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Cylindrical microemulsions : a polymer-like phase ?

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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 mixtures 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] $\xi_1$; for larger length scales, the interfaces are wrinkled, with disordered domains of the characteristic size $\xi_T$.

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, \( \zeta \) depends exponentially on \( 1/T \) due to the larger phase-space for two-dimensional fluctuations [4] at length scales larger than \( \xi_o \), 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 \( x < 1 \)) where the microemulsion 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 orientational 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]

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

where \( R_1(r) \) and \( R_2(r) \) are the local radii of curvature of the interfaces. The surface area element is \( dS \). The spontaneous radius of curvature \( \rho_0 \) 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 convention 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 \( \rho_0 \). The second term in equation (1) represents the energy to distort the surface to a saddle shape [14, 15]. The energies \( K \) and \( \bar{K} \) are related to the elastic constants \( k_c \) and \( \bar{k}_c \) discussed by Helfrich [14] in his treatment of vesicles \((k_c \propto \bar{K} \text{ and } \bar{k}_c \propto K + \bar{K})\). For cylindrically symmetric molecules, which — in the absence of concentration constraints — should pack on the surface of a water in oil sphere of radius \( \rho_0 \), both \( K \) and \( \bar{K} \) are positive [15, 16]. A recent theory [15] for the elastic constants \( K \) and \( \bar{K} \) in terms of molecular properties (e.g. areas per head and tail) estimates \( \bar{K} \ll K \).

The bending free energy per unit volume is \( F = n F_b \), where \( n \) is the number of globules per unit volume. We assume \( K, \bar{K} \gg T \), so that the entropy of mixing can be neglected to a first approximation [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, \( nS \delta = v_w \) and \( nV = x \), where \( S \) and \( V \) are the droplet surface area and volume respectively, and where \( \delta \) 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 constraints discussed above) we define a dimensionless free energy

\[
\tilde{F} = \frac{4}{3} \pi \rho_0^3 K \left[ F - 2 K v_s / \rho_0^2 \delta \right].
\]

Here we consider the case \( \rho_0 \gg 0 \) only.

For infinite lamellae \( \tilde{F} = 0 \). For spheres of radius \( \rho = 3 \delta x / v_w \)

\[
\tilde{F} = 8 \pi x \rho_0^3 [1 - 2/r_0]
\]
where \( r_0 = \rho_0 / \rho \). The energy of the infinite cylinder phase (radius \( b = 2 \rho_0 / 3 \)) is

\[
F_\infty = \pi \rho r_0^3 \left[ \frac{2}{3} \left( 1 + k \right) - 12/r_0 \right].
\]

(4)

where \( k = \bar{K}/K \). Finally, for cylinders of length \( L \) and radius \( b \) where \( \epsilon = b/L \),

\[
F = F_\infty + \frac{\epsilon}{3} \pi \rho r_0^3 \left[ 14 - 10 k - 32/3 r_0 \right] + \ldots
\]

(5)

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

For \( \rho > \rho_0 \), the free energy is minimized by a phase of spherical globules with \( \rho = \rho_0 \) coexisting 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 \( \rho_0 \) 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 \( k = 1/3 \), an increasingly larger region of the parameter space \( (k, \rho_0) \) 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 accommodate the constraints in this concentration range and still maintain a radius of curvature close to \( \rho_0 \).

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 \( \rho / \rho_0 \) and \( \bar{K}/K \). \( \bar{K} \) 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 \( \rho \); \( \rho_0 \) is the spontaneous radius of curvature of the surfactant molecules.](image-url)
\[ \mathbf{R} = X(z) \mathbf{i} + Y(z) \mathbf{j} + z \mathbf{k}, \]
where the cylinder is not permitted to double back on itself. The radii of curvature are given by \( R_1 = b \) and \( R_2 = (b k \cos \theta - 1)/k \cos \theta \), where \( \theta \) is the polar angle in the plane perpendicular to the cylinder axis. The cylinder radius \( b \), is given by \( b = 2 \rho/3 = 2 \delta x/v \). The curvature of the axis \( \kappa \approx [(X')^2 + (Y')^2]^{1/2} \) 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

\[ F = F_\infty + \lambda \sum_q [\left| X_q \right|^2 + \left| Y_q \right|^2] (1 + k) q^4 b^2. \]  

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 \( \lambda = \frac{81}{128 \pi} x r_0^3 \). Using equipartition,

\[ \langle |X_q|^2 \rangle = \frac{2 T}{\pi(1 + k) K b} q^{-4}. \]

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

The persistence length \( \xi_c \) is that length over which the axis of the cylinder is constant in direction. We define \( \Delta(z) = \langle [\mathbf{t}(z) - \mathbf{t}(0)]^2 \rangle \), where \( \mathbf{t}(z) \) is a unit vector along the cylinder axis. We thus find \( \Delta(z) \approx 12 T z/(\pi^2 K b) \) for large \( z \). The persistence length \( \xi_c \) is defined [4] by \( \Delta(z) \approx 1 \) so that \( \xi_c \approx \frac{\pi^2 K}{12 T} b \). 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 \( \xi_c \), the cylinders are rigid (rod-like), for length scales longer than \( \xi_c \), the cylinder axis wanders randomly in space.

The random walk of the cylindrical axis suggests a polymer-like description for length scales larger than \( \xi_c \). 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 \((N \text{ dependent})\) energy of the end caps (see Eq. (5)).

\[ F_N \propto T(v \log v + (1 - x) \log (1 - x)) + K' v \]

where \( v = x/N \) and \( K' = \frac{2 \pi}{27} (14 - 10 k - 32/3 r_0) K \). For values of \( k \) and \( \rho_0 \) 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 \( K' \). Strong, 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 \( K/T \approx 6 \) and \( x \approx 0.1 \), yields a chain length, \( N \approx 150 \). 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 \( b \propto x/v \). By analogy with the theory of semi-flexible polymers [12], we find [28] that for noninteracting chains,

\[ R_g \propto (N \xi_c b)^{1/2} \propto x^{1/2} x/v. \]
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 $> K$). By analogy to the theory of dilute solutions of polymers with strong excluded volume interactions [11, 21] we find [28],

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

(10)

where $\tau \propto (1/2 - \chi)$. 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 ($\chi > 1/2$), 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 $\chi \sim 1/2$ the two phases have volume fractions $x \approx e^{-\beta}$; 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 rheological properties characteristic of polymers.

References

[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 ($\rho_0$ in the present work) was defined as $\rho_1$ while the spherical radius ($\rho$ in the present work) was defined as $\rho_0$.
[10] The possibility of two-phase coexistence of two different shapes is beyond the scope of this work.
Negative values of $\bar{K}$ 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.

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


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.

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 energy cost, and large thermal amplitudes are those where the cylinder cross sections is circular and the axis is allowed to wander.


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 $\bar{N} \propto (x e^{\phi})^{1/2}$, as is the variance.


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.

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 $a = \frac{2}{3} (2 \xi_b/\xi)^{4/5}$. 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 $x_c = \left[ e^{-\phi}/\alpha \right]^{1/9}$. The overlap volume fraction $x_c$ defines a critical value of the chain length $N_c = x_c e^{\phi}$. Since the minimum chain length is $N_c = 1$, a dilute limit can exist only if $\frac{1}{a} (a e^{\phi})^{4/9} > 1$.


