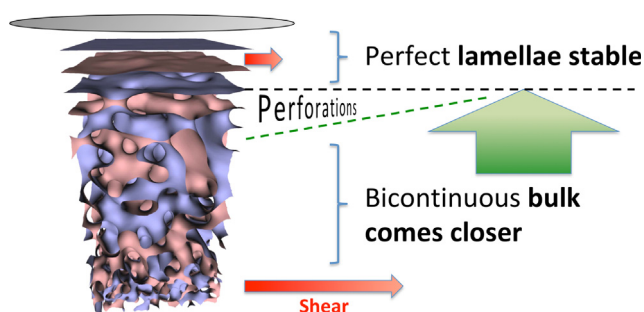


Regular Article

Stability of near-surface ordering of bicontinuous microemulsions in external shear-fields

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GRAPHICAL ABSTRACT



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ABSTRACT

The lubrication effect of bicontinuous microemulsions describes a facilitated flow along hydrophilic planar surfaces because the fluid forms lamellar domains that can slide off along each other much better than randomly ordered domains. The applicability of this effect is based on the prerequisite of the lamellar structure not being destroyed by external shear-fields. In this paper, we demonstrate that the lamellar structure is highly stable for shear rates of up to 600 s^{-1} using neutron reflectivity and grazing incidence small angle neutron scattering experiments. The transition structure that consists of perforated lamellae is attacked by the flow, and the bicontinuous microemulsion comes closer to the solid interface when shear is applied. All of this verifies the stability of the lubrication effect for technical applications.

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1. Introduction

Microemulsions consist of water and oil and a surfactant that mediates between the otherwise immiscible components to form a thermodynamically stable system [1–3]. On microscopic length

scales pure water and oil domains form, observable by scattering experiments [4], with the surfactant molecules as a film in between the two domains. Bicontinuous microemulsions form when nearly equal volumes of water and oil are mixed that lead to sponge-like domains hosting the other domain and vice versa.

When exposing a bicontinuous microemulsion to a planar hydrophilic surface [5], near-surface ordering happens to shape the domains lamellar next to the interface. This lamellar interphase is perfectly ordered within a depth d , and decays gradually by an increasing number of perforations to transit to the bicontinuous

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bulk structure [5]. The dynamics of the lamellar surfactant membranes were about three times faster than the corresponding bulk dynamics [6] that is based on a higher number of modes being present at the interface with higher frequencies at the same time. This effect was also connected to the so-called *lubrication* effect [7] that describes a facilitated flow of lamellar domains along the solid interface. Using clay platelets as planar surfaces with limited extension, the quality of the lamellar order could be rendered [8]. Larger platelets showed faster dynamics due to more long-wavelength modes compared to the small platelets [8]. In macroscopic rheology experiments [9] the lubrication effect with varying quality of lamellar order next to clay platelets with finite dimensions could be verified. Large platelets induced much lower viscosities compared to small platelets. Using crude oils as complex fluid, the viscosity could be even decreased with respect to the bare liquid at lowered temperatures. The formation of lamellar domains adjacent to the clay particles was assumed here as well.

It remains an open question whether the lamellar interphase is stable at elevated shear rates which was inherently assumed for the lubrication effect in applications. This paper verifies the stability of the lamellar interphase as a function of shear rate using neutron reflectometry and grazing incidence small angle neutron scattering (GISANS). The observed reflectivity curves and GISANS patterns are analyzed as a function of shear rate and interpreted by a three-level structure: a perfect lamellar interphase with thickness d , a transition region with thickness ζ , and the bicontinuous bulk phase.

2. Materials and methods

2.1. Materials

N-decane was obtained from Sigma Aldrich. The non-ionic surfactant $C_{10}E_4$ was obtained from Bachem, Weil am Rhein, Germany. Heavy water was obtained from Armar chemicals, Döttingen, Switzerland. All these chemicals were used without further purification. The microemulsions consisted of 17%vol surfactant and 41.5%vol water and oil, respectively. The microemulsion was kept stable at $25\text{ °C} \pm 1\text{ K}$ with a safe distance to the 2-phase regions of at least $\pm 2\text{ K}$. The phase diagram of the symmetric microemulsion with varying surfactant content γ is depicted in Fig. 1. Here, all materials were fully hydrogenous, and the corresponding phase diagram with heavy water needs to be shifted down by 2 K. The

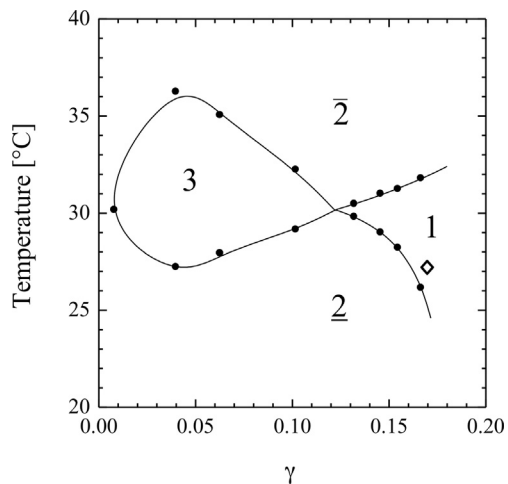


Fig. 1. Phase diagram of the symmetric microemulsion of *n*-decane, normal water and $C_{10}E_4$. The diamond indicates the experimental condition for the neutron experiments. For heavy water, the whole figure is shifted down by 2 K.

experimental condition is indicated by a diamond. There is the important 1-phase bicontinuous microemulsion indicated by “1” that is limited by a lamellar phase towards $\gamma \approx 19\%$. There are 2-phase coexistence regions with expelled oil or water indicated by “ $\bar{2}$ ” and “ $\underline{2}$ ”. The 3-phase coexistence region is indicated by “3” and consists of excess oil and water with a concentrated microemulsion. Further details about phase diagrams of microemulsions with non-ionic surfactants can be found in the literature [10]. The 1-phase microemulsion forms spontaneously, and comes to quick (sub seconds) equilibrium after shaking. When the sample is kept at the equilibrium temperature, as for the neutron experiments, no phase separation occurs.

2.2. Neutron experiments

The flow cell for neutron reflectometry and grazing incidence small angle neutron scattering [5,11] hosted a polished silicon slab ($150 \times 50 \times 20\text{ mm}^2$) with a roughness better than 2 \AA . It was etched before use as described in Refs. 5 and 11 to obtain hydrophilicity. The flow along the slab took place on an area of approx. $120 \times 30\text{ mm}^2$; and the gap was 0.5 mm . The cell was connected with a Luer Lock® System to a peristaltic pump. An average flow speed of up to 50 mm/s could be reached in the cell that translates to an apparent shear rate of 600 s^{-1} at the interfaces with the shear gradient in the normal direction assuming Hagen-Poiseuille flow. The cell was tempered by a water-thermostat to 25 °C , and a limited area around the pump was heated by an electric heat blower. The neutrons impinge on the silicon front face, are reflected from the solid-liquid interface, and leave through the opposite back face.

Neutron Reflectometry was conducted on the instrument MARIA at the MLZ Garching [12,13]. The neutron wavelength was 5 \AA . The entrance and sample slits were $0.4 \times 148\text{ mm}^2$ and $0.4 \times 30\text{ mm}^2$ for the reflectivity data represented here. All data were normalized by a heavy water reference scan such that the total reflectivity plateau was unity. All reflectivities are given as a function of the scattering vector Q . GISANS experiments were conducted with a wavelength of 10 \AA , and all slits were set to $16 \times 2\text{ mm}^2$. The scattering length density (SLD) of the overall microemulsion was $2.456 \times 10^{-6}\text{ \AA}^{-2}$ while the SLD of silicon was $2.07 \times 10^{-6}\text{ \AA}^{-2}$. This resulted in a critical angle of 0.20° . The incidence angles of 0.14° , 0.16° , and 0.18° and 0.20° resulted in the scattering depths of $\Lambda = 7632\text{ \AA}$, 749 \AA , 1018 \AA and virtually infinity (as we refer to them as nominal scattering depths). The experimental scattering depths are smeared out by resolution effects by $\pm 140\text{ \AA}$, $\pm 270\text{ \AA}$, and $\pm 770\text{ \AA}$ correspondingly. These problems are discussed in the literature [14,15] where even the non-linearity is taken into account for more complicated conditions. For simplicity we stay with the nominal scattering depths.

2.3. GISANS formulae

Let's assume the incoming wave is a pure evanescent wave, i.e. $\mathbf{k}_i = (k_{i,x}, k_{i,y}, i/\Lambda)$, and the outgoing wave has negligible damping in z -direction, i.e. $\mathbf{k}_f = (k_{f,x}, k_{f,y}, k_{f,z})$. The scattering probability and, therefore, the scattering intensity is described by the following [16]:

$$I(\mathbf{k}_i, \mathbf{k}_f) = \left| \int d^3\mathbf{r} \rho(\mathbf{r}) \exp(i(\mathbf{k}_i - \mathbf{k}_f)\mathbf{r}) \right|^2 \quad (1)$$

in the hemisphere $z > 0$. A very basic simplification is achieved, if along the z -axis the scattering volumes are decoupled by a rather small correlation length ξ . Then, different sub-volumes of size ξ do not interfere, and the following simplification holds:

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