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Russell W. Duke [a] & Donald B. Dupré [a]
[a] Department of Chemistry, University of Louisville, Louisville, KY, 40208

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Quasielastic Light Scattering from Orientational Fluctuations in a Cholesteric Liquid Crystal

RUSSELL W. DUKE and DONALD B. DUPRÉ

Department of Chemistry, University of Louisville, Louisville, KY 40208

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Examination of the Rayleigh line of a lyotropic cholesteric polypeptide liquid crystal by the techniques of quasielastic light scattering spectroscopy reveals the presence of two new purely dissipative low frequency light scattering modes of comparable intensity. Angular and electric field dependences of the deconvoluted spectra are consistent with the identification of the mechanism as due to twist and viscous-splay normal modes recently predicted theoretically. Analysis of the narrow mode on this basis yields a value of γ_1, the twist viscosity coefficient of the medium. The broader mode results in an estimate of the value of the ratio of the splay to bend elastic moduli, $K_{11}/K_{33} \sim 10^{-5}$, which is shown to be in accord with mean field theoretical calculations for a system of such highly elongated macromolecules.

Thermally induced excitations in condensed and gaseous media have been shown to scatter light through a coupling of the incident radiation field with resultant fluctuations in the spatial components of the local refractive index. In some instances shifts in or a broadening of the frequency of scattered light may be detected. Propagating pressure waves (phonons) give rise to a side-band structure due to an acoustical Raman effect with Stokes and anti-Stokes components corresponding to scattering from sound wave velocity components approaching and receding from the point of observation. The measurement of such spectra in the Brillouin region ($\sim$0.1–10 cm^{-1}) has provided important information on certain high frequency ($\sim$GHz) viscoelastic properties of liquids and solids.[1,2] Shifts of larger magnitude ($\sim$10–100 cm^{-1}) have been analyzed to yield information on shorter wavelength phonon disturbances and molecular rotational relaxation and correlation times.[3] Slowly damped entropy fluctuations which do not propagate in a material are responsible for a portion of light scattered that is unshifted in frequency. Diffusive motions of molecules within the scattering volume, however, broaden in frequency the otherwise almost δ-function Rayleigh component of the spectrum. Recent electronic light-beating techniques that rely on the monochromaticity of laser light permit a spectral resolution sufficient to measure these slight broadenings (~ 10–10^3 Hz) of the Rayleigh line.

In the field of liquid crystal research, spectral analysis of quasielastic Rayleigh scattered light has uncovered the presence of two low-frequency dissipative modes in a nematic monocrystal.[4] These modes correspond to low-amplitude, self-excited superpositions of bending and splay and bending and twist of the directorfield.[5] A detailed study[6] in selected scattering geometries of the angular dependence of the width of the two modes allowed the determination of values of the Leslie viscosity coefficients,[2] α_i. Recent investigations on smectic mesophases, have detected the dynamics of angular twisting of adjoining molecular layers in a smectic-C[8] and non-static layer undulations normal to the molecular planes in a smectic-A liquid crystal.[9] Both modes have been theoretically predicted to scatter light strongly.[10,11] Time analysis of the spectra yielded information on the anisotropy of smectic elastic and viscosity coefficients and on the diffusivity of angular orientation of molecules in this more ordered liquid crystal.

In this report we present a more detailed description of our recent examination[12] of the quasielastic light scattering spectrum of a cholesteric liquid crystal of polypeptide origin. We find that the Rayleigh line of this optically clear lyotropic liquid crystal consists of two overlapping components of comparable intensity, one broad and one sharp. The line shapes and angular dependence of the two components confirm many of the features predicted in the recent theoretical considerations of Fan, Kramer, and Stephen[13] (Rutgers) and Parsons and Hayes[14] (Hawaii). The results thus support the mechanism of these two new modes as originating in twist and viscous-splay normal modes of the chiral medium. Analysis of the sharp mode which we associate with twist deformations leads to a value of K_{22}/γ_1, the ratio of the twist elastic constant to the twist viscosity coefficient. An independent measurement of K_{22}[15] allows the determination of γ_1 for this liquid crystal. A ratio of the splay to bend elastic moduli, $K_{11}/K_{33} \sim 10^{-5}$ is obtained from the broad mode angular dependence. This unusually small ratio is shown to be in accord with mean field theory applied to such a system of highly elongated macromolecules. Experimental results and interpretation will follow a brief résumé of the theoretical predictions of Refs. 13 and 14, which though contradictory in certain aspects are consistent with our observations to the extent of their development within the regimes experimentally accessible to us. To our knowledge our recent letter[12] was the first report of the observation of these two separate light scattering modes centered at the incident laser frequency in a cholesteric liquid crystal and the first attempt to experimentally follow-up the implications of these theoretical developments.

THEORY

Recent theoretical considerations[13,14] of orientational fluctuations in an incompressible cholesteric liquid crystal demonstrate that there are two dominant, slowly relaxing hydrodynamic modes that should be observable by light scattering. One mode corresponds to a twisting and untwisting of the supramolecular spiral arrangement, whereas the other is a combination of viscous-splay motion about the molecular director. Both modes are overdamped and would lead therefore to a broadening but no overall displacement in frequency of scattered laser radiation. Theory suggests several possible means of identifying and separating the modes which in principle should be easier to accomplish than in the case of nematic liquid crystals which also have been shown, both theoretically[5] and experimentally,[4] to exhibit two interesting, purely dissipative light scattering modes. We consider each cholesteric mode separately.

Twist normal mode

The twist normal mode involves a twisting oscillation about the spiral axis of neighboring molecular planes with a restoring force given by the twist elastic constant, K_{22}, and a resistance in proportion to a dissipative coefficient, γ_1. The mode is overdamped and would result, therefore, in a broadening in frequency of scattered laser radiation with a contribution to the halfwidth of the Rayleigh line in the absence of an applied field theoretically given by:

$$\Gamma_t = \frac{K_{22}}{\gamma_1} q^2 \tag{1}$$

where q is the magnitude of the scattering vector. The predicted line shape is Lorentzian and is most intense at momentum transfers corresponding to those required for Bragg scattering, i.e. $\mathbf{q} = 2\mathbf{q}_0$, where π/q_0 is the pitch of the cholesteric helix. In the presence of an applied electric or magnetic field, Eq. (1) is modified.

Application of a small magnetic field perpendicular to the spiral axis, z, produces at band gap in the dispersion curve for the damping constant at $\mathbf{q} = \mathbf{q}_0$. The results of the Hawaii group exhibit no other alteration in the spectral halfwidth except for wavevectors very near $\mathbf{q}_0$. The development of the Rutgers group, which also predicts a field dependent band gap when $\mathbf{q} = \mathbf{q}_0$, contains a multiplicative function which depresses the halfwidth at scattering angles about the gap. Their equations in this regime, however, can be shown to diverge[16] as $H \to O$ and are therefore physically incorrect.

The Hawaii group also carried out exact solutions of the differential equation governing the pitch angle for certain special cases at larger applied field strengths. If the anisotropic diamagnetic susceptibility, χ_a, is positive, a magnetic field applied perpendicular to the z axis of a cholesteric liquid crystal is known to induce an unwinding of the helical superstructure.[17] The resultant pitch dilation, $P(H)$, at larger fields was recognized and incorporated into the development with $q = q_H = \pi/P(H)$. A gap in the dispersion relation was again noted but now shifted to $q = q_H$, corresponding to the increase in pitch. It was also confirmed that Γ_t for the twist mode vanishes with wavevector even in a large field. Unfortunately the case that applies most directly to the field experiments outlined below, $q \gg q_H$, was not included as a simple solution to their exact equation.

Viscous-splay normal mode

The hydrodynamic equations also yield a set of independent relations which are identified with fluctuations about the molecular director in viscous-splay.[5] These modes are also overdamped and one is dominant in light scattering with a damping constant given by

$$\Gamma_s = \beta(K_{33}q_0^2 + K_{11}q^2) \tag{2}$$

where K_{11} and K_{33} are the splay and bend elastic moduli, respectively, and $\beta = (\alpha_2 + \alpha_4 + \alpha_5)/\gamma_1(\alpha_4 + \alpha_5) - \gamma_2\alpha_2$ is a collection of viscosity coefficients. The predicted lineshape of this normal mode is also Lorentzian, but in this case is sharpest at one-half the Bragg condition: $\mathbf{q} = \mathbf{q}_0$. The effect of a weak magnetic field on this spectral halfwidth was also considered. A band gap is shown to occur. In the small field approximation, the damping constant, Eq. (2), is unchanged for $\mathbf{H} \perp \mathbf{z}$. When $\mathbf{H}$ is directed along $\mathbf{z}$, however, the width of the viscous-splay mode decreases in accordance with:

$$\Gamma_s \approx (K_{33}q_0^2 + K_{11}q^2 - \chi_a H^2)/\gamma_1 \tag{3}$$

Both developments were restricted to orientational fluctuations that propagate solely along the cholesteric spiral axis, z. In the general case, which was not developed, where the direction of propagation is at an angle to this axis the hydrodynamics of the directorfield fluctuations becomes more complicated and the above relations for the spectral halfwidths would be presumably modified.

The influence of the two modes on the light scattering spectrum could conceivedly be separated in one of two ways:

a) One mode is shown to scatter light most strongly for momentum transfers exactly equal to the Bragg condition, whereas the other does so at intermediate angles.

b) The angular dependence of the halfwidths of the two contributions, though both quadratic in q, are very different. Eq. (1) for the twist normal mode halfwidth goes to zero at zero scattering angle, whereas Eq. (2) has a finite intercept.

There are complications in either procedure. In case a) one must examine the light scattering spectrum at exceedingly small angles if the periodicity of the cholesteric structure is large (small q_0). For more manageable scattering angles (q_0 large), the periodicity of the structure would have to be the order of the wavelength of light. This is, of course, the condition for strong light scattering and the unique iridescent appearance of cholesteric liquid crystals in white light. Problems with multiple scattering may prevent spectral analysis in this case. On the other hand, if both modes contribute significantly to the light scattering spectrum, a detailed angular dependence study of the halfwidths (case b) may be hampered by the unavailability of a number of viscoelastic constants that appear in equations for the spectral halfwidths and intensities. In our study only procedure b) was practical.

EXPERIMENTAL

Liquid crystal solutions of poly-γ-benzyl-L-glutamate (PBLG) of molecular weight 310,000 were prepared (20% wt/v) in millipore filtered chloroform which had been distilled from NaOH solution to remove traces of water that could result in electrolytic hydrolysis of the polypeptide. The polymer is known to form a lyotropic liquid crystal of the cholesteric structure in this solvent at this concentration.[18] After maturation samples were observed to be of high optical clarity with a zero field pitch corresponding to $q_0 = 7.48 \times 10^2\ \text{cm}^{-1}$. We cannot at this time, however, prepare uniformly oriented homogeneous or homeotropic samples of this liquid crystal, the state of the art of such surface orientation in polypeptide liquid crystals being much less advanced than in the more extensively researched thermotropics. This investigation does not, therefore, strictly meet the condition of the theoretical papers discussed above that $\mathbf{q}$ lie exactly along or perpendicular to the cholesteric $\mathbf{z}$ axis.

Using the techniques of laser light-beating, or quasielastic spectroscopy, the Rayleigh line of scattered laser radiation was examined as a function of scattering angle and applied electric field. Our apparatus is essentially that described elsewhere[19,20] with a 3 mW He–Ne laser as a light source and signal averaging capability provided by a programmable calculator (Wang 600, programmed for 50 channel data accumulation) interfaced to the spectrum analyzer (Tektronix 3L5). The scattering cell was a 12 mm spectrophotometric cuvette fitted internally with two copper disc electrodes separated by 1 cm. The leads were insulated with teflon tubing and exited from the cell through a teflon stopper. The reliability of the apparatus was confirmed by angular studies on two polystyrene sphere solutions of known particle size, utilizing the Stokes–Einstein equation to calculate the translational diffusion coefficient which was compared with the experimental result in each case.

Spectra on cholesteric PBLG solutions were recorded at scattering angles ranging from 20° to 90° in 5° increments with the sample under the influence of an electric field of 0 to 300 V/cm. Fields were applied perpendicular to the scattering plane and were well below the critical value for the electrotropic cholesteric to nematic phase transition as previously determined.[21] Light scattering spectra much below 20° were found to be unsuitable for analysis as they contained both homodyne and heterodyne components. A typical spectrum is shown in Figure 1. Spectra recorded at scattering angles less than 60–90° could not be described by a simple Lorentzian lineshape function. Broad wings of measurable intensity extending in some cases out to

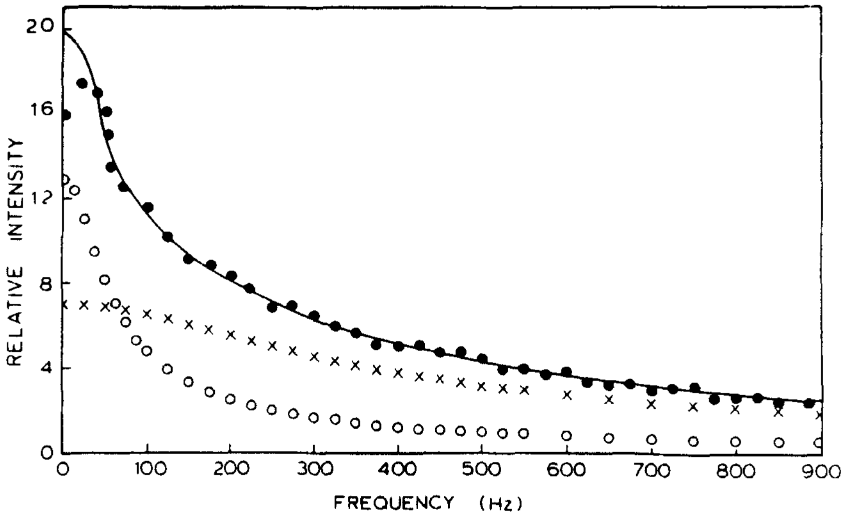

FIGURE 1 Spectral deconvolution for 20° scattering. The closed circles represent the spectral intensity as recorded by the signal averager. The crosses represent the broad component of the deconvoluted spectrum while the open circles represent the narrow component.

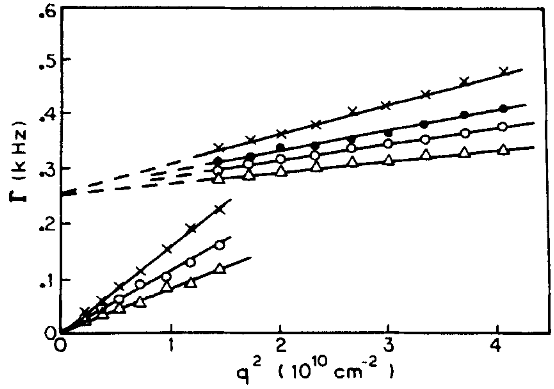

FIGURE 2 Spectral halfwidths, Γ, of the deconvoluted spectra versus the scattering vector, q^2, for a cholesteric polypeptide liquid crystal. The crosses (× × ×) are for scattering with the electric field $E = 0$; solid circles (●●●) for $E = 100$ V/cm; open circles (○○○) for $E = 200$ V/cm; and triangles (△△△) for $E = 300$ V/cm. The broader component with a nonzero intercept when extrapolated to zero scattering angle may be identified with the theoretically predicted viscous-splay normal mode. The narrow component is in accordance with the angular dependence of the lineshape for the cholesteric twist mode.

5000 Hz were evident. In those cases, however, spectra could be separated by a deconvolution process into two overlapping Lorentzian components, one broad and one sharp. The halfwidth of the broader component is quadratic in q and has a non-zero intercept when extrapolated to zero scattering angle (Figure 2). The halfwidth of this mode is depressed with increasing field strength but the intercept is common to all fields. The angular dependence of the narrow component is also quadratic in q, but has a zero intercept. Application of an electric field also depresses the spectral halfwidth of this component.

DISCUSSION

Although the existence of randomly oriented micro-domains within the scattering volume precludes, on the basis of previous theory, a definitive identification of the origin of the two light scattering modes observed, the angular dependence of our results is suggestive that the scattering mechanism giving rise to the broad mode is the cholesteric viscous-splay normal mode and that of the sharp mode is the twist deformation. The reduction is spectral halfwidth at all scattering angles for both modes as seen in Figure 2, however, is not among the conclusions of the theoretical papers for $q \gg q_0$ except for one case (**H**//**z** in the viscous-splay mode). One would expect, however, that such a decrease would take place as the field increases due to

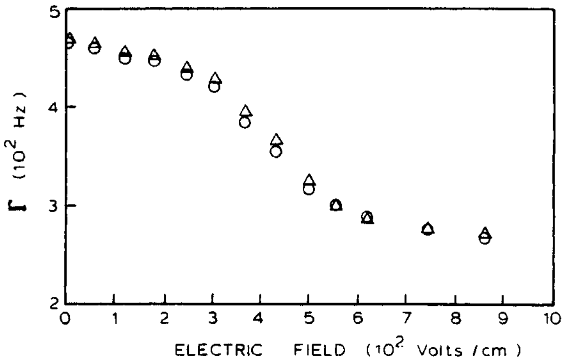

FIGURE 3 Spectral halfwidth, Γ, of a PBLG cholesteric liquid crystal solution as a function of applied electric field. The triangles are the data points for scattering parallel to the electric field; the open circles for scattering perpendicular.

the reduced diffusional mobility resulting from a restriction in the mean-square oscillation amplitude of macromolecules about the imposed field direction. This indeed has been followed experimentally[22] in the PBLG liquid crystal over a wide range of voltages in 90° scattering, where the two modes are not separable due to similar intensities. Figure 3 illustrates a distinct narrowing of the laser line-width as the liquid crystal is subjected to increasingly high electric field strengths. The decline around 300 V/cm has been identified[22] with the cholesteric to nematic phase transition previously reported[21] by optical methods on a similar system.

It is conceivable that since we are dealing with scattering wavevectors $q \sim 10^2 q_0$ that we are actually sampling local nematic order in the cholesteric medium, independent of any spontaneous twist. This possibility can be dismissed by a simple calculation with known parameters of the system. It is, of course, true that as the selected q vector increases the wavelength of the fluctuation sampled goes down. In our case $q \sim 10^5$ cm^{-1} which corresponds to a fluctuation wavelength of ~6000 Å. The PBLG macromolecule in the α-helical configuration is from 15 Å to 25 Å in diameter[23,24] and 2135 Å long.[25] In the liquid crystal, molecules are arranged on a local hexagonal net with long axes separated by a lateral distance of ~ 10–50 Å.[24,26] Consequently, if $\mathbf{q}$, for example, were directed along the cholesteric axis the wavelength of the fluctuation would encompass several 10^2 molecular planes, which is surely enough to sense the effect of the spontaneous twist of the cholesteric structure.

The possibility that the high frequency (broad) mode being due to or interfered by the translations and/or rotations of *single* macromolecules can also be ruled out. It is well established both theoretically and experimentally that the contribution to the Rayleigh line due to translation and rotation of a single rod shaped macromolecule is of the form:[27]

$$\Gamma = D_T q^2 + 6\Theta_R \tag{4}$$

where D_T and Θ_R are the translational and rotational diffusion constants of the macromolecule, respectively. Note that the translational term goes to zero as $q \downarrow 0$, which is not the case for the broad mode of this study. Furthermore, the rotational mobility of the α-helix in this polypeptide system is highly restricted. The magnitude of Θ_R could not account for the large finite intercept of Γ_s as $q \downarrow 0$. Using a modification[28] the Stokes–Einstein relation for Θ_R of a rodlike particle, we calculate that $\Theta_R = 0.09\ \mathrm{sec}^{-1}$ for an individual PBLG macromolecule in this liquid crystal.[29] The intercept of Γ_s is, however, about 0.25 kHz.

Given the above associations, analysis of the angular dependence of the sharp component yields a value of $K_{22}/\gamma_1 = 7.7 \times 10^{-8}$ cgs. Taking $K_{22} = 2.1 \times 10^{-7}$ dyne from a previous experiment[15] we find that $\gamma_1 = 2.7$ poise. This value is an order of magnitude greater than γ_1 reported for a smectic liquid crystal[8] and two orders of magnitude above that for nematic systems.[30] The trend is understandable in terms of the greater response times to external disturbances noted for polypeptide liquid crystals (~10–20 minutes) as compared to thermotropics (~milliseconds).

Although the value of γ_1 derived from the data on the low frequency (sharp) mode is in line with that reported on other systems, viscoelastic constants obtained from the broad mode associated with viscous-splay deformations are very different. Considering Eq. (2), we see that

$$\frac{q_0^2\, d\Gamma_s/d(q^2)}{\Gamma_s(q = 0)} = \frac{K_{11}}{K_{33}} \tag{5}$$

From the slope and intercept of the zero field data of Figure 2, we obtain a ratio of $K_{11}/K_{33} \sim 10^{-5}$. In most liquid crystals all the K_{ii} are of the same order of magnitude although K_{33} is always larger.[31] The elastic moduli, K_{ii}, have been related to molecular dimensions through the use of mean field theory. The theory provides a means of judging the reasonableness of this unusually small ratio for this polymer liquid crystal. Gruler[32] finds that for an axially symmetric, rod like particle

$$K_{11} = K_{22} = x^2 \cdot \tfrac{3}{2} \cdot \left(\frac{N}{V_n}\right)(-\bar{D}) \tag{6}$$

$$K_{33} = z^2 \cdot \tfrac{3}{2} \cdot \left(\frac{N}{V_n}\right)(-\bar{D}) \tag{7}$$

where $\bar{D}$ is the average mean field energy, N/V_n is the packing density and $x(=y)$ and z are the characteristic width and length of the molecule, respectively. Similar expressions have been derived by deGennes[31] using dimensional analysis. Hence the ratio $K_{11}/K_{33} = (x/z)^2$, which is usually the order of 0.1 for small liquid crystal molecules, ranges from 5×10^{-5} if we take the diameter of the PBLG macromolecule to be 15 Å to 1.4×10^{-4} if $x = 25$ Å. The calculation shows that such a small ratio would in fact be expected in a system of such highly elongated macromolecules. The estimated values are in good agreement with our experimental results and make the case for the assignment of the broad mode with viscous splay deformations more appealing. It should be noted however that direct data on K_{11} and K_{33} are not yet available for this system. It may be that these moduli are highly variable. Twist moduli orders of magnitude greater than those of thermotropic systems have been measured[15,33–35] in this polypeptide liquid crystal and are found to be very sensitive to variation in supporting solvent and polymer molecular weight.

Search for the predicted band gaps proved impractical in our system. The large pitch of this liquid crystal, which is fundamentally responsible for its optical clarity, would require a scattering angle of less than 0.5°, which is the order of the angular acceptance of scattered light in our apparatus. We are presently investigating the preparation of a uniform cholesteric polypeptide liquid crystal in an intermediate region of reasonable optical properties and accessible scattering angle. Solutions of the ethyl isomer of polyglutamic acid, for example, are known to have zero field pitch of the order of the wavelength of light which may possibly be suitably modified for study by changes in solvent and concentration of polymer.

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