Elastic Resonance of a Liquid-Crystal Blue Phase

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The blue phase of cholesteryl oleate is shown to exhibit the macroscopic shear elasticity expected for a three-dimensionally ordered structure. The first measurements of blue-phase elastic constants are presented.

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There is now strong evidence, based primarily on optical reflectivity[1,2] and microscopy,[3] that the chiral nematic blue phases are three-dimensionally ordered structures of the nematic director field. Periodic arrays of defects,[4-7] or droplets[8] forming body-centered or simple-cubic lattices have been proposed theoretically as blue-phase (BP) structures. In analogy with typical solids, such three-dimensionally ordered structures should exhibit shear elasticity. In this Letter we present direct evidence for macroscopic elastic behavior in liquid-crystal blue phases and present the first measurements of blue-phase elastic constants.

For motion with wavelengths long compared to the blue-phase lattice constant a, the lattice displacement $\vec{u}$ and the fluid velocity $\vec{v}$ are simply related by the Navier-Stokes equation

$$\rho\dot{\vec{v}} = \eta\nabla^2\vec{v} - \lambda(\vec{v} - \dot{\vec{u}}) \tag{1}$$

and the force balance equation[9,10]

$$\lambda(\vec{v} - \dot{\vec{u}}) + C\nabla^2\vec{u} = 0. \tag{2}$$

The coupled lattice-fluid system is characterized by the (shear or longitudinal) elastic constant C, permeation coefficient λ,[11] fluid shear viscosity η, and mass density ρ. These equations are identical to those describing the motion of colloidal crystals in aqueous suspension[12-16] and the BP should exhibit similar phenomenology. In particular, the fluid incompressibility in both cases requires $\vec{v} = 0$ for longitudinal motion so that permeation must accompany the longitudinal lattice modes. As a result they are overdamped, Eq. (1) giving exponential decay with a rate $\Gamma_q{}^L = Cq^2/\lambda$ for a mode of wave vector q. On the other hand, for transverse modes in the long-wavelength limit, the coupled equations yield $\vec{v} - \dot{\vec{u}} \ll \dot{\vec{u}}$ and $\vec{v} \simeq \dot{\vec{u}}$, that is, permeation disappears and the BP lattice and fluid move together, with damping coming from the fluid shear viscosity η. Note that here η is the shear viscosity that would be measured in absence of the blue-phase structure, i.e., it does not include the large viscosity commonly observed in bulk blue-phase samples, which, as the data of Stegemeyer and Pollman indicate,[17] is a rheological manifestation of the BP elasticity itself. Hence η might be taken to be the viscosity of the isotropic near the BP transition or that of a nematic racemic mixture of the chiral molecules in question. The wave equation, $\rho\ddot{\vec{u}} = \eta\nabla^2\dot{\vec{u}} + c\nabla^2\vec{u}$, obtained from Eqs. (1) and (2) for $\vec{v} \simeq \dot{\vec{u}}$ describes the transverse modes. A small-amplitude mode of wave vector q exhibits the damped harmonic-oscillator dispersion relation $-\omega^2 + i\omega\Gamma_q + \omega_q{}^2 = 0$, with $\Gamma_q = \eta q^2/\rho$ and $\omega_q = (C/\rho)^{1/2} q \equiv vq$. Hence, at sufficiently long wavelengths $(q < q_c \sim v\rho/\eta)$ the transverse modes should become underdamped.

Dimensional analysis can provide an estimate of C to be expected for small deformations of a periodic director structure. The deformation energy of the nematic orientation field is governed by the Frank elastic constants K. For a periodic structure of lattice parameter a we expect $C \sim K/a^2$. Typically, $K \sim 10^{-6}$ erg/cm, $a \sim 0.3$ μm, so that $C \sim 1000$ erg/cm^3, roughly six orders of magnitude smaller than that found in typical atomic or molecular crystals, but comparable with that exhibited by colloidal crystals.[13-16,18] The expected wave velocities $v = (C/\rho)^{1/2}$ are a few centimeters per second. Taking the shear viscosity to be $\eta \sim 1$ g/cm$\cdot$s, the crossover wave vector for transverse-mode underdamping is $q_c \sim 10$ cm^{-1}. Hence shear modes having wavelengths of the order of 1 cm and frequencies of a few tens of hertz should be underdamped, as we observe in cholesteryl oleate.

The experiment is similar in design to those used for colloid elasticity studies.[13,14] Our apparatus consisted of a circular cylindrical plexiglass cup (radius $r_0 = 1.77$ cm) filled to a depth $l = 1.5$ cm with liquid crystal, and made to oscillate rotationally about its axis with fixed amplitude ($\varphi_0 \sim 0.05$ rad) and variable frequency ($0 < f < 50$ Hz). The resulting oscillation of the liquid crystal was probed at its free surface by placing on the center of the surface a cylindrical aluminum foil float to which was attached a small mirror normal to the liquid-crystal surface and parallel to the cylinder axis. The mirror orientation about the cylinder axis was monitored by reflecting laser light from it. The plastic cup was held in a pair of heated concentric aluminum cylindrical cans to provide temperature uniformity and control. The cholesteryl oleate sample, obtained from Kodak and used without further purification, exhibited the following phase behavior: heating, smectic $A \xrightarrow{(42\,^\circ\mathrm{C})}$ helical $\xrightarrow{(47.5)}$ blue phase $\xrightarrow{(48.7)}$ isotropic; cooling, smectic $A \xleftarrow{(42\,^\circ\mathrm{C})}$ blue phase $\xleftarrow{(48.5)}$ isotropic. Note the significant supercooling of the BP. Microscopic observations and the phase behavior of related compounds[19] indicate that we have blue phase I. The BP-isotropic transition exhibited two-phase coexistence over a 0.7 °C range.

Typical data showing the frequency dependence of the float oscillation amplitude $\varphi(\omega)$ divided by its zero-frequency value φ_0 in cholesteryl oleate are presented in Fig. 1. The oscillator response exhibits a sharp resonance peak only at temperatures in the blue phase. In the helical phase, obtained by heating the smectic, the amplitude response was weakly resonant (Fig. 1). In the isotropic phase the response was purely damped as to be expected for a viscous fluid. Furthermore, manual manipulation of the liquid-crystal material reveals a marked gel-like character only in the temperature range of the blue phase.

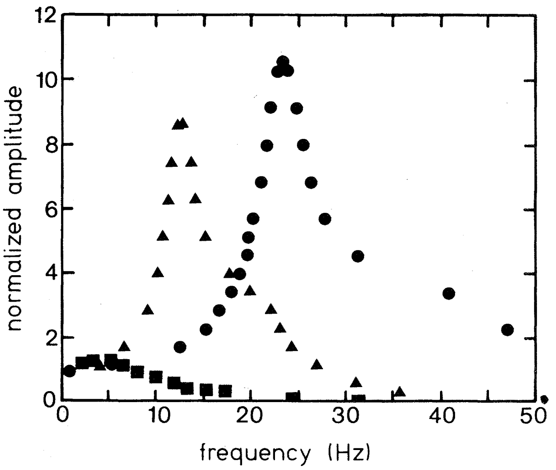

FIG. 1. Typical data showing the dependence on frequency f of the amplitude of the rotational oscillation of the float normalized by the amplitude of the rotational oscillation of the cup, $\varphi(f)/\varphi_0$: helical phase (squares), 43.7 °C; blue phase (circles), 42.8 °C; blue phase (triangles), 47.4 °C. In the BP a sharp resonance, due to the 10 shear mode (see text), is observed. The high-frequency shoulder on the 10 peak is the 20 resonance. The BP below 47 °C is supercooled. The response of the helical phase is characterized by a highly damped lower-frequency resonance. The isotropic response was nonresonant.

To extract the elastic constant C and viscosity η from the blue-phase response curves, we used the weak-damping approximation for the solution of the wave equation for the fluid in an oscillating cup. The float was taken to be massless and to be attached to the BP lattice at the surface center. The normal-mode wave vectors are given in this case (14) by

$$q_{np} = [(\alpha_n/r_0)^2 + \{(2p+1)\pi/2l\}^2]^{1/2},$$

where α_n is the nth zero of the first-order Bessel function J_1. The principal (lowest-frequency) resonance in the blue-phase response curves of Fig. 1 is for $n=1$, $p=0$ ($q_{10}=2.40\ \mathrm{cm}^{-1}$). At higher frequency a weak shoulder corresponding to the $n=2$, $p=0$ and $n=1$, $p=1$ modes is also evident in the blue-phase response curves. The peak oscillation amplitude, normalized by the cup oscillation amplitude, $\gamma_{10}=\varphi_{\max}/\varphi_0$, and the corresponding frequency ω_{10} were taken from the response curves and used to calculate C and η. The temperature dependence of ω_{10} and γ_{10} are shown in Fig. 2(a). Random uncertainty in these data are reflected in the variation of the measured values from smooth curves. Separate runs produced identical temperature dependences, but with a ±2% systematic variation in ω_{10} arising from slightly differing depths assumed by the float on each run. At a weakly damped resonance, the motion of the fluid relative to the cup is nearly that of the undamped normal mode being excited in a fixed cup. With this approximation, the elastic constant C and viscosity η are given by $C = \rho\omega_{10}^2/q_{10}^2$ and $\eta = C/\omega_{10}\gamma_{10}$. Figure 2(b) shows the dependence of C and η on temperature T.

There are several features to note in these data, the first being the very strong temperature dependence of C, with $\omega_{10} \propto \sqrt{C}$ varying linearly with T. Returning to our earlier estimate of $C \sim K/a^2$, we expect $\omega \propto K^{1/2}/a \propto Q/a$, where Q is the nematic order parameter. In the vicinity of the transition to the isotropic, the nematic order parameter typically increases nearly linearly with decreasing T, roughly 10%/°C.[18] Additionally, the BP I lattice parameter is generally found to increase with decreasing T, changing ~ −10%/°C within ~1 °C of the BP-isotropic transition (Refs. 3 and 19–22). On this basis then we would expect very little temperature dependence of ω_{10}.

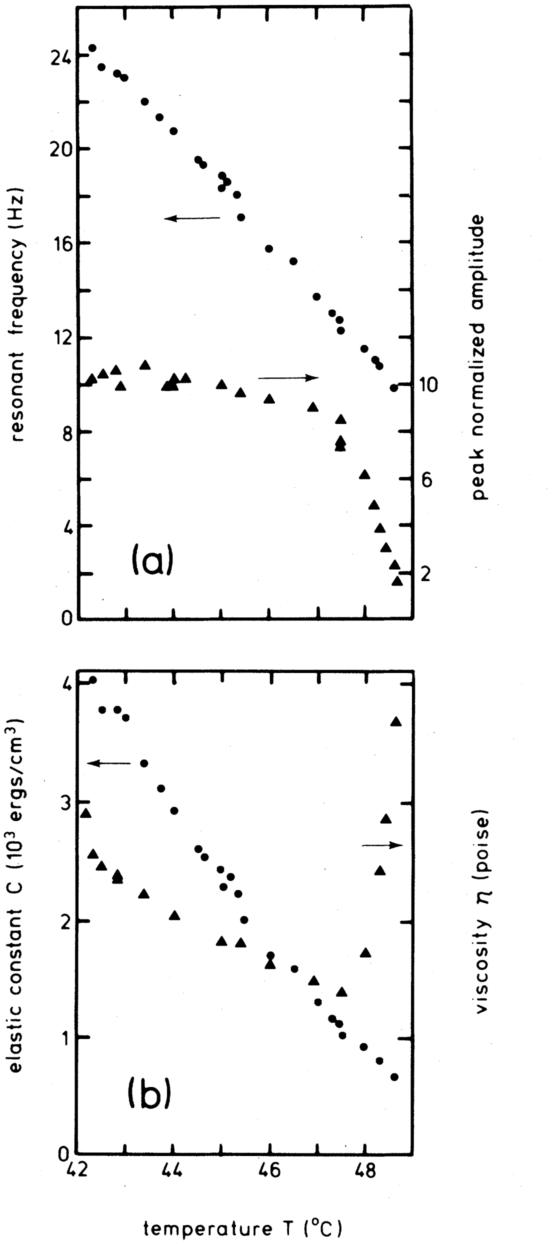

FIG. 2. Elastic resonance data obtained on a polycrystalline sample of the BP of cholesteryl oleate. (a) Normalized peak amplitude of the 10 mode, $\varphi_{\max}/\varphi_0=\gamma_{10}$ (triangles), and peak frequency $f_{10}=\omega_{10}/2\pi$ (circles), vs T. Note the strong dependence of ω_{10} on temperature. (b) Shear elastic constant C (circles) and viscosity η (triangles) obtained from the data of (a). The increase of the apparent viscosity near the BP-isotropic transition is a consequence of BP-isotropic phase coexistence for $48 < T < 48.7$. A thin isotropic layer forms at the cell wall decoupling the BP oscillation from that of the cell. Neglecting this experimental artifact the viscosity, extrapolated to the BP-isotropic transition temperature, of 1.2 P agrees well with that in Ref. 17.

The viscosity data, except for the apparent increase at the BP-isotropic transiton, indicate the expected slowly decreasing viscosity with increasing temperature, with values comparable to bulk measurements in the isotropic phase of this material.[17] The apparent increase in viscosity at the high end of the BP temperature range most likely results from two-phase coexistence—a thin isotropic layer forms at the cup surface and decouples the BP oscillation from that of the cup, reducing the BP oscillation amplitude but having little effect on the frequency.

Returning briefly to the response curves obtained in the helical phase (Fig. 1), it is evident that the helical phase also exhibits finite elastic modulus at frequencies of a few hertz. This is not unexpected since the helix of a random helical structure when subjected to shear (say $\partial u_x/\partial y > 0$) will be dilated when its axis is directed from the origin to where xy is positive and compressed for xy negative. Although these stresses can partially relax internally by rotation and sliding of layers, complete relaxation requires permeation, which is very slow. Qualitatively comparing the helical phase to the blue phase: On the one hand, the incomplete relaxation of stresses in the helical phase should lead to an elasticity somewhat less than but comparable to the blue phase, but on the other hand the relaxation will provide larger damping than found in the blue phase, qualitative differences which are indeed found in the data of Fig. 1. However, definitive evidence on the elasticity of the helical phase requires further experiments.

Although possessing finite elasticity in the range of 10 → 25 Hz, the cholesteryl oleate BP still flows. Thus, either $C=0$ at $\omega=0$, or the BP exhibits a very low yield stress. Given the measured values of C, yield stresses would likely be no larger than ~1 dyn/cm² (pressure ~1 cm of H_2O) and perhaps much smaller. Alternatively, the relaxation processes via which C could disappear with decreasing frequency are permeation or defect (e.g., dislocation) motion of the BP lattice.

In conclusion, our elastic constant measurements show a strong increase of the shear modulus of a polycrystalline sample of the cholesteryl oleate blue phase as the temperature is decreased from the BP-isotropic phase transition temperature. This variation cannot be understood in terms of the temperature dependence of the nematic order parameter or the blue-phase elastic constant. On the other hand, it may reflect the temperature dependence of the isotropic-nematic interfacial energy which enters into several BP models.[7,8] Elasticity has proven to be a powerful probe of the structure, energetics, and dynamic behavior of atomic and colloidal crystals. The present experiment indicates the feasibility of a similar approach to blue-phase structures. We hope that these results will stimulate calculation of BP elastic constants.

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