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Defects, elasticity and flow in lamellar phases*

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Abstract

We present intriguing results from light microscopy and rheometry on a lyotropic lamellar liquid crystal. We find that the rigidity of this structure is in practice controlled mainly by a striking network of oily-streak defects, rather than by the continuum elasticity of the perfectly aligned phase. This network decays under shear, but this decay is retarded substantially by the addition of micron-sized particles which anchor onto its nodes, yielding a particle-stabilised network gel made of line defects. This work was done in collaboration with Geetha Basappa, Suneel, V. Kumaran, Prabhu R. Nott (IISc) and V. M. Naik and D. Rout (Unilever Research India).

Keywords: Surfactants, lamellar liquid crystals, oily-streak defects.

1. Introduction

Surfactants are molecules with a head that likes water and a tail that doesn't. When mixed with water they 'self-assemble'[1] into energy-minimising aggregates such as spherical micelles, cylindrical micelles, vesicles, and macroscopic bilayers. The water-hating tails are sequestered within the aggregates, whose outsides, all head, are in contact with water. A particularly common thermodynamic phase in surfactant solutions is the lamellar or L_α phase which consists of a stack of bilayers. A detailed review of lamellar (also known as smectic) liquid crystals may be found in de Gennes and Prost.[2]

A few words about the ideal, perfectly oriented, defect-free L_α will set the stage for the present work, which is concerned mainly with how defects alter the mechanical properties of this phase. Each bilayer in the stack is a two-dimensional fluid which we shall take to lie parallel to the $x-y$ plane, with layer normal pointing along the z axis. The layer thickness is a and the stacking along z is periodic with a repeat distance d. The z direction is 'solid-like': the surfactant density is a periodic function of z, and dilations or compressions of the layer spacing away from its equilibrium value d, i.e., displacements of the layers along z by an amount which depends on z, incur an elastic energy cost. Displacements parallel to the xy plane attract no such energy penalty. The response of the system to an imposed velocity and gradient in the xy plane, or to a velocity in the xy plane but gradient along z, is that of a viscous fluid. Flow along z with gradient in the xy plane, by contrast, is of a slow, permeative type, like that through a porous medium, underlining the solid-like nature of the structure along z. Accordingly, if the me-

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chanical properties are measured by small-amplitude oscillatory strain, no shear modulus is found at zero frequency

These *predicted* properties of well-aligned lamellar phases are in marked contrast to the *observed* properties of typical samples of this phase The latter are generally found to have a yield stress (a minimum stress below which flow cannot occur) in any direction, and oscillatory shear strain in any direction evokes an elastic response at the lowest frequencies The elastic moduli show a substantial frequency dependence, and the flow in all directions is non-Newtonian How are these observations to be reconciled with what we know about the structure of the phase as a stack of liquid layers? Alternatively, what microstructure can give rise to the observed elasticity?

One of the major motivations for the present work came from recent studies[3, 4] of the L_β phase, also a stack of layers but with the important difference that each layer is solid-like In those studies, particles of size 10 μm or larger were added to the sample and their effect on the elasticity monitored It was found that the shear modulus increased only weakly at first but then rose steeply when the volume fraction of added particles reached a few per cent They speculated that there was an underlying percolation transition of stress-supporting structures, although it was unclear what these structures could be In Shouche *et al*[3] and Reddy *et al*[4] no attempt was made to study the microstructure or to model elasticity from known properties of lamellar phases

My presentation here is rather brief as the work is already published Interested reader can get details from Basappa *et al*[5] Some interesting images may be found at http //144 16 75 130/lcrheol/

2 Earlier theoretical work

The only available theoretical model of the elasticity of disordered lamellar phases is that of Kawasaki and Onuki[6] They begin with the elastic-free energy

$$H = \frac{1}{2}\int d^3x\left[B\left(\frac{\partial u}{\partial z}\right)^2 + K\left(\nabla_\perp^2 u\right)^2\right] \tag{1}$$

for the layer displacement field u describing small, slowly varying distortions about a lamellar phase with layer normal aligned along the z axis B is the layer-compression modulus, and K the bending modulus governing distortions of the layer orientation with wave vector in the $x-y(\perp)$ plane A layer-spacing variation along the z direction thus gives a stress $\sigma_{zz} = B\partial u/\partial z$ Now, for a polydomain lamellar phase with layer normal oriented locally along a direction $\hat{\mathbf{N}}$ which varies slowly from one point of the medium to another, this means that the local layer compression stress is $\sigma_{ij}(\mathbf{r}) = N_i(\mathbf{r})N_j(\mathbf{r})\partial_z u$ Kawasaki and Onuki then consider a lamellar phase consisting of oriented regions of characteristic size ξ The orientation is perfect, apart from thermal fluctuations, within each domain but varies randomly from domain to domain The key idea is to assume that the material is in (metastable) thermal equilibrium with the lamellar structure in each region of size ξ fluctuating with statistical properties governed by equipartition with respect to the energy function (1), but that the domain structure is fixed, not evolving The frequency-dependent response of the material is extracted by looking at time correlations of the macroscopic shear stress Denote the laboratory frame coordinates by $\mathbf{R} = (X, Y, Z)$, distinct from the local coordinates $\mathbf{r} = (x, y, z)$ in each lamellar domain, where the layers are locally normal to the z axis The macroscopic, complex, frequency-dependent shear viscosity for displacements along X and gradients along Y is given by the Kubo formula

$$\eta(\omega) \equiv \eta'(\omega) + i\eta''(\omega) = \frac{1}{k_BT}\int d^3R \int_0^\infty dt \langle \sigma_{XY}(0,0)\sigma_{XY}(\mathbf{R},t)\rangle e^{i\omega t} \tag{2}$$

The average < > is over both the thermal fluctuations and the domain structure Kawasaki and Onuki then note that $\sigma_{XY}(\mathbf{R}, t) = N_X(\mathbf{R})N_Y(\mathbf{R})\partial_z u(\mathbf{R}, t)$ and calculate $\eta(\omega)$ by decoupling the averages over $\hat{\mathbf{N}}$ and the thermal fluctuations u They find a dynamic modulus $G^*(\omega) = G'(\omega) + iG''(\omega) = \omega(\eta'' + i\eta') \propto (i\omega)^{1/2}$, i e that the storage and loss moduli $G'(\omega) + iG''(\omega)$ are equal and vary slowly with frequency This appears to be a good description for the lamellar phase in copolymer systems, and the microstructure there is seen to be polydomain

3 Our work

We study the structure and mechanical properties of lamellar phases as a function of their shear history and the concentration of added particles The mechanical properties were measured in a Rheolyst AR1000N stress-controlled rheometer (TA Instruments) We studied first the effect of shear treatment on elasticity The samples as prepared had storage moduli $G'(\omega)$ of slightly over 1000 Pa at the lowest frequencies ($\simeq$ 1 /s), and growing with ω over the range studied (up to about 100 /s) The samples were then subjected to steady shear (shear rate 1 /s) for durations ranging from 4 to 32 minutes After each run of shear treatment the linear viscoelastic moduli were measured The values found decreased with increasing duration of shear treatment, but the shapes of the $G'(\omega)$ curves were essentially unchanged Indeed, they could be superposed onto a single curve by plotting G'/G_0 vs ω/ω_0 for suitable choices of characteristic modulus G_0 and frequency scale ω_0, both of which decreased with increasing shear treatment When a small (5 % by weight) quantity of spherical latex spheres of about 10 μm diameter is added to the lamellar phase, G' is enhanced by about a factor of 2, and decays much more slowly under shear treatment These observations suggested to us the following picture there must be an underlying structure (on scales larger than the lamellar order) which gives the system its macroscopic rigidity This structure gets more tenuous when the material is sheared, leading to a decrease in the typical rigidity and frequency scales Adding particles somehow anchors this structure and inhibits its decay under shear Clearly, visual information is needed to confirm this guess

4 Defect structure under shear

Accordingly, we studied the structure between crossed polaroids through a polarising microscope (Nikon Optiphot2-Pol) in the laboratory of A K Sood at the Physics Department at IISc If the layers are aligned perfectly parallel to the top and bottom plates of the sample cell the plane of view will be isotropic and should hence appear dark under crossed polars, defects

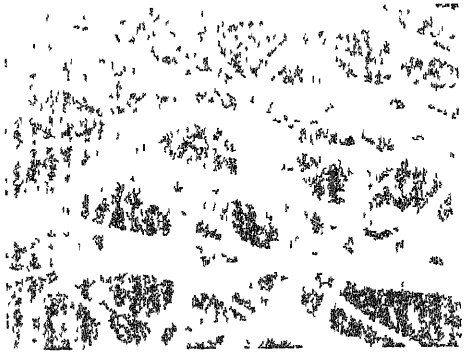

FIG. 1. The oily streak network.

that disrupt this order will then appear as bright objects in the field of view. What we saw initially, in the sample as prepared, was a highly heterogeneous collection of bright regions, indicating a high density of defects. When steady shear (1/s) was applied, the pattern evolved, getting progressively more aligned as signalled by the emergence of macroscopic dark domains. However, these domains coexist with a spectacular network (Fig. 1) of system-spanning line defects called *oily streaks*[5]. This network disappears quite slowly under shear, and even more slowly if added particles are present. The oily-streak network anchors on the particles, inhibiting its decay under shear. The rate of destruction of the network, as quantified by the decay of the brightness of the transmitted image through crossed polars, corresponds well to the rate of decrease of the shear modulus.

These findings are important because they tell us that our lamellar-phase samples, even after a small amount of initial shearing, are well oriented on macroscopic scales. This means that their elastic properties, unlike in Kawasaki and Onuki[6], are not a consequence of a polydomain structure. Presumably, the shear stress is supported by the oily-streak network. A detailed calculation of the elasticity of such a network is not yet available. Our rough theoretical estimates[5] for its rigidity are, however, consistent with our observations.

5 Conclusion

This has been a brief summary of our work on the structure, mechanical properties, and flow behaviour of lamellar phases. We have found that these phases, even when nominally aligned on large scales, behave like weak elastic solids. This behaviour appears to arise from an 'oily-streak' defect network of rather striking appearance, and our estimates of the elasticity of such a network is consistent with the measured values. Further work is needed to understand the mechanics of the network and its interaction with shear fields and particulate additives.

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