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J. Jouffroy, P. Levinson, P.-G. de Gennes. Phase equilibria involving microemulsions (Remarks on the Talmon-Prager model). *Journal de Physique*, 1982, 43 (8), pp.1241-1248. 10.1051/jphys:019820043080124100 . jpa-00209502

HAL Id: jpa-00209502

<https://hal.science/jpa-00209502>

Submitted on 4 Feb 2008

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Classification
 Physics Abstracts
 68.10

Phase equilibria involving microemulsions (Remarks on the Talmon-Prager model)

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(Reçu le 1^{er} mars 1982, accepté le 23 avril 1982)

Résumé. — Nous présentons ici un modèle statistique pour les microémulsions inspiré d'une idée de Talmon et Prager (mais comportant quelques modifications). On suppose que le surfactant est insoluble à la fois dans l'huile et dans l'eau et qu'il est distribué en minces feuillets séparant les domaines d'huile et d'eau. Le feuillet a une longueur de persistance ξ_K . Deux éléments successifs (d'aire ξ_K^2) ont des orientations indépendantes. Ceci apporte au film une certaine entropie S . L'énergie libre inclut : a) la tension interfaciale γ ; b) l'entropie S ; c) un terme de courbure dont le signe est déterminé par la règle de Bancroft. Les effets d'interaction entre gouttelettes (ou autres formes de dispersion) apparaissent simplement comme renormalisation de γ . Nous montrons que, dans ce modèle, tous les équilibres présentant un intérêt ont lieu pour les très faibles valeurs de $\gamma \sim kT/\xi_K^2$, c'est-à-dire au voisinage immédiat d'une courbe bien définie (courbe de Schulman), correspondant à $\gamma = 0$ dans le diagramme de phase ternaire. La structure détaillée des lignes d'équilibre est fortement dépendante de la forme donnée au terme de courbure. Cependant les formes plausibles simples que nous avons introduites pour ce terme ne peuvent engendrer que des équilibres à deux phases et non à trois phases. Nous en concluons que des effets plus complexes (incluant le voisinage d'un point de trouble ou des attractions fortes entre gouttelettes) sont nécessaires pour expliquer les équilibres à trois phases.

Abstract. — We discuss a statistical model for microemulsions, inspired by an idea of Talmon and Prager (but with certain modifications). The surfactant is assumed to be insoluble in both oil and water, and to be distributed in thin sheets, separating oil and water regions. The sheet has a persistence length ξ_K . Consecutive pieces (of area ξ_K^2) have independent orientations. This gives a certain entropy S to the film. The free energy includes : a) the interfacial tension γ ; b) the entropy S ; c) a curvature term whose sign is defined by the Bancroft rule. Interaction effects between droplets (or other shapes) appear simply as a renormalization of γ . We show that in this model all equilibria of interest take place for very low $\gamma \sim kT/\xi_K^2$, i.e. very close to a particular line (the « Schulman line ») corresponding to $\gamma = 0$ in the ternary phase diagram. The detailed structure of the tie lines depends sensitively on the structure of the curvature term. But for plausible forms of this term we are able to generate only 2-phase equilibria, and we do not reproduce 3-phase equilibria. We conclude that more complex effects (involving the vicinity of a cloud point or strong attraction between droplets) are requested to explain the observed 3-phase equilibria.

1. Introduction. — In some favourable cases, a system oil + water + surfactant can exist as a fluid, transparent, isotropic liquid called a microemulsion [1]. In certain limiting cases a microemulsion is simply made of « swollen micelles » : oil droplets in water (or the inverse), the oil/water interface being saturated by surfactant molecules [2]. However when the oil and water fractions are comparable the system is probably « bicontinuous » [3] : the oil regions have the structure of a connected random network and the same property also holds for the water regions. One major question amounts to understand why these structures do not collapse into ordered systems (lyotropic liquid crystals or crystals). In a recent

review [4] C. Taupin and one of us suggested that the answer may depend on the *persistence length* ξ_K of the interface. Small values of ξ_K (~ 100 Å) correspond to very wrinkled interfaces and favour microemulsions, while large ξ_K (~ 500 Å) favour liquid crystal phases. The length ξ_K is an exponential function of the local rigidity of the film, and should thus be very sensitive to additives : in practice microemulsions are often obtained by addition (to the oil/water surfactant base) of a short alcohol (« cosurfactant »). As suggested long ago by Schulman [5] the main role of the cosurfactant is probably to reduce the local rigidity of the film.

Another remarkable feature of microemulsions is

related to their phase equilibria [6]. For instance when increasing the water fraction of a microemulsion (M) made with droplets of water in oil, one often reaches a solubility limit : at this point a phase separation between M and a water rich phase occurs. Various energies contribute to these phase transitions [7] :

1) The oil (or water) regions tend to coalesce because of long range Van der Waals attractions : a system of droplets may show, on a large scale, the analog of the liquid-gas transition of monoatomic fluids.

2) Because the interface is expected to be wrinkled, the *entropy* of the interfacial film may become significant. The role of this entropy has been analysed in a pioneering article by Talmon and Prager (T.P.) [8]. They showed that it could lead to remarkable phase transitions, without any ingredient of type 1). The present work is based on this idea, but with four modifications :

a) T.P. described the geometry of the random film by a subdivision of space into Voronoi polyhedra, with a certain characteristic size ; the meaning of this size was unclear. In our picture this meaning is natural : the size is the persistence length ξ_K ;

b) we replace the Voronoi system by a simpler division of space into cubes of edge ξ_K . This brings in considerable simplifications : the phase transition (for the simplest case) maps directly into an Ising model ;

c) T.P. considered that the interfacial area per surfactant molecule Σ was fixed ($\Sigma = \Sigma^*$) — and thus that the surfactant volume fraction (ϕ_s) controlled entirely the size of the interfacial area (per unit volume). We remove this assumption : starting from a general form for the equation of state of the interfacial film, we show that phase equilibria should occur close to (but not exactly at) a situation of zero interfacial tension γ ;

d) T.P. attempted to incorporate a certain preference for *curved interfaces*, through a geometrical trick. They attributed a lower energy to curved interfaces, but this energy was taken to be the same for both signs of curvature : i.e. for droplets of oil in water or for droplets of water in oil. Models of this type lead rather naturally to 3-phase equilibria (between two microemulsions of opposite curvature, and a microemulsion of zero curvature). Talmon and Prager were aware of the somewhat artificial character of this construction. In the real world, the film tends to bend, with the better solvent of the surfactant on the outside : this is known for macroscopic emulsion droplets as the rule of Bancroft [9]. Thus only one sign of curvature is preferred : we take this dissymmetry into account here, and characterize it by a certain « Bancroft parameter » λ .

All our description is based on the notion of thin surfactant sheets separating regions of oil and water which are larger than the sheets : this means that we

restrict our attention to the vicinity of the O-W edge in a triangular phase diagram.

This restriction may well be inadequate for the discussion of real phase transitions in microemulsions where short range interactions between neighbouring sheets may play an essential role. However we hope that our discussion of this (relatively) simple limit of dilute sheet may provide some useful insights. In particular we show that (contrary to our original belief) the incorporation of curvature energies is probably not sufficient to explain the 3-phase equilibria which are sometimes observed at suitable salinity and temperature.

2. The model free energy. — 2.1 DESCRIPTION OF THE SURFACTANT FILM. — We divide space into adjacent cubes of size ξ_K (volume ξ_K^3). Each cube is filled either with oil (probability ϕ) or with water (probability $1 - \phi$). When two adjacent cubes are filled differently, they are separated by an interface of area ξ_K^2 . The average amount of area available per cube is thus

$$\mathcal{A} = 6 \xi_K^2 \phi(1 - \phi). \quad (1)$$

We assume that the surfactant film at the interface is much thinner than ξ_K : this is an idealization, but it simplifies the notation significantly. If we call ϕ_s the volume fraction of surfactant, we are discussing only the portion of the phase diagram where $\phi_s \ll 1$. We also assume a single surfactant : in many cases an additive (cosurfactant) is included, but there do exist microemulsions with a single surfactant. The number of surfactant molecules per cube is

$$n_s = \phi_s \xi_K^3 w^{-1} \quad (2)$$

where w is the volume of the surfactant molecule. We assume that all the surfactant is at the interface (no solubility in oil or water). The area per surfactant molecule Σ is thus

$$\Sigma = \frac{6 w \phi(1 - \phi)}{\xi_K \phi_s}. \quad (3)$$

The free energy of the film (computed per surfactant molecule) may be written quite generally in the form

$$G(\Sigma) = \gamma_0 \Sigma + G_s(\Sigma) \quad (4)$$

where γ_0 is the interfacial tension of oil/water, while $G_s(\Sigma)$ describes the interactions between surfactant molecules. The energy $G(\Sigma)$ is minimal for a certain value $\Sigma = \Sigma^*$. At this point the interfacial tension

$$\gamma(\Sigma) = \gamma_0 + \frac{\partial G_s}{\partial \Sigma} = \gamma_0 - \Pi(\Sigma) \quad (5)$$

(where $\Pi(\Sigma)$ is the surface pressure) vanishes :

$$\gamma(\Sigma^*) = 0. \quad (6)$$

The importance of the state $\Sigma = \Sigma^*$ has been pointed out first by Schulman and Montagne [11]. We call the state $\Sigma = \Sigma^*$ the « saturated state ». Inserting

$\Sigma = \Sigma^*$ in equation (3) gives a parabola in the (ϕ_s, ϕ) plane. We call this parabola the *Schulman curve* S (Fig. 1). We shall see that in our model, the tie lines describing two-phase equilibria between microemulsions and nearly pure oil or water are expected to end up very near S.

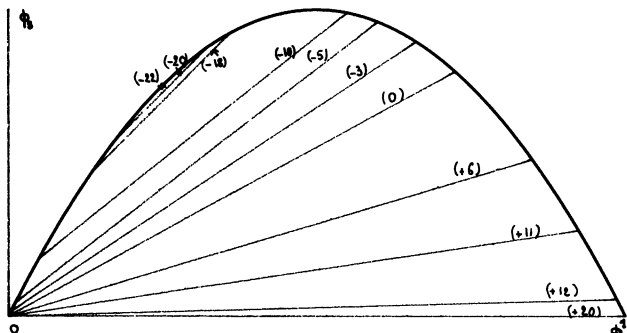


Fig. 1. — « Schulman curve », giving the amount of surfactant required to saturate the interface. This curve is also (very nearly) the limit of the one phase region. We show here the tie lines corresponding to a Bancroft parameter $\lambda/4\pi = 1, 2$, from $\eta = -22$ (flat point) to $\eta = +20$ ($\eta = U_x$).

We shall also show later that a full knowledge of the function $G(\Sigma)$ is usually not required, because G is rapidly very large (when compared to other energies in the problem) when we move out of the Schulman curve. In fact it will be quite sufficient for our purposes to write

$$G(\Sigma) = \frac{1}{2} \gamma'(\Sigma^*) (\Sigma - \Sigma^*)^2 + G_0 \quad (7)$$

where

$$\gamma'(\Sigma) = \frac{d\gamma}{d\Sigma} = - \frac{d\Pi}{d\Sigma}. \quad (8)$$

The main interest of the approximate form (7) is that we need only *one parameter* $\gamma'(\Sigma^*)$ to describe the equation of state of the film. Finally, the surfactant contribution per cube is of the form

$$F_1 = \phi_s \xi_K^3 w^{-1} G(\Sigma). \quad (9)$$

2.2 THE ENTROPY OF THE FLUCTUATING INTERFACE.

— With our division into cubes, this entropy is counted very simply : it is simply the entropy of mixing for a set of cubes filled with oil, mixed with a set of cubes filled with water. In a mean field approximation the resulting free energy is (per cube)

$$F_2 = kT [\phi \ln \phi + (1 - \phi) \ln (1 - \phi)]. \quad (10)$$

2.3 CURVATURE EFFECTS. — Let us return for a moment to a description of the interface as a conti-

nuous surface with a complex shape. At any point on this surface there is a certain curvature

$$C = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

(where R_1, R_2 are the principal radii of curvature). The curvature C may be positive or negative : we choose to take $C > 0$ when the interface is bent as it is in a direct micelle (with the water on the outside) and $C < 0$ for inverse micelles. The energies associated with C are very small. But, because we deal with systems where the interfacial tension γ is ultraweak, the curvature terms cannot be omitted : we shall see that they control the detailed shape of the phase diagram.

The curvature energy for fluid interfaces has been constructed and discussed some years ago by W. Helfrich [10]. It is (per cm^2 of interface)

$$F_c = \frac{1}{2} K (\bar{C}^2 - 2 \bar{C} C_0). \quad (11)$$

The constant K has the dimension of an energy, and is called the rigidity. The constant C_0 has the dimensions of an inverse length, and is called the spontaneous curvature of the interface. The Bancroft rule tells us the sign of C_0 . We wish to map the Helfrich energy (11) into a ϕ dependent contribution to the free energy per cube :

a) The average square term $\frac{1}{2} K \bar{C}^2$ must be minimal where $\phi = 1/2$ and should give a contribution (per cube) $F_3(\phi) = -\rho K \phi(1 - \phi)$ where we have used the simplest (parabolic) form. The parameter ρ can be estimated from the limit $\phi \rightarrow 0$ when we are dealing essentially with isolated droplets of diameter ξ_K . From this remark one concludes that ρ is simply a numerical constant of order unity. We shall not refine the estimate of ρ because as we shall see, F_3 can simply be lumped into F_1 , both having the same ϕ dependence.

b) The cross term $-K C_0 \bar{C}$ in equation (11) is more interesting : we shall see that this term controls the dissymmetry of the phase diagrams [12]. If we take an average of the $C C_0$ term we get (per cube) an energy

$$F_3(\phi) = -\mathcal{A} K C_0 \overline{C(\phi)}. \quad (12)$$

The average curvature $\overline{C(\phi)}$ must change sign when we interchange the oil and the water ($\phi \rightarrow 1 - \phi$). It must also be of order $1/\xi_K$ when $\phi \rightarrow 1$ (i.e. when we deal with isolated droplets of size ξ_K). We may summarize the above properties by setting

$$F_3(\phi) = \lambda k T f_3(\phi) \quad (13)$$

where $f_3(\phi)$ is a dimensionless function, satisfying the conditions

$$\left. \begin{aligned} f_3(1) &= f_3(0) = 0 \\ f_3(1 - \phi) &= -f_3(\phi) \end{aligned} \right\} \quad (14)$$

and λ is a dimensionless constant, which from (12) we may take in the form

$$\lambda = (\text{const.}) \frac{K}{kT} C_0 \xi_K. \quad (15)$$

We shall discuss two (slightly different) plausible forms for $f_3(\phi)$:

a) A simple assumption amounts to put

$$\bar{C} = (\text{const.}) \frac{1}{\xi_K} (\phi - 1/2)$$

and to take the area per cube proportional to $\phi(1 - \phi)$ as before. This then gives a cubic form for $f_3(\phi)$ which we write :

$$f_3 = \phi(1 - \phi)(1 - 2\phi) \quad (\text{cubic}) \quad (16)$$

b) Another, more systematic, approach is then to expand the function $f_3(\phi)$ in a Fourier series where each term satisfies (14)

$$f_3(\phi) = \sum_{p=1}^{\infty} A_p \sin(2\pi p\phi).$$

We now assume that a plausible representation of f_3 is obtained by retaining the first term, and write

$$F_3(\phi) = \lambda f_3(\phi) = \frac{\lambda}{4\pi} \sin 2\pi\phi \quad (\text{sinusoidal}). \quad (17)$$

We shall call λ , as defined above, the *Bancroft parameter* : in ionic systems λ will often be controlled by salinity, while in non ionic systems it will be adjusted through the temperature [1]. Note that all our description makes sense only if the spontaneous curvature C_0 is a weak correction on the scale of ξ_K , or $|C_0| \xi_K < 1$. Since in most cases we expect $K \sim kT$, we then see from (15) that $|\lambda| \approx 1$.

A simplification — hidden in equations (12) to (17) — is that we took F_3 dependent on ϕ , not on ϕ_s . More generally we would expect F_3 to be a function of both ϕ and ϕ_s . However, as already announced, the states of interest will be close to the Schulman curve and ϕ_s is then a known function of ϕ

$$\phi_s = 6 w\phi(1 - \phi)/(\xi_K \Sigma^*). \quad (18)$$

Thus, in a correction term like $F_3(\phi, \phi_s)$ we may substitute equation (18) and obtain a function of one variable $F_3(\phi)$.

The two forms proposed for $F_3(\phi)$ appear very similar at first sight : the graphs for the two curves are very similar (Fig. 3). However, we shall see that for a discussion of phase equilibria what is really relevant is the third derivation $F_3(\phi)$: this is very sensitive to slight changes in the formulation.

3. **Reduction to one variable.** — Using equations (9, 10, 16, 17) we can now write the free energy (per cube) as :

$$F(\phi, \phi_s) = kT\phi_s U(x) + F_2(\phi) + F_3(\phi) \quad (19)$$

$$x \equiv \phi(1 - \phi)/\phi_s \quad (20)$$

$$U(x) \equiv \frac{\xi_K^3}{w} G(6wx/\xi_K). \quad (21)$$

The parameter x is proportional to Σ (interfacial area per surfactant chain).

1) To discuss phase equilibria we write down first the *chemical potentials* μ (conjugate to ϕ) and μ_s (conjugate to ϕ_s). The surfactant potential turns out to depend only on x :

$$\mu_s = kT[U(x) - xU'(x)] \equiv G(\Sigma) + \Sigma\Pi(\Sigma). \quad (22)$$

The last form displays the usual relation between μ_s and the free enthalpy of the film. Our procedure will be to choose a given μ_s — this in turn defines a value of Σ , or a value of x through equation (22).

The oil/water potential μ is

$$\mu = kTU'(x)(1 - 2\phi) + F_2'(\phi) + F_3'(\phi) \quad (23)$$

(where the primes denote derivatives).

2) If we want to have an equilibrium between a phase (ϕ_1, ϕ_{s1}) and a phase (ϕ_2, ϕ_{s2}) we must have the same chemical potentials for both. But we must also ensure that the tangent planes to the free energy surface at points 1 and 2 coincide. (μ and μ_s keep fixed values on this common tangent plane). This imposes ⁽¹⁾

$$\mu(\phi_2 - \phi_1) + \mu_s(\phi_{s2} - \phi_{s1}) = F(2) - F(1). \quad (24)$$

It is then convenient to introduce a reduced potential

$$G_{\mu_s}(\phi) = kTU'(x)\phi(1 - \phi) + F_2(\phi) + F_3(\phi) \quad (25)$$

$$= \gamma(\Sigma)\mathcal{A} + F_2 + F_3. \quad (26)$$

For fixed μ_s (fixed x), the potential G depends only on one variable ϕ , and the condition for equilibrium (24) becomes ⁽²⁾

$$\mu(\phi_2 - \phi_1) = G_{\mu_s}(\phi_2) - G_{\mu_s}(\phi_1). \quad (27)$$

⁽¹⁾ Condition (24) is necessary for equilibrium, but is not always sufficient : the curve $F(\phi, \phi_s)$ must be *above* the tangent plane to ensure a 2-phase equilibrium.

⁽²⁾ Eq. (9) is a special case of a very general theorem on Legendre transforms : if a surface $F_0(\phi, \phi_s)$ has a doubly tangent plane at two points (1, 2), we may consider the curve defined by

$$\begin{cases} \hat{F}_0(\phi, \phi_s) = F_0(\phi, \phi_s) - \phi_s \frac{\partial F_0}{\partial \phi_s} \\ \frac{\partial F_0}{\partial \phi_s} = \mu_s \end{cases}$$

This curve, when projected on the plane (\hat{F}_0, ϕ) has a bitangent at ϕ_1 and ϕ_2 ; the common slope being $\partial F_0/\partial \phi$.

The pairs (ϕ_2, ϕ_1) are then obtained by the classic construction of figure 2.

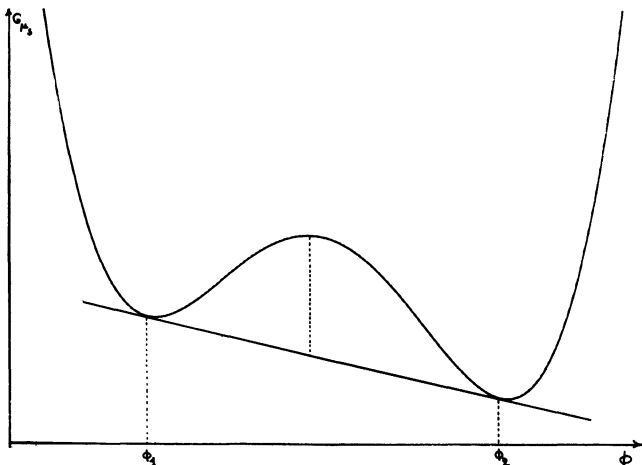


Fig. 2. — Thermodynamic potential versus concentration : ϕ_1, ϕ_2 concentrations correspond to stable two-phase equilibria.

4. Discussion. — 4.1 THE INTERFACE IS NEARLY SATURATED. — It is important to realize at this stage that there is a small parameter in the theory : in equation (26) F_2 and F_3 are of order kT . The first term is of order $\gamma(\Sigma) \xi_K^2$. All terms compute and will be comparable. Thus

$$\gamma(\Sigma) \sim \frac{kT}{\xi_K^2}. \tag{28}$$

Even in the most flexible systems, we expect ξ_K to be of order 50 Å to 100 Å : thus γ is small (≈ 0.1 dyne/cm) and we must be very close to the Schulman curve. More precisely if we use the expansion (7, 8) together with (28) we can write

$$\frac{\Sigma - \Sigma^*}{\Sigma^*} \cong \frac{kT}{\xi_K^2 \Sigma^* \gamma'(\Sigma^*)} = \varepsilon. \tag{29}$$

The parameter ε is expected to be small (of order 0.1 or less). This represents a considerable simplification for all discussions of the phase diagram : in our model, all the tie lines describing 2-phase equilibria have both their extremities very close to the Schulman curve :

a) On figure 3 we show separately the three components to the potential $G_{\mu_s}(\phi)$ when F_3 is « cubic » (Eqs. (16) and (30a)). The overall form of $G_{\mu_s}(\phi)$ with various values of λ and η appears on figure 4. For a given Bancroft parameter λ we find two possibilities : at low η , $\eta < \eta_c(\lambda)$ the plots of $G_{\mu_s}(\phi)$ are entirely convex : we are dealing with a one phase region. At higher η ($> \eta_c(\lambda)$) the potential $G_{\mu_s}(\phi)$ has two inflection points and a bitangent line can be constructed : we have a 2-phase equilibrium.

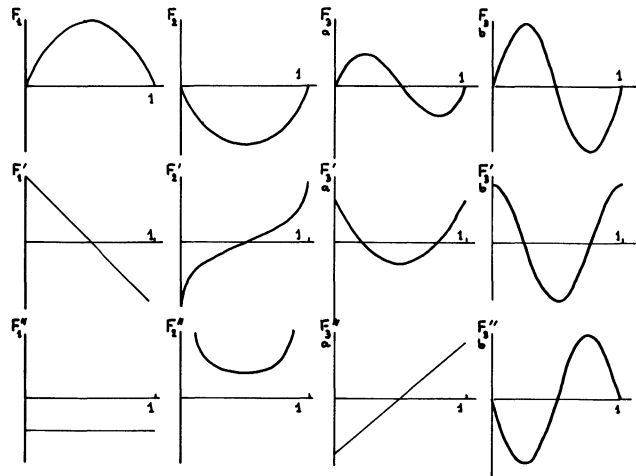


Fig. 3. — Contributions to the free energy versus concentration (together with their 1st and 2nd derivatives). F_1 : interfacial energies ; F_2 entropy term ; F_{3a} curvature energy (cubic shape) ; F_{3b} curvature energy (sinusoidal shape).

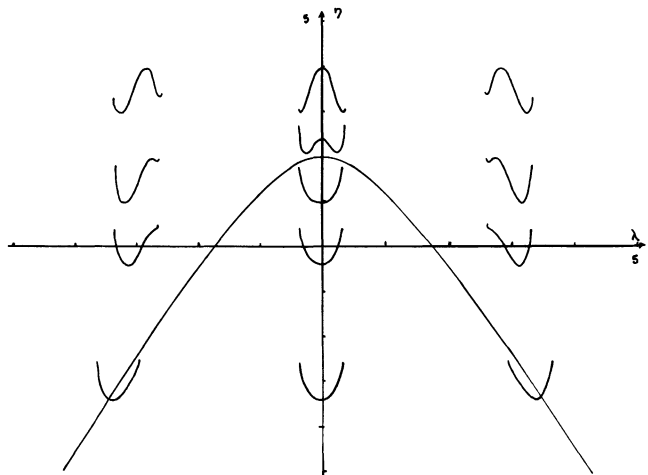


Fig. 4. — Plots of the « reduced potential » G_{μ_s} (with a « cubic » curvature term) for several (η, λ) values. Note the two typical regions. The limiting curve corresponds to $G''_{\mu_s} = G'''_{\mu_s} = 0$.

b) The case where F_3 is « sinusoidal » (Eqs. (17) and (30b)) is more complex. Again we show the three components of $G_{\mu_s}(\phi)$ in figure 3. In figure 5, we show again $G_{\mu_s}(\phi)$ for various values of λ and η . The situation is here more complex : there are regions in the (η, λ) plane which give more than two inflexions. However, the convexity conditions leaves us always with at most a two-phase equilibrium. A typical phase diagram is shown (for $\lambda/4 \pi = 1.2$) on figure 1.

4.2 QUALITATIVE FEATURES. — Let us now apply the construction of figure 2 : we progressively increase the surfactant potential μ_s , or (equivalently) increase the interfacial tension $\gamma(\Sigma)$. (Remember that μ_s and Σ are linked by equation (22)). When $\gamma(\Sigma)$ is negative, the terms $\mathcal{A}\gamma + F_2(\phi)$ in equation (26) coincide

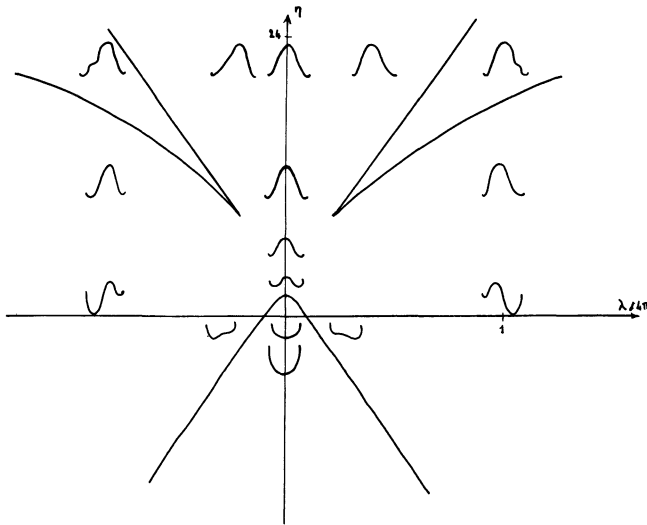


Fig. 5. — Plots of the « reduced potential » G_{μ_s} (with a « sinusoidal » curvature term). Note the three typical regions. The limiting curve corresponds to $G_{\mu_s}'' = G_{\mu_s}''' = 0$.

exactly with what we have in a *compatible* binary mixture, and whenever the third term is small (low $|\lambda|$) we have no phase transition.

Finally when γ reaches a certain critical value γ_c a double root $\phi_1 = \phi_2 = \phi_c$ appears in the construction of figure 2. We can locate the double root by the usual conditions $G_{\mu_s}''(\phi) = G_{\mu_s}'''(\phi) = 0$. The results depend critically on the detailed shape of F_3 :

« Cubic » shape :

$$\left. \begin{aligned} F_3''(\phi_c) &= 12 \lambda \left(\phi_c - \frac{1}{2} \right) = 2 \eta - \frac{1}{\phi_c} - \frac{1}{1 - \phi_c} \\ &\quad \text{with } \eta = U'(x) \\ F_3'''(\phi_c) &= 12 \lambda = \frac{1}{\phi_c^2} - \frac{1}{(1 - \phi_c)^2} = 0 \end{aligned} \right\} \quad (30a)$$

« Sinusoidal » shape

$$\left. \begin{aligned} F_3''(\phi_c) &= -\frac{1}{\pi} \sin 2 \pi \phi = 2 \eta - \frac{1}{\phi_c} - \frac{1}{(1 - \phi_c)} \\ F_3'''(\phi_c) &= -2 \pi^2 \cos 2 \pi \phi = \frac{1}{\phi_c^2} - \frac{1}{(1 - \phi_c)^2} = 0 \end{aligned} \right\} \quad (30b)$$

giving $\eta = \eta_c$ and $\lambda = \lambda_c$ for a given ϕ_c .

5. Conclusions. — 5.1 COMPARISON WITH THE ROBBINS APPROACH. — The first conclusion, due primarily to Talmon and Prager, is that purely entropic effects, for a deformable interface, may lead to phase separations. For instance, if we start with isolated droplets of water in oil, and increase their size progressively (by decreasing the surfactant fraction ϕ_s , while keeping ϕ constant), we expect to reach a limit,

beyond which a pure water phase separates from the microemulsion. In our version of the Talmon-Prager model, the diameter of the droplets at this point is ξ_K . This is very different from the picture set up by Robbins [12], where the size R of the maximal droplets is controlled by the spontaneous radius of curvature R_0 .

We believe that Robbins is right when $|R_0| \ll \xi_K =$ then we have tight spherical droplets, and all our considerations on vary interfaces may become meaningless. On the other hand, for weak spontaneous curvatures and soft interfaces ($|R_0| > \xi_K$) the Robbins approach fades out : in particular, droplets of average size ξ_0 will not be spherical, and will often, in fact, break down into smaller units.

Thus our discussion is restricted to a certain (possibly small) subclass of surfactants. Other restrictions will be discussed below.

5.2 STRUCTURE OF THE PHASE DIAGRAM. — Our free energy (25) contains only two adjustable parameters : the persistence length ξ_K and the Bancroft parameter λ , measuring the ratio ξ_K/R_0 ($|\lambda| \gtrsim 1$). It is interesting to note that all the complex phenomena associated with : a) the Langmuir equation of state of the film, b) the long range Van der Waals interactions can be lumped into such a simple structure !

Accepting (21) as a starting point, we obtain a 2-phase region which lies (in the ternary phase diagram) below a certain « Schulman curve ». The tie lines end up nearly on this curve i.e. in states of very small interfacial tension. The detailed arrangement of the tie lines depends critically on the structure of the curvature energy and on the magnitude of the Bancroft parameter λ .

Within our simple choices for the curvature energy $f_3(\phi)$ we do *not* find any situation where 3 distinct phases coexist (the « type III » equilibria of Winsor [16]). Thus at this point we depart from the initial conclusions of Talmon and Prager [8] : these authors did find type III, but they had to assume a very special form for the curvature energy. Similarly, in our model, if we allow for functions $f_3(\phi)$ which have a rather sharp minimum at some point ($\phi = \phi_m$), we can generate 3-phase equilibria, where a microemulsion (of oil/water fraction close to ϕ_m) coexists with nearly pure oil and nearly pure water⁽³⁾.

But we have not been able to find a convincing argument for the existence of a sharp minimum in $f_3(\phi)$.

5.3 PHYSICAL PROCESSES LEADING TO 3 PHASES EQUILIBRIA. — Two distinct effects, which are *not*

⁽³⁾ For instance, if we add a second Fourier component to the expansion of curvature energy staying :

$$F_3(\phi) = \lambda_1 \sin 2 \pi \phi + \lambda_2 \sin 4 \pi \phi$$

three phases equilibria do appear (cf. Fig. 6).

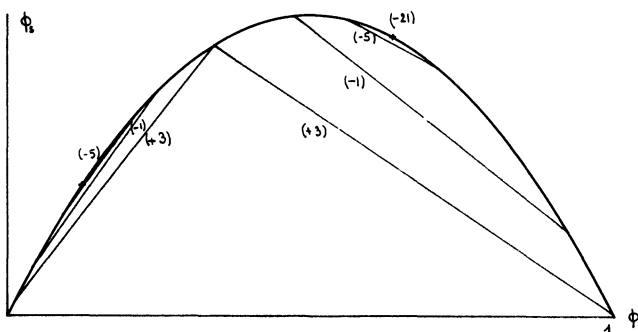


Fig. 6. — Schulman curves with tie lines showing the three phase equilibria which would be obtained with a curvature energy $F_3 = \lambda \sin \pi\phi$ (this choice, however, is probably unrealistic).

incorporated in the present model, may control the Winsor type III equilibria.

5.3.1 *Denser packings.* — Our discussion was based on cubes of size ξ_K . However, if we want to increase the surfactant content, we may, for instance, stack the surfactant films in a lamellar structure with successive O and W regions, and an overall repeat period d which can be relatively short.

These denser packings may be forced in practice by the long range Van der Waals interaction, and lead to phase equilibria which have been discussed by Cantor [15] for non ionic surfactants. The basic idea amounts to assume that consecutive surfactant films will be put into contact by the Van der Waals attractions : any oil or water which is beyond the film is squeezed out and goes as a pure, separate phase. When this is calculated in detail, one does find 3-phase equilibria as shown on figure 7, which do resemble the observations. Of course, in our case, we should not assume an ordered lamellar phase, but a disordered microemulsion (because ξ_K is small). But the principle remains.

Ultimately, for large surfactant fractions, the different surfactant sheets may come into close contact. This may take place when the « two-dimensional distance » and the « three-dimensional distance » of two surfactant molecules come to be of same order :

$$\left[\frac{6\phi(1-\phi)}{\xi_K} \cdot \frac{w}{\phi_s} \right]^{1/2} \approx \left[\frac{w}{\phi_s} \right]^{1/3}$$

for $\phi = 1/2$, $w = 10^{-20}$, $\xi_K = 10^{-6}$. This occurs for $\phi_s \sim 3 \times 10^{-5}$.

We might then focus our attention on the sheet-sheet interaction (rather than on the water-water, or oil-oil interactions). If the sheet density is proportional to $\phi(1-\phi)$, the sheet-sheet interaction would vary like $\phi^2(1-\phi)^2$. This would add to our Ising problem

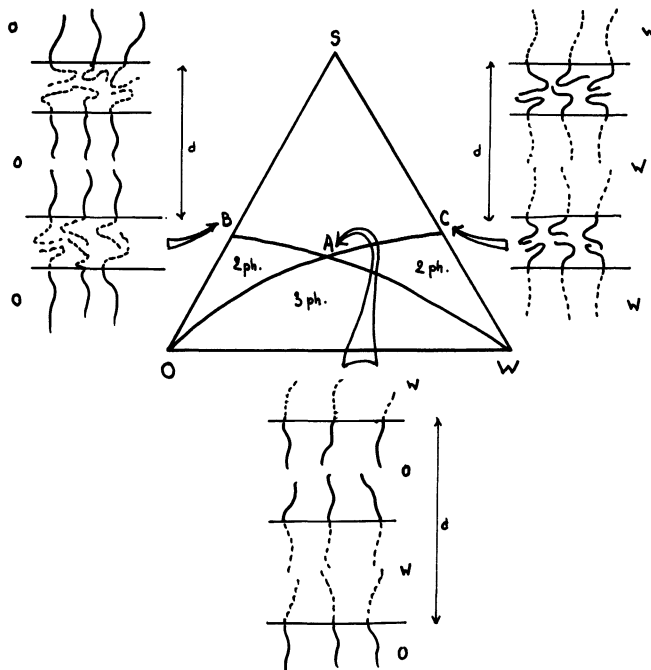


Fig. 7. — Phase diagram for lamellar phases of block copolymers in the model of Cantor [15] where Van der Waals attractions are important. Point C for instance represents a system of stacked lamellae with the hydrophilic parts swollen by water while point A represents lamellae where each part is swollen by its own solvent. The AC line represents « intermediate » lamellae; these are still stacked on the top of each other (because of Van der Waals attractions). The WAC region represents two-phase equilibria between these lamellae and pure water. The OAW region represents 3-phase equilibria.

the analogy of a biquadratic interaction ; the latter is known to favour first order transitions.

5.3.2 *Cloud points.* — All our discussion assumed that oil (water) were both excellent solvents for the corresponding aliphatic (polar) part of the surfactant. When this ceases to be the case, adjacent portions of the film tends to stick in each other, and effects somewhat similar (but more complex) than these discussed in 5.3.1 above, are expected to occur. These attractions will occur for instance near the cloud point of non ionic surfactants, where the polar (ethylene oxide) part of the molecule becomes less soluble in water. We hope to come back to this aspect in future work.

Acknowledgments. — This effort was initiated by a very stimulating seminar of Dr. S. Prager ; the advice and positive criticism of C. Taupin and R. Ober have been of constant help. Remarks by D. Langevin, A. M. Cazabat and J. Meunier are also gratefully acknowledged.

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