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Brillouin Scattering in a Cholesteric Liquid Crystal Near the Cholesteric–Isotropic Transition

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Abstract—Brillouin scattering is used to study the propagation of hypersonic waves in a cholesteric medium at the liquid-to-liquid-crystal transition. Contrary to the results obtained by others, we have found no anomalous change in either the velocity or the attenuation of the hypersonic waves at the transition.

1. Introduction

There have been many investigations of the acoustic properties of substances in the phase transition region. Such diverse transitions as the liquid–vapor, order–disorder, superconducting, ferroelectric and ferromagnetic have been studied rather thoroughly over a wide range of frequencies.⁽¹⁾ These studies have yielded a great deal of information about the dynamical properties of these systems in the transition region. One would hope that similar investigations of the liquid crystal–liquid transition could be just as fruitful. However, so far, there have been only a few reports in existence on the subject.^(2–6)

Hoyer and Nolle,⁽²⁾ using the standard ultrasonic technique have investigated the liquid crystal–liquid transition of *p*-azoxyanisole (P.A.A.) and cholesteryl benzoate in a frequency range of 0.5 to 6 MHz. They observed almost a two order of magnitude increase in the attenuation and a 10% dip in the velocity of the sound waves at the transition. Hoyer and Nolle attributed these effects to structural relaxation⁽⁷⁾ and were able to quantitatively interpret their results.

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Zvereva and Kapustin obtained similar results in the same frequency range for *p,p'*-nonoxybenzaltoluidine,⁽³⁾ cholesteryl caprate⁽⁴⁾ and cholesteryl caprinat.⁽⁵⁾

Durand and Rao⁽⁶⁾ have extended the investigation of the liquid crystal-liquid transition to hypersonic frequencies (10 GHz) using the Brillouin scattering technique. Their investigation of cholesteryl 2-(2 ethoxy ethoxy) ethyl carbonate (CEC) showed that the sound wave became highly damped (large broadening of the Brillouin line) in the transition region, and that its velocity changed by approximately 5%. These effects appear similar to those observed at lower frequencies. However, since in this case, the liquid crystal had domain sizes comparable to the wavelength of the acoustic excitation, we suspect that these effects could be due to an increase of scattering loss induced by the small domains at the transition rather than structural relaxation.

In order to minimize the scattering loss, we should therefore choose a sample with sufficiently large domains. In this paper, we would like to report on our Brillouin scattering measurements at the liquid crystal-liquid phase transition of a thin sample which has domain sizes approximately one hundred times greater than the wavelength of the hypersonic waves. Contrary to the results obtained by Durand and Rao,⁽⁶⁾ we have found no anomalous behavior in the attenuation or in the velocity of the hypersonic wave at the transition.

2. Experimental Methods

Figure 1 shows our experimental set-up which is similar to that of Durand and Pine's.⁽⁸⁾ A coherent Radiation Model 52 argon laser with a 100 mW single-mode output at 5145 Å was used as the light source. The laser beam was focused on the sample by a condensing lens L_1 via a small reflecting mirror (4×3 mm). The sample was surrounded by a copper block which acted like a thermal reservoir and was temperature controlled to $\pm 0.01^\circ\text{C}$. The back-scattered radiation from the sample was spectrally analyzed by a combined set of a Fabry-Perot and a double monochromator. It was collected by the lens L_2 , and focused on a 500μ pinhole after passing through an I_2 absorption cell.⁽⁹⁾ The pinhole was located at the focus of the third

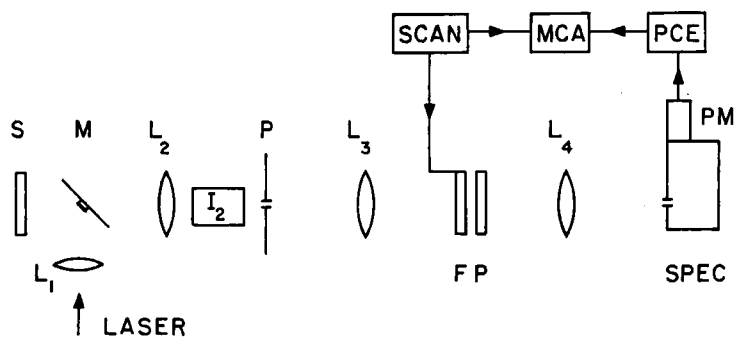


Figure 1. Schematic of experimental setup. S—sample; L_1 , L_2 , L_3 , L_4 lenses with respective focal lengths of 8, 8, 31, and 15 cm; M—small mirror; I_2 —iodine absorption cell; P—500 μ pinhole; FP—Fabry-Perot interferometer; SPEC—SPEX Double monochromator; PM—EMI 9558 photo-multiplier, PCE—Standard photon counting electronics; MCA—multichannel analyzer; SCAN—sawtooth generator for scanning the Fabry-Perot.

lens L_3 . Then, the parallel rays from L_3 were incident on a piezoelectrically scanned Fabry-Perot interferometer whose plates were $\lambda/100$ flat and had a 97.8% reflectivity. The output from the Fabry-Perot was focused by the lens L_4 on the slit of a Spex double monochromator with a bandpass of 20 cm^{-1} centered at 5145 Å. Detection was accomplished using the photon counting method in conjunction with a multichannel analyzer. In this experiment the Fabry-Perot was used in a multiscanning mode to improve the signal-to-noise ratio. A sawtooth voltage applied to the piezoelectric disks periodically scanned the mirrors, in synchronization with the scan of the multichannel analyzer. A typical spectrum was taken in about 2 minutes and consisted of 20 scans. The integration time per channel was 0.4 seconds which yielded a signal to noise ratio of 20 : 1. The Fabry-Perot was aligned before each run and typically had a finesse of 70 over its 1.85 cm aperture. After 20 scans the effective finesse was degraded to approximately 60 which corresponded to a resolution of 0.016 cm^{-1} for the free spectral range of 0.960 cm^{-1} used in our experiments.

The major difficulty often encountered in Brillouin scattering experiments is in the discrimination against elastic scattering from the sample. For clean liquids and homogeneous crystals, the

elastic scattering is about 100 times stronger than inelastic scattering and hence the typical discrimination factor of 1000 of a Fabry-Perot interferometer is sufficient. However, in our case the elastic scattering from the liquid crystal was about seven orders of magnitude stronger than the inelastic scattering and detection of the Brillouin signal would have been impossible without much higher discrimination. Recently, Devlin *et al.*⁽⁹⁾ found that the argon laser frequency at 5145 Å can be tuned to coincide with a strong, but narrow (0.05 cm^{-1}) absorption line of I_2 vapour. One can therefore use an I_2 cell as a very effective filter for the elastically scattered light. Using such a cell at a temperature of 67°C we were able to attenuate the elastic scattering from our sample by five orders of magnitude. Unfortunately I_2 has other absorption lines nearby which may distort the Brillouin lines and make the spectral analysis more difficult. We shall discuss in detail how the observed Brillouin spectra were analyzed in the next section.

The liquid crystal sample used in our experiments was a mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride (by weight). This mixture was in the cholesteric phase from 20 to 56°C with corresponding pitch in the infrared varying from 1.4 to 2.8μ . With this mixture it was relatively easy to make thin film samples 250μ thick which appeared homogeneous and transparent to the naked eye. Under a polarizing microscope, we could however see domains of about 30μ in size. The samples were prepared by pressing a few drops of the mixture between two glass slides. Initially, the sample was hazy, but it became transparent after a few days. The chemicals were obtained from Eastman Kodak and were used without further purification.

3. Results and Data Analysis

In a liquid medium, the spectrum of Brillouin scattering has two components⁽¹⁰⁾ shifted on either side of the exciting frequency ω_0 by the frequency of the hypersonic excitation⁽¹¹⁾

$$\Omega = (2\omega_0 nv/c) \sin(\theta/2) \quad (1)$$

where v is the acoustic velocity, n is the refractive index, c is the light velocity in vacuum, and θ is the angle between the directions of

incident and scattered radiation. In obtaining Eq. (1), we have assumed that each wave propagating in the medium is characterized by a single wave vector. This is not quite true in cholesteric liquid crystals. There, even for waves propagating along the helical axis, each eigenmode is a linear combination of waves with wave vectors k and $k + 4\pi/p$ where p is the helical pitch of the liquid crystal.⁽¹²⁾ However, if the wavelengths involved are far from the periodicity $p/2$, then the component with the wave vector $k + 4\pi/p$ in each eigenmode has a negligibly small amplitude.⁽¹²⁾ In that limit, Eq. (1) is a very good approximation. This is the case for our experiments.

We chose to investigate Brillouin scattering in the backward direction ($\theta = \pi$), corresponding to an acoustic excitation with a frequency of approximately 10 GHz. By varying θ , we can also study the characteristics of the acoustic excitations at lower frequencies. We have not yet carried out such an experiment completely.

In Fig. 2 we show a typical Brillouin spectrum of the liquid crystal taken at room temperature. The Stokes component is distorted by the I_2 absorptions, but the anti-Stokes component, on

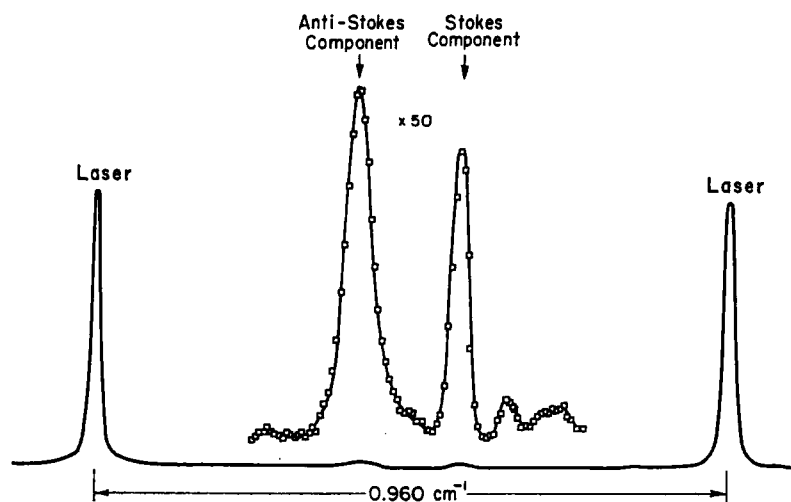


Figure 2. A typical Brillouin spectrum of the cholesteric mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride taken at 20 °C. The Stokes component is somewhat distorted by the I_2 absorptions but the anti-Stokes component is almost undistorted. The structure in the background is due to I_2 absorption lines.

the other hand, is in a flat region of the absorption spectrum and is undistorted. As the temperature increases, the distortion of the Stokes component becomes greater while distortion of the anti-Stokes component remains small. We therefore chose to analyze only the anti-Stokes component and were able to determine its frequency to $\pm 1\%$ and its linewidth to $\pm 10\%$.

We have measured the temperature dependence of the Brillouin shift, Ω , and the Brillouin linewidth, Γ , in the cholesteric liquid crystalline phase and through the liquid crystal-liquid phase transition. Typical values for Ω and Γ are 0.375 cm^{-1} and 0.06 cm^{-1} . The corresponding value for the acoustic velocity v deduced from Eq. (1) is $1.9 \times 10^8 \text{ cm/sec}$. As the temperature of the liquid crystal increased from 20°C and through the phase transition in steps of 0.1°C , Ω gradually decreased (see Fig. 3) and Γ remained constant

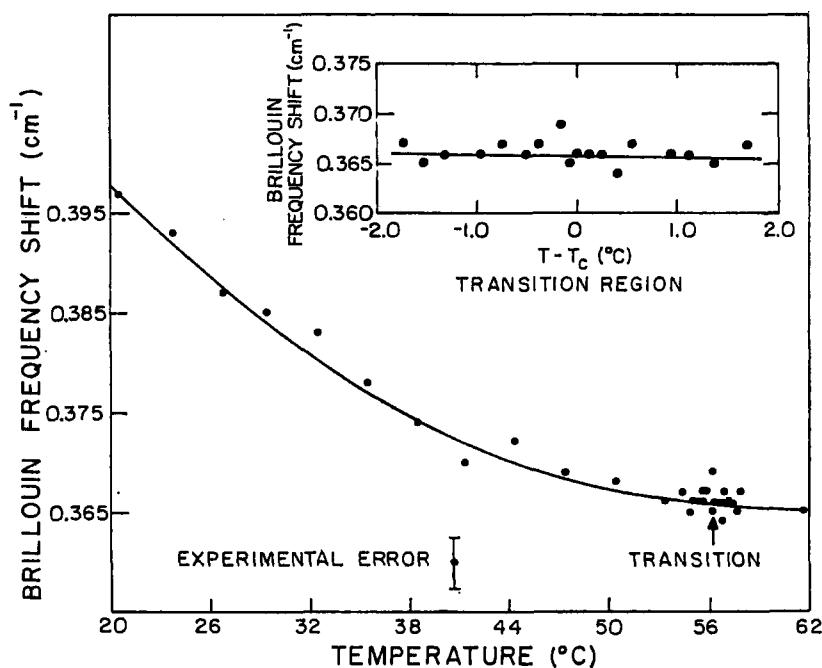


Figure 3. Brillouin frequency shift of the cholesteric mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride as a function of temperature in the liquid crystal phase and through the liquid crystal-to-liquid phase transition. The insert shows the Brillouin frequency shift in the transition region.

within the experimental error. Contrary to the results of the ultrasonic measurements⁽²⁻⁵⁾ and those of Durand and Rao,⁽⁶⁾ no anomalous change in either ν or Γ was observed in the transition region (see Figs. 3 and 4).

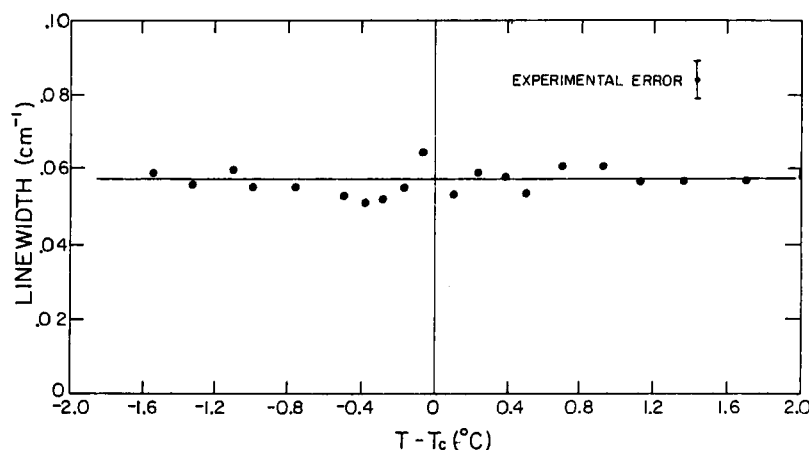


Figure 4. Brillouin linewidth of the cholesteric mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride as a function of temperature in the liquid crystal-to-liquid transition region.

In order to determine the frequency shift and the linewidth of the Brillouin mode accurately, it was necessary to take into account the effects of the I_2 absorption cell which we used to eliminate the elastic scattering. Let $G(\omega)$ be the true Brillouin spectrum and $T(\omega)$ be the transmissivity of the I_2 cell. Then, the observed Brillouin spectrum $S_B(\omega)$ is given by

$$S_B(\omega) = \int_{-\infty}^{\infty} I_B(\omega - \omega_0) T(\omega_0) G(\omega_0) d\omega_0 \quad (2)$$

where $I_B(\omega)$ is the instrumental function of the Fabry-Perot-spectrometer setup, and was obtained in our experiment by using a single-mode laser beam as the incoming source.

We are interested in knowing $G(\omega)$. To find $G(\omega)$, we must first obtain the transmissivity $T(\omega)$ of the I_2 cell. This was done by measuring the transmission of the I_2 cell with broadband radiation shining on the Fabry-Perot-spectrometer setup. The spectrometer

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limited the radiation to a band narrower than the free spectral range of the Fabry-Perot. If $I_T(\omega)$ is the instrumental linewidth in this measurement, the measured transmissivity $S_T(\omega)$ is related to the true transmissivity $T(\omega)$ by the equation

$$S_T(\omega) = \int_{-\infty}^{\infty} I_T(\omega - \omega_0) T(\omega_0) d\omega_0. \quad (3)$$

Then, through deconvolution of Eqs. (2) and (3), we can find $T(\omega)$ and $G(\omega)$.

The standard technique of deconvolution is to substitute a known functional form for the spectral function and vary the parameters in the function until the integral gives a spectrum which fits well with the measured spectrum. In our case, this would be quite difficult since $T(\omega)$ does not have a known functional form. Here, we used the Fourier transform technique to deconvolve our spectra. It is well known that the Fourier transform of a convolution integral

$$\int_{-\infty}^{\infty} A(X - X_0) B(X_0) dX_0$$

is the product of the Fourier transforms of $A(X)$ and $B(X)$.⁽¹³⁾ Therefore, by Fourier-transforming Eqs. (2) and (3), we can find the Fourier transforms of $G(\omega)T(\omega)$ and $T(\omega)$, if the Fourier transforms of the instrumental functions are known. Then, the inverse Fourier transforms enable us to determine the spectral functions $G(\omega)$ and $T(\omega)$ separately.

In our analysis, the instrumental functions were approximated by Airy functions. The fast Fourier transform technique was used to carry out the Fourier transformations on a 6600 Control Data computer. In order to reduce random fluctuations in the spectra, an observed spectrum was first approximated by the best polynomial fit (typically a 20th-order polynomial) and then used in the analysis. Since the sharp structure of the I_2 absorption spectrum coincides with the Brillouin-Stokes frequency, the accuracy of our analysis for the Stokes component was much worse than that for the anti-Stokes component. We therefore chose to analyze only the anti-Stokes component. We were able to determine its peak position to $\pm 1\%$ and its linewidth to $\pm 10\%$.

4. Discussion

Except for the gradual decrease in Ω or ν with increasing temperature which is presumably due to thermal expansion, our results are quite different from those obtained in the Brillouin measurements of Durand and Rao⁽⁶⁾ or the ultrasonic studies of Hoyer and Nolle,⁽²⁾ and Zverera and Kapustin.⁽³⁻⁵⁾ All these workers observed intense acoustic attenuation as well as changes in the velocity of the sound wave in the transition region.

We believe that the difference between our results and those of Durand and Rao⁽⁶⁾ can be explained by the difference in the domain sizes of the samples in the two cases. We realize that scattering of acoustic waves by domain walls increases the damping constant of the acoustic waves. If the domain size is much larger than the mean free path or the attenuation length l_α of the acoustic waves, then most of the acoustic waves excited in a domain decay away before hitting the domain walls, and hence the effect of the domain walls can be neglected. If the domain size is comparable with l_α , then the effective damping constant increases as the domain size decreases. We have observed that at the liquid-crystal-to-liquid transition, the domain size of liquid crystals changes rapidly. It decreases by a factor larger than 2 in a pre-transitional region of about 3°C and then within 0.1°C of the transition, suddenly disappears. This behavior is similar to that of the order parameter.⁽¹⁴⁾ In our case, the domain size in the liquid crystal phase was about 30 μm , and the attenuation length obtained from $l_\alpha = \nu/\Gamma$ was about 0.2 μm . Therefore, it is clear that we should not expect to observe any change in the acoustic damping constant due to scattering by domain walls in the pre-transition region. Since in our experiment, the temperature was raised in steps of 0.1°C, we were also unable to resolve any change which happened within 0.1°C of the transition. In the case of Durand and Rao⁽⁶⁾ the domain size of their sample was about 0.2 μm , which was comparable to l_α . Then, in the pre-transition region, the acoustic damping constant should increase as the domain size decreased. Finally, after the transition, the domains disappeared in the liquid phase, and the acoustic damping returned to its normal value. This explains why Durand and Rao⁽⁶⁾ observed the anomalous increase

of acoustic damping and the corresponding dispersion of acoustic velocity at the transition.

The difference between our results and those of the ultrasonic studies⁽²⁻⁵⁾ can be explained by the difference in the acoustic frequencies in the two cases. The ultrasonic studies have been carried out in the frequency range of 0.5 to 15 MHz. They typically show almost a two order-of-magnitude increase in the ultrasonic attenuation in the transition region. Away from the transition the results of Hoyer and Nolle⁽²⁾ fit the classical absorption coefficient⁽¹⁵⁾ which has an ω^2 frequency dependence. However, in the transition region the acoustic attenuation appears to have a frequency dependence of $\omega^2/(1 + \omega^2\tau^2)$ ⁽¹⁶⁾ which is characteristic of a relaxational process with τ being the relaxation time. Hoyer and Nolle suggested that this attenuation was due to structural relaxation⁽⁷⁾ and using Frenkel's hetrophase fluctuation theory,⁽¹⁷⁾ were able to explain their results fairly well.

The model of structural relaxation is based on the supposition that an increase of pressure can convert a fluid to a more compact local molecular arrangement (larger order parameter) which has a smaller specific volume. This induced change is more pronounced at the phase transition since the pressure affects the equilibrium between the two phases. However, the response of this structural change to the pressure cannot be instantaneous, but has a finite relaxation time τ . Therefore, as a sound wave propagates in the medium, the induced change in the order parameter or in the volume lags in phase behind the pressure wave, and consequently, causes attenuation of the sound wave. The acoustic attenuation constant $\xi (= \Gamma/v)$ due to structural relaxation can be written as^(7,2)

$$\xi/\omega^2 = \frac{1}{2} \frac{v_\infty^2 - v_0^2}{v_0^2 v_\infty^2} \frac{\tau v(\omega)}{1 + \omega^2 \tau^2} \quad (4a)$$

$$v^2(\omega) = \frac{1 + \omega^2 \tau^2}{(1/v_0)^2 + (\omega\tau/v_\infty)^2} \quad (4b)$$

Here v_∞ is the sound velocity at very high frequencies and has no contribution from structural relaxation since the structure or volume change can not respond to a high-frequency pressure wave. v_0 is the sound velocity at very low frequencies and its value depends on how the structure responds to the pressure wave. Since v_0 is not very

different from v_∞ , the frequency dependence of $v(\omega)$ is weak and hence ξ/ω^2 is proportional to $\tau/(1 + \omega^2\tau^2)$ approximately. As the medium approaches the liquid crystal-to-liquid transition, the decrease of v_0 with temperature due to structural relaxation becomes large. This leads to the large acoustic attenuation and the corresponding dip in the velocity $v(\omega)$ at the transition as Hoyer and Nolle have observed.⁽¹⁸⁾ From their results, they found $\tau = 3.5 \times 10^{-8}$ sec at the transition.

In our case, the hypersonic wave probed by the Brillouin scattering was at about 10 GHz. At such a high frequency, ξ/ω^2 should nearly vanish since we do not expect the structural relaxation time to vary much with frequency. Then, the classical acoustic attenuation, which is proportional to ω^2 , should dominate. This was indeed the case. Using Eq. (4) with values of v_0, v_∞ , and τ given by Hoyer and Nolle,⁽²⁾ we found that in our case the linewidth of the Brillouin mode due to structural relaxation should be about $3 \times 10^{-5} \text{ cm}^{-1}$, and the change of acoustic velocity at the transition is less than one part in 10^5 . These effects are of course too small to be observed in the Brillouin scattering measurements.

5. Conclusions

We have used Brillouin scattering to study the hypersonic properties of a cholesteric mixture in the liquid crystal-liquid phase transition region. Contrary to the results of similar measurements by Durand and Rao⁽⁶⁾ and the results of the ultrasonic studies,⁽²⁻⁵⁾ we have found no anomalous change in either the velocity or the attenuation of the hypersonic waves at the transition. We realize that in the case of Durand and Rao, the anomalous change is due to acoustic scattering by the small domains in their sample, and in the case of the ultrasonic studies, it is due to structural relaxation. Neither of these mechanisms has any appreciable effect in our case.

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