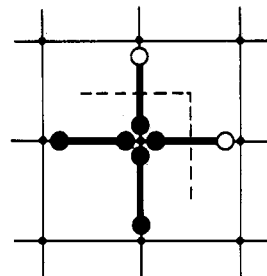


Figure 8. Microscopic lattice model of microemulsions. The dashed lines (really squares in three dimensions) go through the midpoints of the amphiphiles and thus show the microscopic surfactant film.

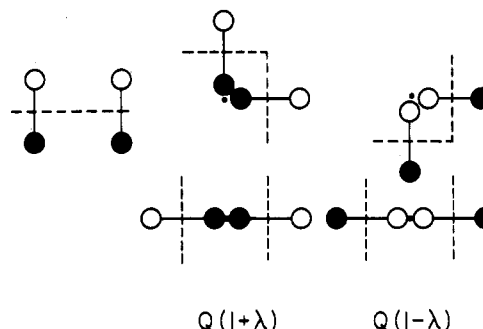


Figure 9. Neighboring amphiphiles when the surfactant film is locally planar, or bent, or in the form of a bilayer. In the latter two cases, according to whether it is the hydrophilic or the hydrophobic (lipophilic) ends of neighboring amphiphiles that are brought together, the excess energy is $Q(1 + \lambda)$ or $Q(1 - \lambda)$.

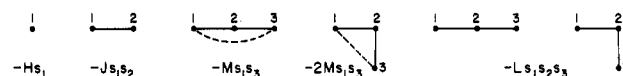


Figure 10. Energies of single spins, pairs of neighboring spins, and connected triples of spins, in the Ising model that is equivalent to the microemulsion model of Figures 8 and 9.

energy, analogous to that associated with the curvature of the surfactant film in Figure 6. The surfactant "film" is just a geometrical construct and is shown in Figure 8 as the dashed lines (or squares, in three dimensions) through the centers of the amphiphiles. The present analogue of Figure 6 is Figure 9, in which we see an energy $Q(1 + \lambda)$ associated with a bend in the film or with a bilayer structure that brings the ● ends of a pair of amphiphiles together at the same lattice site and an energy $Q(1 - \lambda)$ whenever the O ends of two amphiphiles meet. Here λ is analogous to the parameter λ in the phenomenological model.

The model as so defined is equivalent to an Ising model—a model of interacting spins on a lattice. The lattice for the associated Ising model is the same as that in the microemulsion model but has spins at the lattice sites instead of molecules on the bonds. Let $s_i = \pm 1$ be the spin at site i . Then the interactions in this equivalent Ising model are as shown in Figure 10. Each spin s_i interacts with an external magnetic field, with interaction energy $-Hs_i$. Each pair of neighboring spins s_1 and s_2 interact with energy $-Js_1s_2$. A pair of spins separated by two steps on the underlying lattice— s_1 and s_3 in Figure 10—interact with energy $-Ms_1s_3$ if the triple of connected sites 1, 2, and 3 is linear but with energy $-2Ms_1s_3$ if it is nonlinear. The spins at any triple of connected sites 1, 2, and 3, linear or nonlinear, interact also with the three-spin interaction $-Ls_1s_2s_3$. The energy parameters H , J , M , and L are the four parameters of this associated Ising model. They are the counterparts of the two curvature-energy parameters Q and λ and of the two combinations $\mu_a - (\mu_o$

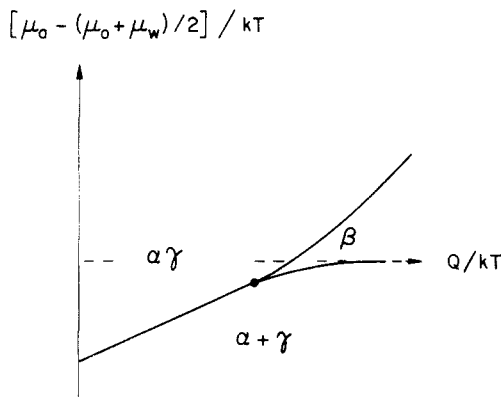


Figure 11. Schematic phase diagram for the lattice microemulsion model in its symmetric states. Region $\alpha\gamma$ is that of homogeneous oil-water-surfactant solutions, structurally different from those of the microemulsion phases β ; region $\alpha + \gamma$ is where oil-rich α is in equilibrium with water-rich γ . The boundary between $\alpha\gamma$ and $\alpha + \gamma$ is a line of critical-solution points (consolute points); that between β and $\alpha\gamma$ is a second-order-transition line; and that between β and $\alpha + \gamma$ is a first-order-transition line, hence a locus of triple points.

$+ \mu_w)/2$ and $\mu_w - \mu_o$ of the configurational chemical potentials μ_a , μ_o , and μ_w of the amphiphile, oil, and water, in the microemulsion model. The connections for the simple-cubic lattice in three dimensions are

$$J/k\theta = \{5Q - [\mu_a - (\mu_o + \mu_w)/2]\}/2kT \quad (2)$$

$$M/k\theta = -Q/4kT \quad (3)$$

$$H/k\theta = [15\lambda Q/2 + 3(\mu_w - \mu_o)]/2kT \quad (4)$$

$$L/k\theta = -\lambda Q/4kT \quad (5)$$

where θ is the absolute temperature in the Ising model when T is that in the microemulsion model.

The minus sign in (3) is crucial. The bending energy Q is taken as positive to encourage the formation of extended structures in the microemulsion. That, by (3), implies $M < 0$, favoring antiparallel alignment of the spins at second-neighbor sites. This antiferromagnetic interaction can then compete with ferromagnetic interactions of neighboring spins ($J > 0$) to produce a multiplicity of complex structures that differ little in free energy and to give low tensions of the interfaces between coexisting phases.

Thanks to recent and continuing work by M. D. Lipkin, K. A. Dawson, and P. Balbuena, many of the properties of this model are now known. Most results to date have been obtained within the mean-field approximation, and for the special case $H = L = 0$, i.e., for the fully symmetric case $\lambda = 0$ and $\mu_o = \mu_w$. Figure 11 shows, schematically, the phase diagram in the plane of the remaining parameters Q/kT and $[\mu_a - (\mu_o + \mu_w)/2]/kT$. It resembles in several respects the analogous phase diagram of the earlier phenomenological model.²³ The region marked $\alpha\gamma$ is a homogeneous solution of oil and water, rendered mutually soluble by a high concentration of amphiphile. It is the paramagnetic (disordered) region of the equivalent Ising model. In this symmetric case with $\lambda = 0$ and $\mu_o = \mu_w$ there are equal concentrations of oil and water in the $\alpha\gamma$ phase. That phase nevertheless differs from the microemulsion phase β , which is also a homogeneous oil-water-amphiphile solution with equal concentrations of oil and water but which has complex, large-scale structures that distinguish it from $\alpha\gamma$.

The region β in Figure 11 consists of a complex network of subregions, separated by first-order-transition lines. The structure of the microemulsion is different in each subregion. The structures that have so far been studied are periodic. All imaginable periodicities, both commensurate and incommensurate with that of the underlying lattice, are represented. The $\beta, \alpha\gamma$ phase boundary is a locus of second-order transitions; the amplitudes of the periodic modulations of chemical composition vanish within $\alpha\gamma$ and on the boundary and are nonvanishing in the β region.

There is an alternative lattice model of microemulsions²⁴ in which the disordered states of the kind that are here called $\alpha\gamma$, i.e., the paramagnetic states of an equivalent Ising model, are themselves identified as the microemulsion, so that there are not distinguishable $\alpha\gamma$ and β regions separated by a phase boundary. Separate regions, such as are found in the present model, are found also in the earlier phenomenological model,¹⁹ where they are distinguished by the cell size ξ the system chooses so as to minimize its free energy: in the $\alpha\gamma$ phase $\xi = a$, the lower limit of the allowed sizes, while in the microemulsion ξ is greater than a , and often much greater.

It is not known whether in real microemulsions there are distinguishable $\alpha\gamma$ and β phases or whether, as in the model of Pandit et al.,²⁴ there is only one such region of homogeneous oil-water-amphiphile solutions. Nor is it yet known, in the lattice model that has been described here, whether in some augmented thermodynamic space, of which Figure 11 would be merely a subspace, $\alpha\gamma$ and β might not be seen to belong to the same continuous manifold of states. The distinction between $\alpha\gamma$ and β , which is seen in the lower dimensional space of Figure 11, would then not be a fundamental and permanent one. The issue is an important one and is another aspect of the question raised earlier with respect to the wetting or nonwetting of the interface between the oil- and water-rich phases by the β phase, viz., whether microemulsions are basically the same as the less structured oil-water-amphiphile solutions formed by smaller amphiphiles or are qualitatively different.

The region $\alpha + \gamma$ in Figure 11 is that of coexisting oil-rich and water-rich phases. The boundary that separates it from β is a locus of triple points, i.e., of three-phase states. These are the three-phase equilibria characteristic of microemulsions. The line between the $\alpha\gamma$ and $\alpha + \gamma$ regions is a locus of critical-solution points (consolute points). The $\beta, \alpha + \gamma$ triple-point line has the Q/kT axis, along which $\mu_a = (\mu_o + \mu_w)/2$, as an asymptote, which it approaches exponentially rapidly. After just a short distance along the triple-point line from the point where the regions $\alpha\gamma$, $\alpha + \gamma$, and β all meet, the separate α and γ phases are nearly pure oil and pure water, while the β phase is $1/9 = 11\%$ amphiphile and $4/9 = 44\%$ each of water and oil. (The β phase then consists of parallel planes, each plane of uniform composition, but alternating by threes between planes that are mostly of \circ sites and planes that are mostly of \bullet sites.)

Dawson²⁵ remarks that the tension $\sigma_{\alpha\gamma}$ of the oil-water interface vanishes at the point in Figure 11 where the $\alpha\gamma$, $\alpha + \gamma$, and β regions all meet, because that is a point on the line of α, γ critical points, and that²² $\sigma_{\alpha\gamma} \rightarrow 0$ as $Q/kT \rightarrow \infty$ along the Q/kT axis [where $\mu_a = (\mu_o + \mu_w)/2$] and

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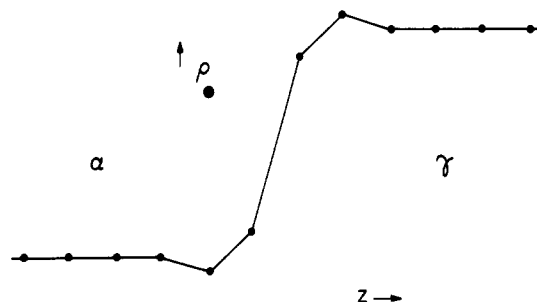


Figure 12. Schematic of Dawson's density profile of the $\alpha\gamma$ interface, giving the density of \bullet sites in planes parallel to the interface as a function of the index z of the planes. The bulk α and γ phases are at $z = \pm\infty$.

hence also as $Q/kT \rightarrow \infty$ along the $\beta, \alpha + \gamma$ triple-point line, so that somewhere along that triple-point line $\sigma_{\alpha\gamma}$ has a maximum value. He calculates that maximum value to be

$$\max \sigma_{\alpha\gamma} = (2 \times 10^{-3})kT/a^2 \quad (6)$$

in excellent accord with the $(1 \times 10^{-3})kT/a^2$ found¹⁸ in the phenomenological model at $\lambda = 0$, as seen here in Figure 7. We should note that there are no adjustable parameters in (6); in obtaining the dimensionless coefficient 2×10^{-3} we do not assign a value to any parameter. The tensions of the interfaces in the microemulsion phase equilibria in this model are thus ultralow in an absolute sense. To be sure, the coefficient in (6) is likely to be lattice-dependent and has so far only been found to be 2×10^{-3} for the simple-cubic lattice, on which the calculations have been based, but it is unlikely to be very different for any of the other simple three-dimensional lattices.

Dawson²⁵ has also obtained the chemical-composition profiles of the interfaces in these microemulsion phase equilibria. His results for the $\alpha\gamma$ interface, along the triple-point line as it approaches its asymptote, are shown here schematically in Figures 12 and 13. In Figure 12 is shown the mean density of \bullet sites in lattice planes parallel to the interface. The planes are indexed by z . Figure 13 shows the mean density of $\circ-\bullet$ bonds, i.e., of amphiphiles, that lie between the planes at z and at $z + 1$ on bonds perpendicular to the interface. (The smaller concentration of amphiphiles lying parallel to the interface is not shown.) The bulk α and γ phases are at $z = \pm\infty$. The density of \bullet sites is low in the α phase and high in the γ phase, and vice versa for the \circ sites. The concentration of amphiphiles is low in both bulk phases and strongly peaked in the interface.

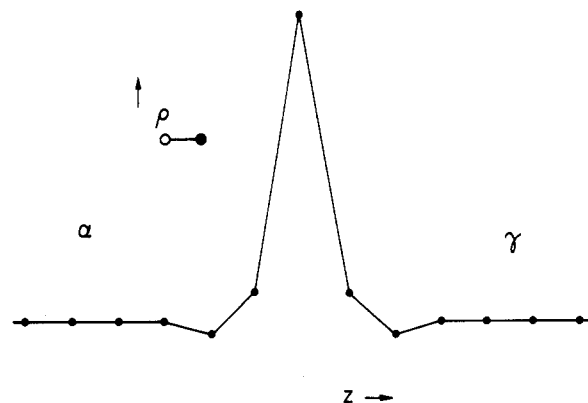


Figure 13. Schematic of Dawson's profile of the density of amphiphiles through the $\alpha\gamma$ interface, giving the mean density of amphiphiles that lie between the planes at z and at $z + 1$ on bonds perpendicular to the interface. The bulk α and γ phases are at $z = \pm\infty$.

The approach to the bulk α and γ phases as $z \rightarrow \pm\infty$ is oscillatory but with an exponentially damped amplitude of oscillation, so on the scale of Figures 12 and 13 the oscillations are not visible more than two lattice spacings away from the interface's symmetry plane. The oscillation has a half-wavelength of three lattice spacings, which is reminiscent of the structure of the coexisting β phase, but we see in Figures 12 and 13 that the $\alpha\gamma$ interface consists of only a microscopic, not a macroscopic, layer of this β -like phase. Thus, β does not wet the $\alpha\gamma$ interface. Dawson confirms this by the quantitative relation among the interfacial tensions: he finds²⁵ $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ (here $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ by symmetry), although the difference between $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ is only slight, as in the phenomenological model¹⁸ (Figure 7). The nonwetting of the $\alpha\gamma$ interface by β , we have seen, is apparently characteristic of real microemulsion phase equilibria.

Figure 13 shows that the interface consists primarily of a monolayer of oriented surfactant, with minor perturbations in the immediately adjacent layers, and little else. This is in agreement with the early picture shown schematically in Figure 3 and is still another respect in which the model seems to be providing some useful insights.

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