

Observations of the Collapse of Dilute Lyotropic Lamellar Phases under Shear Flow

A. Al kahwaji and H. Kellay

Centre de Physique Moléculaire Optique et Hertzienne, U. Bordeaux I, 351 cours de la Libération, 33405 Talence, France

(Received 8 July 1999)

Experimental evidence of the collapse of dilute lamellar phases due to shear flow is presented. Two systems are used: one composed of brine and an ionic surfactant, and another composed of water, a nonionic surfactant, and cosurfactant. We observe this transition for a range of lamellar spacings and brine salinity. The results are in reasonable agreement with recent theory in which the suppression of fluctuations by shear plays an important role.

PACS numbers: 47.55.Kf, 47.15.Fe, 47.20.Hw

Microstructured soft materials such as liquid crystals, block copolymers, and self-assembled surfactant systems can sustain different types of fluctuations due to thermal agitation. In many cases, the fluctuations of the system are responsible for the stability of its structure. A shear flow, which can couple even weakly to such fluctuations, can induce structural transformations of such materials. Examples of such shear induced effects have been observed in the isotropic to lamellar transition in block copolymers [1] and in the disordered sponge phase to lamellar phase transition in self-assembled surfactant systems [2]. Other shear flow effects such as the development of several defects in smectic-A liquid crystal films [3] and the transformation of lyotropic lamellar phases to a dispersion of onionlike objects [4] have also been evidenced. Other systems such as binary mixtures near critical points have also been used to evidence shear effects on the behavior of the fluctuations in such systems [5]. A widely invoked idea is that shear can influence both the shape and lifetime of these fluctuations, which may have drastic effects on the stability of the system. Here, we show for a class of self-assembled surfactant systems, namely the lyotropic lamellar phase, which is stabilized (among other factors) by the fluctuations or undulations of its individual membranes, that shear suppression of these fluctuations leads to the collapse of the lamellar phase. In particular, our experiments present a rare instance in the physics of self-assembled surfactant systems where a shear induced transition can be understood quantitatively. Other instances such as the sponge to lamellar transition and the lamellar to onion transition have resisted quantitative interpretation so far. It is plausible that the mechanisms leading to the destabilization of the lamellar phase in our experiments apply to other layered structures such as smectic-A liquid crystals and block copolymer lamellar phases.

Now, take a lyotropic lamellar phase (a stack of flexible fluid membranes intercalated by a solvent), and subject it to shear flow. If the velocity and the gradient of the velocity are in the plane of the layers, the phase can be unstable. A theory along these lines has been put forth a few years ago [6]. The main ingredient of the theory is that a stack of flexible membranes subjected to such a flow configuration sees a reduction in the entropy of its membranes. Basi-

cally, long-wavelength amplitude fluctuations of the membranes are preferentially suppressed by shear resulting in a smaller entropical repulsion. It is precisely this reduction of the amplitude of out-of-plane fluctuations of the membranes that causes the instability as the stack is stabilized by entropical repulsion, usually referred to as the Helfrich interaction [7,8]. This class of complex fluids turns out to be ideal for the study of shear effects on the stability of the structure. Here we present an experiment which tests such ideas. Our work is possible using a recently developed Couette cell which allows for shearing thin films of material in the above mentioned flow configuration. So far the effect of shearing fluids in such a geometry has focused on smectic-A liquid crystals and soap films [3,9]. Experiments using smectic-A liquid crystal films [3] have reported a strong increase of turbidity above a certain shear rate; this transition is accompanied by the appearance of several defects in the film. We use this apparatus to shear thin films of lyotropic lamellar phases made up of surfactant bilayers intercalated by brine or water. Our main observation is that above a certain rotation frequency which we refer to as the threshold, the thin film which is transparent to the eye in the absence of shear, becomes turbid and scatters light strongly a short time after starting the shear. Clearly, the lamellar phase has developed large scale structures and the lamellar texture has become unstable giving rise to other forms of structures besides flat membranes.

We describe these experiments and give the results for the threshold frequency or equivalently the threshold shear rate as a function of the different parameters characterizing the phase, namely the surfactant concentration, which fixes the lamellar spacing, and the brine salinity which affects both the viscosity of the lamellar phase and possibly the rigidity of the membranes. Theory [6] predicts that the threshold shear rate Ω_c varies as $(kT)^3/(\eta\kappa^2d^3)$, where k is Boltzmann's constant, T is the temperature, η is the viscosity, d is the lamellar spacing, and κ is the rigidity constant of the membranes. Our results show reasonable agreement with such a prediction provided the viscosity used is that of the lamellar phase rather than the interstitial fluid viscosity which is water in our case.

The Couette cell [Fig. 1(a)] is made of an outer ring and an inner disk. The rings used can have diameters of 4.4 or

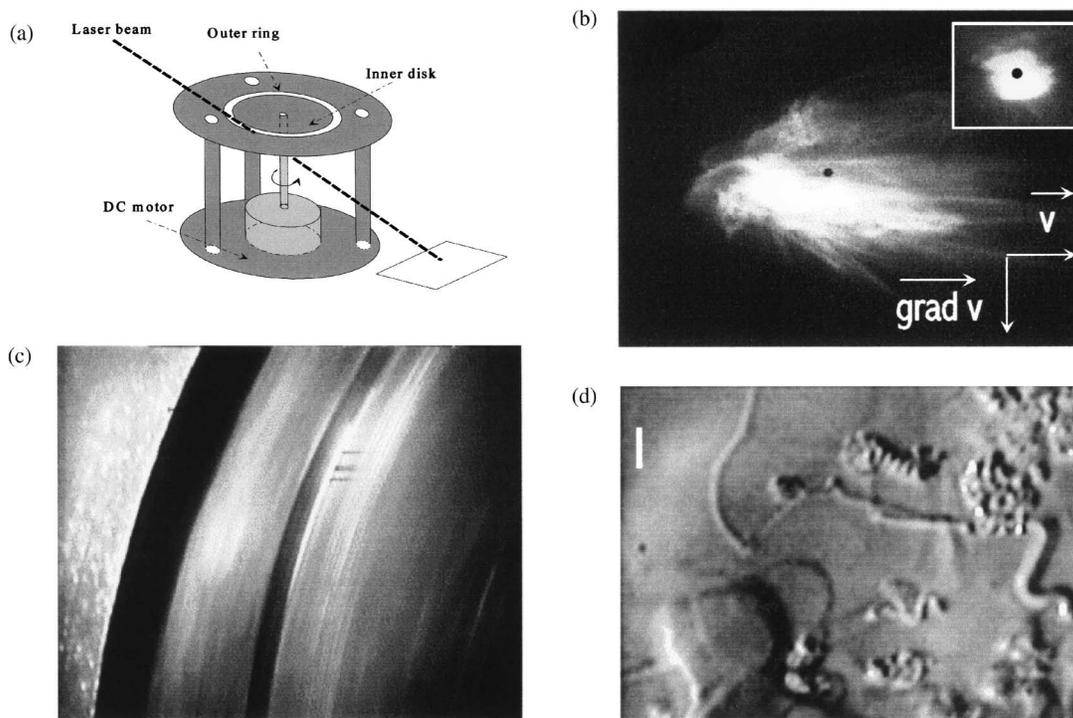


FIG. 1. (a) Couette cell used and the light scattering geometry. (b) Forward scattering pattern above Ω_c (1.2% salt, 7% AOT, $\Omega = 845 \text{ s}^{-1}$, $\Omega_c = 297 \text{ s}^{-1}$); inset in (b): scattering pattern below Ω_c [same as (b) with $\Omega = 123 \text{ s}^{-1}$]. (c) Visualization of the film above Ω_c using white light (1.4% salt, 7% AOT, $\Omega = 1400 \text{ s}^{-1}$). (d) New structures such as tubes and vesicles are present in the film above Ω_c (optical microscopy photo; the white bar is $10 \mu\text{m}$ in length) (1.3% salt, 10% AOT, $\Omega = 2160 \text{ s}^{-1}$, $\Omega_c = 1500 \text{ s}^{-1}$).

4.6 cm. The inner edge of the ring is tapered to obtain a very thin edge. The inner disks used, whose edges are also tapered to obtain thin edges, are 4.0, 4.1, or 4.2 cm in diameter. We used different diameters for the inner disk and outer ring to modify the gap from 1 to 3 mm. Both the inner disk and outer ring are made of stainless steel. The inner disk is fixed to a dc motor with variable speed. One can estimate the shear rate in the Couette cell as $\dot{\gamma} = \Omega = 2\pi Rf/b$, where R is the radius of the inner disk, f is the rotation frequency, and b is the gap. A thin film is formed by depositing a small drop of the fluid used and spreading it over the gap to form a freely suspended thin film. To our surprise these films can be spun at rotation frequencies of several Hz without breaking. The fluids used for most of our experiments are mixtures of an ionic surfactant (AOT, bis-ethyl hexyl sulfosuccinate) and brine. The surfactant concentration was varied between 5.5 and 12 wt % in brine giving lamellar spacings d ranging from about 200 to 500 Å. The brine salinity was also varied from 1 to 1.6 wt % of NaCl. In this region of surfactant and salt concentrations, a lamellar phase is obtained [10]. This phase is birefringent and host to many defects such as focal conics and dislocations [11]. In order to further test the dependence on the lamellar spacing d , we have carried out experiments using another system composed of a nonionic surfactant (C_{12}E_5 : penta-ethyleneglycol mono n -dodecyl ether), a cosurfactant (Hexanol), and pure water. For this mixture, a lamellar phase is obtained with a range of lamellar spacings extending from 300 to 3500 Å

depending on the surfactant and cosurfactant concentration [12]. The cosurfactant to surfactant mass ratio was fixed to 0.27. Both the surfactant and cosurfactant was then added to pure water containing the cosurfactant at 0.3% mass fraction. The surfactant and cosurfactant concentration was then varied between 1% and 10% volume fraction to obtain different lamellar spacings. For both systems we estimate the lamellar spacing as $d = \delta/\phi$ where δ is the bilayer thickness (21 and 33 Å for the AOT and C_{12}E_5 systems, respectively) and ϕ is the volume fraction of surfactant or surfactant and cosurfactant [12,13].

Lytotropic lamellar phases can be oriented in flat capillaries by subjecting the fluid to flow [14,15]. The lamellas then orient with the membranes parallel to the cell walls. In our case where thin films of the fluid are used, we will assume that the membranes are preferentially parallel to the interfaces of the film. This is a plausible configuration since the interfaces of the thin film are made of a surfactant monolayer as in soap films. The surfactant molecules in the monomolecular layer at the interface have their aliphatic tails in contact with air and their polar heads in contact with water. These monolayers will favor the membranes beneath or above them to be parallel to them. Some evidence that the lamellas are parallel to the flat sides of the film comes from transmission electron microscopy where one observes flat lamellas for the phases used in this study [16].

As mentioned above, the initially transparent film becomes very turbid above the threshold frequency or shear

rate Ω_c . To record the forward scattering patterns below and above Ω_c , a 20 mW HeNe laser beam is used at oblique incidence with respect to the film plane and the scattering pattern is visualized on a screen. Here, the incident beam is in the vorticity-velocity plane and is at an angle of 60° with respect to the vorticity axis which is normal to the plane of the film. Both the velocity and the gradient of the velocity are in the plane of the film. Below Ω_c the film is transparent and the scattering pattern around the transmitted beam is a small symmetric spot [inset of Fig. 1(b)]. Above Ω_c the film becomes turbid and the scattering pattern [Fig. 1(b)] becomes more intense and fluctuating. Strong scattering in the forward direction clearly indicates the presence of large scale structures in the film which are not present below threshold. Note also that the pattern is slightly asymmetric with respect to the transmitted beam with more scattering in the velocity direction. Since the film becomes highly turbid, multiple scattering from the film must dominate the pattern. Above Ω_c , one can also observe strong scattering around the reflected beam. As the incident beam is oblique to the plane of the film, strong scattering around the reflected beam may indicate the presence of out of plane fluctuations. In Fig. 1(c) we show a photo of the film above Ω_c . This photo is taken using white light and shows the strong scattering of light by part of the film, the white band surrounded by dark regions. The film becomes turbid to the eye after it was totally transparent at first (dark under the lighting conditions used). An optical microscopy photo of the state of the film above Ω_c is shown in Fig. 1(d). New structures form above Ω_c . The most notable are thin flexible cylinders and large vesicles. Upon cessation of the shear one can observe the flexible cylinders change to form other structures which may be coiled cylinders or aggregates of small vesicles. A second set of results is shown in Fig. 2 where we plot Ω_c versus d . Clearly Ω_c increases as d decreases which is consistent with the theory of Ref. [6]; however, the expected dependence on d is not verified. Here we decided to measure the

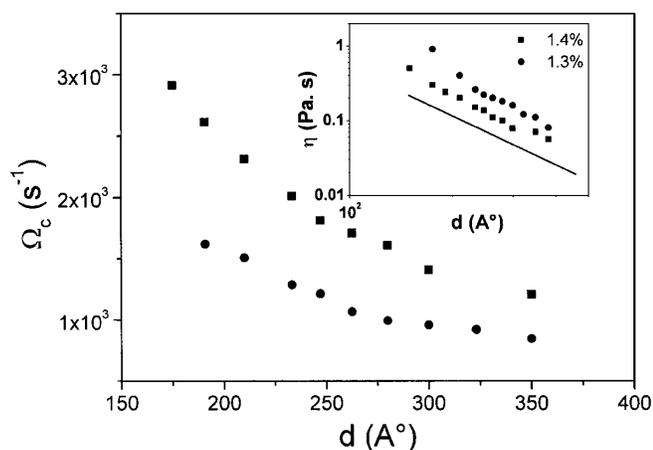


FIG. 2. Ω_c versus lamellar spacing d . Circles and squares correspond, respectively, to 1.3 wt% and 1.4 wt% NaCl. Inset: zero shear viscosity of the phases versus d ; the line has a slope of -2 .

shear viscosities of these phases as a function of d or surfactant concentration. The shear viscosity of all the phases used was measured on a Reologica Stress-Tech rheometer in a Couette cell with a gap of 1 mm. The zero shear viscosity η_0 (obtained by extrapolation) of these phases varies with d as approximately d^{-2} as can be seen in the inset of Fig. 2. When we plot the product $\eta_0\Omega_c$ versus d we find a rough agreement with the d^{-3} dependence as can be seen in Fig. 3. In this figure we have plotted both the data from the AOT system as well as the data from the $C_{12}E_5$ system to have a larger span of d values. For the latter system we have also used η_0 as the relevant viscosity. The variation we find is approximately linear in this double-logarithmic plot; the solid line has a slope of 1 as expected from theory. It must be noted that while the exponent is close to 1 for the AOT system, it is smaller for the $C_{12}E_5$ system. At the present time, this deviation is not understood, but it could be due to changes in the rigidity constant as the concentration of surfactant changes. Nonetheless, the collapse of the data from the two different systems on this universal curve is encouraging.

The above observations raise a serious question, however. Namely, what is the relevant viscosity to be considered? Is it the viscosity of the interstitial solvent (water) or is it the viscosity of the lamellar phase (water and surfactant)? This question must be intimately related to whether the interactions between membranes are strong or weak. Usually in studies of the hydrodynamics of lamellar phases [17–19], one considers the viscosity of the interstitial solvent in estimating the dissipation [18]. This is so because fluctuations of the membranes engender solvent flow between the bilayers, and for no slip conditions on the membranes this flow is subject to dissipation as in porous media. Now, if the interactions are strong, then the fluctuations of

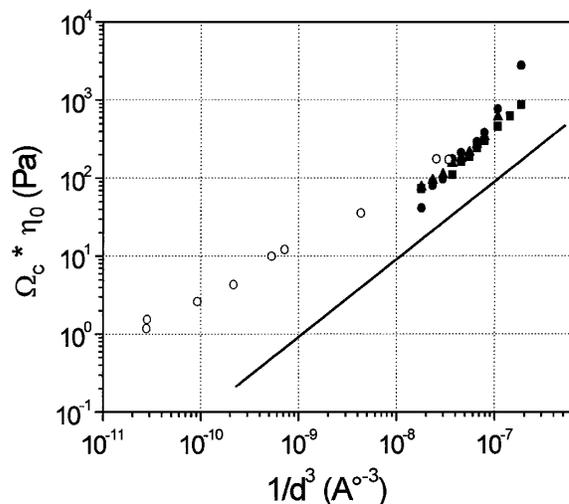


FIG. 3. $\Omega_c \eta_0$ versus $1/d^3$. The line has a slope of 1 as predicted by theory. Filled circles and triangles correspond to two different realizations for AOT lamellar samples at 1.3 wt% NaCl. Squares are for AOT samples at 1.4 wt% NaCl. The open circles are for a lamellar phase of a nonionic surfactant $C_{12}E_5$ and cosurfactant (Hexanol).

one membrane can couple to the fluctuations of the other membranes and therefore cause dissipation in a different fashion. Bruinsma and Rabin [20] have used the viscosity of the lamellar phase as well as its dependence on surfactant concentration in their theory for the effects of shear flow on the dynamics of lyotropic lamellar phases. More recently, Zilman and Granek [21] also found it necessary to use the viscosity of the lamellar phase to explain the transition from a lamellar phase to an onion phase in surfactant systems.

A third test is the dependence of Ω_c on salt concentration for a fixed surfactant concentration of AOT. Here again it is necessary to use the zero shear viscosity of the phase (inset of Fig. 4) and, in fact, Ω_c turns out to be approximately proportional to $1/\eta_0$. We have also estimated the variation of the rigidity κ of the membranes as a function of salinity using dynamic light scattering [15] but this variation turns out to be small (from 1.2 to 0.5 kT). The variation of Ω_c is therefore consistent with the variation of the viscosity of the bulk phase with salt concentration. In Fig. 4, we plot the variation of Ω_c as a function of $1/\eta_0\kappa^2$. The results seem to be consistent with theory.

A crucial issue is whether the lamellar phases used are mostly stabilized by entropic repulsive interactions (the Helfrich interaction). For the nonionic $C_{12}E_5$ system it is known that the lamellar phase is stabilized by the entropic repulsion. For the ionic AOT system, we have carried out a series of measurements about the relation between the compressibility modulus \bar{B} and the elasticity modulus K of the lamellar phases used [15]. The elasticity modulus measures the undulations of the bilayers while \bar{B} measures the interactions between membranes. Our results [15] show that the compressibility modulus is inversely proportional to the elasticity modulus of the membranes. This is the signature of the Helfrich interaction. While the bilayers are

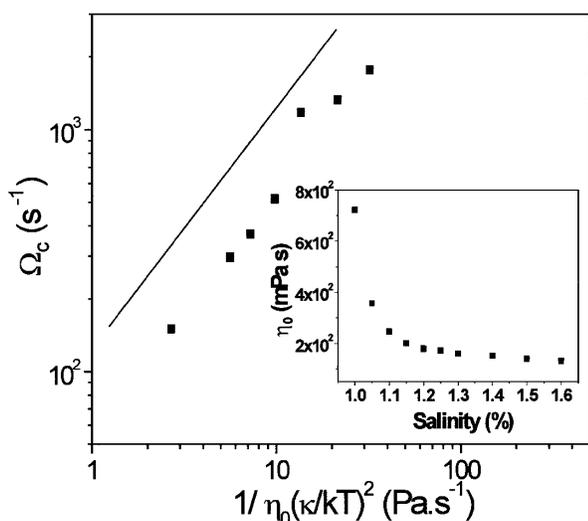


FIG. 4. Ω_c versus $1/\eta_0\kappa^2$ for a surfactant concentration of 7 wt %. The line has a slope of 1 as predicted by theory. Inset: η_0 versus salinity. (κ values are 1.2, 1, 0.8, 0.6, and 0.5 kT for 1.1, 1.2, 1.3, 1.5, and 1.6% salt, respectively).

definitely interacting via electrostatic interactions, it appears that the Helfrich interaction is important for their stability. Considering that bilayers have rigidities of about a kT , their undulations are important. Also, since the lamellar phases contain salt the electrostatic interactions must be strongly screened.

In conclusion, we show that a lamellar phase of brine or water and surfactant can be destabilized under shear flow. The experiments are carried out using thin films of lamellar phases subjected to shear using a recently introduced Couette apparatus. This scheme is crucial for the collapse of the phase since both the velocity and the gradient of the velocity need to be in the plane of the membranes composing the lamellar phase. Our results are consistent with recent theory on the effects of shear flow on the stability of lyotropic lamellar phases.

We thank X.L. Wu for help with the initial stages of this work and for a careful reading of the manuscript. We thank J. Meunier, D. Bonn, and O. Greffier for discussions. We thank A. Léon for the viscosity measurements and M. Behure for making our Couette cells.

-
- [1] K. Koppi, M. Tirrell, and F.S. Bates, Phys. Rev. Lett. **70**, 1449 (1993).
 - [2] J. Yamamoto and H. Tanaka, Phys. Rev. Lett. **77**, 4390 (1996); H.F. Mahjoub *et al.*, Phys. Rev. Lett. **81**, 2076 (1998).
 - [3] D. Dash and X.L. Wu, Phys. Rev. Lett. **79**, 1483 (1997).
 - [4] O. Diat, F. Nallet, and D. Roux, J. Phys. II (France) **3**, 1427 (1993).
 - [5] A. Onuki and K. Kawasaki, Ann. Phys. **121**, 456 (1989); A. Onuki, Physica (Amsterdam) **140A**, 204 (1986).
 - [6] S. Ramaswamy, Phys. Rev. Lett. **69**, 112 (1992). Note that the formula given in the first page of this reference contains an error [S. Ramaswamy (private communication)].
 - [7] W. Helfrich, Z. Naturforsch. **30c**, 841 (1975); **33a**, 305 (1978).
 - [8] T.C. Lubensky, J. Prost, and S. Ramaswamy, J. Phys. (Paris) **51**, 933 (1990).
 - [9] X.L. Wu *et al.*, Phys. Rev. Lett. **75**, 236 (1995).
 - [10] O. Ghosh and C. A. Miller, J. Phys. Chem. **91**, 4528 (1987).
 - [11] P. Boltenhagen, O. Lavrentovich, and M. Kléman, J. Phys. II (France) **1**, 1233 (1991).
 - [12] E. Freyssingas, F. Nallet, and D. Roux, J. Phys. II (France) **7**, 913 (1997).
 - [13] M. Skouri *et al.*, J. Phys. II (France) **1**, 1121 (1991).
 - [14] D. Roux and C. Knobler, Phys. Rev. Lett. **60**, 373 (1988).
 - [15] A. Alkahwaji *et al.* (to be published).
 - [16] D. Bonn (private communication).
 - [17] P.C. Martin, O. Parodi, and P.S. Pershan, Phys. Rev. A **6**, 2401 (1972).
 - [18] F. Brochard and P.G. de Gennes, Pramana Suppl. **1**, 1 (1975).
 - [19] F. Nallet, D. Roux, and J. Prost, J. Phys. (Paris) **50**, 3147 (1989).
 - [20] R. Bruinsma and Y. Rabin, Phys. Rev. A **45**, 994 (1992).
 - [21] A.G. Zilman and R. Granek, Eur. Phys. J. B **11**, 593 (1999).