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Physica B 350 (2004) e963–e966
PHYSICA B
www.elsevier.com/locate/physb

Relaxation of a shear-induced lamellar phase measured with time-resolved small-angle neutron scattering

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Abstract

We have measured the relaxation of Couette shear-induced L_α lamellar states to their isotropic L_3 "sponge" equilibrium phases in the cetylpryridinium–hexanol/dextrose–brine system by (cycled) time-resolved small-angle neutron scattering. Although diffusive motions of adjacent membrane sheets may be estimated to bring them into contact with frequencies ~ 10 kHz, we observe structural relaxation times on the order of seconds. This indicates a significant activation energy against the re-establishment of the passages characterizing the convoluted sponge structure.

PACS: 82.70.Dd; 87.16.Dg; 47.20.Hw; 61.12.Ex

Keywords: SANS; Shear; Relaxation; Sponge phase; Lamellar phase

The isotropic L_3 "sponge" phase consists of a single self-assembled surfactant bilayer spanning solution volume in a convoluted multi-connected network and separating two equivalent sub-volumes, which interpenetrate through randomly directed passages [1]. Despite this extended structure, these phases are typically highly fluid and show little or no response to applied shear, as the passages can rapidly reorient to relieve stresses on the membrane and allow free flow of the solvent [2]. When they occur in a chemical system L_3 phases are found in narrow regions of stability adjacent to those of the very different L_α lamellar phases. In the L_α morphology surfactant membranes are stacked in regular smectic order. L_α phases are anisotropic and strongly birefringent, and while viscous at low shear rates shear-thin as the membranes align in the flow field. This latter response is easily observed in shear-cell scattering measurements.

Dilute sponge phases do exhibit one interesting dynamical response—transient birefringence upon gentle stirring. This immediately suggests a shear-induced sponge to lamellar transition. Cates and Milner [3], treating shear as quasi-thermodynamic parameter in the free energy for isotropic phases,

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doi:10.1016/j.physb.2004.03.305

predicted that shear should induce an L_3 to L_α transition by suppressing the fluctuations that stabilize the phase, with critical shear rates varying as the cube of the membrane volume fraction ϕ and inversely as the solvent viscosity η_s. At the typical concentrations convenient to structural and rheological measurement such a transition occurs at very high shear rates. However, in measurements on hyperswollen $C_{12}E_5$ sponges under oscillatory shear in thin film cells Yamamoto and Tanaka [4] were able to observe an optical diffraction signal consistent with a transition to L_α membrane ordering.

Recently, we directly addressed the question of shear-induced sponge to lamellar transitions and in particular the predicted ϕ^3/η_s scaling of this response. Rather than working with very dilute samples we pursued an alternative strategy of adding a thickener to the solvent, which if inert (excluded from the membranes) should have little effect on phase behavior while slowing its dynamics. We found that dextrose can play this role in the well-known cetylpyridinium (CPCl)–hexanol/brine system. Small-angle scattering (SANS) measurements showed that L_α structure is maintained to dextrose concentrations of up to 40% volume fraction while the viscosity of the solvent by increases by over an order of magnitude [5].

Slowed diffusive motion of the membranes in these ''sweetened'' sponges causes strong structural and rheological responses to applied shear at easily accessible shear rates ($<2000\,s^{-1}$). In rheological measurements an initial Newtonian constant viscosity response is followed by shear-thinning region, and a final quasi-Newtonian region. Consistent with the predicted scaling, appropriately normalized viscosities for a range of samples (volume fraction ϕ of: 3–10%, η_s: 1.1–16.3×10^{-3} Pa s) for which the onset of shear-thinning varied by about two orders of magnitude fell to a master curve plotted against a rescaled shear rate $(d\gamma/dt)\eta_s/\phi^3$. Parallel Couette shear SANS showed that the shear-thinning response corresponds to a shear-induced L_3 to L_α transition, with the appearance of strong anisotropy in the scattering patterns and the eventual appearance of definite Bragg peaks in tangential Couette SANS data (beam along the flow direction) indicating ''c'' lamellar stacking (normals along the shear gradient). In region III this signal disappears rapidly, presumably indicating a collapse of the shear-induced L_α phase and strong scattering emerging at small scattering vectors indicates some as yet unidentified larger scale ordering [6].

The shear-induced L_α signal saturates indicating full alignment of the membranes over about a factor of two in $(d\gamma/dt)\eta_s/\phi^3$ and is easily accessible for lower ϕ and higher η_s (dextrose) samples. We have recently been successful in measuring the relaxation from this ''passage free'' L_α state to the equilibrium L_3 phase upon cessation of shear. This re-establishment of the L_3 structure disrupted by shear offers a strong clear signal of the fusion of membranes to (re)form passages. A process which usually occurs in dynamic equilibrium (creation/destruction) against a background of other phenomena.

Even with the slowed dynamics of our system relaxation takes only a few seconds. These short times (for SANS) required that we time multiplex the NIST NG3 2D SANS detector output into several memory modules, rather than measure sequential runs. To achieve adequate statistics we cycled through the process of shearing to a steady L_α state, stopping, and relaxing fully to L_3 several thousand times (see Fig. 1). Each data acquisition cycle was synchronized at a delay to a stop signal to our ORNL Couette shear cell [7,8]. Repeated cycling did not degrade these samples and data was completely reproducible. Finally, in order to obtain sufficient points on the relaxation curve we hardware rebinned the detector output from 128×128 to a 32×32 array by dropping the

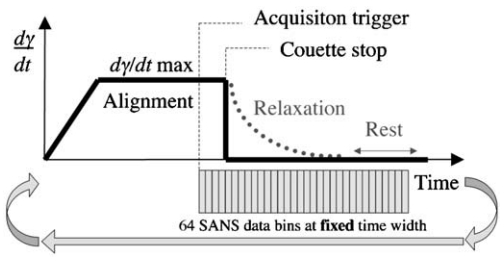

Fig. 1. Cycled time-resolved SANS data acquisition.

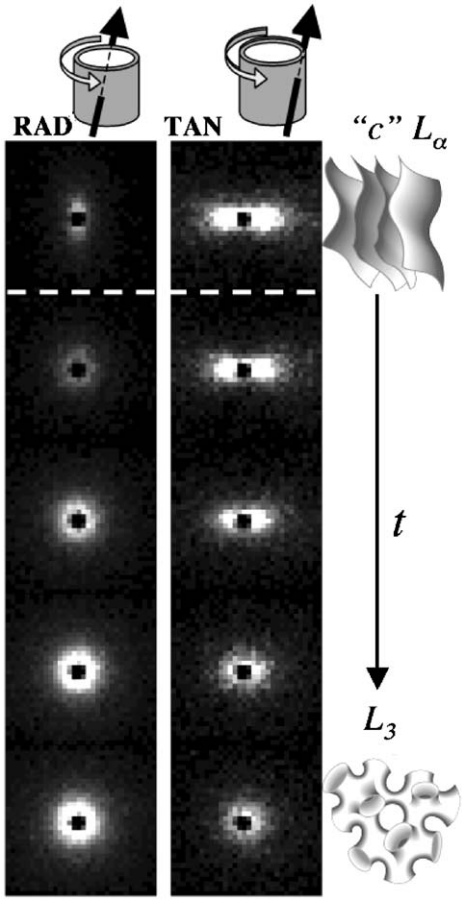

Fig 2. SANS time bin patterns for L_α to L_3 relaxation.

lower two bits of the addressing, thus swapping spatial for time resolution to obtain 64 time bins.

Fig. 2 shows the scattering measurements for series in radial and tangential Couette scattering geometries for a volume fraction of 3% CPCl–hexanol sample at a dextrose concentration of 40% ($\eta_s = 16.3 \times 10^{-3}$ Pa s) relaxing from L_α saturation (applied shear rate $d\gamma/dt = 500\,s^{-1}$). The patterns represent 0.5 s bins and are taken are 1 s apart in the time series. The first frames show the anisotropic scattering of the shear-induced L_α state. (Note Bragg peaks in the tangential geometry data.) The final frames show isotropic scattering from an essentially fully restored sponge.

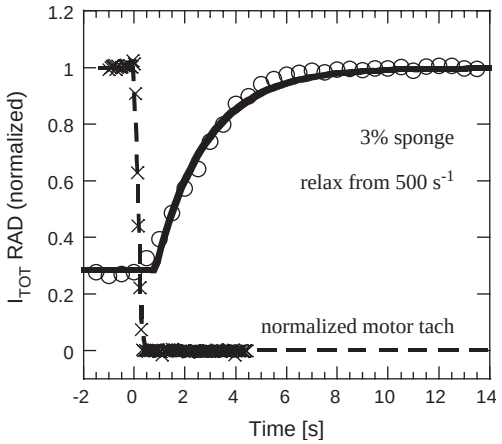

Fig 3. Total SANS intensity radial Couette geometry and motor stopping signal (both normalized to max).

In Fig. 3, we plot the total signal for the radial geometry SANS data for 16 s of the series. Since Bragg scattering from the "*c*" aligned membranes contributes very little to the signal in this geometry it gives a good indication of the re-establishment of the isotropic scattering. An exponential fit to the data gives an L_α to L_3 relaxation time constant $\tau = 2.0$ s. (The stopping time constant for shear is 0.1 s. Dotted line fit to Couette tachometer signal.) Dynamic light scattering measurements [5] allow us to estimate a frequency of diffusive contacts between adjacent membranes $\sim$10 kHz indicating a significant activation energy barrier against passage (re)formation.

The NG3 SANS instrument is operated by NIST, US Department of Commerce, with funding from the US National Science Foundation under agreement DMR-9986442. ORNL is managed by UT-Battelle LLC for the US Department of Energy under contract DE-AC05-00OR22725. G.G.W. acknowledges Australian Nuclear Science and Technology Organization and Australian Research Council support.

The identification of any commercial or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

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