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Ultrasonic absorption studies in the cholesteric and isotropic phases of cholesteryl valerate

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Ultrasonic absorption has been measured in the cholesteric and isotropic phases of cholesteryl valerate as a function of both temperature and frequency. The anomalous absorption observed in the cholesteric phase has been interpreted by considering the coupling of the sound wave to the director fluctuations. In the isotropic phase coupling of the sound wave to the tensor order parameter is considered to analyse the absorption results.

1. Introduction

The anomalous ultrasonic absorption in the cholesteric and isotropic phases of cholesteric liquid crystals have been reported by several investigators for cholesteryl benzoate [1, 2], cholesteryl linoleate and cholesteryl linolenate. To interpret the anomalous absorption in the isotropic phase, Hoyer and Nolle [2] adopted Frenkel's heterophase fluctuation theory. Zvereva [3] has discussed the anomalous absorption in cholesteryl caprinate, based on the relaxation theory, considering the reorientation of molecular groups in the ultrasonic field. Subsequently, Edmonds and Orr [4], by studying the propagation of ultrasonic waves in three 18-carbon unsaturated fatty acid esters of cholesterol and their mixtures of the esters, concluded that a summation of two or more relaxation mechanisms are necessary to explain their data.

In this paper we have made an attempt to explain the anomalous absorption observed in the cholesteric and isotropic phases of cholesteryl valerate (CV), considering two relaxation processes. In the cholesteric phase we consider coupling of the sound wave to the director fluctuations. In the isotropic phase we consider coupling of the sound wave to the tensor order parameter fluctuations.

In § 2 we formulate the expressions for ultrasonic absorption in cholesteric and isotropic phases. The experimental results are presented on § 3. Finally in § 4 we analyse the experimental results considering the two relaxation mechanisms discussed in § 2.

2. Theoretical

The cholesteric phase is characterised by the helical arrangement of the molecules and hence the cholesteric free energy depends on the relative orientation between the pitch axis and the local nematic director [5]. Thus in cholesterics the amplitude of the order parameter remains constant and the spatial variations allow the twisted equilibrium conformation. In the cholesteric phase it is expected that the fluctuations of the tensor order parameter only influence the director. According to recent theories, cholesterics cannot exist without phase biaxiality which is induced by helicity [6]. Thus fluctuations are anisotropic which reflect the non-vanishing phase biaxiality.

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In the isotropic phase of cholesterics the chirality exists only over a short temperature range [7]. At higher temperatures it is reasonable to expect that the helical order disappears to give the isotropic liquid of a quasi-nematic phase.

The passage of sound waves causes thermal fluctuations in the medium. In cholesteric phase it is expected that the fluctuations of the tensor order parameter only contain fluctuations of the director. But in the isotropic phase, as the magnitude of the scalar order parameter becomes zero, we must consider the fluctuations of the tensor order parameter. Hence, we have considered the coupling of sound waves to the fluctuations of the director in the cholesteric phase and to the tensor order parameter fluctuations in the isotropic phase through the oscillating temperature.

2.1. *Cholesteric phase*

The free energy as a function of director is given as [8]

$$\begin{aligned} F(\mathbf{n}) &= \tfrac{1}{2}K_1(\operatorname{div}\mathbf{n})^2+\tfrac{1}{2}K_2(\mathbf{n}\cdot\operatorname{curl}\mathbf{n}+q_0)^2 \\ &\quad +\tfrac{1}{2}K_3(\mathbf{n}\times\operatorname{curl}\mathbf{n})^2. \end{aligned} \tag{1}$$

For mathematical convenience the average Frank elastic constant

$$K=(K_1+K_2+K_3)/3 \tag{2}$$

is considered as an approximation and the free energy then equals

$$F(\mathbf{n})=\tfrac{1}{2}K\sum_{ij}(\nabla_i n_j)(\nabla_i n_j). \tag{3}$$

Equation (3), obtained for the cholesteric phase, can be considered as a good approximation for blue phases [9]. In the present analysis this assumption is quite legitimate, as we have not observed any anomalous behaviour in absorption in the cholesteric blue phase transition region of cholesteryl valerate. However, the absorption data at temperature $T<(T_c-0{\cdot}5^\circ\mathrm{C})$ have only been analysed using the present theory. The blue phase region for CV is $\sim 0{\cdot}3^\circ\mathrm{C}$ [10].

Sound wave propagation in the medium causes a change in the equilibrium values of the thermodynamic functions. The passage of the sound wave is responsible for a small change in the equilibrium value of the director

$$\mathbf{n}=\mathbf{n}+\Delta\mathbf{n}. \tag{4}$$

The condition $\mathbf{n}$ is a unit vector that requires $\mathbf{n}\cdot\Delta\mathbf{n}=0$ by considering

$$\left.\begin{aligned} \Delta n_x &= -\phi\sin\phi_0 \\ \Delta n_y &= \phi\cos\phi_0, \\ \text{and}\qquad \phi_0 &= q_0 z. \end{aligned}\right\} \tag{5}$$

The fluctuations of the twisted cholesteric phase are represented by the parameter

$$|\phi|^2=|\Delta n_x|^2+|\Delta n_y|^2. \tag{6}$$

It is clear that these fluctuations are biaxial. The component Δn_z represents the tilting of the cholesteric axis. Substitution of equations (4) and (5) in (3) gives the free energy as

$$F(\mathbf{n})=\tfrac{1}{2}K\int_V d\mathbf{r}(\nabla\phi)^2+4q_0\Delta n_z\left\{\cos\phi_0\frac{\partial\phi}{\partial x}+\sin\phi_0\frac{\partial\phi}{\partial y}\right\}+q_0^2(\Delta n_z)^2+(\nabla n_z)^2. \tag{7}$$

The quadratic form can be partially diagonalized by introducing

$$W = \Delta n_z + q_0^{-1}[\cos\phi_0(\partial\phi/\partial x) + \sin\phi_0(\partial\phi/\partial y)] \tag{8}$$

substituting this equation in equation (7)

$$F(\mathbf{n}) = \tfrac{1}{2}K\int_V d\mathbf{r}\Bigg[q_0^2W^2 + (\nabla W)^2 + (\nabla\phi)^2 + 4\frac{\partial\phi}{\partial z}\left\{\sin\phi_0\frac{\partial W}{\partial x} - \cos\phi_0\frac{\partial W}{\partial y}\right\} + \ldots\Bigg] \tag{9}$$

Assuming that W and ϕ vary slowly when compared to the pitch, and then averaging equation (9) over many pitch lengths the free energy becomes

$$\langle F\rangle = \tfrac{1}{2}K\int_V d\mathbf{r}\Bigg[q_0^2W^2 + (\nabla W)^2 + (\nabla\phi)^2 + \tfrac{1}{2}q_0^{-2}\frac{\partial^2}{\partial z^2}\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right) + \tfrac{1}{2}q_0^{-2}\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right)^2\Bigg]. \tag{10}$$

Expanding W and ϕ in Fourier components gives

$$\langle F\rangle = \tfrac{1}{2}K\sum_q[(q_0^2 + q^2)\langle|W|^2\rangle + \{q^2 + \tfrac{1}{2}q_0^{-2} \times (q_z^2q_\perp^2 + q_\perp^4)\}\langle|\phi|^2\rangle], \tag{11}$$

where $q_\perp^2 = q_x^2 + q_y^2$. The average free energy can be written as a sum of two energy terms, pertaining to fluctuations of W and ϕ. Hence

$$\langle F\rangle = \langle F_W\rangle + F_\phi\rangle. \tag{12}$$

The entropy density associated with the fluctuations is obtained by differentiating this equation with respect to temperature

$$\langle\Delta S\rangle = \langle\Delta S_W\rangle + \langle\Delta S_\phi\rangle. \tag{13}$$

Using the equipartition theorem the mean square fluctuations of W and ϕ can be written, from equation (11), as

$$\langle|W|^2\rangle = \frac{kT}{K(q_0^2 + q^2)}, \tag{14}$$

$$\langle|\phi|^2\rangle = \frac{kT}{Kq^2 + 1/2Kq_0^{-2}q_\perp^2(q_z^2 + q_\perp^2)} = \frac{kT}{Kq^2 + \varepsilon}, \tag{15}$$

where ε is assumed to be a temperature dependent constant.

Explicitly fluctuations in W mean fluctuations in n_z and the fluctuations in ϕ are along n_x and n_y, i.e. these fluctuations are in two directions, which show the biaxiality and hence one can expect a high frequency relaxation [11, 12]. In deriving the expression for attenuation it is assumed that the fluctuations of W and ϕ are not interdependent. Further, it is also assumed that the term Kq_0^2 is a constant.

(*a*) *Fluctuations of W*

The fluctuations of W are described by the equilibrium correlation function

$$G(\mathbf{q}) \sim \langle |W|^2 \rangle = \frac{kT}{Kq^2}. \tag{16}$$

The coupling of the sound wave with the fluctuation of W can be achieved by considering the temperature variation of K and the oscillating temperature produced by the sound waves. The induced changes in $G(\mathbf{q})$ and K can be written as

$$\left.\begin{aligned} K &\to K + \frac{\partial K}{\partial T} T_\omega \exp(i\omega t), \\ G(\mathbf{q}) &\to G(\mathbf{q}) + G(\mathbf{q}, \omega) \exp(i\omega t). \end{aligned}\right\} \tag{17}$$

The sound attenuation arises due to delay in the response of the correlation function $G(\mathbf{q})$ to local temperature oscillations. The relaxation equation of $G(\mathbf{q})$ is

$$\nu_1 \frac{\partial}{\partial t} G(\mathbf{q}, t) = Kq^2 G(\mathbf{q}, t), \tag{18}$$

where ν_1 is the effective viscosity coefficient. Substitution of equation (17) into equation (18), and using equation (16), the excess entropy due to fluctuations of W can be obtained as

$$\langle \Delta S_W \rangle = \frac{-1}{16\pi^3} \frac{\partial K}{\partial T} \int_0^{q_{\max}} G_1(\mathbf{q}, \omega) q^2 \, d\mathbf{q}. \tag{19}$$

The dynamic heat capacity is given by

$$\Delta C_W^* = T \frac{\partial \langle \Delta S_W \rangle}{\partial T}. \tag{20}$$

The ultrasonic attenuation is proportional to the imaginary part of ΔC_W^* [13] and can be obtained upon substitution of $G_1(\mathbf{q}, \omega)$ in equation (19)

$$\begin{aligned} \alpha_W \lambda &= \frac{\pi(\gamma_0 - 1)}{C_\mathrm{p}^0} \operatorname{Im} \Delta C_W^* \\ &= \frac{kT^2(\gamma_0 - 1)}{4\pi C_\mathrm{p}^0} \left(\frac{\partial K}{\partial T}\right)^2 K^{-2} q_{\max}^3 G(x), \end{aligned} \tag{21}$$

where

$$G(x) = x\left[1 - \frac{x^{1/2}}{2^{5/2}} \left\{ \ln \left| \frac{1 + (2x)^{1/2} + x}{1 - (2x)^{1/2} + x} \right| + 2 \tan^{-1} \left| \frac{(2x)^{1/2}}{x - 1} \right| \right\} \right],$$

$$x = \frac{\omega}{\omega_0}, \quad \omega_0 = \frac{Kq_{\max}^2}{\nu_1}, \quad \gamma_0 = C_\mathrm{p}^0 / C_\mathrm{V}^0.$$

Here C_p^0 and C_V^0 are the zero frequency heat capacities at constant pressure and volume. These equations are similar to the equations derived for $\alpha\lambda$ in the nematic phase. The value $G(x)$ can be calculated numerically and from the maximum value of $G(x)$, assuming $\omega_\mathrm{r} = \omega_{\max}$, the value of $(\alpha_W \lambda)_{\max}$ can be written as

$$(\alpha_W \lambda)_{\max} = 0{\cdot}3 \frac{kT^2(\gamma_0 - 1)}{4\pi C_\mathrm{p}^0} \left(\frac{\partial K}{\partial T}\right)^2 K^{-2} q_{\max}^3 \tag{22}$$

and

$$\omega_r = \omega_{\max} = 0{\cdot}6\omega_0,$$

which predicts that both $\nu_1\omega_r$ and $(\alpha_W\lambda)_{\max}$ diverge at the transition point as K and $(\partial K/\partial T)^2 K^{-2}$, respectively. At any particular temperature equation (21) can be expressed as

$$\alpha_W/f = A_1(T)G(x), \tag{23}$$

where

$$A_1(T) = \frac{kT^2(\gamma_0 - 1)}{4\pi C_p^0 c_0}\left(\frac{\partial K}{\partial T}\right)^2 K^{-2} q_{\max}^3,$$

where c_0 is the ultrasonic velocity and it is assumed that the velocity dispersion is less. It can be seen that the value $A_1(T)$ diverges like $(\partial K/\partial T)^2 K^{-2}$. Also this constant $A_1(T)$ is proportional to the excess specific heat C_p in the zero frequency limit [14].

(*b*) *The fluctuations of the parameter* ϕ

With regards to the fluctuations of the parameter ϕ the correlation function can be written as

$$G(\mathbf{q}) \sim \langle|\phi|^2\rangle = \frac{kT}{Kq^2 + \varepsilon}. \tag{24}$$

The passage of the sound wave causes a variation in temperature and induces the changes in coefficients K, and $G(\mathbf{q})$ and can be represented in the form

$$\left.\begin{aligned} K &\rightarrow K + \left(\frac{\partial K}{\partial T}\right)T_\omega \exp(i\omega t), \\ \varepsilon &\rightarrow \varepsilon + \left(\frac{\partial \varepsilon}{\partial T}\right)T_\omega \exp(i\omega t), \\ G(\mathbf{q}) &\rightarrow G(\mathbf{q}) + G_1(\mathbf{q}, \omega)\exp(i\omega t). \end{aligned}\right\} \tag{25}$$

The relaxation equation for $G(\mathbf{q}, t)$ is

$$\nu_2 \frac{\partial G(\mathbf{q}, t)}{\partial t} = -(Kq^2 + \varepsilon)G(\mathbf{q}, t), \tag{26}$$

where ν_2 is the effective viscosity coefficient. From equations (24), (25) and (26) the excess entropy due to the passage of the sound wave can be obtained as

$$\langle \Delta S_\phi \rangle = \frac{-1}{16\pi^3}\int_0^{q_{\max}} \left\{ q^2\left(\frac{\partial K}{\partial T}\right) + \left(\frac{\partial \varepsilon}{\partial T}\right)\right\} G(\mathbf{q})\, d\mathbf{q}. \tag{27}$$

From the complex heat capacity

$$\Delta C_\phi^* = T\frac{\partial \langle \Delta S_\phi \rangle}{\partial T}, \tag{28}$$

an expression for the absorption coefficient can be obtained. The integration is solved following the procedure given by Kamenskii and Kats [12]. The equation for the excess absorption is obtained as

$$\begin{aligned}\alpha_{\phi}\lambda &= \frac{\pi(\gamma_0-1)}{C_{\mathrm{p}}^0}\operatorname{Im}\Delta C_{\phi}^{*},\\ &= \frac{kT^2(\gamma_0-1)}{2\pi C^0}\left(\frac{\partial K}{\partial T}\right)^2 K^{-2}q_{\max}^3 I,\end{aligned} \tag{29}$$

where

$$I=\operatorname{Im}\int_0^1 \frac{(\delta+t^2)^2t^2\,dt}{(\beta+t^2)(\beta+t^2-id)},$$

$$\beta=\varepsilon/Kq_{\max}^2,$$

$$d=\omega v_2/Kq_{\max}^2,$$

$$\delta=\left(\frac{\partial\varepsilon}{\partial T}\right)\Big/\left(\frac{\partial K}{\partial T}\right)q_{\max}^2,$$

and

$$\gamma_0=C_{\mathrm{p}}^0/C_{\mathrm{V}}^0.$$

The total attenuation in the cholesteric phase is due to the fluctuations of W and ϕ, i.e. to the director fluctuations. The total attenuation can be expressed as

$$\alpha/f=\alpha_W/f+\alpha_{\phi}/f, \tag{30}$$

substituting the corresponding equations

$$\alpha/f=\frac{kT^2(\gamma_0-1)}{4\pi C_{\mathrm{p}}^0 c_0}\left(\frac{\partial K}{\partial T}\right)^2 K^{-2}q_{\max}^3[G(x)+2I]. \tag{31}$$

For the sake of convenience the integral I is represented as a sum of three terms

$$I=\delta^2 I_1+2\delta I_2+I_3, \tag{32}$$

where

$$\begin{aligned}I_1 &= \beta^{1/2}\{t^{-1}\tan^{-1}(\beta^{1/2})-L-A\},\\ I_2 &= \beta^{1/2}[t^{-1}\tan^{-1}(\beta^{1/2})-\{2+(t^2+1)^{1/2}\}L\\ &\quad -\{2-(t^2+1)^{1/2}\}A],\\ I_3 &= \beta^{3/2}[t\beta^{-1/2}-t^{-1}\tan^{-1}(\beta^{-1/2})\\ &\quad +\{3-t^2+2(t^2+1)^{1/2}\}L\\ &\quad +\{3-t^2-2(t^2+1)^{1/2}\}A].\end{aligned}$$

Here

$$L=\frac{\{(t^2+1)^{1/2}-1\}^{1/2}}{2^{5/2}t}\ln\left[\frac{1+(2\beta)^{1/2}\{(1+t^2)^{1/2}-1\}^{1/2}+\beta(t^2+1)^{1/2}}{1-(2\beta)^{1/2}\{(1+t^2)^{1/2}-1\}^{1/2}+\beta(t^2+1)^{1/2}}\right],$$

$$A=\frac{\{(t^2+1)^{1/2}+1\}^{1/2}}{2^{5/2}t}\left[\pi-2\tan^{-1}\frac{\beta(t^2+1)^{1/2}-1}{(2\beta)^{1/2}\{(t^2+1)^{1/2}+1\}^{1/2}}\right]$$

and

$$t=\frac{\omega v_2}{\varepsilon}.$$

The values of I_1, I_2 and I_3 are calculated for the arbitrary values of t and β. It is found that I_1, I_2 and I_3 follow the approximate relation

$$h=\frac{I_1}{I_2}=\frac{I_2}{I_3}\sim 2 \text{ to } 3. \tag{33}$$

Now equation (31) can be written as

$$\alpha/f=A_1(T)\{G(x)+pI_3\}, \tag{34}$$

where

$$p=2(\delta h+1)^2$$

$$x=zt$$

and

$$z=\beta v_1/v_2.$$

The value of $A_1(T)$ is given by equation (23). The function $\{G(x)+I_3\}$ is plotted against t in figure 1 for $z=5$ and $\beta=0{\cdot}5$. The value v_1/v_2 fixes the position of the maximum in the low frequency range, whereas the value of β fixes the position of the maximum in the

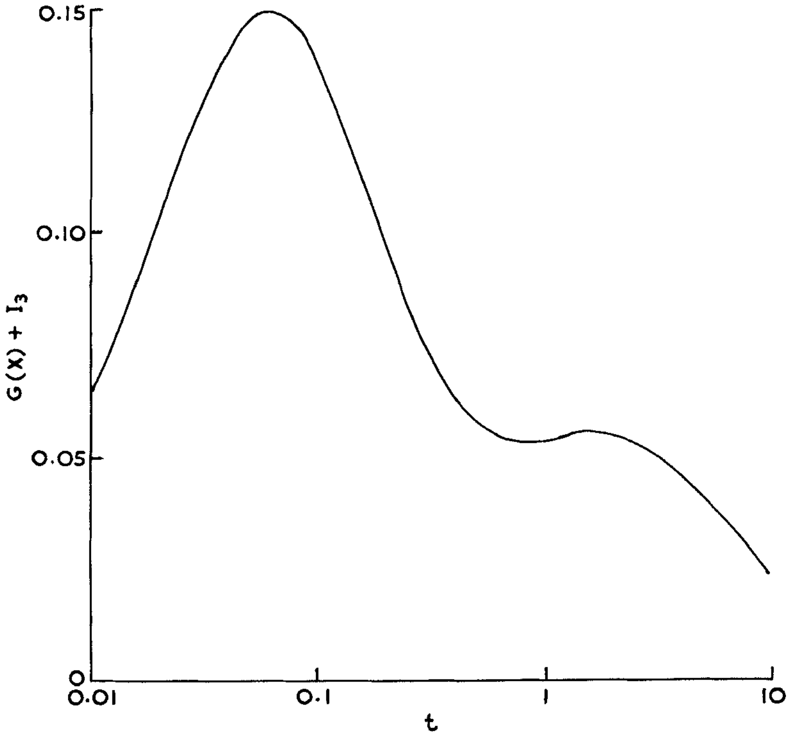


Figure 1. $G(x)+I_3$ versus t at $\beta=0{\cdot}5$ and $z=5$.

high frequency range. Depending on the value of β and v_1/v_2 the maximum value of I_3 will give the value of $d_{\max}$ and the corresponding $\omega_{\max}$ can be assumed to be equal to the relaxation frequency.

According to the proposed theory the excess absorption is described by two relaxational mechanisms. One is due to the fluctuations of the director along the z axis, and is characterized by the relaxation frequency f_{r1}. The second mechanism is due to the biaxial fluctuations of the director, which are characterized by the relaxation frequency f_{r2}. The relaxation frequencies f_{r1} and f_{r2} diverge like K/v_1 and K/v_2, respectively. Further the value of $pA_1(T)$ is proportional to the excess specific heat arising due to the biaxial fluctuations in the zero frequency limit. Thus cholesterics show multiple relaxation phenomena. The high frequency relaxation may be attributed to the phase biaxiality.

In the cholesteric phase two types of viscosities can be expected depending on whether the substance is stressed parallel or perpendicular to the plane of layers [15]. These viscosities may be identified as the viscosities for homeotropic and focal conic textures of cholesteric phase. The experimental value of the ratio of viscosities is found to be ~2·5 in cholesterics [16]. The effective viscosities v_1 and v_2 may be assumed to be proportional to these viscosities.

Another process responsible for the excess anomalous absorption is due to the relaxation of the pitch. Papoular [17] has given the expression for the relaxation time of helical pitch as

$$1/\tau = \frac{K_{22}q_0^2}{v}. \tag{35}$$

It is found that the relaxation frequency associated with the pitch will be of the order of 10^3 Hz. As such the influence of the pitch relaxation on the above mechanisms considered, which will be in the MHz range, may be ignored.

2.2. *Isotropic phase*

It is known that the pretransitional effects in the isotropic phase emerge due to the presence of chiral aggregates. de Gennes [18] has given the free energy for the isotropic phase of cholesterics as

$$\begin{aligned} F = {} & \tfrac{1}{2}A\mathbf{Q}_{\alpha\beta}\mathbf{Q}_{\beta\alpha} + \tfrac{1}{2}L_1\partial_\alpha\mathbf{Q}_{\beta\gamma}\partial_\alpha\mathbf{Q}_{\beta\gamma} \\ & + \tfrac{1}{2}L_2\partial_\alpha\mathbf{Q}_{\alpha\gamma}\partial_\beta\mathbf{Q}_{\beta\gamma} + q_0L_1\varepsilon_{\alpha\beta\gamma}\mathbf{Q}_{\alpha\mu}\partial_\gamma\mathbf{Q}_{\beta\mu}, \end{aligned} \tag{36}$$

where the convention of summation over repeated Greek indices has been adopted. From the Fourier spectra of this equation de Gennes arrived at the averages

$$\left.\begin{aligned} \langle Q\rangle &= \frac{2kT}{3(A+L_1q^2)+2L_2q^2}, \\ \langle|Q_{xy}|^2\rangle &= \frac{kT(1+\xi_1q^2)}{2A\{(1+\xi_1^2q^2)^2-4q_0^2q^2\xi_1^4\}}, \\ \xi_1^2 &= L_1/A. \end{aligned}\right\} \tag{37}$$

As the other components Q_{xz} and Q_{yz} give similar results to that for Q_{xy} the terms are not considered. Neglecting the q^4 terms and replacing

$$\left.\begin{aligned} L' &= \tfrac{3}{2}(L_1 + 2L_2) \\ A' &= \tfrac{3}{2}A \\ A'' &= 2A \\ \text{and}\qquad M &= \left(2L_1 - \frac{4q_0^2L_1^2}{A}\right), \end{aligned}\right\} \tag{38}$$

equation (37) can be written in a convenient form as

$$\left.\begin{aligned} \langle Q^2\rangle &= \frac{kT}{A' + L'q^2}, \\ \langle |Q_{xy}|^2\rangle &= \frac{kT}{A'' + Mq^2}. \end{aligned}\right\} \tag{39}$$

From these equations it can be seen that the fluctuation of the tensor order parameter is a combined effect of fluctuations of Q and the cross term Q_{xy}, which includes the chirality. If L_1 is a temperature independent constant the temperature dependence of M is only due to the chiral term. As already pointed out earlier we may expect, at higher temperatures, M is a temperature insensitive constant and the problem turns into a quasi-nematic form.

To derive the ultrasonic attenuation it is assumed that the coupling of the sound wave is achieved through the temperature variation of A and M. The expression for the absorption coefficient is derived following the methodology used in the previous case.

2.3. *Fluctuations of Q*

For the fluctuations of Q the equations are the same as those derived by Imura and Okano [19]

$$\alpha_z\lambda = \frac{kT2(\gamma_0 - 1)}{16\pi C_p^0}\left(\frac{3}{2}\right)^{3/2}(a/L')^2(A/L')^{-1/2}F(x), \tag{40}$$

where

$$F(x) = (2x)^{1/2}[x + (x^2 + 1)^{1/2}]^{1/2} - (2x),$$

$$x = \omega_0/\omega, \quad \omega_0 = (3/2)A(T)/v_1 \quad \text{and} \quad \gamma_0 = C_p^0/C_V^p.$$

2.4. *Fluctuations of Q_{xy}*

As the sound wave passes through the medium, it is assumed that the coupling of the sound wave to the correlation function is through the temperatures variation of A'' and M. The excess entropy due to the passage of the sound wave can be derived as

$$\langle \Delta S_{xy}\rangle = \frac{1}{16\pi^3}\int_0^{q_{\max}}\left\{q^2\left(\frac{\partial M}{\partial T}\right) + \frac{\partial A''}{\partial T}\right\}G(\mathbf{q})\,d\mathbf{q}. \tag{41}$$

From the complex heat capacity,

$$\Delta C_{xy}^* = \mathrm{T}\,\frac{\partial\langle \Delta S_{xy}\rangle}{\partial T}, \tag{42}$$

the expression for the absorption coefficient can be obtained. The integration is solved using the procedure given by Kamenskii and Kats [12]. The equation derived for the excess absorption is

$$\alpha_{xy}\lambda = \frac{kT^2(\gamma_0 - 1)}{2\pi C_p^0} q_{\max}^3 \left(\frac{\partial M}{\partial T}\right)^2 M^{-2} I, \tag{43}$$

where

$$I = \mathrm{Im} \int_0^1 \frac{(\delta + t^2)^2 t^2 \, dt}{(\beta + t^2)(\beta + t^2 - id)},$$

$$\beta = \frac{2A}{Mq_{\max}^2}, \quad d = \frac{\omega v_2}{Mq_{\max}^2} \quad \text{and} \quad \delta = \frac{\mathrm{A}A}{(\partial M/\partial T) q_{\max}^2}.$$

The total excess absorption is a sum of these two processes

$$\alpha/f = \alpha_z/f + \alpha_{xy}/f \tag{44}$$

substituting the corresponding equations

$$\alpha/f = -\frac{kT^2(\gamma_0 - 1)}{16\pi C_p^0 c_0} \frac{(3/2)^{1/2}(a/L')^2(A/L')^{1/2}}{8} \{F(x) + pI_3\}, \tag{45}$$

where

$$p = \frac{8(\partial M/\partial T)^2 M^{-2} q_{\max}^3}{(3/2)^{1/2}(a/L')^2(A/L')^{-1/2}} (\delta h + 1)^2,$$

$$t = \frac{\omega v_2}{2A}, \quad x = zt \quad \text{and} \quad z = \frac{4}{3}\frac{v_1}{v_2}.$$

This equation can be expressed as

$$\alpha/f = A_1(T)\{F(x) + pI_3\}, \tag{46}$$

where

$$A_1(T) = \frac{kT^2(\gamma_0 - 1)}{16\pi C_p^0 c_0} \frac{(3/2)^{1/2}(a/L')^{1/2}(A/L')^{-1/2}}{8}.$$

The integral I_3 is given in equation (32).

Thus even in the isotropic phase multiple relaxation phenomena can be expected. It is clear that when the chiral terms are absent these equations reduce the equations derived by Imura and Okano for the isotropic phase. When the chiral terms are present the relaxation frequency f_{r2} in the high frequency tail is a decreasing function of temperature.

2. Experimental results

The ultrasonic absorption has been measured using a variable path pulse transmission technique. The equipment used was Chesapeak U-100 signal generator, an Arenberg PA-620B tuned preamplifier and an Arenberg WA-600E amplifier along with Marconi step attenuator. For path length variations a micrometer carries the upper delay rod. Horizontal and vertical alignment between the two rods is ensured by the measurement of absorption at several frequencies in standard liquids, like benzene and water.

The temperature of the sample under investigations was controlled to within ±0·1 °C using a thermostat and was kept at the desired temperature for at least 4 hours, to attain the equilibrium temperature, before any absorption measurement was made. The CV sample was obtained from Aldrich and has the transition temperatures:

$$\text{Solid} \xleftrightarrow{93^{\circ}\mathrm{C}} \text{Cholesteric} \xleftrightarrow{\sim 103{\cdot}2^{\circ}\mathrm{C}} \text{Blue phase} \xleftrightarrow{103{\cdot}5^{\circ}\mathrm{C}} \text{Isotropic}$$

The transition temperatures were measured using a polarizing microscope in conjunction with a hot stage. All of the transitions are found to be in close agreement with those in literature.

In order to avoid any possible contamination, at most of the temperatures, fresh samples of the same batch were used and a uniform thermal history of the sample was maintained. (The rate of sample heating was ~0·3°C per minute).

Absorption measurements were performed by maintaining the amplitude of the receiver signal constant, an increase in attenuation for increased path length being compensated by decreasing the attenuation of the attenuator.

All of the measurements were performed in the Fresnel diffraction region and the total distance over which the measurements were made was kept as uniform as possible. The absence of thermal gradients was ensured by observing the attenuation when the transducer was moved up and down. Further care was taken not to move the fused quartz delay rod too fast, in order to disturb the sample as little as possible. At all frequencies and temperatures the absorption was measured for three to four different acoustic path lengths and the average value is presented. To obtain a set of absorption measurements at any frequency took about 30 min. The accuracy of absorption measurements is better than ±3 per cent.

The temperature dependence of the ultrasonic absorption coefficient (α/f^2) for certain frequencies is shown in figure 2. At lower frequencies the absorption coefficient shows a prominent increase near the mesophase–isotropic transition. As the frequency is increased, however, the absorption maximum becomes less prominent and at frequencies above 25 MHz the absorption is nearly temperature independent.

Figure 3 shows the frequency dispersion of absorption at different temperatures. From these figures it is clear that the absorption of ultrasonic waves shows anomalous behaviour near the cholesteric–isotropic transition.

4. Discussion

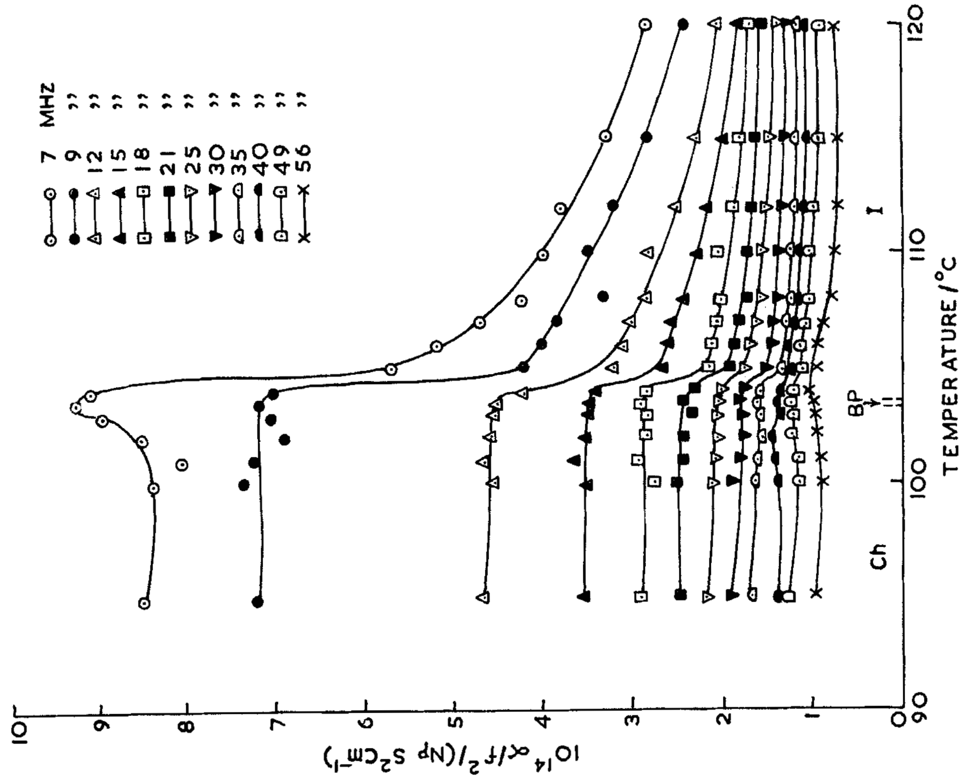
4.1. *Cholesteric phase*

It has already been mentioned that the theoretical frequency dispersion of the ultrasonic absorption of the cholesteric phase is characteristic of multiple relaxation behaviour. In fact our experimental results show a deviation from the single relaxation curve given by

$$\alpha/f^2 = \frac{A}{1+(f/f_r)^2} + B,$$

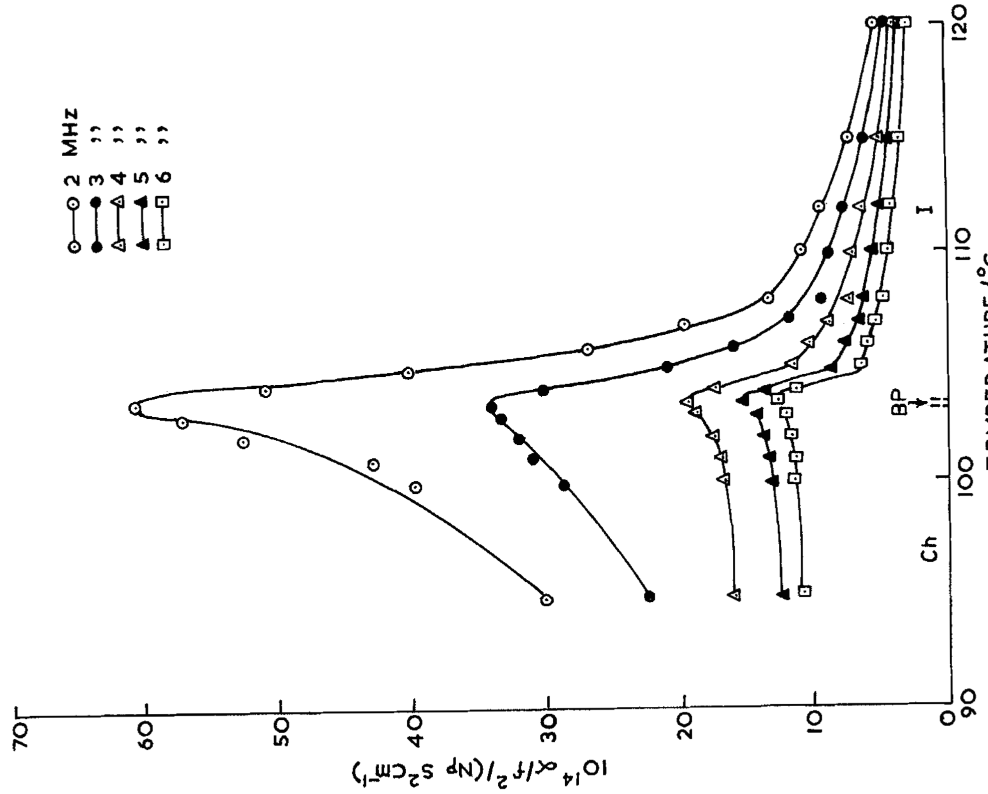
where A and B are constants. We have therefore fitted the ultrasonic absorption data in the cholesteric phase, to the double relaxation equation

$$\alpha/f^2 = \sum_{i=1}^{2} \frac{A_i}{1+(f/f_{ri})^2} + B$$



7 MHz
9 ,,
12 ,,
15 ,,
18 ,,
21 ,,
25 ,,
30 ,,
35 ,,
40 ,,
49 ,,
56 ,,
$10^{14}\alpha/f^2/(\mathrm{Np\ s^2 cm^{-1}})$
0
1
2
3
4
5
6
7
8
9
10
90
100
110
120
Ch
BP
I
TEMPERATURE /°C

(b)



2 MHz
3 ,,
4 ,,
5 ,,
6 ,,
$10^{14}\alpha/f^2/(\mathrm{Np\ s^2 cm^{-1}})$
0
10
20
30
40
50
60
70
90
100
110
120
Ch
BP
I
TEMPERATURE /°C

(a)

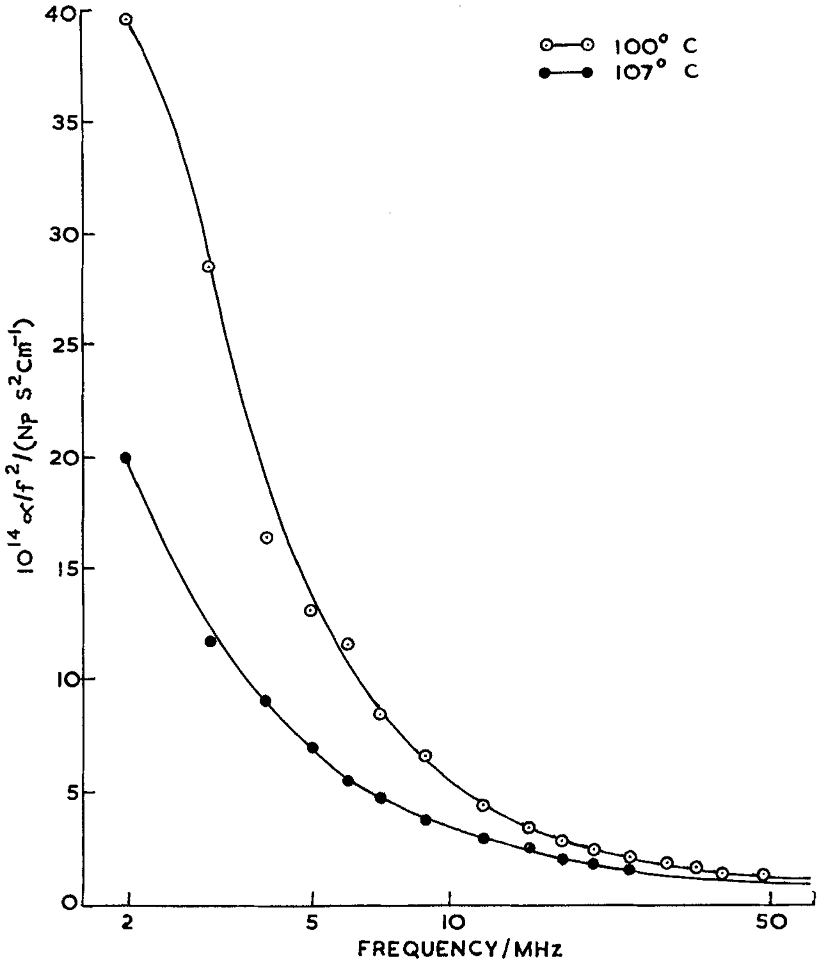


Figure 3. Frequency dispersion of α/f^2 in CV at different temperatures.

Computed values of f_{r1}, f_{r2}, $A_1(T)$, p together with their standard deviation (s.d.) and v_1/v_2 for cholesteric an isotropic phases of CV at different temperatures.

Temperature °C	f_{r1} MHz	f_{r1} s.d.	f_{r2} MHz	f_{r2} s.d.	$A_1(T) \times 10^8$ Np s cm^{-1}	$A_1(T)$ s.d.	p	p s.d.	v_1/v_2
115	18·6	2·1			64·4	10·6			
112	11·9	1·2			78·4	12·3			
110	10·5	0·8			90·8	9·1			
108	9·7	0·6			87·8	8·7			
107	8·4	0·6			106·6	6·8			
106	6·5	0·3			127·2	8·0			
105	4·0	0·3	14·8	2·1	593·8	27·4	0·6	0·03	4·9
104	2·7	0·1	18·4	4·0	1719·6	52·2	0·3	0·01	9·0
103·5	2·7	0·1	13·5	2·0	603·9	35·5	0·3	0·02	2·5
103	2·6	0·1	14·0	1·9	568·5	29·4	0·4	0·02	2·7
102	3·0	0·2	14·5	2·0	521·5	29·0	0·5	0·03	2·4
101	3·0	0·2	17·5	8·0	480·4	17·2	0·6	0·02	2·9
100	3·3	0·2	15·7	2·4	443·7	22·7	0·7	0·04	2·3
95	4·3	0·2	16·7	2·6	381·6	15·0	0·6	0·02	1·9

following the method of Ito *et al.* [20]. The values of the relaxation frequencies thus obtained are presented along with the estimated standard deviations in the table. The values obtained for f_{r1} are of the same order of magnitude as that reported for cholesteryl caprinate by Zvereva [3] and for uniaxial nematics.

At this stage to have an idea about the order of magnitude of the values of ν_1/ν_2, $A_1(T)$ and p, the absorption results in the mesomorphic phase are fitted to equation (34). The best fit values of the parameters ν_1/ν_2, $A_1(T)$ and p together with their standard deviations are presented in the table. The theoretical values of α/f calculated for some temperatures from the best fit values of the parameters are compared with the experimental values in figure 4.

The values of ν_1/ν_2 obtained from this analysis are in close agreement with the ratio of viscosities of focalconic and homeotropic textures of the cholesteric phase [16] and can be interpreted as verifying the proposed theory.

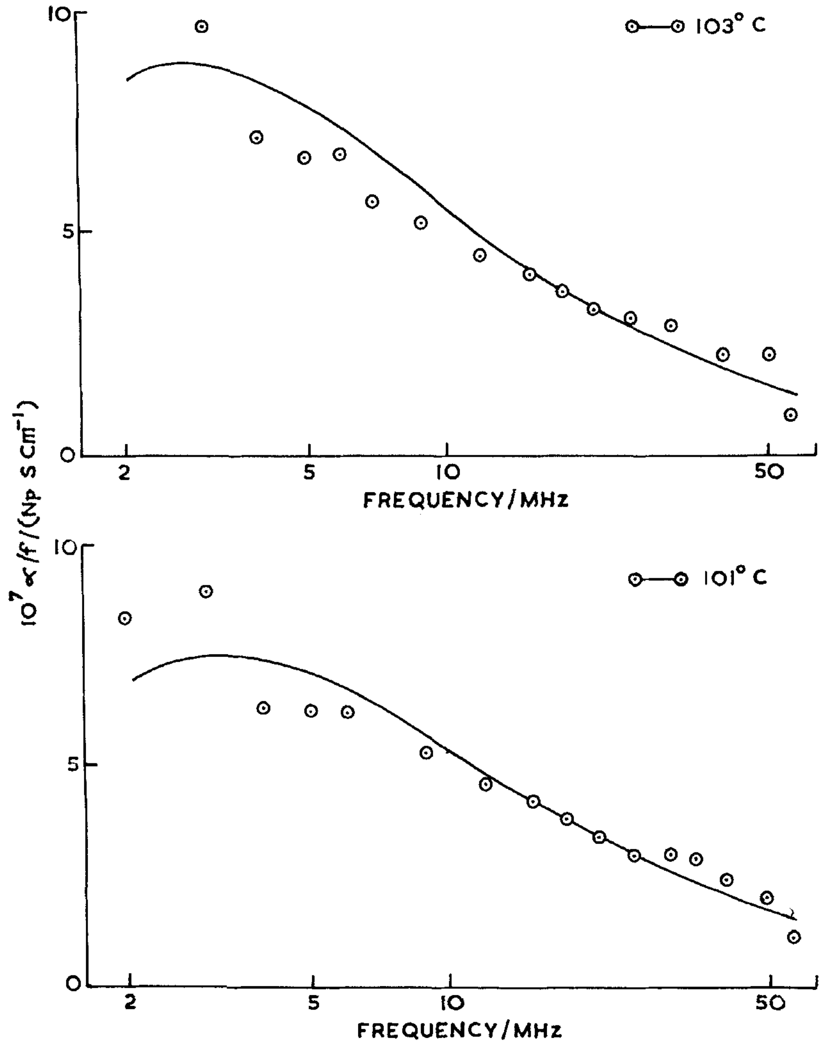


Figure 4. Comparison of theoretical and experimental α/f values in the cholesteric phase of CV at 103°C and 101°C. The solid line is theoretical and the points are experimental.

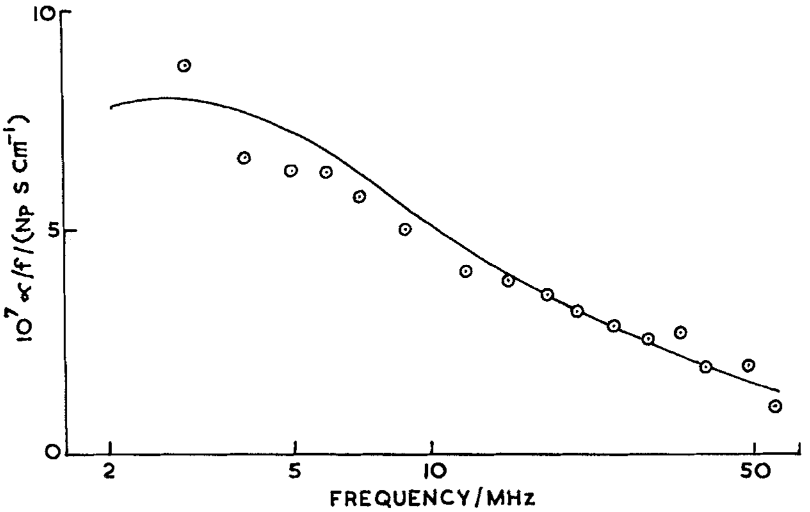


Figure 5. Comparison of theoretical and experimental α/f values in the isotropic phase of CV at 104°C. The solid line is theoretical and points are experimental.

4.2. *Isotropic phase*

Equation (46) suggests that the absorption in the isotropic phase is also characterized by the two relaxation frequencies. As such we have compared the experimental data to the double relaxation equation. However, it is found that at most of the temperatures the absorption agrees well with the single relaxation equation. This may be due to the reason that the chirality exists only over a limited temperature range. In the limited temperature range ~2°C (see the table), over which the absorption showed double relaxation behaviour, the higher relaxation frequency f_{r2} is found to be a decreasing function of temperature. Now the absorption results in the isotropic phase are fitted to equation (46). The best fit values of v_1/v_2, $A_1(T)$ and p are presented in the table. The best fit theretical absorption values and experimental absorption results at 104°C are compared in figure 5.

In conclusion, the absorption in the cholesteric and isotropic phases of CV could be satisfactorily explained by assuming that both fluctuations of n_z and the biaxiality contribute to the absorption. In analysing the results, however, we have not taken into account the effect of low frequency pitch relaxation ($\sim 10^3$ Hz), as its contribution to the absorption in the present experimental frequency range is much smaller.

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