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Résumé. — Nous calculons les zones de stabilité des phases de microémulsions sphériques, cylindriques et lamellaires en théorie de champ moyen. Dans la phase cylindrique, les fluctuations thermiques déterminent une longueur de persistance dépendant de la température. A une échelle inférieure à cette longueur les cylindres sont rigides (bâtonnets), tandis qu'à plus grande échelle, les cylindres sont flexibles (comme des polymères). La longueur de ces cylindres flexibles dépend de la concentration et de la température. Nous calculons également leur rayon de giration.

Abstract. — The regions of stability of spherical, cylindrical, and lamellar phases of microemulsions are calculated within mean-field theory. In the cylindrical phase, thermal fluctuations determine a temperature dependent persistence length below which the cylinders are rigid (rod-like) and above which the cylinders are flexible (polymer-like). The length of the polymer-like chains depends on concentration and temperature. The radii of gyration of these flexible microemulsions are also calculated.

Three-component microemulsions (liquid mixures of water, oil, and surfactant) are characterized by domains or globules of water in oil (or oil in water) with surfactant at the interfaces [1]. The large energies associated with the water/oil repulsion and the surfactant-tail hydrophobic and the surfactant-polar-head hydrophilic interactions constrain the surfactant to the interface [2]. The physics of these systems thus differs from general three component fluids. On the other hand, the phase diagrams of the systems are richer than those of suspensions of rigid colloidal particles [3] (e.g. polystyrene spheres in water) due to the internal degrees of freedom of the globules. The sizes and shapes [2] of the microemulsion globules can be varied by changing the concentration, temperature T, or salinity [4, 5]. Although most phase behaviour studies have modelled microemulsions as spherical globules [5-7] (e.g. water-in-oil spheres), recent theories have also considered disordered [8], lamellar-like structures. These lamellae are flat on length scales smaller than a persistence length [4, 9] ξ_1; for larger length scales, the interfaces are wrinkled, with disordered domains of the characteristic size ξ_1.

This paper introduces the possibility of a new cylindrical microemulsion phase. Within mean-field theory, we analyse the bending free energy and obtain stability regions [10] of the spherical, cylindrical and lamellar phases as a function of the concentrations and the spontaneous curvature. We then focus on the properties of the cylindrical phase. We find that the cylinders are rigid over a persistence length $\xi_c \propto 1/T$, which also scales with the cylinder radius and hence is a function of

the concentrations. (For lamellae, ξ_1 depends exponentially on $1/T$ due to the larger phase-space for two-dimensional fluctuations [4] at length scales larger than ξ_c, the cylinders from polymer-like chains.) Pursing the polymer analogy, we study the radius of gyration [11, 12] R_g, of these chains on the surfactant, water and oil concentrations. The unusual dependence of R_g on the surfactant, water, and oil concentrations should enable detection of these cylindrical, polymer-like phases by scattering probes.

We assume that all water/oil interfaces are saturated [4, 13], i.e. all the surfactant resides at the interfaces. In addition, we assume incompressibility of the surfactant molecules compared with their resistance to orientational distortions (bending of the surfactant layer). Thus, the area per surfactant (as well as the volume per water or oil molecule) is taken to be constant [2, 4, 6, 8]. Finally, we focus on the dilute limit (microemulsion volume fraction $x \ll 1$) where the micro-emulsion can be pictured as a collection of non-interacting globules of oil in water (or water in oil) with the surfactant at the interfaces. The remaining degrees of freedom involve only the orienta-tional interactions of the surfactants along the interface and result in a form for the bending energy of a single globule given by [2, 4, 14]

$$F_b = \frac{K}{2} \int \left[\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{\rho_0} \right]^2 dS + \frac{\overline{K}}{2} \int \left[\frac{1}{R_1} - \frac{1}{R_2} \right]^2 dS \tag{1}$$

where $R_1(\mathbf{r})$ and $R_2(\mathbf{r})$ are the local radii of curvature of the interfaces. The surface area element is dS. The spontaneous radius of curvature ρ_0 represents the tendency of the interface to bend either towards the water ($\rho_0 > 0$) or towards the oil ($\rho_0 < 0$) regions. We apply a similar conven-tion to define positive radii of curvature $R_{1,2} > 0$ for local bending towards the water (applicable for water drops in oil) and negative radii of curvature $R_{1,2} < 0$ for local bending towards the oil (applicable for oil drops in water). The first term in equation (1) is the usual [15] bending energy of a general interface with spontaneous radius of curvature ρ_0. The second term in equation (1) represents the energy to distort the surface to a saddle shape [14, 15]. The energies K and $\overline{K}$ are related to the elastic constants k_c and $\overline{k}_c$ discussed by Helfrich [14] in his treatment of vesicles ($k_c \propto \overline{K}$ and $\overline{k}_c \propto K + \overline{K}$). For cylindrically symmetric molecules, which — in the absence of concentration constraints — should pack on the surface of a water in oil sphere of radius ρ_0, both K and $\overline{K}$ are positive [15, 16]. A recent theory [15] for the elastic constants K and $\overline{K}$ in terms of molecular properties (e.g. areas per head and tail) estimates $\overline{K} \leqslant K$.

The bending free energy per unit volume is $F = nF_b$, where n is the number of globules per unit volume. We assume $K, \overline{K} \gg T$, so that the entropy of mixing can be neglected to a first approxi-mation [6]. F is minimized subject to the constraints of constant total surface area and constant volume [2]. These constraints arise from the incompressibility of the components as discussed above. Thus, $nS\delta = v_s$ and $nV = x$, where S and V are the droplet surface area and volume respectively, and where δ is a typical surfactant molecular length. For example, for water globules in oil, defining v_w as the water volume fraction and v_s as the surfactant volume fraction, the volume fraction of globules is $x = v_w + \frac{1}{2} v_s$ [17].

We have used (1) to calculate the bending energy for spheres, finite cylinders (with spherical caps), and lamellae. Since the term proportional to nS in (1) is shape independent (by the con-straints discussed above) we define a dimensionless free energy

$$\hat{F} = \frac{4 \pi \rho_0^3}{3 K} [F - 2 K v_s / \rho_0^2 \delta] . \tag{2}$$

Here we consider the case $\rho_0 \geqslant 0$ only.

For infinite lamellae $\hat{F} = 0$. For spheres of radius $\rho = 3 \delta x / v_s$,

$$\hat{F} = 8 x r_0^3 [1 - 2/r_0] \tag{3}$$

where $r_0 = \rho_0/\rho$. The energy of the infinite cylinder phase (radius $b = 2\,\rho/3$) is

$$\tilde{F}_\infty = \pi x r_0^3 [\tfrac{9}{2}(1 + k) - 12/r_0]\,. \tag{4}$$

where $k = \overline{K}/K$. Finally, for cylinders of length L and radius b where $\varepsilon = b/L$,

$$\tilde{F} = \tilde{F}_\infty + \frac{\varepsilon}{3}\,\pi x r_0^3 [14 - 10\,k - 32/3\,r_0] + \cdots \tag{5}$$

The second term in (5) is the energy due to the spherical end caps in the limit of small ε.

For $\rho \geqslant \rho_0$, the free energy is minimized by a phase of spherical globules with $\rho = \rho_0$ coexisiting with excess water (emulsification failure [6]). As the ratio x/v_s is decreased, there exist first-order transitions between spherical, cylindrical, and lamellar phases, as shown in figure 1. For all values of ρ_0 and $k > 0$ where the cylindrical phase is lower energy than the lamellar or spherical phases, infinite cylinders are of lower energy than finite cylinders. The introduction of the saddle splay energy — which favours $R_1 = R_2$ (i.e. sphere or lamellae) — reduces the range of stability of the cylindrical phase and for $k > 1/3$ eliminate it altogether. As k is decreased, below $k \doteq 1/3$, an increasingly larger region of the parameter space (k, ρ_0) has the infinite cylindrical phase as the lowest energy state. At $k = 0$, the cylindrical phase is the lowest free energy state for $3/8 < \rho/\rho_0 < 7/8$, where $\rho = 3\,\delta x/v_s$. The physical origin of this stability is the ability of the cylinder to accomodate the constraints in this concentration range and still maintain a radius of curvature close to ρ_0.

The quasi-one-dimensional structure of these cylinders suggests that thermal fluctuations can substantially perturb the mean-field (zero-temperature) structure. The effects of thermal fluctuations are calculated by considering the free energy of a cylinder with a circular cross-section whose axis is permitted to wander through space [18-20]. The position of the cylinder axis is given by
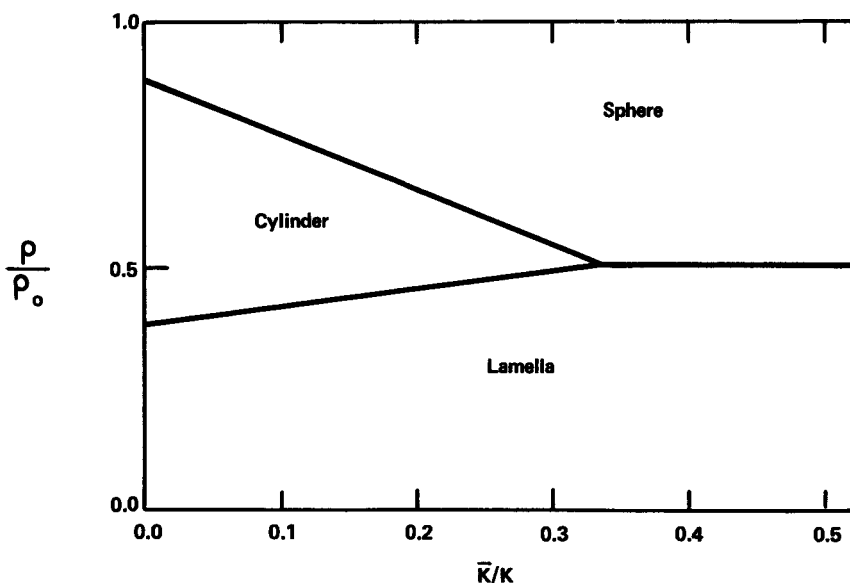
Fig. 1. — The region of stability of the spherical, cylindrical, and lamellar phases of microemulsions as a function of the ratio of ρ/ρ_0 and $\overline{K}/K$. $\overline{K}$ is the saddle-splay energy and K is the splay energy. The ratio of the microemulsion volume fraction x to the surfactant volume fraction v_s defines the characteristic radius ρ; ρ_0 is the spontaneous radius of curvature of the surfactant molecules.

$\mathbf{R} = X(z)\,\hat{x} + Y(z)\,\hat{y} + z\hat{z}$, where the cylinder is not permitted to double back on itself. The radii of curvature are given by $R_1 = b$ and $R_2 = (b\kappa \cos\theta - 1)/\kappa \cos\theta$, where θ is the polar angle in the plane perpendicular to the cylinder axis. The cylinder radius b, is given by $b = 2\,\rho/3 = 2\,\delta x/v_s$. The curvature of the axis $\kappa \cong [(X')^2 + (Y')^2]^{1/2}$ where the prime denotes differentiation with respect to z. We use (1) and (5) subject to the constraints of constant total volume and surface area, and find

$$\hat{F} = \hat{F}_\infty + \lambda \sum_q [|X_q|^2 + |Y_q|^2](1 + k)\,q^4\,b^2 . \tag{6}$$

Here X_q and Y_q are the Fourier transforms of the functions X and Y, q is the wavevector in the z direction, and $\lambda = \dfrac{81}{128\,\pi} x r_0^3$. Using equipartition,

$$\langle\,|X_q|^2\,\rangle = \frac{2\,T}{\pi(1 + k)\,KbL}\,q^{-4} . \tag{7}$$

The divergence of these modes at small q results from the translational symmetry of the cylinder axis.

The persistence length ξ_c is that length over which the axis of the cylinder is constant in direction. We define $\Delta(z) = \langle\,[\hat{t}(z) - \hat{t}(0)]^2\,\rangle$, where $\hat{t}(z)$ is a unit vector along the cylinder axis. We thus find $\Delta \cong 12\,Tz/(\pi^2\,Kb)$ for large z. The persistence length ξ_c is defined [4] by $\Delta(z) \cong 1$ so that $\xi_c \cong \dfrac{\pi^2\,K}{12\,T}\,b$. Unlike the lamellar case [4], $\xi_c \propto K/T$ due to the stronger nature of the one-dimensional fluctuations. For length scales shorter than ξ_c, the cylinders are rigid (rod-like), for length scales longer than ξ_c, the cylinder axis wanders randomly in space.

The random walk of the cylindrical axis suggests a polymer-like description for length scales larger than ξ_c. However, for real polymers, the chain length N is fixed by the polymerization process; for cylindrical microemulsions, the number N of persistence lengths per chain must be determined self-consistently by minimizing the total free energy. The « polymerization » is thus self-organizing [21]. The relevant free energy F_N, consists of the entropy of mixing [12, 21] of the finite length chains with N persistence lengths per chain, and the (N dependent) energy of the end caps (see Eq. (5)).

$$F_N \propto T(v \log v + (1 - x)\log(1 - x)) + K'\,v \tag{8}$$

where $v = x/N$ and $K' = \dfrac{2\,\pi}{27}(14 - 10\,k - 32/3\,r_0)\,K$. For values of k and ρ_0 where the cylindrical phase is lower energy than the spherical or lamellar phase (see Fig. 1), $K < K' < 3\,K$. The entropy of mixing favours short chains, while the energy term favours long chains (fewer end caps). Weak interactions between segments tend to renormalize K'. Stong, attractive interactions could lead to deformations of the cylindrical segments, but a detailed treatment is beyond the scope of this work. Minimizing F_N with respect to v, we find [22] that $N = x\,e^\beta$ with $\beta = K'/T + 1$. Typical values of $K/T \sim 6$ and $x \cong 0.1$, yields a chain length, $N \cong 150$. For $K/T \ll 1$, the chains are short ($N \to 1$) and the microemulsions are rod-like. In this limit, for high enough density, the cylindrical globules should align in a nematic phase [23-27]. In the limit $K/T \gg 1$, the chains form flexible polymer-like chains, with N persistence lengths per chain.

For $N \gg 1$, the polymer analogy predicts the radius of gyration R_g of these chains to be a function of the volume fraction x of microemulsion and of the cylinder radius $b \propto x/v_s$. By analogy with the theory of semi-flexible polymers [12], we find [28] that for noninteracting chains,

$$R_g \propto (N\xi_c\,b)^{1/2} \propto x^{1/2}\,x/v_s . \tag{9}$$

For the case of interacting chains, we augment (8) by a term $T\chi x(1 - x)$, which represents the mean-field interaction between segments [11, 21].

We first discuss the case where the interaction between segments (of one persistence length) is strongly repulsive ($\chi < 0$) so that deformations of the chains are energetically unfavourable (excluded volume interaction $\gg K$). By analogy to the theory of dilute solutions of polymers with strong excluded volume interactions [11, 21] we find [28],

$$R_g = (2\,N)^{3/5}\,\tau^{1/5}(\xi_c/b)^{1/5}\,b \propto x^{3/5}\,x/v_s \qquad (10)$$

where $\tau \propto (\frac{1}{2} - \chi)$. Thus, a characteristic dependence of R_g on the microemulsion volume fraction is predicted [29].

For the case of attractive interactions ($\chi > 0$), the chains tend to collapse instead of stretching. For sufficiently large attractions ($\chi > \frac{1}{2}$), the solution of chains separates into a high density phase and a low density phase [28, 30]. In the low density phase, $x < e^{-\beta}$, forcing $N = 1$, while the high density phase may still have $N \gg 1$. For $\chi \sim \frac{1}{2}$ the two phases have volume fractions $x \cong e^{-\beta}$; the critical point for this phase separation thus occurs at very low concentrations. This phase separation differs from the usual polymer case [11, 21] due to the concentration dependence of N in this self-organizing system.

In this paper, we have explored the stability range for microemulsions of various shapes, and have noted the possibility of a cylindrical phase. Depending on the concentrations and the interactions, this cylindrical phase can manifest itself as short, rigid rods or as long, wandering chains. These ideas may be of use in interpreting the recent observations of cylindrical micelles [26, 27], and of birefringent microemulsions [31]. The polymer-like phase should be recognizable through the concentration dependence of the radius of gyration as well as through peculiar rehological properties characteristic of polymers.

References

[1] For a general survey, see *Micellization, Solubilization, and Microemulsions*, edited by K. W. Mittal (Plenum, N. Y.) 1977.

[2] SAFRAN, S. A., *J. Chem. Phys.* **78** (1983) 2073. The notation in this reference, as well as in reference [6] is slightly different : the spontaneous radius of curvature (ρ_0 in the present work) was defined as ρ_1 while the spherical radius (ρ in the present work) was defined as ρ_0.

[3] VINCENT, B., *Adv. Colloid Interface Sci.* **4** (1974) 193.

[4] DE GENNES, P. G. and TAUPIN, C., *J. Phys. Chem.* **86** (1982) 2294.

[5] HUH, C., *J. Colloid Interface Sci.* **71** (1979) 408 and unpublished.

[6] SAFRAN, S. A. and TURKEVICH, L. A., *Phys. Rev. Lett.* **50** (1983) 1930.

[7] ROBBINS, M. L., Ref. [1], p. 713 ;
MILLER, C. A. and NEOGI, P., *AIChE J.* **26** (1980) 212 ;
RUCKENSTEIN, E. and CHI, J. C., *J. Chem. Soc. Faraday Trans.* 2 **71** (1975) 1690.

[8] TALMON, Y. and PRAGER, S., *J. Chem. Phys.* **69** (1978) 2984.

[9] JOUFFROY, J., LEVINSON, P. and DE GENNES, P. G., *J. Physique* **43** (1982) 1241.

[10] The possibility of two-phase coexistence of two different shapes is beyond the scope of this work.

[11] *Scaling Concepts in Polymer Physics*, DE GENNES, P. G. (Cornell University Press, Ithaca, N.Y.) 1979.
FLORY, P., *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, N.Y.) 1971.

[12] SCHAEFER, D. W., JOANNY, J. F. and PINCUS, P., *Macromolecules* **13** (1980) 1280.

[13] SCHULMAN, J. H. and MONTAGNE, J. B., *Ann. N.Y. Acad. Sci.* **92**, 366 (1961).

[14] HELFRICH, W., *Z. Naturforsch.* **28** (1973) 693.

[15] PETROV, A. G., NITOV, M. D. and DERZHANSKI, *Phys. Lett.* **65A** (1978) 374.

[16] Negative values of $\overline{K}$ can stabilize saddle-shaped structures. Non-cylindrically symmetric molecules can possibly yield such structures. Saddle-shaped structure for microemulsions are discussed by L. E. Scriven, in reference [1], p. 877.

[17] We have split the surfactant volume between the internal (water) an external (oil) components. We have also assumed that $\delta < \rho$ so that $S\delta$ is the volume occupied by surfactant.

[18] SERVUSS, R. M., HARBICH, W. and HELFRICH, W., *Biochim. Biophys. Acta.* **436** (1976) 900.

[19] SCHNEIDER, M. B., JENKINS, J. T., WEBB, W. W., *Biophys. J.* (in press). We note that this study of dynamic effects does not treat the volume and surface constraints as we have.

[20] We have also calculated the free energy for general shape fluctuation of a cylinder in the small amplitude limit. We have found that the only fluctuations with small free energy cost, and large thermal amplitudes are those where the cylinder cross sections is circular and the axis is allowed to wander.

[21] TOBOLSKY, A. V. and EISENBERG, A., *J. Am. Chem. Soc.* **81** (1959) 780.
WHEELER, J. C. and PFEUTY, P., *Phys. Rev. A* **24** (1981) 2050.

[22] This mean-field minimization yields the most probable value of N. As is well known for self-assembling systems with end caps.
ISRAELACHVILI, J. N., MITCHELL, D. J. and NINHAM, B. W., *J. Chem. Soc. Faraday Trans.* II **72** (1976) 1525, the distributions obtained are very broad. The mean value of the chain length $\overline{N} \propto (x\, e^{\beta})^{1/2}$, as is the variance.

[23] DE GENNES, P. G., *Physics of Liquid Crystals* (Oxford University Press, Oxford, U.K.) 1974, p. 34.

[24] ONSAGER, L., *Ann. N.Y. Acad. Sci.* **51** (1949) 627.

[25] GELBART, W. (unpublished).

[26] KUMAR, S., YU, L., LITSTER, J. D., *Phys. Rev. Lett.* **50** (1983) 1672.

[27] MISSEL, P. J., MAZER, N. A., BENEDEK, G. B., YOUNG, C. Y., CAREY, M. C., *J. Phys. Chem.* **84** (1980) 1044.
APPELL, J., PORTE, G. and POGGI, Y., *J. Colloid Interface Sci.* **87** (1982) 492.

[28] Again, this is the result using the most probable value of the chain length (mean-field theory). In general, since the distribution of lengths is broad there will be a distribution of R_g. The severity of such polydispersity in N has been treated for polymer systems by JOANNY, J. F., GRANT, P., PINCUS, P. and TURKEVICH, L. A., *J. Physique* **42** (1981) 1045, *J. Appl. Phys.* **52** (1981) 5943.

[29] The range of applicability of the dilute limit is given by the criterion $c/c^* < 1$, where c^* is the concentration of chains and c is the concentration of persistence lengths. In our case, $c^* = 3\,N/4\,\pi R_g^3$ and hence $c/c^* = a \times N^{4/5}$. Where $a = \frac{8}{3}(2\,\xi_c/b)^{4/5}\,\tau^{3/5}$. Thus, for small values of x a dilute limit with $c/c^* < 1$ is possible. The overlap volume fraction x_c where $c/c^* = 1$ is given by $x_c = [e^{-\beta}/a]^{5/9}$. The overlap volume fraction x_c defines a critical value of the chain length $N_c = x_c\, e^{\beta}$. Since the minimum chain length is $N_c = 1$, a dilute limit can exist only if $\frac{1}{a}(a\, e^{\beta})^{4/9} > 1$.

[30] APPELL, J. and PORTE, G., *J. Physique Lett.* **44** (1983) L-689.
PORTE, G., *J. Phys. Chem.* **87** (1983) 3541.

[31] MEYER, C. T., POGGI, Y., MARET, G., *J. Physique* **43** (1982) 827.
LANGEVIN, D. (unpublished), HIRSCH, E., DEBEAUVAIS, F., CANDAU, F., LANG, J. and ZANA, R. (preprint).