# Shear-induced orientations in a lyotropic defective lamellar phase

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# Shear-induced orientations in a
# lyotropic defective lamellar phase

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**Abstract.** – The influence of shear on a defective lamellar phase of the ternary mixture sodium
dodecyl sulphate/decanol/$D_2O$ was studied using small-angle neutron scattering (SANS), small-
angle light scattering (SALS) and birefringence. Shear flow leads to an alignment of lamellae but
in addition to previous studies, we found a reorientation from "perpendicular" lamellae, *i.e.* with
the layer normal along the vorticity direction, to "parallel" lamellae with the layer normal
along the velocity gradient direction at increasing shear rates. The reorientation processes were
accompanied by a decrease of viscosity.

*Introduction.* – Shear flow is known to have a strong influence on the structure of complex
fluids. Especially samples with lamellar morphology attracted attention in the last few years
in order to find unifying principles in different types of materials as, *e.g.*, aqueous surfactant
solutions and block copolymer melts. Although these materials are rather different concerning
molecular structure and composition, similar effects of shear orientation have been observed.
In both cases, a shear-induced alignment of the lamellae was found, which can be characterised
by comparing the orientation of the layer normal with the direction of flow, the direction of
the velocity gradient and the vorticity direction, respectively. Following the terminology used
in other work [1], we denote the real-space orientation with the layer normal pointing along
the neutral direction, the flow direction and the velocity gradient direction as *perpendicular,
transpose* and *parallel*, respectively.

In block copolymer melts large-amplitude oscillatory shear has usually been employed and
different orientations of the lamellae were found [2-4]. Often the "parallel" layer orientation is
found at low frequencies, and the "perpendicular" orientation at higher frequency deformation.
It has been suggested that layer fluctuations close to the order-disorder transition increase the

stability of the perpendicular orientation at higher frequencies [5]. Recently, there was a report on two transitions from *parallel-to-perpendicular-to-parallel orientation* which, as far as we know, is not yet theoretically understood [3].

In lyotropic surfactant lamellar phases steady shear is employed usually. Roux and co-workers [6] detected a parallel alignment of lamellae, whereas a transition from parallel to perpendicular orientation at high shear rates was observed in other systems, similar to the behaviour of block copolymer melts [7-10]. However, one characteristic difference between lyotropic and polymer melt systems is the shear-induced formation of multilamellar vesicles ("onions") which is frequently found in lyotropic systems [6, 8, 11, 12].

In the present work, we report on small-angle neutron and light scattering (SANS, SALS) as well as birefringence experiments obtained from a *defective* lyotropic lamellar phase containing sodium dodecyl sulphate (SDS), decanol and water [13]. As will be shown below, these samples do not form vesicles but show a reorientation from "perpendicular" to "parallel" lamellae with increasing shear. This indicates that the "*perpendicular-to-parallel*" transition might be a general feature of complex fluids with lamellar morphology.

*Experimental details.* – 1-Decanol (99%) was purchased from Sigma-Aldrich, sodium dodecyl sulphate (> 99%) from Fluka. All chemicals were used without further purification. The defective lamellar phase consisted of sodium dodecyl sulphate/decanol/$D_2O$ with a $D_2O$ mass fraction of 0.679. Two samples with different molar fraction $x_c$ in the surfactant/co-surfactant mixture were investigated. The decanol content was $x_c = 0.285$ and $x_c = 0.301$.

SANS experiments were performed on the instrument D11 of the Institut Laue-Langevin, Grenoble, using neutrons of wavelength 4.5 Å ($\Delta\lambda/\lambda = 10\%$). The Couette-type shear cell consisted of two concentric quartz cylinders with a gap of 1.0 mm. Two beam configurations were used. The radial position, where the beam direction is parallel to the velocity gradient direction and the tangential beam position, where the neutrons pass through the sample along the flow direction. In the latter case, a rectangular aperture of 0.25 mm × 10 mm was used. Data were collected on a two-dimensional detector and will be discussed mostly qualitatively. For quantitative measurements with the tangential beam, it is necessary to correct for the different pathlengths and the smearing of the directions. Procedures are in preparation to enable quantitative measurements with the tangential beam position.

For rheo-optical studies, a stress-controlled Bohlin CS-10 rheometer equipped with a quartz glass cone/plate or plate/plate shear geometry was used. The incident laser beam of a He-Ne laser passes through the sample along the direction of the velocity gradient and perpendicular to the flow direction. For birefringence the retardance was determined using the method described by Lim and Ho [14]. The actual experimental setups are given elsewhere [15, 16]. All experiments were performed at 25 °C.

*Neutron scattering at rest.* – Figure 1 displays neutron scattering curves from both samples at rest. There are two characteristic features: i) Sharp Bragg-peaks from the layer spacing at high $q$ (with $q_{max} = 0.107$ Å$^{-1}$ for $x_c = 0.285$ and $q_{max} = 0.106$ Å$^{-1}$ for $x_c = 0.301$, in agreement with X-ray scattering data of Berger and Hiltrop [13]). ii) A broad peak corresponding to the distance between defects within the surfactant bilayers with $q_{max} = 0.071$ Å$^{-1}$ for $x_c = 0.285$ and $q_{max} = 0.066$ Å$^{-1}$ for $x_c = 0.301$. $q_{max}$-values of the peaks were not influenced by shear flow. In the following we will use the terms "Bragg-peak" and "defect-peak" for the two scattering maxima.

*Sample with lower decanol content $x_c = 0.285$.* – SANS patterns under shear are shown in fig. 2 for the sample with the lower decanol content of $x_c = 0.285$. The scattering patterns are
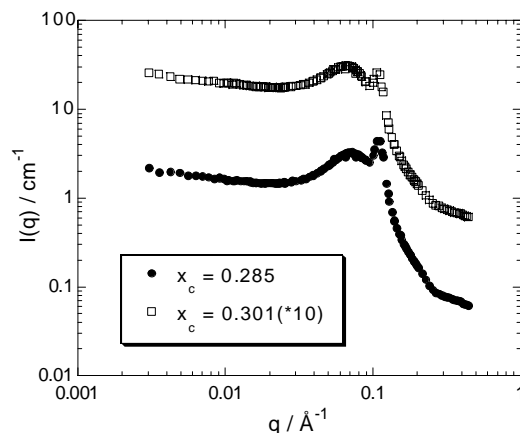
Fig. 1. – Angular dependence of SANS from the defective lamellar phase at rest.

strongly anisotropic and a shear rate dependence can be observed with both beam positions. At low shear rate, the radial beam (top part of fig. 2) shows the strong Bragg-peak only along the vorticity direction, whereas the defect-peak is isotropically distributed on the two-dimensional detector. At high shear rate, the intensity of the Bragg-peak is very weak but the defect-peak intensity is not changed. The results from the radial beam clearly show that no transposedly aligned lamellae are present. Thus the radial beam data indicate a transition from perpendicular to parallel orientation.

A disadvantage of the radial beam position is that the Bragg-peak of lamellae which are oriented parallel to the walls cannot be detected. Thus, the tangential beam provides additional, important information. Results from the tangential beam are displayed in the bottom part of fig. 2 for the same shear rates. The reorientation process is obvious also in this beam position, but detailed information on the degree of orientation is obtained. At low shear rates, the intensity of the Bragg-peak along the vorticity direction (corresponding to the
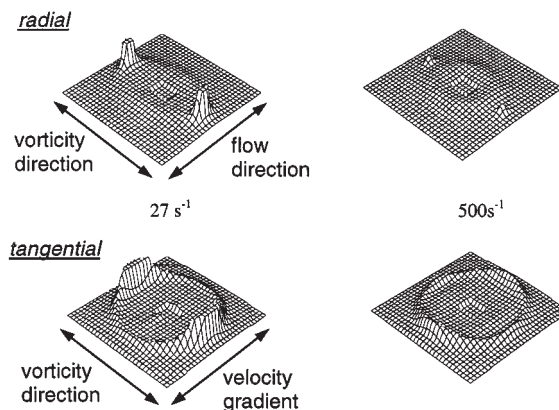


Fig. 2. – Neutron scattering patterns of the defective lamellar phase at $x_c = 0.285$ at shear rates of $27 \text{ s}^{-1}$ (left) and $500 \text{ s}^{-1}$ (right). Top: radial beam. Bottom: tangential beam. The intensities are scaled to the same maximum for each beam direction.
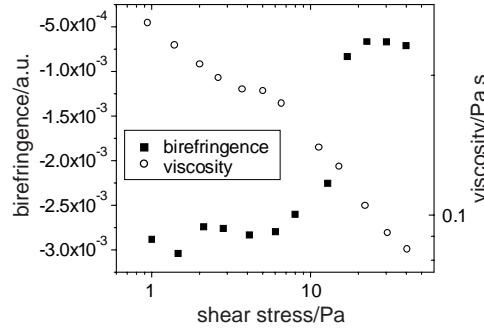
Fig. 3. – Viscosity and flow birefringence of the defective lamellar phase at $x_c = 0.285$.

perpendicular orientation) is higher as compared to the Bragg-peak along the velocity gradient direction. Thus at low shear rates, the perpendicular orientation of the surfactant bilayers is dominating. However, at high shear rates the parallel orientation is dominant (by a factor of 1.7). Thus the results from radial- and tangential-beam positions provide evidence for a *reorientation of lamellae from perpendicular to parallel orientation with increasing shear rate.*

Results from flow birefringence are shown in fig. 3. In birefringence measurements, the retardance is detected and due to the periodicity it is sometimes difficult to determine the absolute value for strongly birefringent samples. A negative value is expected for lamellae adopting the perpendicular orientation. Due to the long axis of the molecule aligned parallel to the layer normal, a negative flow birefringence results since the molecules are aligned along the neutral direction, perpendicular to the flow direction. However, surfactant molecules adopt a homeotropic orientation when the lamellae are aligned parallel to the walls. In this case, the long axis of the molecule is parallel to the direction of the velocity gradient (*i.e.* parallel to the incident light beam) and only a small absolute birefringence value is detected. This is true for the high shear region in fig. 3, while in the low shear region, the perpendicular orientation predominates. Thus the flow birefringence experiments provide additional evidence for the transition from perpendicular-to-parallel layer orientation at ca. $100 \text{ s}^{-1}$ ($\sigma = 15$ Pa). Figure 3 also shows that this transition is accompanied by a kink in the viscosity-stress curve.

*Sample with higher decanol content $x_c = 0.301$.* – Figure 4 displays SANS patterns at three different shear rates for radial (top) and tangential (bottom) beam positions. Three different states were found with this sample. A comparison with fig. 2 shows that the lamellae are aligned parallel to the walls at low and high shear rates. In the radial beam position, the Bragg-peak is much weaker as compared to the defect-peak and the tangential beam shows a higher Bragg-peak intensity along the velocity gradient direction as compared to the vorticity direction.

The behaviour of this sample seems to be quite similar to what was observed by Roux and co-workers [6]. They found the parallel orientation at low and high shear rates as well. At intermediate shear rates, they observed multilamellar vesicles ("onions"). However, in our case the behaviour at intermediate shear rate is different.

The radial SANS pattern at intermediate shear rates shows a strong Bragg-peak *only* along the vorticity direction but not along the flow direction. If vesicles were present, the Bragg scattering from the layer spacing would be observable on the entire azimuthal trace on the two-dimensional multidetector [12]. The radial SANS scattering pattern thus indicates the presence of perpendicularly aligned lamellae, similar to the behaviour of the sample at
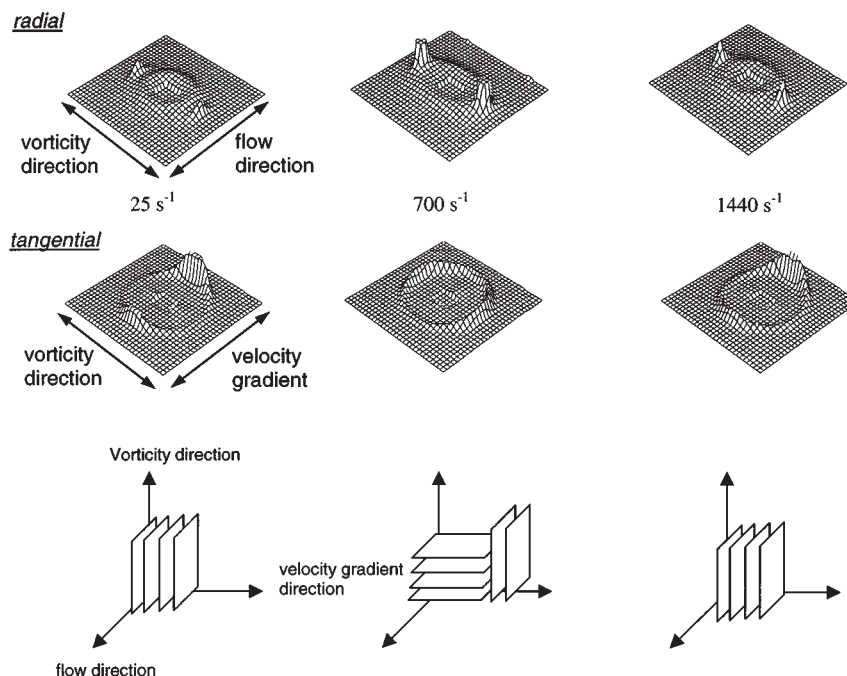
Fig. 4. – Neutron scattering patterns of the defective lamellar phase at $x_c = 0.301$ under shear for different rates of 25 s$^{-1}$, 700 s$^{-1}$ and 1440 s$^{-1}$ (left to right). Top: radial beam. Bottom: tangential beam. The dominating layer orientation is schematically shown below the scattering patterns. The intensities are scaled to the same maximum for each beam direction.

$x_c = 0.285$ at low shear rates. Again, the tangential beam provides more detailed information. The Bragg-peak intensity along the vorticity direction is, by a factor of 2, higher as compared to the velocity direction. Thus, the lamellae are predominately oriented perpendicularly at intermediate shear rates. With a further increase of shear, a reorientation of lamellae from *perpendicular-to-parallel orientation* is observed above 1000 s$^{-1}$ which is similar to the behaviour of the sample with lower decanol content.

Thus, the sample at $x_c = 0.301$ behaves differently as compared to the system studied by Roux and co-workers. Further rheo-optical experiments were performed in order to clarify whether or not multilamellar vesicles were formed at intermediate shear rates, see fig. 5. Obviously, the three different regions could be distinguished in flow birefringence, small-angle light scattering and viscosity as well. The birefringence curve shows low birefringence values at low and high shear rates supporting the homeotropic orientation with surfactant bilayers parallel to the walls of the shear cell. At intermediate shear rates, strong negative values were found, which, following the discussion presented above with the sample of low decanol content, indicate a perpendicular orientation of the lamellae.

Figure 5 also includes contour plots of depolarized (HV) SALS patterns obtained under shear. The flow direction in the contour plots is *vertical*. The scattering pattern of region I is characterized by a rather diffuse intensity distribution with slightly enhanced scattering intensity along and perpendicular to the flow direction. The pattern indicates the presence of defects in the texture as already discussed by Diat *et al.* [6]. Region II is characterized by an intense streak perpendicular to the flow direction. This indicates the presence of an ordered texture with defect lines aligned in the flow direction. Furthermore, this scattering pattern
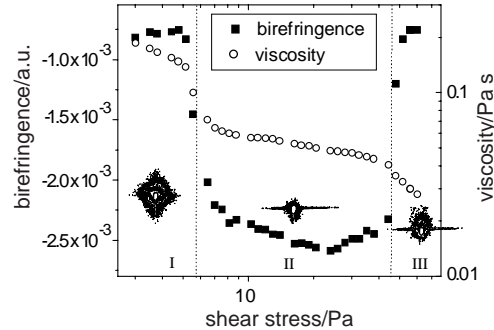
Fig. 5. – Viscosity, flow birefringence and SALS pictures of the defective lamellar phase at $x_c = 0.301$.

provides strong evidence against the presence of multilamellar vesicles. It has been shown before that multilamellar vesicles give rise to four-lobe pattern in depolarized SALS [8, 12]. Region III also shows a streak; however, the total scattering intensity is much weaker as compared to regions I and II. Obviously, only few defects are present at high shear rates, which is in agreement with the observations by Roux and co-workers [6].

The rheological behavior provides further evidence against the formation of vesicles. The sample was shear thinned and the viscosity showed two transitions at ca. $\sigma = 5.5$ Pa ($\dot{\gamma} = 55$ s$^{-1}$) and $\sigma = 44$ Pa ($\dot{\gamma} = 1200$ s$^{-1}$), respectively. It has been observed before that changes in layer orientation are connected with a decrease of viscosity, whereas Diat *et al.* already pointed out that the formation of vesicles leads to a viscosity increase [6].

Thus SANS, SALS and rheology provide strong evidence that the intermediate region II does not contain vesicles. In a previous study we examined the behaviour of a sample with a decanol content of $x_c = 0.354$; there we found vesicles [17]. In order to find out whether the different behaviour observed in the present study is due to slower transition kinetics, we sheared the sample with $x_c = 0.301$ at intermediate stresses for four hours ($\sigma = 4$ Pa, $\dot{\gamma} \approx 25$ s$^{-1}$), but we neither observed a four-lobe HV-SALS pattern nor an increase of viscosity. Of course, we cannot exclude that vesicles could be formed eventually, but in the experimentally accessible time scale where evaporation is not yet a problem, we could not observe indications of vesicle formation. We wish to note that vesicles are easily formed at higher decanol content.

Therefore, we conclude that the sample with $x_c = 0.301$ shows three regions of oriented lamellae. Reducing the shear rate revealed that the transitions are reversible. The results from SANS in the tangential beam showed that the orientation in region II was not perfect. We performed preliminary birefringence and SANS experiments at different gap size which indicate that the parallel orientation is preferred near the walls. A gap size effect in lamellar systems is known [18, 19] and will be investigated more in detail in the future. The first transition from parallel to perpendicular alignment has been observed in other surfactant systems before [7-10], but, to our knowledge, the opposite behaviour has not been reported before for lyotropic systems.

*Conclusions.* – Rheological, SANS, birefringence and SALS experiments from a defective lyotropic lamellar phase showed that shear flow can lead to different states of lamellae orientation. The sample with $x_c = 0.285$ displayed two regions whereas three regions were found when $x_c = 0.301$. However, both samples revealed a *reorientation from perpendicular to parallel* alignment. Similar behaviour was observed with block copolymer melts where oscillatory shear was applied. Apparently, surfactant mesophases and polymer melts can show

similar behaviour under shear. This indicates that the "*perpendicular-to-parallel*" transition might be a general feature of complex fluids with lamellar morphology.

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