Structure of a Lyotropic Lamellar Phase under Shear

Philippe Sierro and Didier Roux
Centre de recherche Paul-Pascal, CNRS, Ave Dr Schweitzer, 33600 Pessac, France
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The effect of shear on a lyotropic lamellar phase is studied by the means of small-angle light scattering and direct microscopic observations. We found a complex behavior that can be described by a shear diagram. This diagram exhibits successively as a function of shear four different steady states. After a transition to a phase of monodisperse multilamellar vesicles with no long-range order there is a transition to the same vesicles exhibiting long-range order. At even higher shear rates, there is a transition between this ordered population of vesicles of size typically 1 μm to another ordered state made of vesicles which are much bigger (from 10 to 50 μm). [S0031-9007(97)02380-6]

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Recently, it has been shown that the effect of shear on both lyotropic and thermotropic lamellar phases can be described by a shear diagram describing a succession of stationary states of orientations separated by dynamic transitions [1–3]. In the first system studied [2], the shear diagram exhibited three different orientation states. At very low shear, a partially oriented state with the normal to the smectic layers mainly parallel to the shear gradient direction was observed until a transition to a state of monodisperse multilayered vesicles (named spherulites) was observed (around 1 s^{-1}). At even higher shear rate ($10-1000$ s^{-1} depending upon the lyotropic sample) another transition was observed between the state of vesicles to another oriented state with no defect in the direction of the flow but some defects remaining in the vortex direction. The connection between the rheological properties of the lamellar phase and the shear diagram has been made [4].

More recently while studying a different system, another type of transition has been observed. In the multilayered vesicle state, a layering transition has been observed [5] similar to the shear ordering transition observed in colloids [6]. Indeed, in increasing the shear rate, the multilayered vesicle state that does not exhibit any long-range order between the vesicles spontaneously orders under shear to show a long-range order of layers of vesicles sliding on each other.

We report here a more complex behavior observed on a lyotropic lamellar phase. In addition to the transitions previously described as a function of shear, this system exhibits a new transition between two states of ordered multilayered vesicles. These two states can be easily differentiated by the vesicle size, and the transition between these two states is observed as a jump from small to big vesicles when either the shear rate or the temperature is increased. This transition which is in general discontinuous becomes continuous above a critical temperature. The shear diagram of this system is established.

The system studied is a quaternary lyotropic lamellar phase which phase diagram has already been published [7]. It is composed of water, sodium dodecyl sulfate (SDS), octanol, and sodium chloride. One unique sample has been studied whose composition is, respectively, in weight 85.6% of water containing 20 g/l of NaCl, 6.5% of SDS, and 7.9% of octanol. This system is studied as a function of both temperature and shear rate. Note that the behavior described below is very sensitive to the exact composition and purity of the chemicals used and a slight translation in the absolute values of the transitions can be observed. To observe the effect of shear on the lamellar phase we used a homemade transparent Couette cell [2]. This cell is thermostated (0.1 °C of accuracy); we used a 1 mm gap between the two cylinders. A laser beam can be sent through the cell, and small-angle light scattering is observed on a screen placed at some distance from the cell. A video camera digitalizes the image obtained on the screen. For direct space observations, a plate/plate cell has been made that will be described elsewhere [8]. When, in the Couette cell, the shear rate is homogeneous for Newtonian fluid, in the plate-plate cell the shear rate varies linearly from the center to the side allowing an observation at different shear rates.

Let us first describe what is observed in the reciprocal space using small-angle light scattering. The experimental setup has been previously described [2]; briefly the laser beam goes through the Couette cell parallel to the gradient shear direction. Figure 1 shows a series of patterns obtained when the shear rate $\dot{\gamma}$ is increased at a constant temperature ($T = 24.3$ °C). Below $\dot{\gamma} = 1$ s^{-1}, no characteristic pattern is observed, only some small-angle scattering around the laser beam can be recorded. Above $\dot{\gamma} = 1$ s^{-1} an isotropic ring of scattering [see Fig. 1(a) appears characteristic of the multilayered vesicle state [1,2]. This ring corresponds to the characteristic size of the close packed vesicles. It changes size with the shear rate increasing in size, indicating that the vesicle size decreases with the shear rate [1,2]. The isotropy of the ring is the signature of no long-range order in the positions of the vesicles. Above a well defined shear rate of 10 s^{-1} a modulation in the radial intensity of the ring

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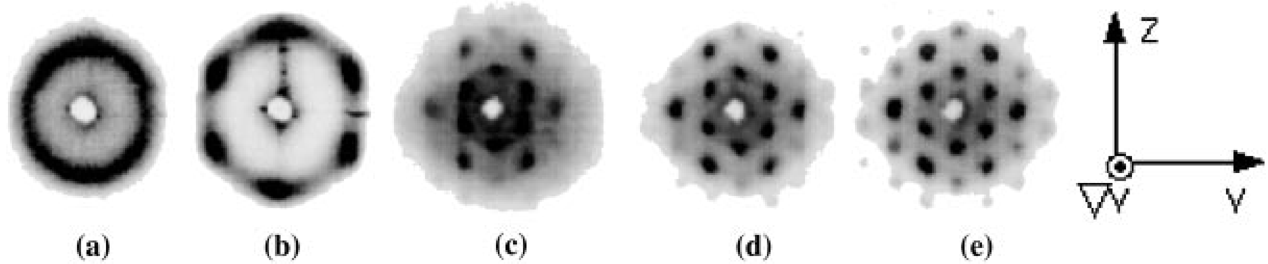

FIG. 1. Evolution of the small-angle light scattering as a function of the shear rates. 1(a) $\dot{\gamma} = 10\ \mathrm{s}^{-1}$; the ring is isotropic and corresponds to an ensemble of monodispersed multilayered vesicles. 1(b) $\dot{\gamma} = 80\ \mathrm{s}^{-1}$; the ring of scattering is replaced by six dots. The organization exhibits now a long-range order. 1(c) $\dot{\gamma} = 200\ \mathrm{s}^{-1}$; the small-angle pattern after the transition of size. The characteristic size of the vesicles is now much bigger and several orders of scattering can be easily seen. 1(d) $\dot{\gamma} = 0\ \mathrm{s}^{-1}$; same as (c) but after a rapid stop of the shear. The long-range order is kept and even more pronounced. 1(e) $\dot{\gamma} = 0\ \mathrm{s}^{-1}$; same as (d) but after a few oscillations of small amplitude (made by hand). The long-range order is even better; more than 5 orders of diffraction can be seen.

appears to lead to a well defined six spots pattern above $\dot{\gamma} = 50\ \mathrm{s}^{-1}$ [see Fig. 1(b)]. This is the sign of the so-called layering transition which corresponds to the ordering of the multilayered vesicles in planes exhibiting a hexagonal order [5]. This transition does not affect the vesicle size since the dots appear on the ring. Consequently, the size of the vesicles before and after the transition is practically the same and is around 3–4 microns at the transition. After the transition, the size evolves very slowly with the shear rate, still decreasing when the shear rate increases (see Fig. 2). When a shear rate of $200\ \mathrm{s}^{-1}$ is reached, a new phenomenon is observed. The previous pattern made of the six dots evolves toward two rings of scattering: One is at the previous position, and a new ring appears at smaller angles. With time, the former ring of scattering disappears and a clear new set of dots is seen at a much smaller angle than the previous one. After some time (typically from 20 min to a couple of hours), the pattern shown in Fig. 1(c) is observed under shear. This new pattern corresponds to an ordered structure of spherulites as the state previously described but is constituted of much bigger vesicles (around 10 μm $T = 24.3\,^\circ$C). Moreover, even under shear, several orders of diffraction can be observed (up to 3–4). Contrarily to the previous ordered state, when the shear is stopped the pattern remains [see Fig. 1(d)]. It can even be improved quite a lot in applying very small amplitude oscillations on the cell [see Fig. 1(e)]. We have been able to keep this ordered structure after the shear has been stopped for several days.

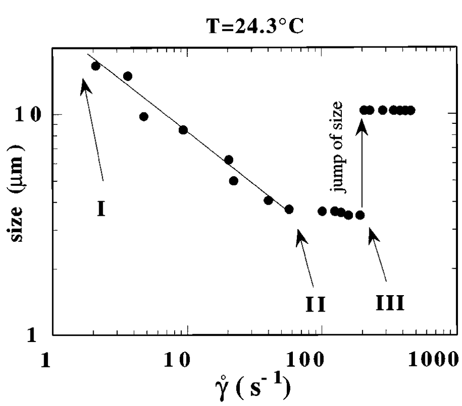

FIG. 2. Evolution of the spherulite size as a function of the shear rate for $T = 24.3\,^\circ$C. The arrows indicate the approximate position of the transitions: (I) between a partially oriented state and the sperulite state (II) between the "glassy" (no long-range order) and the layered state (long-range ordered), and (III) the position of the jump in size.

Figure 2 presents the evolution of the vesicle size as a function of the shear rate. The first part of the curve where the size decreases with the shear rate corresponds to a scaling law $R \propto \dot{\gamma}^{-0.5}$ as previously observed [1,2]. The positions of the three transitions are shown on the curve.

The plate/plate cell allowed us to make direct space observations. Figure 3 presents the evolution of the sample through the transition between small and big vesicles. In this case for practical reasons the transition is observed after a temperature jump (21 to 24.3 °C). At 21 °C only the small population is present whatever the shear rate is, and at 24.3 °C the transition between the small and the big populations happens at $200\ \mathrm{s}^{-1}$. The microscopic observation is done after stopping the shear. Before the temperature jump the texture is very thin, appearing nearly as continuously grey. This is characteristic of small multilayered vesicles. After the temperature jump and waiting a few minutes some very big vesicles nucleate randomly [Fig. 3(a)]. The concentrations of big vesicles increases with time, and they start to line up one below another [Fig. 3(b)]. Then the lines of big vesicles merge together to fill up the high shear side of the cell. Because in the plate/plate cell the shear rate increases with the distance from the center, in the stationary state the space is divided between the big vesicles (in the high shear region) and small vesicles (in the low shear region) [Fig. 3(c)]. In the big vesicles region if one applies, after stopping the shear rate, very small amplitude oscillations, one clearly observes a well ordered texture [see Fig. 3(d)].

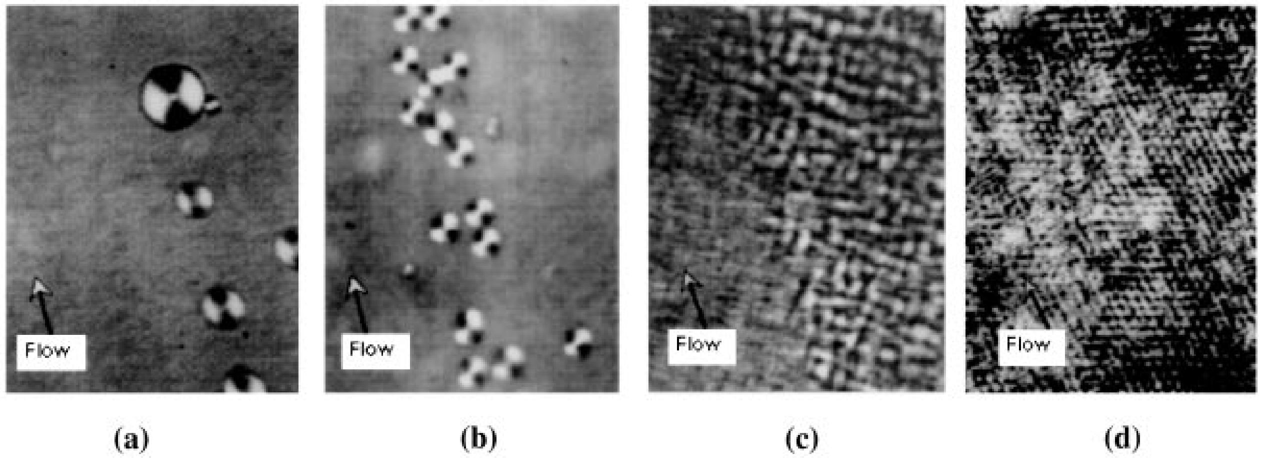

FIG. 3. The jump in size transition seen in the direct space (optical microscopy). The transition is controlled here by a change in temperature (21 to 24.3 °C). The shear direction is horizontal. 3(a) After a few minutes some big spherulites appear randomly; 3(b) they are then collected in lines; 3(c) the small and big populations coexist; 3(d) the big population once stopped and after some small amplitude oscillations.

The transition between small and big vesicles can be mapped in the $\dot{\gamma}/\mathrm{T}$ plane. Figure 4 presents a series of light scattering measurements obtained at steady shear and varying temperature. Below 26 °C a clear jump in the size of the vesicles is observed, and the evolution of the scattering pattern as a function of time is presented in Figs. 5(a)–(d). Figures 5(b) and 5(c) show clearly a population of small particles (large scattering circle) coexisting with a population of big particles (small-angle scattering peaks). However, above 26 °C no jump is observed and the increase of size is continuous. Figures 5(e)–5(h) show the evolution as a function of time. Clearly the ring is shrinking continuously, indicating that the onion size is increasing with time as the long-range order is built.

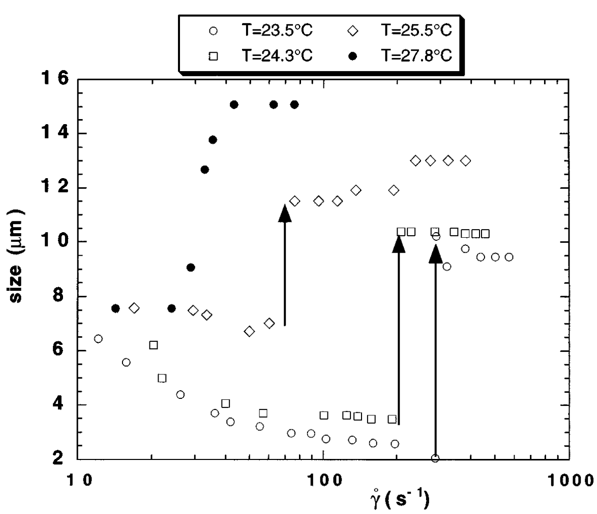

FIG. 4. The evolution of the spherulite size as a function of the shear rate for different temperatures. Above 26 °C the transition cannot be seen and a continuous evolution of size replaces the jump seen previously.

One concludes that the transition that was discontinuous below $T = 26$ °C becomes continuous above. Figure 6 shows the shear diagram obtained from these measurements. The two regions of ordered vesicles (small and big) are separated by a line corresponding to a discontinuous transition. This line ends on a "critical point" at $\dot{\gamma} = 40\ \mathrm{s}^{-1}, T = 26$ °C.

It seems difficult with the knowledge we have on these systems to give a theoretical interpretation of this complex behavior, even if some hand waving arguments can be given to explain the lamellar-spherulite [1–2,4] instability and some similarity with colloidal systems invoked for the layering transition [5]. However, the fact that well defined transitions can be determined confirms that the correct way of describing the effect of shear on complex fluids is to use the shear diagrams methodology. Moreover, because these systems are out of equilibrium

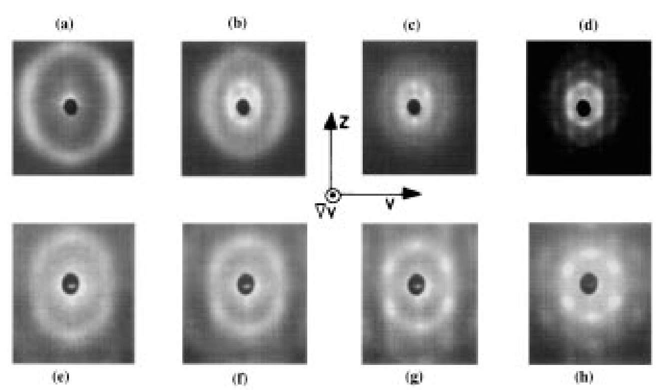

FIG. 5. Evolution of the scattering pattern after a shear jump below 26 °C [continuous transition, 5(a)-5(d)] and above 26 °C [continuous transition, 5(e)–(h)]. Note that the intermediate times show two populations in 5(b) and 5(c) corresponding to the discontinuous transition when it looks continuous in 5(f) and 5(g).

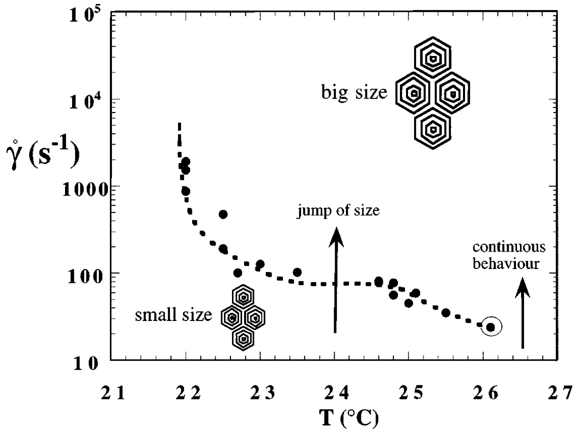

FIG. 6. The shear diagram of the jump in size transition. The full dots are the experimental points, the dashed line is a guide for the eye, and the circled dot is the location of critical point where the discontinuous transition is replaced by a continuous evolution.

and the transitions between different orientation states are discontinuous or continuous, one should expect a richer behavior. In particular, we are looking for nonstationary states near the bifurcation points.

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