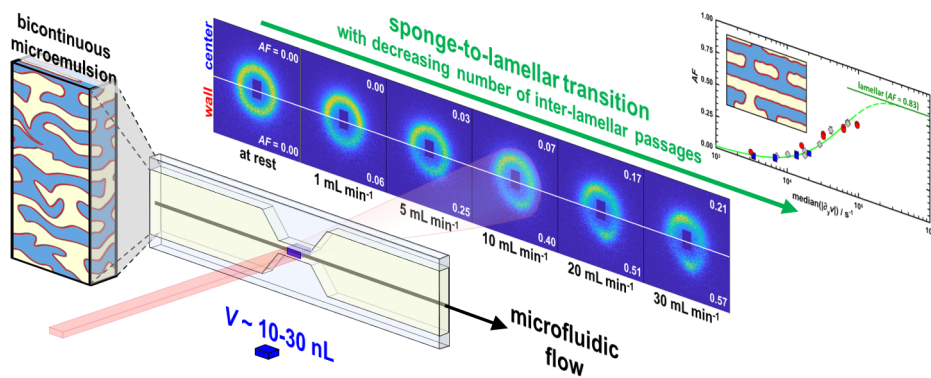


Graphical Abstract

Shear-Induced Sponge-to-Lamellar Transition in Bicontinuous Microemulsions Evidenced by Microfluidic-SANS

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Shear-Induced Sponge-to-Lamellar Transition in Bicontinuous Microemulsions Evidenced by Microfluidic-SANS

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Abstract

Hypothesis: Shear flow applied to bicontinuous microemulsions is expected to induce a transition to lamellae via the suppression of surfactant monolayer fluctuations. Compared to the topologically analogous L_3 (sponge) phase, composed of surfactant bilayers, this transition is likely to occur at much higher shear rates.

Experiments: We examine the flow response of a model bicontinuous microemulsion, D_2O/n -octane/ $C_{10}E_4$ by coupling microfluidics with small-angle neutron scattering (SANS), attaining wall shear rates in excess of 10^5 s^{-1} . The reduction of probed sample volumes down to $\sim 10 \text{ nL}$ allows the spatial mapping of the structural and orientation changes within the microchannel, as a function of the flow field components.

Findings: With increasing flow rate, we observe a gradual increase in scattering anisotropy, accompanied by a decrease of the microemulsion domain size along the main flow orientation. A consistent description of the degree of anisotropy was obtained when considering the velocity gradient along the scattering plane perpendicular to the flow. We discuss the flow dependence of the effective bending rigidity, rationalizing a strong influence of shear on thermal membrane fluctuations. Assuming a similar shear dependence for the saddle splay modulus, the bicontinuous-to-lamellar transition can be attributed to the gradual disappearance of inter-lamellar passages.

Keywords: bicontinuous microemulsion, surfactant monolayers, sponge-to-lamellar transition, microfluidics, self-assembly, shear deformation, small-angle neutron scattering

1. Introduction

Sponge-like (L_3) nanostructures, formed by self-assembled surfactant bilayer membranes, are a unique feature of aqueous surfactant systems [1–3]. The topology of this phase, characterized by two interwoven water domains, differs significantly from lamellar (L_α) structures, formed by stacks of smectically ordered bilayer membranes separated by unconnected water layers. Although the two structures possess distinct optical and rheological properties, both exhibit zero mean bilayer curvature $\langle H_{\text{bilayer}} \rangle = 0$ and lie adjacently in the phase diagram. However, while for the sponge-like L_3 -phase the mean curvature $\langle H_{\text{mono}} \rangle$ of the monolayers constituting the bilayer is negative, $\langle H_{\text{mono}} \rangle = 0$ for the monolayers forming the smectically ordered bilayers [4, 5].

Transitions between the two topologies can be readily induced through changes of monolayer curvature by altering temperature or composition [1, 6–9]. Cates and Milner [10] predicted that a sponge-to-lamellar transition could also

be induced by suppressing membrane fluctuations through the application of shear flow. The critical shear rate for the transition $\dot{\gamma}_c$ was predicted to depend on viscosity η and domain size ξ , or equivalently on membrane volume fraction ϕ_m and membrane thickness δ [10]:

$$\dot{\gamma}_c \sim \frac{k_B T}{\eta \xi^3} \sim \frac{k_B T}{\eta} \left(\frac{\phi_m}{\delta} \right)^3, \quad (1)$$

where k_B is the Boltzmann constant. Diat and Roux first observed experimentally this shear-induced sponge-to-lamellar transition for highly dilute L_3 phases with rheo-SANS and -birefringence measurements at shear rates of up to 10^4 s^{-1} [11]. Considerable work has since focused on the influence of membrane volume fraction on the shear-induced L_3 -to- L_α transition of both neat and oil-swollen bilayers and its associated relaxation behavior [12–14].

Bicontinuous microemulsions are topological analogues of the L_3 phase, but formed by surfactant monolayers separating water and oil domains at the nanoscale. Here, the zero mean curvature $\langle H_{\text{mono}} \rangle = 0$ of the sponge-like monolayer results from principal curvatures being of different sign. Due to the ultra-low oil/water interfacial tension and excellent wetting behavior [17–22], bicontinuous microemulsions in particular find practical application in cosmetics, foods, agrichemicals, enhanced oil recovery, etc

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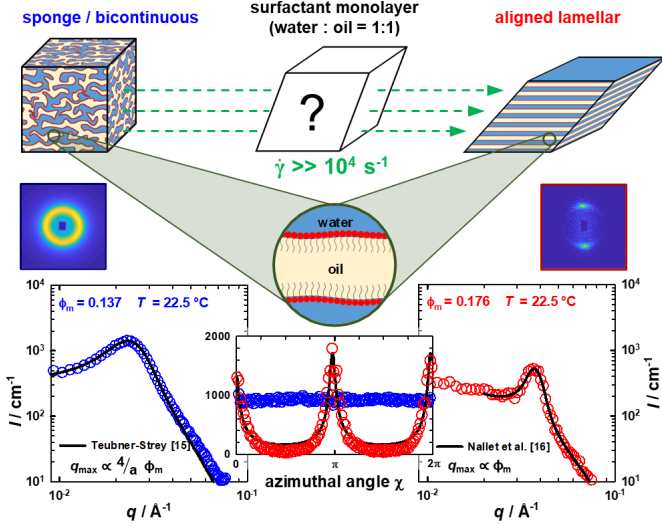


Figure 1: 2D-, 1D- and azimuthal scattering pattern of a non-sheared bicontinuous microemulsion ($\phi_m = 0.137$) and an aligned lamellar phase ($\phi_m = 0.176$) of the studied model system D_2O/n -octane/ $C_{10}E_4$, recorded at the phase inversion temperature $T = 22.5^\circ C$ with equal volumes of D_2O and n -octane. The schematic representations of a bicontinuous microemulsion and a lamellar structure illustrate our hypothesis of a shear-induced transition to smectically ordered lamellae at high shear rates.

[23–27], while exhibiting shear flow (e.g., in mixers, through nozzles or porous media) during processing and application. Given its industrial and academic relevance, the influence of shear on the rheology of bicontinuous microemulsions has been previously investigated [28, 29], but an understanding of the associated structural response at the nanoscale has remained elusive, thus motivating the present work.

Figure 1 illustrates the expected bicontinuous to lamellar transition, and the characteristic 2D scattering patterns of these two structures along with the radially- and azimuthally-averaged scattering profiles, measured under quiescent conditions by changing ϕ_m . From Eq. (1), the shear rate required to induce a transition from bicontinuous domains to lamellae can be estimated (assuming $\phi_m = 0.1$; $\eta = 7.0$ mPa s; $\delta = 10$ Å) to be $\sim 2 \times 10^5$ to 10^6 s $^{-1}$ [13]. Although such high shear rates can occur in applications [30], their influence on the microstructure of complex fluids could not be examined so far with conventional rheometers coupled with small-angle X-ray and neutron scattering (rheo-SAXS and -SANS, reaching $\dot{\gamma} \lesssim 10^4$ s $^{-1}$). The advent of microfluidic-SANS [31–35] has enabled the investigation of wall shear rates exceeding 10^5 s $^{-1}$ while exploiting the flux increase ($\sim 10^8$ n cm $^{-2}$ s $^{-1}$) of neutron facilities.

In this paper, we use microfluidic-SANS to study the impact of flow on the structure of a symmetric bicontinuous model microemulsion, D_2O/n -octane/ $C_{10}E_4$. For this purpose, we allow the microemulsion to flow at different flow rates through a microchannel with linear constriction providing adjustable shear rates in excess of 10^5 s $^{-1}$. By interrogating small sample volumes of ~ 10 -30 nL we were

able to map the response of the bicontinuous structure within the microchannel spatially and thus as a function of flow field components. The subsequent azimuthal and radial analysis of the recorded 2D scattering data provides the flow field dependence of the alignment factor AF , the periodicity d_{TS} , the amphiphilicity factor f_a as well as the effective bending rigidity κ_{eff} . We discuss the variation of the latter using a shear-dependent renormalization due to fluctuations and conclude the variation of the structure within the flow field, from lamellar sheets at the wall to sponge-like structures in the center of the microchannel.

2. Materials and Methods

2.1. Materials and Sample Preparation

Deuterium oxide (D_2O , 99.9 %) and n -octane (98 %) were purchased from *Sigma-Aldrich*, Tetraethylene glycol monododecyl ether ($C_{10}E_4$, 99 %), a linear non-ionic surfactant, was purchased from *Bachem*. Note that D_2O , which was used to adjust bulk contrast in the SANS measurements, was also used in all other experiments for comparability. All chemicals were used without further purification. The samples were prepared by weighing surfactant, oil and D_2O (in that order) with an accuracy of $\Delta m = \pm 0.001$ g into either test tubes (phase diagram studies and viscosity measurements) or glass vials (SANS measurements).

To calculate the membrane volume fraction ϕ_m , the mass fractions were converted to volume fractions using the respective densities. Accounting for the amount of monomerically dissolved $C_{10}E_4$ in n -octane ($\phi_{C,mon,b}$) [36], ϕ_m was calculated from the total surfactant volume fraction $\phi_C = \phi_m + \phi_{C,mon,b}$. Note that the monomeric solubility of $C_{10}E_4$ in water can be neglected [36].

2.2. Phase Behavior

Before investigating the properties of complex multi-component systems, such as flow behavior or structure, their phase behavior should be characterized. Accordingly, the temperature-dependent phase behavior of the ternary system D_2O/n -octane/ $C_{10}E_4$ was studied as a function of the membrane volume fraction ϕ_m at equal volumes of D_2O and n -octane. For the determination of the phase behavior, a sealed test tube containing the respective sample was placed in a water bath whose temperature was adjusted with a thermostat (*Thermo-Haake* DC30, $\Delta T = \pm 0.02$ K) while the sample was homogenized with a magnetic stirrer. After reaching temperature equilibrium, stirring was stopped to determine the number and appearance of the phases. Note that the lamellar phase was characterized by its birefringence, detected with crossed polarizers. In this way the phase transition temperatures were determined with a precision of $\Delta T = \pm 0.05$ K.

Fig. 2a shows the recorded phase diagram exhibiting the typical features of microemulsions stabilized by non-ionic surfactants [17, 37]. Its main feature is the temperature-induced phase inversion. At low temperatures an oil-in-water microemulsion coexists with an oil-excess phase (2),

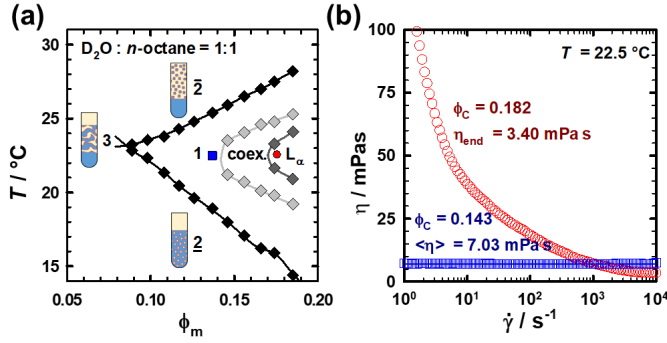


Figure 2: (a) Phase diagram of the system $\text{D}_2\text{O}/n\text{-octane}/\text{C}_{10}\text{E}_4$ as a function of the membrane volume fraction ϕ_m at equal volumes of D_2O and $n\text{-octane}$. The bicontinuous microemulsion (blue square, $\phi_m = 0.137$) and lamellar phase (red circle, $\phi_m = 0.176$) are both examined at the phase inversion temperature of $T = 22.5^\circ\text{C}$ close to the two-phase coexistence of microemulsion and lamellar phase. (b) Flow curve reveals Newtonian flow behavior for the bicontinuous microemulsion (blue squares, $\phi_m = 0.137$) with an average viscosity of $\langle\eta\rangle = 7.03\text{ mPa}\cdot\text{s}$ and characteristic shear-thinning behavior for the lamellar phase (red circles, $\phi_m = 0.176$).

while a coexistence of a water-in-oil microemulsion with a water-excess phase is found at high temperatures ($\bar{2}$). At intermediate temperatures and low membrane volume fractions $\phi_m < 0.085$ a three-phase coexistence (3) of a microemulsion and two (water and oil) excess phases is found. When the volume fraction of the membrane is increased, a single-phase microemulsion (1) forms between $\phi_m = 0.085$ and 0.142 at the phase inversion temperature $T = 22.5^\circ\text{C}$, where the mean curvature of the surfactant monolayer is known to be zero. The examined bicontinuous (blue square, $\phi_m = 0.137$) and lamellar structure (red circle, $\phi_m = 0.176$) are both located close to the two-phase coexistence of microemulsion and lamellar phase (coex.) between $\phi_m = 0.142$ and 0.170 .

2.3. Viscosity Measurements

The viscosity measurements were performed with the rotational rheometer Physica MCR 501 from Anton-Paar. A double gap geometry (DG26.7) with a gap size to internal radius ratio of 0.035 (gap sizes $416\text{ }\mu\text{m}/466\text{ }\mu\text{m}$) was used due to the expected low viscosities. Before every measurement the rheometer was set to the measurement temperature with a Peltier element and left for 30 min to equilibrate. Then a glass pipette was used to fill the gap with around 3.8 mL of the respective sample, while ensuring that the sample remained homogeneous. The viscosity was determined for 10 s at a steady shear rate $\dot{\gamma}$ ranging from 1 to 10^4 s^{-1} . Every measurement was repeated three times.

The resulting $\eta(\dot{\gamma})$ -diagram in Fig. 2b reveals Newtonian flow behavior for the bicontinuous microemulsion (blue squares, $\phi_m = 0.137$) with an average viscosity of $\langle\eta\rangle = 7.03\text{ mPa}\cdot\text{s}$, while the lamellar phase (red circles, $\phi_m = 0.176$) shows characteristic shear-thinning behavior.

2.4. Small-Angle Neutron Scattering

The shear-induced changes in the nanostructure of the system $\text{D}_2\text{O} - n\text{-octane} - \text{C}_{10}\text{E}_4$ were investigated via small-angle neutron scattering (SANS). All measurements were carried out at the D22 spectrometer of the Institut Laue-Langevin (ILL) in Grenoble (France) with a wavelength of $\lambda = 6\text{ }\text{\AA}$ ($\Delta\lambda/\lambda = 0.1$).

The experiments were performed at two different collimation/detector distances ($8.0\text{ m}/8.0\text{ m}$ for the bicontinuous microemulsion and $8.0\text{ m}/5.6\text{ m}$ for the lamellar phase) adjusting q -ranges from 7.1×10^{-3} to $9.3 \times 10^{-2}\text{ }\text{\AA}^{-1}$ and 1.3×10^{-2} to $6.3 \times 10^{-1}\text{ }\text{\AA}^{-1}$. Note that an additional side detector was employed at the shorter distance, extending the q -range to higher values. All SANS measurements were performed with the microfluidic-SANS setup (see Section 2.5)

The recorded scattering intensities were normalized to absolute scale using direct beam measurements. All data were reduced taking into account empty cell and background scattering as well as the transmission using the Matlab-based software *Grasp*.

2.5. Microfluidic-SANS Setup

The microflow response of the bicontinuous microemulsion was studied via SANS in a custom, glass microfluidic device with a linear constriction of cross-section $305\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$, depicted in Fig. 3a. Constriction lengths of 1 and 2 mm were found to yield equivalent microflow response of the bicontinuous microemulsion, within measurement uncertainty. The microdevice was fabricated using boron-free crown glass (*Dolomite Microfluidics*), yielding a high neutron transmission ($\approx 91\%$), despite its considerable overall thickness (4 mm) required to withstand high pressures, thus enabling us to reach large flow velocities and wall shear rates, detailed below.

Volume driven flow was controlled by a dual syringe pump (*Harvard Apparatus* 33 DDS) connected to the chip via FEP (fluorinated ethylene propylene) tubing from *Cole Parmer*. Spatial resolution of our flow measurements inside the microfluidic channel was achieved by mounting the chip onto a high precision xy stage from *Physik Instrumente* ($\pm 10\text{ }\mu\text{m}$). In order to map the fluid structures along the flow field, a Cd slit aperture of $420\text{ }\mu\text{m} \times 175\text{ }\mu\text{m}$ was fabricated, defining an exceptionally small sample volume of $\sim 10\text{-}30\text{ nL}$ within the microchannel (edge to center). The whole setup (syringe pump, tubing and chip with mounting) was placed in a home-built box tempered via air flow ($\Delta T = \pm 0.5\text{ K}$). For each experiment approximately 40 mL of the single-phase sample were filled into a 50 mL stainless steel syringe (*Harvard Apparatus*) connected to the tubing. In order to avoid demixing of the sample, the filling process took place in the box adjusted to the measurement temperature. Then, trapped air in syringe, tubing, and chip was removed by pushing some sample through it, followed by connecting another steel syringe of the same type to the tubing at the other end

of the chip channel. Before the two syringes were placed in the syringe pump, the remaining small amounts of air were collected in a bubble trap connected to the system. Finally, the tempered box was closed and sealed.

The flow experiments were carried out in a reciprocating pumping cycle to increase counting statistics. For simplicity, all results are presented in uniform flow direction and respective results in the opposite direction were mirrored during analysis. During the experiment, the flow rate was varied from 0 to 30 mL min⁻¹, resulting in average flow velocities up to 5.5 ms⁻¹. The resulting velocity and gradient profiles of the fully developed laminar flow used for analysis, shown in Fig. 3b, were calculated numerically under the assumption of a no-slip boundary condition and Newtonian flow behavior [38] (for a more detailed discussion see S2, Supplementary Material).

3. Results

The model Newtonian bicontinuous microemulsion, consisting of equal volumes of D₂O and *n*-octane and the nonionic surfactant tetraethylene glycol monodecyl ether (C₁₀E₄), under flow within the microfluidic constriction, exhibits clear changes in the 2D scattering pattern. The pattern, which is isotropic for bicontinuous microemulsions (Fig. 1, left), becomes increasingly anisotropic (Fig. 3a and Fig. 4a). To gain information on how the flow field affects the alignment as well as length scales and morphology of the structure, the recorded 2D scattering patterns were systematically analyzed, azimuthally (Section 3.1) as well as radially (Section 3.2).

3.1. Membrane Alignment

From the azimuthally-averaged data, illustrated in Fig. 1 (and S1, Supplementary Material), the degree of anisotropy was quantified using an ‘alignment factor’

$$AF \equiv \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \quad (2)$$

in accordance to previous studies on the shear-induced L_3 -to- L_α transition [11, 13]. $I_{\max}$ and $I_{\min}$ are the maximum and minimum intensity observed at the azimuthal angles $\chi_{\max}$ and $\chi_{\min} = \chi_{\max} + 90^\circ$, respectively. Accordingly, $AF = 0$ corresponds to an isotropic sponge-like, and $AF \sim 1$ to a lamellar structure, perfectly aligned parallel to the incident neutron beam and free from membrane fluctuations. Fig. 3b shows the alignment factor AF measured along the y -position at two flow rates, 5 and 20 mL min⁻¹, together with the velocity and gradient fields, calculated by the Navier-Stokes equations [38] (S2, Supplementary Material). The magnitude of the error bars reflect the inspected sample volumes and thus decrease towards the wall due to the only partial illumination of the microchannel by the neutron beam. As expected, AF increases with flow rate at all positions. The hyperbolic shape of the AF profile, symmetric about the channel centerline, indicates

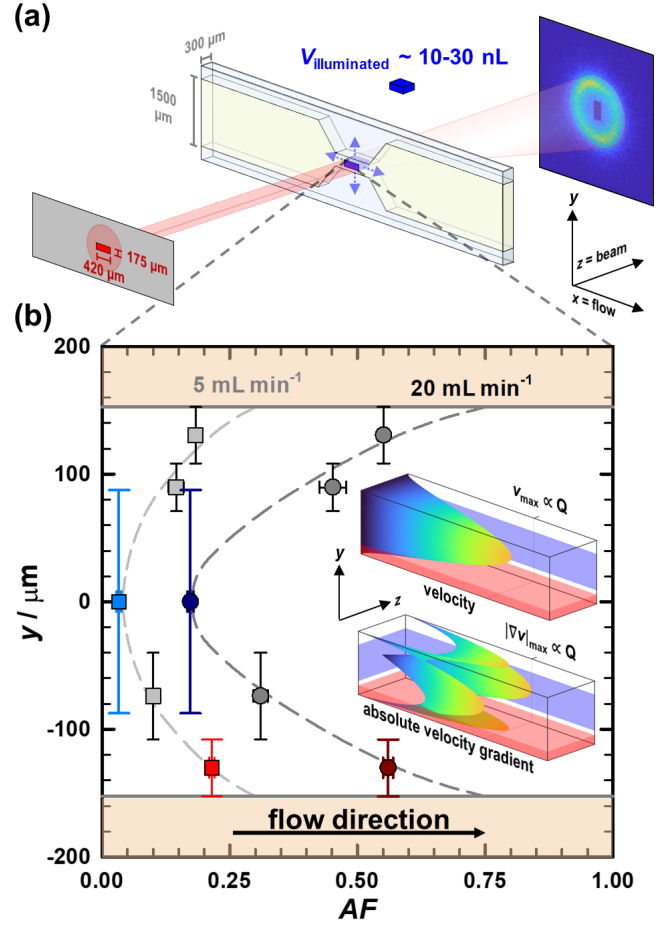


Figure 3: (a) Microfluidic-SANS setup depicting the slit diaphragm enabling the inspection of the flow behavior of minute sample volumes (~ 10 -30 nL), spatially resolved within the microchannel. (b) Influence of flow on the microemulsion alignment, quantified by the ‘alignment factor’ AF (Eq. (2)) along the y -direction, perpendicular to flow (illustrated at 5 and 20 mL min⁻¹), including a hyperbolic guide to the eye, symmetric along the channel centerline. The inset depicts the calculated velocity and gradient fields (detailed in S2, Supplementary Material).

that the structure evolves from near isotropic at the center to increasingly anisotropic near the walls.

The 2D SANS scattering patterns recorded along the channel cross-section as a function of flow rate Q are shown in Fig. 4a, exhibiting marked differences as the rate increases. The alignment factor at the channel wall increases strongly from $AF = 0$ to $AF = 0.57$, but only to $AF = 0.21$ in the center, as Q increases to 30 mL min⁻¹. At $Q = 1$ mL min⁻¹, isotropic scattering is observed at the channel center, while slight anisotropy is seen near the wall. Comparing the finite beam footprint with the channel dimensions, we conclude that, at such low flow rates, the microemulsion structure remains largely unaffected in more than half of the channel cross-section. The anisotropic region of aligned surfactant monolayers thus appears to grow from the channel walls towards the center. Besides, the scattering peak deviates from the vertical position, slightly rotating counterclockwise ($\chi_{\max} < 0$), indicating a tilted orientation of

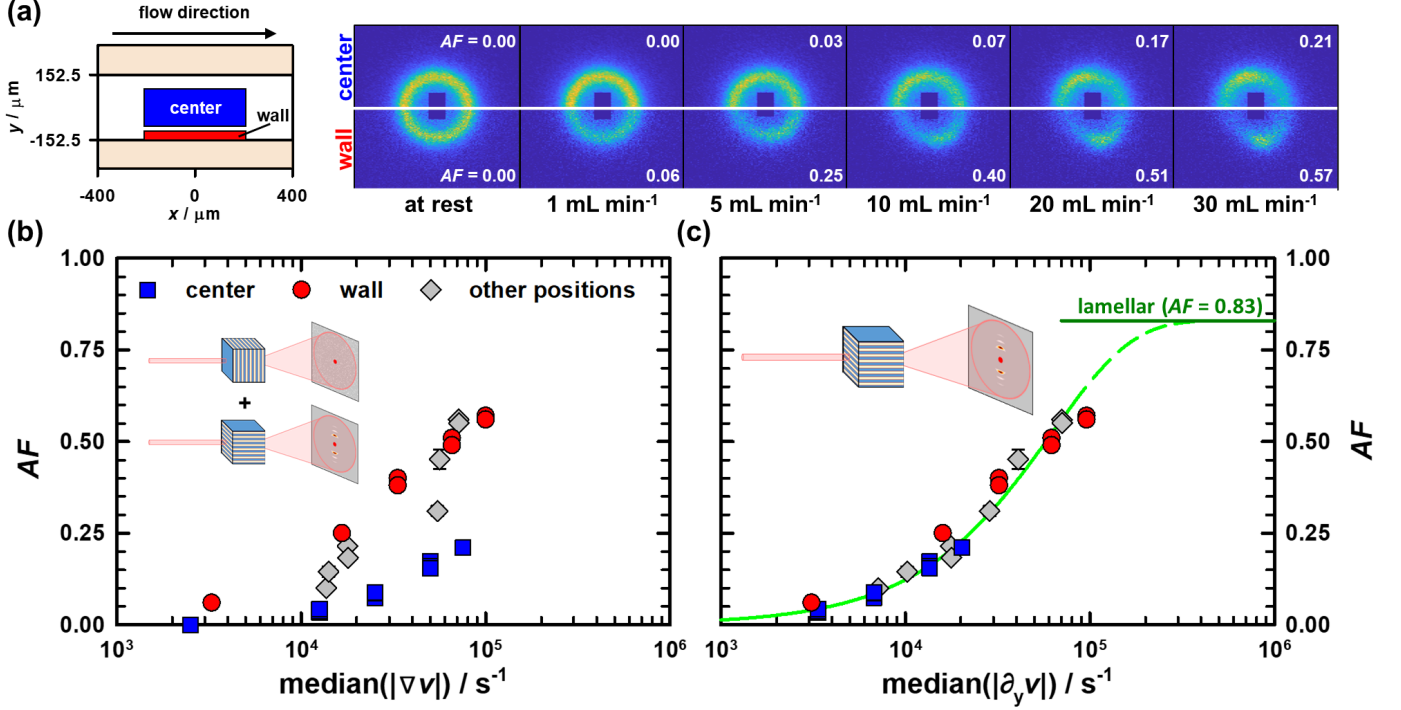


Figure 4: Flow rate-dependent microfluidic-SANS measurements performed at selected positions along the channel transversal y direction. (a) Schematic of the central part of the microchannel constriction (entire chip geometry shown in S2, Supplementary Material) and corresponding 2D scattering patterns at the microchannel center and wall, acquired at different flow rates. (b) Experimentally determined alignment factor AF plotted as a function of the total velocity gradient ∇v . (c) Collapse of AF data onto a master curve when plotted against $|\partial_y v|$, recognizing that only the gradient in y direction contributes to the scattering signal. The line is an exponential rise to $AF=0.83$, determined experimentally for the lamellar phase ($\phi_m = 0.176$) under very mild flow.

the flow-induced anisotropic structure. Interestingly, the tilt angle approaches zero both when the flow rate is increased as well as when moving from the center towards the wall of the microfluidic channel (detailed in S3, Supplementary Material). Similar observations were reported for anisotropic colloidal objects in shear flow [39, 40]. To rationalize how flow influences the structure of the bicontinuous microemulsion, various descriptors of the flow field were considered, including the median velocity gradient $|\nabla v|$ (Fig. 3b and S2, Supplementary Material), which is equivalent to the shear rate $\dot{\gamma}$, spatially averaged by the SANS beam. The median was selected (e.g. instead of the mean) to better reflect the scattering volume average within the velocity gradient. The alignment factor AF , recorded at different flow rates and channel positions, is found to increase with the velocity gradient $|\nabla v|$, regardless of the transversal channel position (y), and is strongest at the channel wall, as shown in Fig. 4b. The insensitivity to the channel position should stem from the connection between membrane orientation and obtained scattering signal.

For surfactant bilayer membranes, Porcar et al. [13] observed that shear-induced lamellar structures align parallel to the flow direction and normal to the velocity gradient vector. In a microchannel with flow along the x direction and a respective velocity gradient vector of $\nabla v =$

$(0, \partial_y v, \partial_z v)$, the lamellar membranes are expected to align concentrically around the channel centerline. In this case, essentially only membranes aligned parallel to the beam with $\nabla v \sim (0, \partial_y v, 0)$, contribute to coherent scattering, while those aligned normal to the neutron beam, or $\nabla v \sim (0, 0, \partial_z v)$ do not contribute, as illustrated in Fig. 4b. Accordingly, a collapse of all AF data onto a master curve is expected when plotted as a function of the median velocity gradient $|\partial_y v|$, which is indeed observed experimentally, as shown in Fig. 4c. The line is an exponential rise profile to a value of $AF = 0.83$, which was experimentally found for a lamellar phase ($\phi_m = 0.176$ and $T = 22.5^\circ\text{C}$) near the wall under very mild flow ($Q = 0.1 \text{ mL min}^{-1}$), detailed in S4, Supplementary Material. Note that thermally fluctuating lamellar monolayers are expected to exhibit lower alignment factors than $AF = 1$ (which holds for perfectly ordered lamellar phases). Capillary RheoSANS [41] measurements may reveal whether the assessed values for the critical shear rate of $\sim 5 \times 10^5 \text{ s}^{-1}$ and the corresponding alignment factor of $AF = 0.83$ are quantitatively correct for the investigated bicontinuous C_{10}E_4 microemulsion.

3.2. Length Scales and Morphology

To determine how the flow field, and in particular the velocity gradient $|\partial_y v|$, affects the length scales and morphology of the bicontinuous microemulsion, we next ana-

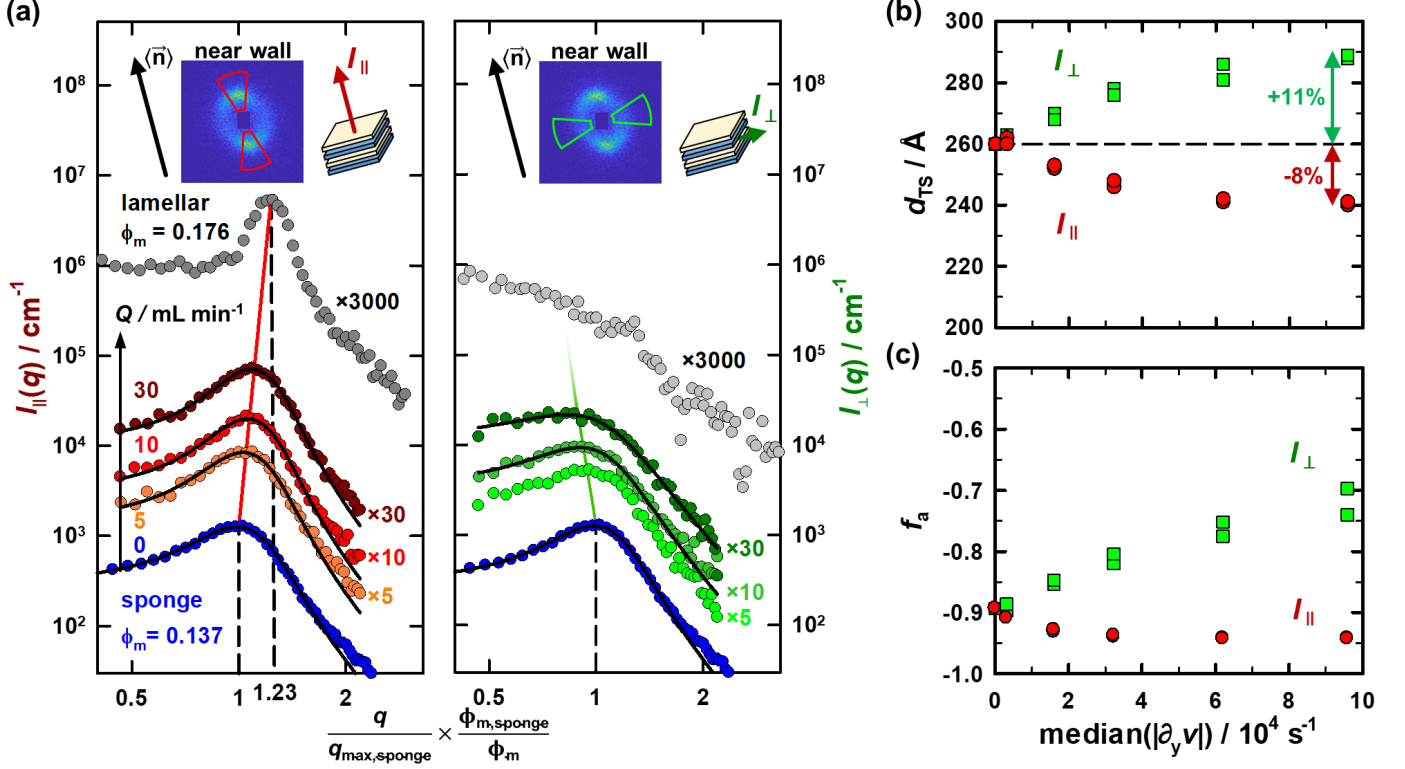


Figure 5: (a) Scattering profiles obtained from sector analysis of the 2D patterns near the channel wall with increasing flow rate Q . $I_{\parallel}(q)$ curves show a scattering peak that sharpens and shifts toward higher q values, while the peak in $I_{\perp}(q)$ moves to lower q values and nearly vanishes. (b) Periodicity d_{TS} and (c) amphiphilicity factor f_a as a function of $\text{median}(|\partial_y v|)$ obtained from the analysis of $I_{\parallel}$ (red) and $I_{\perp}$ (green) using the Teubner-Strey model [15].

lyze the recorded 2D scattering patterns sector-wise radially (Fig. 5a). Here, the scattering intensity $I_{\parallel}$ (red) in the two sectors located in the $\chi_{\max}$ direction originates from surfactant monolayers with a normal vector parallel to the mean orientation $\langle \vec{n} \rangle$ of the induced structure, while the scattering intensity $I_{\perp}$ (green) in the two sectors in the $\chi_{\min}$ direction rather originates from monolayers with a normal vector perpendicular to $\langle \vec{n} \rangle$.

In Fig. 5a, scattering curves recorded near the channel wall of the sheared bicontinuous microemulsion ($\phi_m = 0.137$) are shown alongside those of the reference lamellar phase ($\phi_m = 0.176$) gently aligned at 0.1 mL min^{-1} . A scaled q axis was used to compare the peak position of the bicontinuous microemulsion and the lamellar phase despite their different membrane volume fractions (unscaled data in S5, Supplementary Material). At rest, the former shows a scattering curve characteristic of sponge-like bicontinuous microemulsions with a peak located at $\frac{q}{q_{\max}} \times \frac{\phi_{m,\text{sponge}}}{\phi_m} = 1$, while the much sharper scattering peak of the lamellar phase is located at 1.23. This implies that the mean membrane distance in the bicontinuous microemulsion is a factor ~ 1.23 larger than that in the lamellar phase at the same membrane volume fraction. Simple geometric models of the bicontinuous structure predict factors of 1.46 [42] or 1.5 [43], but do not account, however, for thermal fluctuations.

The orthogonal sectors of the scattering pattern of the bicontinuous microemulsion respond to flow in opposite manner: with increasing flow rate Q , the scattering peak in $I_{\parallel}(q)$ becomes sharper and shifts towards higher q values, while the peak in $I_{\perp}(q)$ moves towards lower q values and almost vanishes. As such, the scattering features of the sheared bicontinuous microemulsion increasingly approach those of the lamellar phase, without showing the abrupt change expected for a first-order bicontinuous-to-lamellar transition.

Considering the bicontinuous nature of the studied $\text{D}_2\text{O}/n$ -octane/ C_{10}E_4 microemulsion at rest, which has been demonstrated by means of freeze fracture transmission electron microscopy [44], we used the Teubner-Strey model [15]:

$$I(q) = \frac{1}{c_2 q^4 + c_1 q^2 + a_2} \quad (3)$$

to quantify the systematic variation of the structure with shear. Here, a_2 , c_1 and c_2 are the coefficients of the order parameter expansion of the free energy density f [45]. Eq. (3) is obtained by Fourier transformation of the spatial correlation function:

$$\gamma(r) = \frac{\sin(kr)}{kr} \times \exp\left(\frac{-r}{\xi_{TS}}\right) \quad (4)$$

where $k = 2\pi/d_{TS}$. This function combines the two well-known properties of symmetric bicontinuous microemul-

sions. First, water and oil are separated by an amphiphilic film, forming alternating domains of size $\xi = d_{\text{TS}}/2$. Second, there is no long-range order, characterized by the correlation length ξ_{TS} . In terms of a_2 , c_1 and c_2 , these two structural length scales are given by:

$$d_{\text{TS}} = 2\pi \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} - \frac{c_1}{4c_2} \right]^{-1/2} \quad (5)$$

and

$$\xi_{\text{TS}} = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} + \frac{c_1}{4c_2} \right]^{-1/2} \quad (6)$$

Thus, the model delivers a simple but effective ansatz to extract structural information from the scattering of bicontinuous microemulsions [46, 47]. Note that the random wave description of Marčelja et al. [48, 49] formally gives the same scattering intensity function as Eq. (3), while the clipped random wave model of Chen et al. [50, 51] uses an additional third length scale introduced by a higher order term in the spectral density function.

The flow influence on the periodicity d_{TS} of the bicontinuous structure is shown in Fig. 5b by plotting d_{TS} as a function of $\text{median}(|\partial_y v|)$. In agreement with the observed shift of the scattering peaks shown in Fig. 5a, $d_{\text{TS},\parallel}(q)$ (red circles) decreases with increasing flow, while $d_{\text{TS},\perp}(q)$ (green squares) increases. The variation of correlation length ξ_{TS} with shear flow is shown in S5, Supplementary Material. However, here we discuss the flow influence on the structural order by means of the amphiphilicity factor [46]

$$f_a = \frac{c_1}{2\sqrt{a_2 c_2}}. \quad (7)$$

For well-structured bicontinuous microemulsions, an amphiphilicity factor below -0.6 is typically found, with the value becoming more negative as the structural order increases [46]. For a highly ordered ideal lamellar phase L_α the correlation length is expected to diverge, resulting in an amphiphilicity factor f_a of -1 . Considering the variation of the amphiphilicity factor with $\text{median}(|\partial_y v|)$ shown in Fig. 5c, a systematic decrease of $f_{a,\parallel}$ (red circles) from -0.89 to -0.94 is clearly seen, indicating an increasing degree of structural ordering with increasing flow in the direction of the main orientation. In contrast, the pronounced increase of the amphiphilicity factor $f_{a,\perp}$ (green squares), points to a strong loss of structural ordering in the perpendicular direction.

The recorded microfluidic-SANS data and their analysis so far lead us to the preliminary conclusion that the bicontinuous microemulsion is deformed into a lamellar-like structure in response to shear flow. However, both the finding that $f_{a,\parallel}$ is not -1 and the presence of remnants of a less ordered structure perpendicular to the main orientation suggest that the transition to a lamellar structure is not yet completed and raise the question of the nature in which the shear-induced structure is formed in the microchannel.

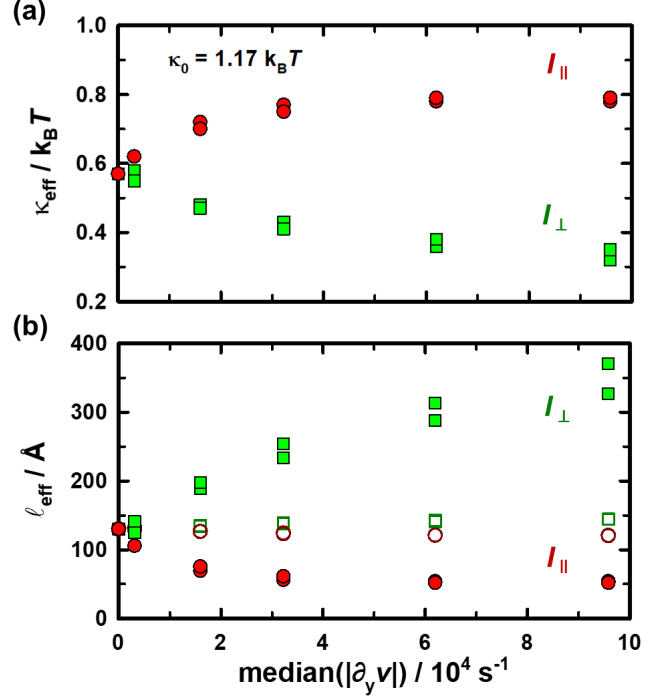


Figure 6: Effective bending rigidity κ_{eff} (a) and effective fluctuation length scale ℓ_{eff} (b) as a function of $\text{median}(|\partial_y v|)$ obtained from the sector analysis of the scattering data. (a) The effective bending rigidity $\kappa_{\text{eff},\perp}$ (green squares) decreases systematically, while $\kappa_{\text{eff},\parallel}$ (red circles) increases with increasing shear flow (calculated from the model of random interfaces [52] [47]). (b) ℓ_{eff} values, calculated assuming a length scale-dependent renormalization of the bending rigidity (Eq. (11)), show a strong influence of shear on the thermal membrane fluctuations when compared to the characteristic length scale $\xi = d_{\text{TS}}/2$ (open symbols).

4. Discussion

In order to further elucidate the structural response of a bicontinuous microemulsion to microflow, we discuss the morphology of the induced lamellar-like structure in the context of the so-called Helfrich energy

$$\mathcal{H} = \int \left[\frac{\kappa}{2} (2H - c_0)^2 + \bar{\kappa} K \right] dS, \quad (8)$$

characterized by the bending rigidity κ , the saddle splay modulus $\bar{\kappa}$ as well as the mean, Gaussian and spontaneous curvature $-H$, K and c_0 of a membrane of surface S [53]. We use the approach of Gompper et al. [47] based on the model of random interfaces [52] and calculate the effective bending rigidities of the surfactant monolayers along both scattering directions $I_{\parallel}$ and $I_{\perp}$. Following the assumption that both moduli κ and $\bar{\kappa}$ are renormalized by thermal fluctuations [54–58], the results are discussed in terms of the flow-induced suppression of those fluctuations proposed by Cates and Milner [10]. Expecting a similar shear dependence of the effective saddle splay modulus, we propose that the bicontinuous-to-lamellar transition can be attributed to the gradual disappearance of the inter-lamellar passages.

4.1. Influence of Shear on Bending Moduli

Following Gompper et al. [47], the model of random interfaces [52] can be used to determine the bending rigidity

$$\kappa = \frac{10\sqrt{3}\pi}{64} \frac{\xi_{\text{TS}}}{d_{\text{TS}}} k_{\text{B}}T \quad (9)$$

of surfactant monolayers from the two length scales d_{TS} and ξ_{TS} . Using the values of d_{TS} (Fig. 5b) and ξ_{TS} (S5, Supplementary Material) from the sector-wise scattering analysis, we determined the values of a kind of effective bending rigidity along the main ($\parallel$) and perpendicular orientation ($\perp$), which are plotted as a function of the median velocity gradient $|\partial_y v|$ in Fig. 6a. As can be seen, the values of the effective bending rigidity $\kappa_{\text{eff},\perp}$ (green squares) decreases systematically, while $\kappa_{\text{eff},\parallel}$ (red circles) increases with increasing shear flow.

According to Cates and Milner, these flow-induced variations in bending rigidity result from changes in thermal membrane fluctuations [10]. The latter are suggested to cause length scale-dependent renormalization of the rigidity according to

$$\kappa = \kappa_0 - \frac{\alpha}{4\pi} \ln\left(\frac{\ell}{a}\right) k_{\text{B}}T \quad (10)$$

[54–58], where κ_0 is the bare bending rigidity of a non-fluctuating membrane and $\alpha = 3$ the renormalization prefactor. The ratio ℓ/a between the structural and the molecular length scale characterizes the excess area stored in the fluctuating surfactant membrane [59]. While the former determines the maximum length scale of the fluctuation amplitude, the latter is often referred to as the membrane thickness δ [58]. For the studied bicontinuous microemulsion at rest with $l = d_{\text{TS}}/2 = 130 \text{ \AA}$ and $a = \delta = 10.7 \text{ \AA}$ [60] yields a bare bending rigidity of $\kappa_0 = 1.17 k_{\text{B}}T$, which agrees almost quantitatively with neutron spin echo measurements [61]. These values now can be used to extract the effective fluctuation length scale

$$\ell_{\text{eff}} = \delta \times \exp\left(\frac{4\pi}{\alpha} \frac{\kappa_0 - \kappa_{\text{eff}}}{k_{\text{B}}T}\right) \quad (11)$$

from the effective bending rigidity κ_{eff} assuming that shear does not effect the value of the prefactor α (see also S6, Supplementary Material). Fig. 6b shows ℓ_{eff} as a function of the median velocity gradient $|\partial_y v|$. In main orientation, $\ell_{\text{eff},\parallel}$ decreases systematically with $|\partial_y v|$, which is in agreement with the prediction of Cates and Milner that flow induces the suppression of thermal membrane fluctuations [10]. Thus, ℓ_{eff} is increasingly smaller than the characteristic length scale $d_{\text{TS}}/2$ (Fig. 6b, open symbols) of the structure.

More difficult to understand, however, is the increase of the effective fluctuation length scale $\ell_{\text{eff},\perp}$ in the perpendicular orientation. This trend appears clearer when viewed in the context of the renormalized saddle splay modulus

$$\bar{\kappa} = \bar{\kappa}_0 + \frac{\bar{\alpha}}{4\pi} \ln\left(\frac{\ell}{a}\right) k_{\text{B}}T. \quad (12)$$

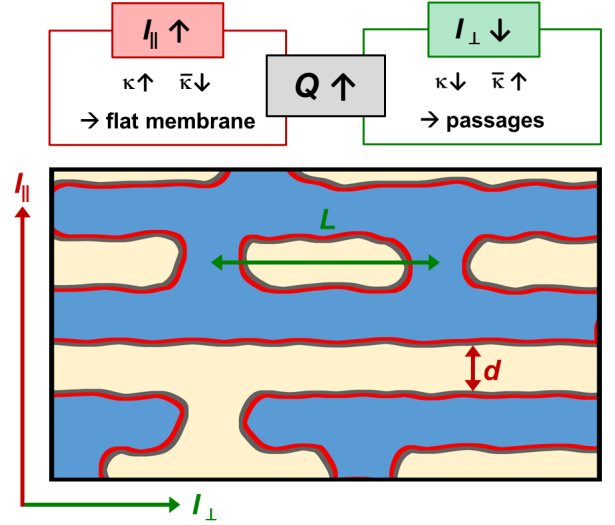


Figure 7: Cross-sectional schematic of the microemulsion structure under high shear, depicting the formation of lamellar-like surfactant membranes connected by inter-lamellar passages. The length scales $d_{\text{TS},\parallel}(q)$ and $d_{\text{TS},\perp}(q)$ obtained from the sector-wise analysis of the scattering data (Fig. 5b) can be related to the lamellar spacing d ($\parallel$) and the distance between passages L ($\perp$).

Here, $\bar{\kappa}_0$ is the bare saddle splay modulus of a non-fluctuating membrane and $\bar{\alpha} = 10/3$ the corresponding prefactor [55]. Although the value of the saddle splay modulus is not easily accessible experimentally, Eq. (12) can be used to predict its flow-induced changes. It is readily apparent that the opposite sign of the renormalization term in Eq. (10) and Eq. (12) leads to inverse trends in κ and $\bar{\kappa}$ with shear flow.

4.2. Shear Induced Structure

In the framework of Helfrich’s bending energy, the structure of the surfactant membrane depends strongly on the bending moduli κ and $\bar{\kappa}$ (Eq. (8)). Smaller values of $\bar{\kappa}$ combined with high bending rigidities κ stabilize the formation of the lamellar structure. On the contrary, sponge-like structures with a large number of passages inter-connecting both structural domains (water/oil or water/water) dominate at large values of $\bar{\kappa}$. [56–58, 62, 63] Driving force of this stabilization is the formation of passages where, according to Golubović [56], the energy cost of a single passage is proportional to $-\bar{\kappa}$ and κ .

In this context, the observed increase of $\kappa_{\text{eff},\parallel}$ and the inferred decrease of $\bar{\kappa}_{\text{eff},\parallel}$ along the main orientation ($\parallel$) of the induced structure point to the flow-induced formation of lamellae. However, perpendicular to the main orientation, the variation of $\kappa_{\text{eff},\perp}$ and $\bar{\kappa}_{\text{eff},\perp}$ rather suggest the stabilization of passages. One obvious reason for this stabilization could be the flow perpendicular to them, which the passages must resist by locally reducing the bending rigidity κ and increasing the saddle splay modulus $\bar{\kappa}$, presumably facilitated by increasing the effective fluctuation length scale $\ell_{\text{eff},\perp}$ (Fig. 6b). Together with the

shear-induced alignment (Fig. 4), the trends of the bending elastic moduli suggest that the induced structure, which is formed when the flow is not strong enough to complete the transition from bicontinuous to lamellar, partially retains its original bicontinuous nature by maintaining a number of passages connecting the lamellae.

These interpretations allow us to infer the 2D schematic of the microemulsion structure formed under high shear shown in Fig. 7. It depicts lamellar-like surfactant membranes separating water- and oil-domains connected by inter-lamellar passages and nicely explains the different length scales obtained from the sector-wise analysis of the scattering data (Fig. 5b). While $d_{TS,\parallel}(q)$ relates to the lamellar spacing d , which decreases with increasing flow, $d_{TS,\perp}(q)$ is a measure for the passage distance L . The latter increases with flow, indicating a decreasing number of passages, which is also evidenced by a vanishing scattering intensity $I_{\perp}$. The existence of passages also explains the rather small decrease of the length scale in the main direction (Fig. 5b), which was also found by Yamamoto and Tanaka [12] studying the bilayer sponge (L_3) phase of pentaethylene glycol monododecyl ether ($C_{12}E_5$) in water (1.8 wt.%).

As the shear rate or velocity gradient $|\nabla v|$ also depends on the position within the microchannel, increasing towards the channel wall, the entire continuum of this transition can be observed within the microfluidic constriction (compare Fig. 3b), as shown schematically in Fig. 8. It depicts the evolution from a bicontinuous structure at the center of the channel to a lamellar structure with passages, the number of which decreases towards the wall, until a lamellar structure without defects is formed at the wall.

5. Conclusion

In summary, we examine and spatially map the effect of flow on bicontinuous microemulsions formed by surfactant monolayers, enabled by recent advances in microfluidic SANS. We demonstrate that shear flow induces a gradual evolution towards a lamellar structure, facilitated by the disappearance of inter-lamellar passages. Measurements along the cross-section of the microfluidic constriction (Fig. 3b), and thus as a function of the velocity gradient $|\nabla v|$, show the evolution from a bicontinuous structure at the center of the channel to a lamellar structure at the wall, as shown in Fig. 8. At the highest investigated shear rates in excess of 10^5 s^{-1} achieved near the wall (Fig. 4c), a degree of anisotropy of up to $\sim 70\%$ ($AF_{\text{max}}/AF_{\text{lamellar}}$) was found. The degree of anisotropy is consistently described when the velocity gradient along the scattering plane perpendicular to the flow is considered. The length scales $d_{TS,\parallel}(q)$ and $d_{TS,\perp}(q)$ (Fig. 5b) obtained from a sector-wise analysis of the 2D scattering patterns along the main ($\parallel$) and perpendicular direction ($\perp$), relate to the lamellar spacing d ($\parallel$) and the distance between passages L ($\perp$), respectively. As a result of the flow-induced suppression of thermal fluctuations, d is found to decrease, while L

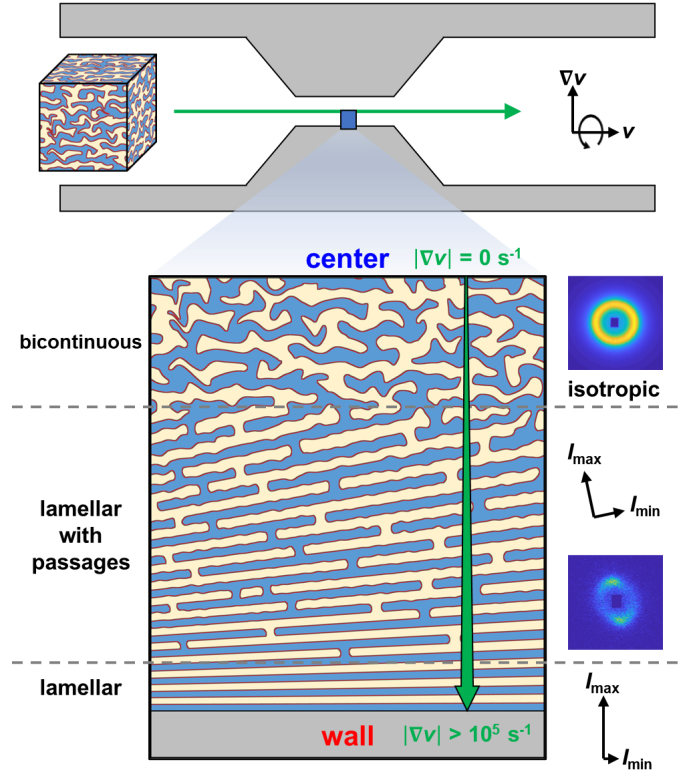


Figure 8: Schematic representation of the flow-induced structure inside the microfluidic channel. With increasing velocity gradient $|\nabla v|$, the structure shows a gradual transition from the initial bicontinuous structure, preserved at the center, towards a lamellar structure at the channel wall. The transition is facilitated by membrane alignment along the flow direction and normal to the velocity gradient vector ∇v as well as the desintegration of remaining inter-lamellar passages by flow.

increases, indicating a decreasing number of passages. Simultaneously, the opposite trend of the amphiphilicity factors $f_{a,\parallel}$ and $f_{a,\perp}$ (Fig. 5c) reveals an increasing and decreasing ordering of the structure in the main and perpendicular directions, respectively. We further demonstrate that the variation of the effective membrane bending rigidity κ_{eff} , obtained by means of the random interface model, is related to a flow-induced variation of the effective fluctuation length scale (Fig. 6). Assuming a similar shear dependence for the effective saddle splay modulus $\bar{\kappa}_{\text{eff}}$, the opposite variation of κ_{eff} and $\bar{\kappa}_{\text{eff}}$ along both directions, $\parallel$ and $\perp$, strongly suggests a flow-induced evolution of the bicontinuous microemulsion toward a lamellar structure through a gradual decrease of the connecting passages. Further increasing the shear rate (e.g., using capillary rheoSANS [41]) might result in a complete transition from a bicontinuous to a lamellar structure and, moreover, additional structural transitions might arise [64]. In addition, manipulation of membrane properties by doping with amphiphilic block polymers might allow a far greater shear deformability of the membrane [65–68].

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