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Shear Induced Order in Dilute Lamellar Systems

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Abstract

Certain lyotropic surfactant systems, including microemulsions, form smectic phases at very low volume fractions of surfactant (in the few percent range). Upon further dilution these melt into an isotropic state. The effect of a steady shear flow on this transition has been considered from the point of view of time-dependent Landau Ginzburg theory. In the absence of a cubic term in the Landau expansion, the theory predicts, in a suitable temperature range, a transition from the isotropic to the lamellar phase at a critical shear rate D^*. (Preliminary experiments suggest D^* of only a few reciprocal seconds for certain highly diluted bilayer-forming surfactant systems.) In the presence of a cubic term (as expected for most microemulsions, on symmetry grounds), there is the further possibility of an hexagonal phase. In this case we predict that the hexagonal phase is stabilized by shear even more effectively than the lamellar one. Hence we expect systems to exist for which hexagonal order is induced by a flow, whereas lowering the temperature produces a lamellar phase instead.

1. Introduction

Certain lyotropic surfactant systems [1–3] and microemulsions [4, 5] (in common with diblock copolymers blends and solutions [6–8]) may undergo a transition from a liquid-like homogeneous disordered phase to a long-range ordered state. Several different ordered structures can result, depending upon the intrinsic asymmetry of the system. Very asymmetric systems tend to form spherical objects, packed in a three-dimensional body-centre cubic lattice. For smaller asymmetries the tendency is to form cylinder-like aggregates, packed in a two-dimensional hexagonal lattice, or one dimensional lamellar structures. In microemulsions, for example, the intrinsic asymmetry is controlled by the spontaneous curvature of the surfactant film at the oil/water interface, and by the ratio of water and oil contents. In suitable systems, hexagonal liquid crystalline phases, as well as lamellar (smectic) ones, are seen [9].

At the level of the mean-field approximation, the Landau–Ginsburg formalism (which is expected to correctly describe the second-order or weakly first-order phase transitions) predicts a second order [7, 10] isotropic-lamellar transition for symmetric systems but a first order one when there is finite asymmetry. Symmetric systems include (as an idealization) perfectly "balanced" microemulsions with no spontaneous curvature and equals amounts of water and oil. A more exact realization of such a system may be provided by the sponge-like L_3 phase [11–13], in which it is thought that a surfactant bilayer divides random domains of the same solvent. [In this case the two sides of the sheet are identical and the symmetry is exact unless it is spontaneously broken.] If fluctuations are taken into account at the Hartree level [14] the transition becomes first order even for symmetric systems. The Hartree treatment leads also to a negative shift into the temperature at which the transition occurs [6, 14].

Under an applied shear flow ($\boldsymbol{u}_x = (Dy, 0, 0)$) the two preceding descriptions correspond to two limiting situations [15]: (a) for small enough shear rates D, the time for a fluctuation to be convected away from the critical shell ($|\boldsymbol{k}| = k_0$) is longer than its spontaneous relaxation time, and the flow has only a weak effect on the phase transition which remains "Hartree-like"; (b) for large shear rates the fluctuations are convected away before they would otherwise have time to relax, and are less and less effective in suppressing the phase transition which, at high shear rates, therefore acquires a strong mean-field character.

In the case of symmetric systems the transition temperature increases with shear rate [16, 17] and, for large enough shear rates, approaches exponentially its mean-field value. Hence, close to the static transition temperature, there is a region where the disordered homogeneous phase becomes unstable to a lamellar phase at high enough shear rate. For asymmetric systems one obviously need to consider also the formation of two dimensional structures. We study the formation of a two-dimensional hexagonal phase, and the corresponding isotropic–lamellar (I–L), isotropic–hexagonal (I–H) and the hexagonal–lamellar (H–L) phase transitions. We review first some well known results of the mean-field treatment [7] and of the Hartree approximation of Brazovskii [14]. Then we discuss the role of the shear field on the I–H and H–L phase transitions and conclude by outlining the practical relevance of this work for surfactant systems.

2. Mean-field and Hartree descriptions of the transitions

Our starting point is the Landau–Ginsburg expansion [18] for the free-energy density as a function of the order parameter ϕ (in units of $k_B T$):

$$F[\phi_k] = \frac{1}{2!}\int_k (\tau + (k - k_0)^2)\phi_k\phi_{-k} + \frac{\mu}{3!}\int_k\int_{k'}\phi_k\phi_{k'}\phi_{-k-k'} + \frac{\lambda}{4!}\int_k\int_{k'}\int_{k''}\phi_k\phi_{k'}\phi_{k''}\phi_{-k-k'-k''} \quad (1)$$

τ being a temperature-like control variable. The order parameter is chosen to vanish on average in the homogeneous disordered phase and has a non-zero value in the ordered phases. The third order coefficient μ is a measure of the intrinsic asymmetry, being zero for completely symmetric systems.

We first recall the predictions of the mean-field theory for the formation of the lamellar and hexagonal mesophases. The one dimensional lamellar phase along the z-axis is described by

$$\phi(\boldsymbol{r}) = 2a_l \cos(k_0 z) \quad (2)$$

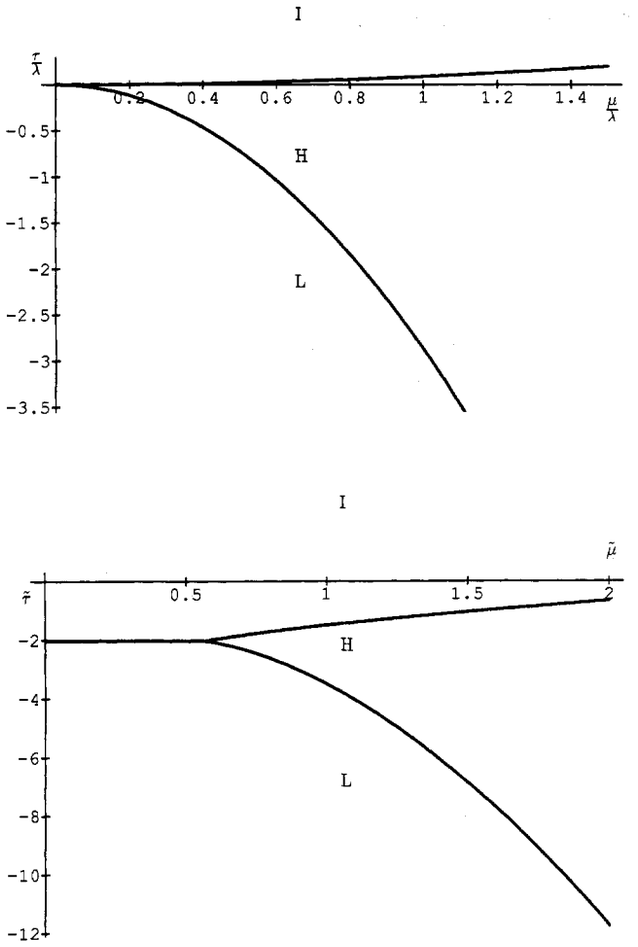

Fig. 1. (a) Mean-field phase diagram of the isotropic (I), hexagonal (H) and lamellar (L) structures. τ is a temperature related parameter and μ the measure of the intrinsic asymmetry. λ is the fourth coefficient of the Landau–Ginsburg free-energy and accounts for the relative importance of the spontaneous fluctuations. The I–H and H–L lines are parabolas of equations $\tau = (4/45)\mu^2/\lambda \simeq 0.089\mu^2/\lambda$ and $\tau = -(7 + 3\sqrt{6}/5)\mu^2/\lambda \simeq 2.87\mu^2/\lambda$, respectively [7]. (b) Hartree phase-diagram of the isotropic (I), hexagonal (H) and lamellar (L) structures. The coordinates of the triple point are $\tilde{\tau}_c = -2.308$ $\tilde{\mu}_c = 0.564$. For high values of $\tilde{\mu}$ the transition lines approach their mean-field values.

and for the two dimensional hexagonal phase in the $Y - Z$ plane we have

$$\phi(\boldsymbol{r}) = 2a_h \left\{ \cos(k_0 z) + \cos\left(k_0 \frac{\sqrt{3}y - z}{2}\right) + \cos\left(k_0 \frac{-\sqrt{3}y - z}{2}\right) \right\} \tag{3}$$

Replacing these forms of the order parameter in the Landau–Ginsburg free energy (1), minimizing with respct to the amplitudes a_h and a_l and then comparing the values at the minima, leads to the determination of the isotropic–lamellar (I–L), isotropic–hexagonal (I–H) and lamellar–hexagonal (L–H) phase transitions. The phase diagram may be displayed in a convenient way in the $[\tau/\lambda, \mu/\lambda]$ plane (Fig. 1(a)). As expected we have an homogeneous disordered phase at high temperatures. For symmetric systems ($\mu = 0$) there is a second-order phase transition from the isotropic to the lamellar phase at $\tau = 0$. For asymmetric systems ($\mu \neq 0$) the transitions are first order. Unde cooling the hexagonal phase appears first but at lower temperatures the stablestructure is the smectic.

The role of the fluctuations on the phase transition has been previously considered by Brazovskii [14] who showed that, within a self-consistent Hartree approximation, the renormalized inverse susceptibilities of the isotropic (r_0), lamellar (r_l) and hexagonal (r_h) phases satisfy the following equations [6, 14], where $\alpha = k_0^2/(4\pi)$:

$$\begin{aligned} r_0 &= \tau + \sigma_0 = \tau + \frac{\alpha\lambda}{r_0^{1/2}} \\ r_l &= \tau + \sigma_l + \lambda a_l^2 = \tau + \frac{\alpha\lambda}{r_l^{1/2}} + \lambda a_l^2 \\ r_h &= \tau + \sigma_h + 3\lambda a_h^2 = \tau + \frac{\alpha\lambda}{r_h^{1/2}} + 3\lambda a_h^2 \end{aligned} \tag{4}$$

The difference to the mean-field picture resides in the presence of the σ-terms which are the explicit contributions of the fluctuations, self-consistently calculated from

$$\sigma_i = \frac{1}{2}\frac{\lambda}{(2\pi)^3}\int \frac{d\boldsymbol{k}}{r_i + (k - k_0)^2} \simeq \frac{\alpha\lambda}{r_i^{1/2}} \tag{5}$$

The phase diagram can be obtained by minimization of the thermodynamic potentials (with renormalized susceptibilities) and by comparison of their minimized values [6, 17]. We summarize in Fig. 1.b the results plotted in the plane $\tilde{\tau}$, $\tilde{\mu}$ where $\tilde{\tau} = \tau\alpha^{-2/3}\lambda^{-2/3}$, $\tilde{\mu} = \mu\lambda^{-5/6}\alpha^{-1/3}$.

There are two main differences with the mean-field phase-diagram. First, the isotropic-lamellar phase transition is shifted to negative values of the temperature ($\tilde{\tau}_c = -2.03$) and the transition is first order even for symmetric systems (the spinodal line, given by $r_0 = 0$ is shifted to $\tau = -\infty$). In the symmetric case the lamellar structure first appears from the isotropic phase with a finite amplitude $a_l = 1.45\alpha^{1/3}\lambda^{-1/6}$. The second difference is the existence of a finite region of small $\tilde{\mu}$ for which the hexagonal phase is never stable. Only for asymmetries larger than $\tilde{\mu}_c = 0.564$ does this structure appear.

3. The effect of a shear flow on the phase diagram

We now investigate how an applied shear flow modifies the transitions described above. Our arguments follow those of Cates and Milner [16], and the works of Fredrickson [19] and Onuki [20]. The starting point is the "Hartree version" of the Fokker–Planck equation for the probability $P\{\phi(\boldsymbol{k})\}$ of the $\boldsymbol{k}$ Fourier component of the order parameter [21]

$$\int \frac{d\boldsymbol{k}}{(2\pi)^3}\frac{\delta}{\delta\phi(\boldsymbol{k})}\left\{\zeta\left[\frac{\delta}{\delta\phi(-\boldsymbol{k})} + [r + (k - k_0)^2]\phi(-\boldsymbol{k})\right] - Dk_x\frac{\partial\phi(\boldsymbol{k})}{\partial k_y}\right\} P\{\phi(\boldsymbol{k})\} = 0 \tag{6}$$

where ζ is the Onsager mobility coefficient, approximated by its value at k_0. This gives an equation for the flow-distorted $S(\boldsymbol{k})$ [19, 20]

$$[r + (k - k_0)^2]S(\boldsymbol{k}) - \frac{D}{2\zeta}k_x\frac{\partial S(\boldsymbol{k})}{\partial k_y} = 1 \tag{7}$$

The main assumption in this formulation is that the flow field $\boldsymbol{u}_x = (Dy, 0, 0)$ is fixed by an externally imposed perturbation. This completely neglects any reaction of the flow field to local fluxtuations in the order parameter, but it is a good approximation for the disordered state and presumably also in weakly ordered phases (since the order parameter is small everywhere).

In the limit of small shear rates we obtain the perturbative correction of the fluctuation integral (5), which now reads, to the leading order in D and small r

$$\sigma(D) = \sigma(0) + \frac{\pi}{24}\left(\frac{D}{D^*}\right)^2\left(\frac{|\tau_c|}{r}\right)^{7/2}\tau_c \tag{8}$$

where $\tau_c = -2.03(\alpha\lambda)^{2/3}$ and $D^* = \zeta\lambda\alpha^{1/2}$. The negative sign of this contribution shows that, as expected, the shear flow reduces the fluctuations. In the limit of large shear rates the fluctuation integral is (at the leading order in r) [16, 20]

$$\sigma(D) \simeq \left(\frac{D}{D^*}\right)^{-1/3}|\tau_c| - \left(\frac{D}{D^*}\right)^{-1} r[\ln \beta r]^2 \tag{9}$$

with $\beta \simeq |\tau_c|^{-1}(D/D^*)^{2/3}$. This integral vanishes with increasing shear rates, even in the limit $r \to 0$. Accordingly the behavior approaches that of mean-field theory, as D^*/D approaches zero. The crossover from the Hartree to the mean-field description is roughly at $D = D^*$. We now set $\Delta = D/D^*$ and discuss how the phase diagram changes when Δ varies from 0 to ∞.

Following the above scheme, the phase diagram for the crystallization of the lamellar and hexagonal structures is still obtained by minimization of the "static" thermodynamic potentials where the contributions from the fluctuations to the renormalized susceptibilities (equations 1 and 5) are now flow-dependent (equations 8 and 9). In the regime of small shear rates we have solved these equations by a perturbation method, to first order in Δ^2. For large shear rates we indicate the general trends of the solutions, which may be determined largely by applying topological arguments to the phase diagram.

The new phase diagram which accounts for the role of the shear flow is set in a three-dimensional space $[\tilde{\tau}, \tilde{\mu}, \Delta]$. The $\Delta = 0$ and $\Delta = \infty$ planes correspond, respectively, to the static Hartree (Fig. 1(a)) and mean-field (Fig. 1(b)) phase-diagrams. The $\tilde{\mu} = 0$ plane corresponds to the situation previously analyzed by Cates and Milner [16]. This situation arises for completely symmetric systems, and the only two possible phases are the lamellar and the isotropic. The I–L transition temperature $\tilde{\tau}_c = -2.03$ for zero shear rate, to reach the infinite shear rate value of $\tau_c = 0$. In the region of small flow rate the first correction to the temperature is quadratic in the flow rate

$$\tilde{\tau}_c(\Delta) - \tilde{\tau}_c = 3.323\Delta^2 \tag{10}$$

approaching exponentially the spinodal line $\tau_s \sim \Delta^{-1/3}$

$$\tilde{\tau}_c(\Delta) - \tilde{\tau}_s \sim \Delta^{-5/6}\exp\{-\Delta^{1/2}\} \tag{11}$$

for large values of Δ.

When $\tilde{\mu} \neq 0$ the phase diagram in the plane $[\tilde{\tau}, \Delta]$ at constant $\tilde{\mu}$ is qualitatively different for values of $\tilde{\mu}$ larger or smaller than $\tilde{\mu}_c = 0.564$. In the large $\tilde{\mu}$ case ($\tilde{\mu} > \tilde{\mu}_c$) three different phases already exist at zero shear rate: the homogeneous disordered phase at high temperatures, the hexagonal phase at intermediate temperatures and the lamellar phase at lower temperatures. Thus, by increasing the shear rate at constant $\tilde{\mu}$ the only effect is to shift each of the two correspondent transition lines. For small rates there is a parabolic departure from the Hartree values.

In the intermediate $\tilde{\mu}$ case ($0 < \tilde{\mu} < \tilde{\mu}_c$), only two phases are present in the static Hartree phase diagram, but three phases do exist in the mean field limit. Therefore the I–L transition line must split in the two I–L and H–L lines for some value of Δ (Fig. 2). Correspondingly, the triple point located at $[\tilde{\tau}_c, \tilde{\mu}_c, \Delta = 0]$ in the static case moves towards its $[\tilde{\tau} = 0, \tilde{\mu} = 0, \Delta = \infty]$ position in the mean-field diagram. Thus an interesting situation arises if $\tilde{m}$ is smaller than but close to the triple point value $\tilde{\mu}_c = 0.56$), and for temperatures such that $\tilde{\tau}$ is greater than but close to its I–L value $\tilde{\tau}_c = -2.03$: in this region close to the static triple point, the same isotropic system can transform either into the lamellar or into the hexagonal phase according to whether it is cooled or sheared.

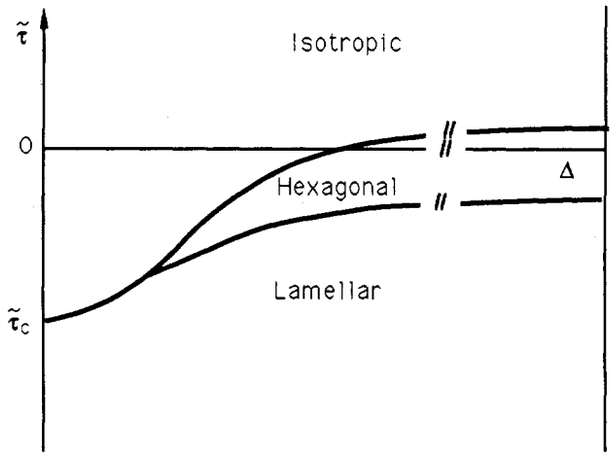

Fig. 2. Schematic phase diagram for the transition between the isotropic, hexagonal and lamellar mesophases for systems with small asymmetry ($0 < \tilde{\mu} < \tilde{\mu}_c = 0.564$).

4. Applications to surfactant systems

The results presented above can be applied directly to surfactant systems, with some extra input from experimental results to estimate the parameter values. Here we consider mixtures of oil, water and surfactant which form thermodynamically stable phases. The isotropic phase is a microemulsion; at low temperatures (and/or high concentrations) this is unstable, typically to lamellar ordering, although hexagonal phases are sometimes seen [9]. The relevant parameters of the thermodynamic description of the system are: ϕ the volume fraction of water; ϕ_s the volume fraction of the surfactant (which resides in the surface dividing the water and oil domains); $\delta = \xi_k/a$ where ξ_k is the persistence length of that surface and a its thickness, and x_0 which is the ratio of the persistence length to the spontaneous radius of curvature of the interface. We may expand a suitable estimate of the free-energy [5] $G(\phi, \phi_s, x_0, \delta)$ for these systems in powers of the order parameter $\psi = \phi - \bar{\phi}$, with $\bar{\phi}$ the average value of the water fraction in the homogeneous disordered phase and ϕ its spatially dependent value in an ordered phase. Assuming the existence of corresponding gradient terms, and comparing the coefficients of the expansion with the parameters of the Landau-Ginsburg free-energy, we obtain an estimate for the asymmetry parameter $\tilde{\mu}$ as

$$\tilde{\mu} = 2\pi^{1/3}\frac{(1-\beta)^{1/6}}{k_0}f_2^{1/6}f_4^{-5/6}f_3 \tag{12}$$

Here β is the value of $S(0)/S(k_0)$ in the isotropic phase at coexistence with a lamellar state; this parameter is for microemulsions of order unity [22]. The other relevant quantities are $f_i = \partial_\phi^{(i)}G(\phi)|_{\phi=\bar{\phi}}$. Within the framework of the model

of Andelman *et al.* [22] the value of k_0 is of the order of $\pi\phi_s/(6\bar{\phi}(1-\bar{\phi}))$. If one calculates the values of $\tilde{\mu}$ as a function of $\bar{\phi}$ for sensible parameter choices (for example $\beta = 0.5$, $\phi_s = 0.2$, $\delta = e^{10}$ and $x_0 = 0$; see e.g., Ref [22]) it turns out that the asymmetry parameter can easily be in the region of $\tilde{\mu}_c$ even for quite small asymmetries of the water/oil contents. Obviously the above estimate is only reliable to within (at best) a factor of order unity but still we expect that the cubic terms should be significant in microemulsions that are not carefully tuned to lie at the oil/water symmetry point.

To investigate the possibility of a microemulsion exhibiting a shear-induced hexagonal or lamellar phase, we need to estimate the crossover shear rate D^*. This was done by Cates and Milner [16] on the basis of a hydrodynamic estimate of the relaxation time τ_0 for piece of surfactant film of the characteristic size (related to the persistence length). However, their estimate neglects the fact that full structural relaxation requires topological reconnections of the film, for which there may be a significant activation energy E [23]. This suggests instead a relaxation time $\tau \sim \tau_0 e^{E/k_B T}$, whih may allow a reduction of D^* from rather high rates (perhaps of order 10^4–$10^6\ s^{-1}$) toward values more readily accessible experimentally. In particular for suitable sponge phases [1, 2] the I–L transition appears to be induced by simple agitation of the test tube; this suggests an activation factor τ/τ_0 of order 100. [The hydrodynamic relaxation time in this system is already quite long ($\sim 10^{-3}$ s) since the characteristic length is of order 1000 Å, larger than usually seen in microemulsions.] While this is an extreme case, D^* values of order a few hundred s^{-1} for normal microemulsions should be attainable, allowing flow effects on the phase diagram to be probed experimentally.

5. Conclusions

We have studied the effect of shear on the transition from isotropic (I) to hexagonal (H) and lamellar (L) phases in weakly ordering systems, such as microemulsions, and lyotropic surfactant solutions. [Applications to block copolymer systems may also be significant and are described elsewhere [17].] The role of shear is to move the system away from Hartree and toward mean-field behaviour. For the case of the I–L phase transition temperature that increases with flow rate; thus for suitable temperatures a shear induced I–L transition is predicted. Preliminary observations on sponge-like L_3 phases [11–13] are in accord with this prediction, which was made originally for symmetric systems [16] (of which the L_3 phase may in fact be an example). In the asymmetric case the same tendency to suppress fluctuations can lead to more subtle effects on the phase diagram. When the cubic coefficient $\tilde{\mu}$ is large enough, a hexagonal phase is stabilized relative to lamellae at all flow rates. However, the most interesting case arises when there is a relatively *small* cubic term. Under these conditions a mean field calculation (valid at high flow rate) show that the hexagonal phase is stable whereas the Hartree results for the static case show that the lamellar phase is preferred. This results in the phase diagram of Fig. 2, which shows that hexagonal order may be induced under shear in systems that have no phase of this symmetry in their static phase diagram. This is particularly interesting since, although static hexagonal order is found in a minority of microemulsion-forming systems [9], lamellar order is much more common. Our treatment suggests that at least some of these systems will order hexagonally under a shear flow; we await with interest experimental tests of this prediction.

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