

# On the frequency dependence of ultrasonically induced birefringence in isotropic phase of liquid crystal: 5CB (*p*-*n*-pentyl *p*'-cyanobiphenyl)

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Theoretical expressions for the ultrasonically induced birefringence of liquids are obtained in the frame work of de Gennes' phenomenological theory. The intensity and frequency dependence of ultrasonically induced birefringence in the isotropic phase of *p*-*n*-pentyl *p*'-cyanobiphenyl (5CB) was measured in order to examine the usefulness of birefringence measurements for investigating dynamical properties liquids. The observed birefringence was proportional to the square root of ultrasonic intensity. The birefringence divided by the square root of ultrasonic intensity increases with increasing frequency and appears to saturate when the ultrasonic frequency approaches the relaxation frequency of molecular reorientation. The observed values of birefringence were reproduced satisfactorily by the expression derived in this paper. © 1999 American Institute of Physics. [S0021-9606(99)51728-5]

## I. INTRODUCTION

Birefringence has been observed in some liquids and solutions under the irradiation of longitudinal ultrasound.<sup>1-8</sup> For large particles of anisotropic shape such as rodlike and planar colloidal particles, ultrasonic radiation pressure produces a stationary torque on the particles and induces reorientational order as a whole, because the orientational relaxation frequency of particles is much smaller than that of ultrasound frequency. In this case, the induced birefringence is proportional to the ultrasonic intensity.<sup>1-5</sup> The dynamical properties of large particles can be investigated by following the decay of the birefringence after rapid cessation of ultrasonic irradiation.<sup>1-5</sup>

For neat liquids, however, a sinusoidal velocity gradient can directly produce sinusoidal orientational order. The reorientational order produced is not uniform but propagates as waves and the induced birefringence should be proportional to the ultrasonic amplitude, that is, the square root of the ultrasonic intensity.<sup>1,6-8</sup> In the neat liquids, we cannot obtain the transient decay curve after rapid cessation of ultrasonic irradiation. If the relaxation frequency for reorientational motion is close to the applied ultrasound frequency, the birefringence per amplitude of the applied ultrasonic wave should be affected by the reorientational relaxation processes of the molecules. Measurement of birefringence as a function of frequency gives information of the reorientational motion in liquids.

Problems with regard to the coupling of the reorientational mode to the translational mode have been investigated mainly by flow birefringence and depolarized VH light scattering.<sup>9-18</sup> Theories for the flow birefringence and the depolarized VH light scattering were constructed independently on the basis of the de Gennes' phenomenological

theory<sup>9-12</sup> and irreversible statistical mechanics.<sup>12-18</sup> In both theories, the coupling of reorientational mode to the shear mode was taken into account. The expressions derived from both theories are consistent each other.<sup>12</sup> In the case of ultrasonically induced birefringence, where coupling of the reorientational mode to the longitudinal mode should be taken into account, the formula for the birefringence from the irreversible statistical treatment has already been derived by Lipeles and Kivelson.<sup>19</sup> The problem of the coupling of the reorientational mode to the longitudinal mode should be also taken into account in derivation of the spectra density for the polarized VV and the depolarized HH light scattering. Kivelson and co-workers have extensively investigated the problem from the irreversible statistical mechanics.<sup>20</sup> Grubbs and MacPhail investigated the line shape of stimulated Brillouin gain spectra and discussed the coupling of the reorientational mode to the longitudinal mode.<sup>21</sup> Unlike the earlier theory of Lipeles and Kivelson,<sup>19</sup> they used four independent variables to derive the spectral density for the VV light scattering. On the other hand, Wang derived formulae for the spectrum of density fluctuation of the VV light scattering from the de Gennes' approach.<sup>22</sup> In this paper, we will present a theoretical expression of the ultrasonically induced birefringence in terms of the de Gennes' phenomenological theory and compare it to that obtained by Lipeles and Kivelson. We also compare our results with the earlier theories.<sup>1,23-25</sup>

The isotropic phase of liquid crystals is most appropriate to examine the expression obtained here, because the relaxation frequencies of the orientational motions are the same order of magnitude as the ultrasonic frequencies usually used for ultrasonic relaxation studies.<sup>26</sup> Besides, the flow birefringence for isotropic phase of liquid crystal, 5CB, has been already reported by Martinoty *et al.*<sup>7</sup> The values of the flow birefringence and the relaxation frequencies are required to reproduce the frequency dependence of the ultrasonically induced birefringence.

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To confirm our expression quantitatively, we measured the ultrasonically induced birefringence of *p*-*n*-pentyl *p*'-cyanobiphenyl (5CB) in the isotropic phase as a function of frequency.

## II. THEORY

Stress induced birefringences in liquids of anisotropic molecules, such as those induced ultrasonically or by flow, can be understood in the theoretical frame work of de Gennes' phenomenological treatment<sup>9,10</sup> of the coupling of the reorientational order parameter to the strain rate tensor for an anisotropic molecule in liquids and solutions. First, we will present the generalized transport equations taking into account coupling of the orientational order to the strain rate tensor. Second, we will discuss the expressions for ultrasonically induced birefringence.

### A. Transport equations

To obtain general expressions for the transport equations, we need the following the equations of mass and momentum conservation:

$$\delta\dot{\rho} + \rho\partial_k v_k = 0, \quad (1)$$

$$\rho\dot{v}_\alpha = \partial_\beta(\sigma_{\alpha\beta} - \delta p\delta_{\alpha\beta}), \quad (2)$$

where  $\rho$  is the equilibrium density,  $\delta\rho$  and  $\delta p$  are the mass and pressure fluctuations, respectively,  $\sigma_{\alpha\beta}$  is the stress tensor and  $v_\alpha$  is the velocity vector and repeated indices are summed. For the sake of simplicity, we have neglected here the effects of temperature fluctuations. The stress tensor and strain rate tensor,  $\sigma_{\alpha\beta}$  and  $A_{\alpha\beta}$ , can be written as the sum of isotropic and anisotropic parts:

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^i + \sigma_{\alpha\beta}^a, \quad (3)$$

$$A_{\alpha\beta} = A_{\alpha\beta}^i + A_{\alpha\beta}^a. \quad (4)$$

The isotropic and anisotropic parts of the strain rate tensor are, respectively, written as follows:

$$A_{\alpha\beta}^i = \partial_k v_k \delta_{\alpha\beta} / 3, \quad (5)$$

$$A_{\alpha\beta}^a = (\partial_\alpha v_\beta + \partial_\beta v_\alpha) / 2 - \partial_k v_k \delta_{\alpha\beta} / 3. \quad (6)$$

To consider the coupling of translational mode to reorientational mode, we will use de Gennes' phenomenological treatment and take the tensor order parameter of molecular reorientation  $Q_{\alpha\beta}$  and its conjugated stress  $\phi_{\alpha\beta}$  as internal variables.<sup>9,10</sup> Since the tensor order parameter is anisotropic (i.e., traceless), the anisotropic part of  $\sigma_{\alpha\beta}$  and  $A_{\alpha\beta}$  can couple to the reorientational mode. The relation between "force" and "flow" can thus be written by the expression of nonequilibrium thermodynamics as follows:

$$\sigma_{\alpha\beta}^i = 3\eta_V A_{\alpha\beta}^i, \quad (7)$$

$$\sigma_{\alpha\beta}^a = 2\eta_S A_{\alpha\beta}^a + 2\mu\dot{Q}_{\alpha\beta}, \quad (8)$$

$$\phi_{\alpha\beta} = 2\mu A_{\alpha\beta}^a + \nu\dot{Q}_{\alpha\beta}, \quad (9)$$

where  $\eta_V$  is the volume viscosity,  $\eta_S$  is the shear viscosity, and  $\mu$  and  $\nu$  are viscosity parameters introduced by de Gennes:  $\mu$  is a measure of coupling between  $Q_{\alpha\beta}$  and the

anisotropic part of the flow field, and  $\nu$  is related to the relaxation of  $Q_{\alpha\beta}$ . The dot above  $Q_{\alpha\beta}$  denotes taking the time derivative.

In the original de Gennes' theory, the strain rate tensor  $A_{\alpha\beta} = (\partial_\alpha v_\beta + \partial_\beta v_\alpha) / 2$  (Refs. 9, 10) was used in Eqs. (8) and (9). He only dealt with incompressible fluids in which case the relation  $A_{\alpha\beta} = A_{\alpha\beta}^a$  holds. To extend his treatment to the general case, for example plane sound wave propagation, the anisotropic part of the strain rate tensor should be coupled to the tensor order parameter  $Q_{\alpha\beta}$ . If the fluctuation of  $Q_{\alpha\beta}$  is small, the relation of  $Q_{\alpha\beta}$  and  $\phi_{\alpha\beta}$  is written as<sup>9,10</sup>

$$\phi_{\alpha\beta} = -A Q_{\alpha\beta}, \quad (10)$$

where  $A$  is the quadratic expansion coefficient of free energy in  $Q_{\alpha\beta}$ . We also need the following thermodynamic relation:

$$\delta\rho = (\partial\rho/\partial p)_s \delta p = c_0^{-2} \delta p, \quad (11)$$

where  $c_0$  is the sound velocity in the low frequency limit.

From Eqs. (1) to (11), we can deduce the following linearized transport equations:

$$\delta\dot{\rho} + \rho\partial_k v_k = 0, \quad (12)$$

$$\rho\dot{v}_\alpha = \partial_\beta(3\eta_V A_{\alpha\beta}^i + 2\eta_S A_{\alpha\beta}^a + 2\mu\dot{Q}_{\alpha\beta} - \delta\rho c_0^2 \delta_{\alpha\beta}), \quad (13)$$

$$-A Q_{\alpha\beta} = 2\mu A_{\alpha\beta}^a + \nu\dot{Q}_{\alpha\beta}. \quad (14)$$

For a longitudinal velocity field with  $\partial_x v_x \neq 0$ ,  $\partial_y v_y = \partial_z v_z = 0$ , Eq. (12) to Eq. (14) can be written as:

$$\delta\dot{\rho} + \rho\partial_x v_x = 0, \quad (15)$$

$$\dot{v}_x = \frac{1}{\rho} \left( \eta_V + \frac{4}{3}\eta_S \right) \partial_x^2 v_x + 2\frac{\mu}{\rho} \partial_x \dot{Q}_{xx} - \frac{c_0^2}{\rho} \partial_x \delta\rho, \quad (16)$$

$$\dot{Q}_{xx} = -\Gamma Q_{xx} - \frac{4}{3} \frac{\mu}{\nu} \partial_x v_x, \quad (17)$$

$$\dot{Q}_{yy} = -\Gamma Q_{yy} + \frac{2}{3} \frac{\mu}{\nu} \partial_x v_x, \quad (18)$$

$$\dot{Q}_{zz} = -\Gamma Q_{zz} + \frac{2}{3} \frac{\mu}{\nu} \partial_x v_x, \quad (19)$$

where  $\Gamma$  is the relaxation frequency of reorientational order, which is related to  $\nu$  and  $A$  as  $\Gamma = A/\nu$ . Taking into account the traceless character of the tensor order parameter and the requirement from the longitudinal symmetry, the relations  $Q_{xx} + Q_{yy} + Q_{zz} = 0$  and  $Q_{yy} = Q_{zz}$  must hold. Equations (17) to (19) satisfy these requirements and the transport equations can be written by only three independent variables  $\delta\rho$ ,  $v_x$ ,  $Q_{xx}$ . Equations (15) to (17) are fundamental equations for the sound propagation and the ultrasonically induced birefringence. The dispersion relation for sound propagation is discussed in Appendix A and is compared with Grubbs and MacPhail's treatment based on irreversible statistical mechanics.

## B. Ultrasonically induced birefringence

In this section, we will derive an expression for the ultrasonically induced birefringence using the transport equations obtained in the previous section. Birefringence is induced when the local dielectric tensor becomes anisotropic due to the local orientational order of the anisotropic molecules.

The tensor order parameter  $Q_{\alpha\beta}$  is related to the local dielectric tensor as<sup>11</sup>

$$Q_{\alpha\beta} = \frac{3}{2} \frac{(\varepsilon_{\alpha\beta} - \bar{\varepsilon} \delta_{\alpha\beta})}{\Delta\varepsilon}, \quad (20)$$

where  $\varepsilon_{\alpha\beta}$  is the dielectric tensor,  $\bar{\varepsilon}$  is the mean dielectric constant in the absence of external perturbations and  $\Delta\varepsilon$  is the anisotropy in the dielectric constant if all molecules are perfectly aligned in one direction. We choose  $x$  to be the direction in which ultrasonic wave is propagating and  $z$  to be direction of the optical beam whose polarization lies in the  $yz$  plane. The direction of the polarization is at  $45^\circ$  from the  $y$  axis.

Ultrasound propagating in the  $x$  direction induces a non-zero component of  $Q_{\alpha\beta}$  and the resultant breakdown in the isotropy of the dielectric tensor causes the birefringence. The relation of  $Q_{\alpha\beta}$  to the birefringence can be obtained as follows:

$$\begin{aligned} \Delta n &= \sqrt{\varepsilon_{xx}} - \sqrt{\varepsilon_{yy}} \\ &= \sqrt{\bar{\varepsilon} + 2\Delta\varepsilon Q_{xx}/3} - \sqrt{\bar{\varepsilon} + 2\Delta\varepsilon Q_{yy}/3} \\ &\cong \frac{\Delta\varepsilon}{3\sqrt{\bar{\varepsilon}}} (Q_{xx} - Q_{yy}). \end{aligned} \quad (21)$$

As mentioned in the previous subsection, the relations  $Q_{xx} + Q_{yy} + Q_{zz} = 0$  and  $Q_{yy} = Q_{zz}$  hold. Therefore, Eq. (21) can be written as

$$\Delta n = \frac{\Delta\varepsilon}{2\bar{n}} Q_{xx}, \quad (22)$$

where  $\bar{n}$  is the mean refractive index which refers to the dielectric constant as  $\bar{n} = \sqrt{\bar{\varepsilon}}$ . We consider a plane wave propagating in the  $x$  direction:  $Q_{xx} = \tilde{Q}_{xx} \exp[i(\omega t - kx)]$ ,  $\delta\rho = \delta\tilde{\rho} \exp[i(\omega t - kx)]$ ,  $v_x = \tilde{v}_x \exp[i(\omega t - kx)]$ .

Equations for the density conservation and the relaxation of the order parameter are written as

$$i\omega \delta\tilde{\rho} - ik\rho\tilde{v}_x = 0, \quad (23)$$

$$i\omega \tilde{Q}_{xx} + \Gamma \tilde{Q}_{xx} - ik \frac{4\mu}{3\nu} \tilde{v}_x = 0. \quad (24)$$

Eliminating  $\tilde{v}_x$  from Eqs. (23) and (24), the relation of  $\delta\tilde{\rho}$  to  $\tilde{Q}_{xx}$  is obtained as

$$\tilde{Q}_{xx} = \frac{4}{3} \frac{\mu}{\nu} \frac{\delta\tilde{\rho}}{\rho} \frac{i\omega}{i\omega + \Gamma}. \quad (25)$$

Substituting the thermodynamic relation,

$$\delta\tilde{\rho} = (\partial\rho/\partial p)_s \delta\tilde{p} = c_0^{-2} \delta\tilde{p}, \quad (26)$$

where  $\delta\tilde{p}$  is the amplitude of the pressure perturbation, into Eq. (25) and using the definition of the ultrasonic intensity,  $W_U = \delta\tilde{p}^2/2\rho c_0$ , the modulus of  $\tilde{Q}_{xx}$  is obtained as

$$|\tilde{Q}_{xx}| = \frac{4}{3} \frac{\mu}{A} \sqrt{\frac{2W_U}{\rho c_0^3}} \frac{\omega}{\sqrt{1 + (\omega/\Gamma)^2}}. \quad (27)$$

The root mean square of the ultrasonically induced birefringence  $\Delta n_{\text{rms}}$  is acquired as

$$\Delta n_{\text{rms}} = \frac{\Delta\varepsilon}{2\bar{n}} \cdot \frac{|\tilde{Q}_{xx}|}{\sqrt{2}} = \frac{2\Delta\varepsilon\mu}{3\bar{n}A} \sqrt{\frac{W_U}{\rho c_0^3}} \frac{\omega}{\sqrt{1 + (\omega/\Gamma)^2}}. \quad (28)$$

The flow birefringence  $\Delta n_f$  under a constant shear strain rate  $G$  is obtained as Eq. (B4) in Appendix B:

$$\Delta n_f = -2\mu G \Delta\varepsilon / (3\bar{n}A). \quad (29)$$

Thus, the ultrasonically induced birefringence is related to the flow birefringence by

$$\Delta n_{\text{rms}} = \left| \frac{\Delta n_f}{G} \right| \sqrt{\frac{W_U}{\rho c_0^3}} \frac{\omega}{\sqrt{1 + (\omega/\Gamma)^2}}. \quad (30)$$

Frenkel derived an expression for the ultrasonically induced birefringence similar to Eq. (28).<sup>23,24</sup> His treatment is very akin to ours in coupling the anisotropy tensor of the molecular orientation to the traceless part of the strain rate tensor. Our treatment, however, is based on a standard theory of irreversible thermodynamics and gives a concrete expression for the proportionality constant that appeared in his theory.

Peterlin derived the following expression for ultrasonically induced birefringence using the rotational diffusion equation for an ellipsoid under a longitudinal ultrasound:<sup>24,25</sup>

$$\begin{aligned} \Delta n_{\text{rms}}^{\text{Peterlin}} &= \bar{n} \left( \frac{\bar{n}^2 + 2}{3\bar{n}} \right)^2 \frac{4\pi}{5} N_0 (\alpha_1 - \alpha_2) \\ &\quad \times \frac{\bar{\beta}}{6D} \sqrt{\frac{W_U}{\rho c_0^3}} \frac{\omega}{\sqrt{1 + (\omega/6D)^2}}, \end{aligned} \quad (31)$$

where  $N_0$  is the number density of the ellipsoid,  $\alpha_1$  and  $\alpha_2$  are the polarizability along and perpendicular to the principal axis of the ellipsoid, respectively, and  $D$  is the rotational diffusion constant.  $\bar{\beta}$  is a constant depending on the molecular shape and defined as  $\bar{\beta} = (a_1^2 - a_2^2)/(a_1^2 + a_2^2)$ , where  $a_1$  and  $a_2$  are the long and short diameters of the ellipsoid, respectively. Although the collective effect was not included in Peterlin's theory, the intensity and frequency dependence is the same as that in Eq. (28), if the term  $6D$  is replaced by  $\Gamma$ . The formula for flow birefringence is also obtained in the same framework as<sup>24,25</sup>

$$\left| \frac{\Delta n_f}{G} \right|^{\text{Peterlin}} = \bar{n} \left( \frac{\bar{n}^2 + 2}{3\bar{n}} \right)^2 \frac{4\pi}{5} N_0 (\alpha_1 - \alpha_2) \frac{\bar{\beta}}{6D}. \quad (32)$$

Substituting Eq. (32) into (31), the following relation is obtained:

$$\Delta n_{\text{rms}}^{\text{Peterlin}} = \left| \frac{\Delta n_f}{G} \right|^{\text{Peterlin}} \sqrt{\frac{W_U}{\rho c_0^3}} \frac{\omega}{\sqrt{1 + (\omega/6D)^2}}. \quad (33)$$

This equation is the same form as Eq. (30).

Martinoty and Bader obtained Eq. (28) for the ultrasonic birefringence of the isotropic phase of liquid crystals substituting Eq. (B4) in place of  $|\Delta n_f/G|^{Peterlin}$  into Eq. (33). Their indirect derivation of Eq. (28) is confirmed by this paper.

Expressions for flow<sup>14</sup> and ultrasonically induced birefringence<sup>19</sup> were obtained by Kivelson and co-workers based on an irreversible statistical treatment as

$$\left| \frac{\Delta n_f}{G} \right|^{Kivelson} = \frac{1}{\bar{n}} \left( \nu_K \cdot \frac{R_{Total} \Delta_\mu}{1 + \Delta_\mu} \cdot \frac{\eta}{k_B T} \cdot \frac{R}{\Gamma} \right)^{1/2} \frac{\lambda_0^2}{\pi}, \quad (34)$$

$$\Delta n_{rms}^{Kivelson} = \frac{1}{2\bar{n}} \left( \nu_K \cdot \frac{R_{Total} \Delta_\mu}{1 + \Delta_\mu} \cdot \frac{\eta}{k_B T} \cdot \frac{R}{\Gamma} \right)^{1/2} \times \frac{\lambda_0^2}{\pi} \sqrt{\frac{W_U}{\rho c_0^3} \frac{\omega}{\sqrt{1 + (\omega/\Gamma)^2}}}, \quad (35)$$

where  $R_{Total}$  is the total light scattering per unit volume,  $\Delta_\mu$  is the depolarization ratio,  $\nu_K$  is the ratio of the central Lorentzian HH Rayleigh line relative to the total depolarized light scattering intensity,  $k_B$  is the Boltzmann constant,  $T$  is the temperature and  $R$  is the coupling parameter of the molecular reorientation to the translational motion. It should be noted, however, the proportionality constant in Eqs. (30) and (33) differs by a factor of 2 from that implied by Eqs. (34) and (35).

### III. EXPERIMENT

Details of the experimental system are described in our previous papers.<sup>3-5</sup> In this study, the  $\lambda/4$  plate was not used to detect the birefringence signal in a way of square law detection. In this case, the root mean square of the birefringence  $\Delta n_{rms}$  is obtained from the following relation:

$$\Delta n_{rms} = (\lambda/\pi d) \sin^{-1} \sqrt{I/I_0}, \quad (36)$$

where  $\lambda$  is the wavelength of the laser light in the air,  $d$  is the optical path length (16 mm),  $I$  is the light intensity increment due to the birefringence, and  $I_0$  is the light intensity in the absence of the sound wave with the polarizer and the analyzer being parallel.

To discuss the frequency dependence of the birefringence, the ultrasonic intensity must be measured precisely. To do so, we measured the ultrasonic intensity on the basis of the light diffracted by the propagating the sound waves. The Raman-Nath parameter  $\nu_R$  is defined as

$$\nu_R = \frac{2\pi d}{\lambda} \left( \frac{\partial n}{\partial \rho} \right) \delta \rho, \quad (37)$$

where  $n$  is the refractive index and  $\delta \rho$  is the density perturbation caused by ultrasound. The Raman-Nath parameter can be estimated from the diffracted light intensity using the numerical calculation given by Klein and Cook.<sup>27</sup> The Raman-Nath parameter is related to the ultrasonic intensity  $W_U$  as

$$W_U = \frac{c_0^3}{2\rho} \left( \frac{\lambda}{2\pi d} \right)^2 \left( \frac{\partial \rho}{\partial n} \right)^2 \nu_R^2. \quad (38)$$

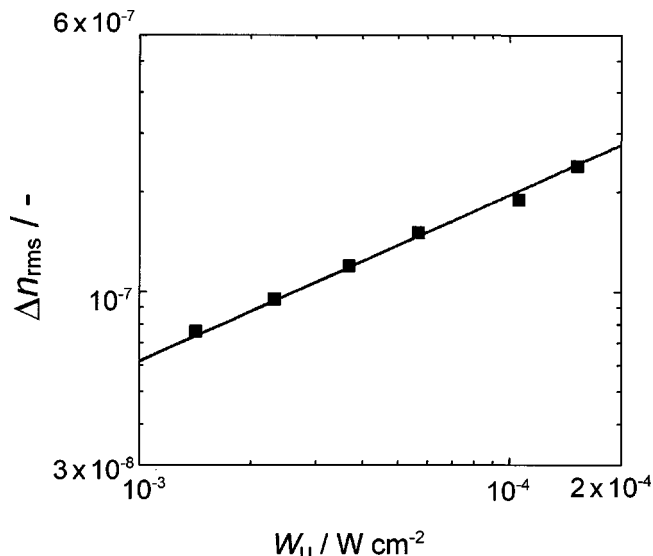


FIG. 1. Ultrasonic intensity dependence of the root mean square of the induced birefringence of 5CB (closed square) at 50 °C. The solid line indicates the slope of 0.5.

The value of  $(\partial n/\partial \rho)$  was estimated from an empirical formula given by Gibson and Kinkaid:<sup>28</sup>

$$\rho \left( \frac{\partial n}{\partial \rho} \right) = \frac{(n-1)(n^2 + 1.4n + 1.4)}{n^2 + 0.8n + 1}. \quad (39)$$

The sample of *p-n*-pentyl *p'*-cyanobiphenyl (5CB) used was purchased from BDH Co. Ltd. and used without further purification. All measurements were carried out at 50 and 55 °C and measured frequencies were 3, 5, 7, 11 and 13 MHz.

### IV. RESULTS AND DISCUSSION

Figure 1 shows the ultrasonic intensity dependence of the birefringence in 5CB at 50 °C. The slope of the solid line for this logarithmic plot is 0.5, indicating the birefringence is proportional to the square root of the ultrasonic intensity. This result is in good agreement with Eq. (30). Figure 2

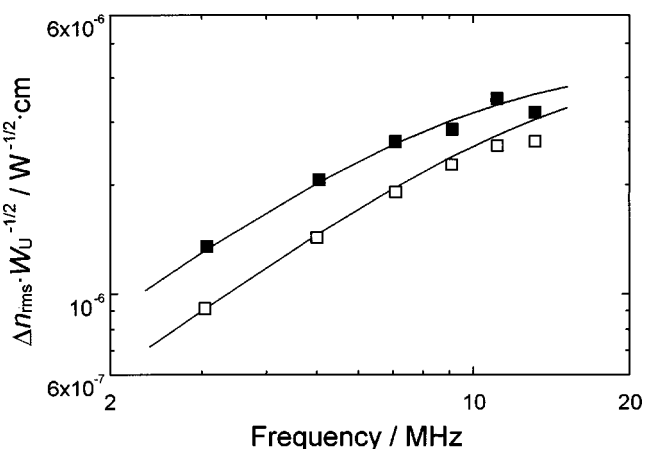


FIG. 2. Frequency dependence the birefringence per the square root of the ultrasonic intensity at 50 (closed) and 55 (open) °C. Solid curves indicate the estimation from Eq. (30). The detailed explanations are given in the text.

shows frequency dependence of  $\Delta n_{\text{rms}} W_U^{-1/2}$ . The value of  $\Delta n_{\text{rms}} W_U^{-1/2}$  increases but the slope  $\partial(\Delta n_{\text{rms}} W_U^{-1/2})/\partial f$  decreases with increasing frequency. The solid curves in Fig. 2 are calculated ones obtained by substituting into Eq. (30) the values of  $|\Delta n_f/G|$  from flow birefringence measurements<sup>11</sup> and  $\Gamma$  from optical beating light scattering experiments.<sup>26</sup> The values of  $|\Delta n_f/G|$  are 1.86 and 1.26 ns and those of  $\Gamma/2\pi$  are 10.0 and 15.3 MHz at 50 and 55 °C, respectively. The observed values of  $\Delta n_{\text{rms}} W_U^{-1/2}$  in this study are satisfactorily reproduced by Eq. (30).

Martinoty and Bader measured the ultrasonically induced birefringence for the isotropic phase of liquid crystals.<sup>3,4</sup> In their experiment, however, only the relative values of the ultrasonic intensity were measured and they examined Eq. (30) in terms of the temperature dependence of the birefringence at three different frequencies.

In this work, we measured directly the ultrasonically induced birefringence as a function of frequency and ultrasonic intensity. Our results are reproduced completely by the equation derived here. Moreover, the absolute values of ultrasonically induced birefringence obtained in this work are in good agreement with those calculated using the flow birefringence and reorientational relaxation frequency obtained by light scattering. This indicates that our theoretical treatment is valid and the method of ultrasonic intensity measurement presented here is very useful.

## APPENDIX A: COMPARISON BETWEEN IRREVERSIBLE STATISTICAL TREATMENT AND DE GENNES' PHENOMENOLOGICAL ONE

From Eqs. (15) to (17), we can obtain the dispersion relation of the sound waves as

$$-i\omega^3 - \omega^2 \left( \frac{k^2}{\rho} \left( \eta_V + \frac{4}{3} \eta_S \left( 1 - \frac{2\mu^2}{\eta_S \nu} \right) \right) + \Gamma \right) + i\omega \left( \frac{k^2}{\rho} \left( \eta_V + \frac{4}{3} \eta_S \right) \Gamma + c_0^2 k^2 \right) + c_0^2 k^2 \Gamma = 0. \quad (\text{A1})$$

Alms *et al.*<sup>12</sup> compared the irreversible statistical treatment on the reorientational-translational coupling with the de Gennes phenomenological one for the purely shear case. They derived the relationship of the coupling parameter “ $R$ ” between reorientational and transverse translational modes to the phenomenological transport coefficients  $\mu$  and  $\nu$  as

$$R = \frac{2\mu^2}{\eta_S \nu}. \quad (\text{A2})$$

Although the coupling of the longitudinal translation to the reorientational mode is considered in this paper, Eq. (A2) is valid in our case for the following reason. In our approach, the longitudinal velocity gradient and its conjugated stress are divided into isotropic and anisotropic terms and only the latter terms are coupled to the tensor order parameter and its conjugated stress variable, as introduced by de Gennes. The definition of parameters  $\mu$  and  $\nu$  is the same as that for the purely shear case.

Equation (A1) can be expressed as follows:

$$\frac{\omega^2}{k^2} = c_0^2 + i\omega \frac{1}{\rho} \left( \eta_V + \frac{4}{3} \eta_S \left( 1 - R \frac{i\omega}{i\omega + \Gamma} \right) \right). \quad (\text{A3})$$

If the coupling parameter  $R$  is zero, Eq. (A3) reduces to the ordinary dispersion relation of sound waves. It should also be noted that in the case of simple shear, de Gennes derived an effective dynamic shear viscosity  $\eta_S^*(\omega)$ ,<sup>9,10</sup>

$$\eta_S^*(\omega) = \eta_S \left( 1 - R \frac{i(\omega/\Gamma)}{1 + i(\omega/\Gamma)} \right). \quad (\text{A4})$$

If Eq. (A4) is substituted in place of the shear viscosity  $\eta_S$  in the ordinary dispersion relation, Eq. (A3) is obtained again.

In the limit  $\text{Im}(k)/\text{Re}(k) \ll 1$ , we obtain from Eq. (A3) approximate expressions for the sound velocity dispersion and absorption coefficient:

$$c = c_0 \left( 1 + \frac{2}{3\rho c_0^2} \eta_S R \frac{\omega^2 \Gamma}{\omega^2 + \Gamma^2} \right), \quad (\text{A5})$$

$$\alpha = \frac{\omega^2}{2c_0^3 \rho} \left( \eta_V + \frac{4}{3} \eta_S (1 - R) + \frac{4}{3} \eta_S R \frac{\Gamma^2}{\omega^2 + \Gamma^2} \right). \quad (\text{A6})$$

In the low frequency limit, Eq. (A5) reduces to  $c = c_0$ , and Eq. (A6) becomes the ordinary classical sound absorption:

$$\alpha = \frac{\omega^2}{2c_0^3 \rho} \left( \eta_V + \frac{4}{3} \eta_S \right). \quad (\text{A7})$$

Grubbs and MacPhail have derived the VV light scattering intensity density function from the following equations:<sup>21</sup>

$$\dot{D}_{xx-yy} = -\Gamma D_{xx-yy} - i\Gamma(\alpha R)^{1/2} p_x, \quad (\text{A8})$$

$$\dot{D}_{zz} = -\Gamma D_{zz} - i\Gamma(\alpha R/3)^{1/2} p_x, \quad (\text{A9})$$

$$\dot{n} = -ic_0 k p_x, \quad (\text{A10})$$

$$\dot{p}_x = -i\Gamma(\alpha R)^{1/2} D_{xx-yy} - i\Gamma(\alpha R/3)^{1/2} D_{zz} - ic_0 k n - \Gamma \alpha \left[ \eta_V / \eta_S + (1 - R)4/3 \right] p_x, \quad (\text{A11})$$

where  $D_{xx-yy}(k, t)$  and  $D_{zz}(k, t)$  are the orientational density tensor components,  $n(k, t)$  is the number density,  $p_x(k, t)$  is the longitudinal momentum density, and  $\alpha = k^2 \eta_S / \rho \Gamma$ . Unlike in the original theory of Lipeles and Kivelson,<sup>19</sup> the coupling to  $D_{zz}(k, t)$  term is considered. Using Fourier transforms, the dispersion relation is obtained from Eqs. (A8) to (A11) as

$$(i\omega + \Gamma) \left[ i\omega^3 - \omega^2 \left( \frac{k^2}{\rho} \left( \eta_V + \frac{4}{3} \eta_S (1 - R) \right) + \Gamma \right) + i\omega \left( \frac{k^2}{\rho} \left( \eta_V + \frac{4}{3} \eta_S \right) \Gamma + c_0^2 k^2 \right) + c_0^2 k^2 \Gamma \right] = 0. \quad (\text{A12})$$

The term in the second parenthesis is identical to the left hand of the Eq. (A1). The relation  $i\omega + \Gamma = 0$  represents the nonpropagating mode, thus the expressions for the sound velocity and absorption are identical to Eqs. (A5) and (A6). The sound velocity and absorption relations which appeared in the Lipeles and Kivelson paper were not identical to those obtained here since the coupling to  $D_{zz}(k, t)$  term was not

taken into account in their paper.<sup>19</sup> However, the Lipeles–Kivelson expression for ultrasonically induced birefringence still remains as in Eq. (35), since only Eqs. (A8) and (A10) are necessary to derive the expression of ultrasonically induced birefringence.

Since Eqs. (A9) to (A12) are not equivalent to Eqs. (15) to (19), the spectral density functions for the VV light scattering obtained from our transport equations are different from those obtained by Grubbs and MacPhail. For example, the spectral density of  $Q_{zz}$ ,

$$J_{QQ}(k, \omega) = \text{Re} \int_0^\infty dt \exp(i\omega t) \langle Q_{zz}(k, t) Q_{zz}^*(k, 0) \rangle / \langle |Q_{zz}(k, 0)|^2 \rangle, \tag{A13}$$

is approximately obtained using the Laplace–Fourier transform<sup>16</sup> when  $c_0 k \gg \eta_v k^2 / \rho, \eta_s k^2 / \rho$  as

$$J_{QQ}(k, \omega) = \left( 1 + \frac{4}{3} \eta_s \frac{k^2}{\rho} \Gamma R \frac{\Gamma^2 c_0^2 k^2}{(\Gamma^2 + c_0^2 k^2)^2} \right) \frac{\Gamma_R}{\omega^2 + \Gamma_R^2} - \frac{2}{3} \eta_s \frac{k^2}{\rho} \Gamma \frac{\Gamma^2 - c_0^2 k^2}{(\Gamma^2 + c_0^2 k^2)^2} \left( \frac{\Gamma_B}{(\omega - \omega_B)^2 + \Gamma_B^2} + \frac{\Gamma_B}{(\omega + \omega_B)^2 + \Gamma_B^2} \right) - \frac{4}{3} \eta_s \frac{k^2}{\rho} \Gamma \frac{c_0 k \Gamma}{(\Gamma^2 + c_0^2 k^2)^2} \left( \frac{\omega_B - \omega}{(\omega - \omega_B)^2 + \Gamma_B^2} + \frac{\omega_B + \omega}{(\omega + \omega_B)^2 + \Gamma_B^2} \right), \tag{A14}$$

where  $\Gamma_R$ ,  $\omega_B$  and  $\Gamma_B$  are given by the equations,

$$\Gamma_R = \Gamma - \frac{4}{3} \frac{k^2}{\rho} \eta_s R \frac{\Gamma^2}{\Gamma^2 + c_0^2 k^2}, \tag{A15}$$

$$\omega_B = c_0 k \left( 1 + \frac{2}{3} \frac{k^2}{\rho} \eta_s R \frac{\Gamma}{\Gamma^2 + c_0^2 k^2} \right), \tag{A16}$$

$$\Gamma_B = \frac{1}{2} \left( \frac{k^2}{\rho} \left( \eta_v + \frac{4}{3} \eta_s \left( 1 - R \frac{c_0^2 k^2}{\Gamma^2 + c_0^2 k^2} \right) \right) \right). \tag{A17}$$

Equation (A14) is different from Eq. (8b) of Ref. 21. Wang derived the spectral density of the density fluctuation  $\delta\rho$  as<sup>22</sup>

$$J_{\rho\rho}(k, \omega) = \text{Re} \int_0^\infty dt \exp(i\omega t) \langle \delta\rho(k, t) \delta\rho^*(k, 0) \rangle / \langle |\delta\rho(k, 0)|^2 \rangle = \text{Re} \left( \frac{i\omega + \frac{k^2}{\rho} \left( \eta_v + \frac{4}{3} \eta_s \left( 1 - R \frac{i\omega}{i\omega + \Gamma} \right) \right)}{c_0^2 k^2 + i\omega \left( i\omega + \frac{k^2}{\rho} \left( \eta_v + \frac{4}{3} \eta_s \left( 1 - R \frac{i\omega}{i\omega + \Gamma} \right) \right) \right)} \right). \tag{A18}$$

The same results can be obtained from Eqs. (15) to (19). Eq. (A18) is not identical with Eq. (8a) of Ref. 21. The differences demonstrated above come from the difference in the choice of the coupled variables. In the statistical approach, the reorientational densities  $D_{xx-yy}$  and  $D_{zz}$  were chosen and were directly coupled to the longitudinal momentum density. On the other hand, in our treatment, the translational term was divided into isotropic and anisotropic components and only the latter couples to the reorientational mode.

### APPENDIX B: FLOW BIREFRINGENCE

The formula for flow birefringence has been already obtained.<sup>9–11</sup> For ease of comprehension, we will here mention its derivation.

Consider a stationary shear strain rate  $G$  in which fluid flows in the  $x$  direction with its gradient parallel to the  $y$  axis. Taking into account the stationary condition, Eqs. (13) and (14) relate the order parameter to the strain rate as

$$-A Q_{xy} = -A Q_{yx} = \mu G. \tag{B1}$$

The dielectric tensor is then written as

$$\begin{pmatrix} \bar{\epsilon} & \delta\epsilon & 0 \\ \delta\epsilon & \bar{\epsilon} & 0 \\ 0 & 0 & \bar{\epsilon} \end{pmatrix}, \tag{B2}$$

where  $\delta\epsilon$  is defined as  $\delta\epsilon = -2\mu G \Delta\epsilon / 3A$ . By choosing new axes  $XY$ , which are rotated counterclockwise from the  $xy$  axes by  $45^\circ$ , the dielectric tensor can be written as

$$\begin{pmatrix} \bar{\epsilon} + \delta\epsilon & 0 & 0 \\ 0 & \bar{\epsilon} - \delta\epsilon & 0 \\ 0 & 0 & \bar{\epsilon} \end{pmatrix}. \tag{B3}$$

The birefringence  $\Delta n_f$  is then obtained from

$$\begin{aligned}
 \Delta n_f &= \sqrt{\varepsilon_{XX}} - \sqrt{\varepsilon_{YY}} \\
 &= \sqrt{\bar{\varepsilon} + \delta\varepsilon} - \sqrt{\bar{\varepsilon} - \delta\varepsilon} \\
 &\cong \frac{\delta\varepsilon}{\sqrt{\bar{\varepsilon}}} = -\frac{2\mu G \Delta\varepsilon}{3\bar{n}A}. \tag{B4}
 \end{aligned}$$

<sup>1</sup>H. G. Jerrard, *Ultrasonics* **2**, 74 (1964).

<sup>2</sup>H. D. Ou-Yang, R. A. MacPhail, and K. D. Kivelson, *Phys. Rev. A* **33**, 611 (1986).

<sup>3</sup>K. Yasuda, T. Matsuoka, S. Koda, and H. Nomura, *Jpn. J. Appl. Phys.* **33**, 2901 (1994).

<sup>4</sup>K. Yasuda, T. Matsuoka, S. Koda, and H. Nomura, *J. Phys. Chem.* **100**, 5892 (1996).

<sup>5</sup>K. Yasuda, T. Matsuoka, S. Koda, and H. Nomura, *J. Phys. Chem. B* **101**, 1138 (1996).

<sup>6</sup>R. Lipeles and D. Kivelson, *J. Chem. Phys.* **72**, 6199 (1980).

<sup>7</sup>P. Martinoty and M. Bader, *J. Phys. (Paris), Colloq.* **42**, 1097 (1981).

<sup>8</sup>M. Bader and P. Martinoty, *Mol. Cryst. Liq. Cryst.* **76**, 269 (1981).

<sup>9</sup>P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **12**, 193 (1971).

<sup>10</sup>P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993), Chap. 2.

<sup>11</sup>P. Martinoty, F. Kiry, S. Nagai, and S. Candau, *J. Phys. (Paris), Colloq.* **38**, 159 (1977).

<sup>12</sup>G. R. Alms, T. D. Gierke, and G. D. Patterson, *J. Chem. Phys.* **67**, 5779 (1977).

<sup>13</sup>G. R. Alms, D. R. Bauer, J. I. Baruman, and R. Pecora, *J. Chem. Phys.* **59**, 5304 (1973).

<sup>14</sup>S. J. Tsay and D. Kivelson, *Mol. Phys.* **29**, 1 (1975).

<sup>15</sup>D. Kivelson, T. Keyes, and J. Champion, *Mol. Phys.* **31**, 221 (1976).

<sup>16</sup>B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Chap. 11.

<sup>17</sup>P. J. Chappell, M. P. Allen, R. I. Hallem, and D. Kivelson, *J. Chem. Phys.* **74**, 5929 (1981).

<sup>18</sup>M. P. Allen, P. J. Chappell, and D. Kivelson, *J. Chem. Phys.* **74**, 5942 (1981).

<sup>19</sup>R. Lipeles and D. Kivelson, *J. Chem. Phys.* **67**, 4564 (1977).

<sup>20</sup>P. J. Chappell and D. Kivelson, *J. Chem. Phys.* **76**, 1742 (1982).

<sup>21</sup>W. T. Grubbs and R. A. MacPhail, *J. Chem. Phys.* **97**, 8906 (1992).

<sup>22</sup>C. H. Wang, *Mol. Phys.* **58**, 497 (1986).

<sup>23</sup>J. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946), Chap. 5.

<sup>24</sup>N. C. Hilyard and H. G. Jerrard, *J. Appl. Phys.* **33**, 3470 (1962).

<sup>25</sup>A. Peterlin, *J. Phys. Radium* **11**, 45 (1950).

<sup>26</sup>T. Shibata, T. Matsuoka, S. Koda, and H. Nomura, *J. Chem. Phys.* **109**, 2038 (1998).

<sup>27</sup>W. R. Klein and B. D. Cook, *IEEE Trans. Sonics Ultrason.* **SU-14**, 123 (1967).

<sup>28</sup>R. B. Gibson and Kinkaid, *J. Am. Chem. Soc.* **60**, 511 (1938).