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Light Scattering Spectrum of a Nematic Liquid†

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Abstract—We measured the intensity and the spectrum of light scattered by the nematic liquid crystal *p*-methoxybenzylidene *p-n*-butylaniline as a function of temperature. The measurements yield the temperature dependence of the amplitude and dynamics of orientational fluctuations in the ordered phase. We analyze the results in terms of two theories of normal modes of liquid crystals, and examine the extensions required to make the macroscopic elastic theory consistent with experiment.

Introduction

We report here the results of an experimental study of the temperature dependence of the intensity and spectrum of light scattered by fluctuations in the nematic phase of *p*-methoxybenzylidene *p-n*-butylaniline (MBBA). From these measurements we deduce the mean squared amplitude and time dependence of the fluctuations, and we compare our results with two phenomenological theories of the normal modes of a liquid crystal.

The ordered phase of nematic liquid crystal is characterized by a long range parallel orientational ordering of the anisotropic rod-like molecules that constitute the compound. The cooperative interaction means the molecules are not free to rotate about directions perpendicular to their long axis, and the normal modes of the ordered phase consist of collective orientational oscillations about the equilibrium direction. Since the electric polarizability of the molecules is highly anisotropic, the orientational fluctuations cause large changes in the refractive index and are, therefore, readily studied by light scattering.

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Let incident light of wave vector $\mathbf{k}_i$ with polarization along **i** be scattered in a direction with wave vector $\mathbf{k}_f$ and polarization along **f**. Then this light will be scattered[1] only by a particular spatial Fourier component of the fluctuations in the element ϵ_{if} of the dielectric constant tensor whose wave vector is $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. The intensity of the scattered light is proportional to the mean squared fluctuations, $\langle \delta\epsilon_{if}^2(\mathbf{q}) \rangle$. The spectrum gives the Fourier transform of the correlation function $\langle \delta\epsilon_{if}(\mathbf{q}, 0)\ \delta\epsilon_{if}(\mathbf{q}, \tau) \rangle$ and hence the time dependence of $\delta\epsilon_{if}(\mathbf{q})$. Exponentially decaying fluctuations, for example, give therefore a Lorentzian spectrum to the scattered light.

Phenomenological Theories

There are at present two phenomenological theories of the normal modes of liquid crystals. In this section of our paper we outline the basic features of these two models and how their predictions may be compared with the results of light scattering experiments. In a subsequent section we shall present the measurements we made and compare our results with each model.

If we consider a nematic liquid crystal of uniaxial symmetry, the order on a macroscopic scale may be specified by two quantities: (i) the average alignment direction (optic axis) of the molecules in a small volume, and (ii) the degree of alignment (birefringence) of the molecules along this direction. Therefore, we may write the Cartesian dielectric constant and susceptibility tensors as

$$\epsilon_{\alpha\beta} = \bar{\epsilon}\delta_{\alpha\beta} + (Q\Delta\epsilon/3)(3n_\alpha n_\beta - \delta_{\alpha\beta}) \tag{1}$$

$$\chi_{\alpha\beta} = \bar{\chi}\delta_{\alpha\beta} + (Q\Delta\chi/3)(3n_\alpha n_\beta - \delta_{\alpha\beta}) \tag{2}$$

Here, n_α, n_β are the Cartesian components of a unit vector (called the director) parallel to the local optic axis. An order parameter that specifies the degree of alignment[2] is $Q = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$ where θ is the angle between the long axis of a molecule and the optic axis. The quantities $\Delta\epsilon$ and $\Delta\chi$ are, respectively, the anisotropies of the dielectric constant and diamagnetic susceptibility for a completely ordered ($Q = 1$) liquid crystal. It is clear from (1) that both fluctuations in Q and **n** will scatter light. In the nematic phase the most intense scattering comes from thermally excited fluctuations in the orientation of **n**; it is these fluctuations we have

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studied in MBBA. From (1) it is also apparent that re-orientations of the director cause large fluctuations only in ϵ_{31} and ϵ_{32} if we choose the undisturbed director to lie along the 3 direction. Then, for example, we may carry out experiments with the incident polarization **i** along 3 and the scattered polarization **f** along 1 or 2, respectively, to study the mean squared fluctuations in n_1 or n_2 (from the intensity) and the time dependence of these fluctuations (from the spectrum).

The Orsay Liquid Crystal Group[3] has proposed a model to explain the intensity and spectrum of the scattered light. In this model they derive an equation of motion for the director using the Frank[4] elastic model for liquid crystals and Leslie's hydrodynamic equations[5] for anisotropic fluids. The fluctuations in **n** are heavily overdamped and lead to a Lorentzian spectrum of the scattered light. Since the Orsay theory deals directly with optic axis (director) motions, we may obtain directly from it expressions for the intensity and spectrum of the scattered light.

The theory of Martin, Pershan, and Swift (MPS)[6] discusses the normal modes of a liquid crystal in terms of strains $u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i)$. Coordinates are chosen so that the 3 axis is a symmetry axis in the unstrained crystal. In order to use the MPS theory to interpret optical and magnetic measurements on liquid crystals it is necessary to relate the optic axis displacements to the strains u_{ij}. In the unstrained uniaxial liquid the dielectric polarizability tensor is diagonal at any point; the major axis of the corresponding polarizability ellipsoid (the optic axis) coincides at any location with the overall symmetry axis. The polarizability ellipsoid can be distorted through rotations, which correspond to fluctuations in the off-diagonal elements of the tensor, or by deformations, which involve only the diagonal elements of the corresponding dielectric polarizability tensor. The fluctuations measured by our experiments (i.e., those that arise from the reorientation of the optic axis) will in general be given by ($j = 1$ or 2)

$$\delta\epsilon_{3j} = Q\Delta\epsilon(A\,\partial_3 u_j + B\,\partial_j u_3) \tag{3}$$

where A and B are parameters relating the optic axis motion to the MPS displacements u_i. Note that, in general, the optic axis can be rotated both by the symmetric part (center of mass flow) and the

antisymmetric part (reorientation of molecular axis) of the displace ment gradient.†

A comparision of Eqs. (1) and (3) shows that director displacements are related to strains ($j = 1$ or 2) as

$$\delta n_j = A\,\partial_3 u_j + B\,\partial_j u_3 \tag{4}$$

Analysis of Light Scattering Experiments

Since the liquid crystal possesses symmetry about the 3 axis, we may, without loss of generality, choose the scattering wave vector **q** to lie in the 1–3 plane. Our experiments were carried out, as detailed in the Appendix, under three different conditions which led to the following configurations:[8] (a) $q_1^2 < 0.078\,q_3^2$, **i** along 3 and **f** in the 1–3 plane; (b) $q_1^2 < 0.0026\,q_3^2$, **i** along 2, and **f** in the 1–3 plane; (c) $q_3 = 0$, **i** along 3, and **f** along 1. Under the conditions a, b, and c, we therefore measured the mean squared amplitude and time dependence of $f_1\,\delta\epsilon_{13}$, $f_3\,\delta\epsilon_{23}$, and $\delta\epsilon_{13}$, respectively, where f_1 and f_3 are the components of the unit vector **f** along 1 and 3, respectively.

We may then use the Orsay model to calculate the intensities for our three configurations to be proportional to:

$$\langle \delta\epsilon_{if}^2(\mathbf{q}) \rangle = Q^2 \Delta\epsilon^2 f_1^2\, kT/K_{33}\, q_3^2 \tag{5a}$$

$$= Q^2 \Delta\epsilon^2 f_3^2\, kT/K_{33}\, q_3^2 \tag{5b}$$

$$= Q^2 \Delta\epsilon^2 kT/K_{11}\, q_1^2 \tag{5c}$$

Here we have ignored the small contributions of q_1^2 in configurations *a*, and *b*, and have used the notation of the original references[3] for the elastic constants. Equations (5a)–(5c) refer to the configurations *a–c*, respectively.

From the MPS theory and Eq. (3) we obtain:

$$\langle \delta\epsilon_{if}^2(\mathbf{q}) \rangle = Q^2 \Delta\epsilon^2 A^2 f_1\, kT/M_5\, q_3^2 \tag{6a}$$

$$= Q^2 \Delta\epsilon^2 A^2 f_3^2\, kT/M_5\, q_3^2 \tag{6b}$$

$$= Q^2 \Delta\epsilon^2 B^2\, kT/L_5\, q_1^2 \tag{6c}$$

where, again, we use the notation of the original reference[6] for elastic constants.

† Amazingly enough, this point in the case of solids has only recently been noted.[7]

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We used the known temperature dependence of the refractive indices of MBBA[9] to correct for the variation of reflection at the liquid crystal surfaces, the geometrical factors f_1 or f_3, and the wave vectors q_1 or q_3. In Fig. 1 we show kT divided by the intensity of

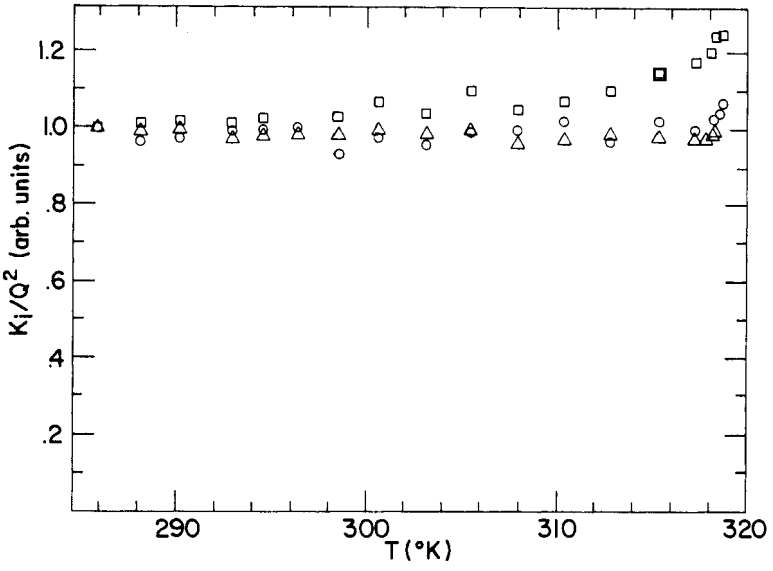

Figure 1. The temperature dependence of normalized light intensity scattered by fluctuations in the nematic phase of MBBA. The squares, triangles, and circles correspond respectively to the experimental configurations a, b and c discussed in the text.

the scattered light normalized to unity at 286 °K. We see that K_{33}/Q^2, K_{11}/Q^2, M_5/A^2Q^2, and L_5/B^2Q^2 are all independent of temperature within the accuracy of our measurements. (We did not correct for the temperature dependence of the effect of the q_1 component in a; we believe this explains the slight rise near the transition temperature for this configuration in Fig. 1).

The spectrum of the scattered light was found to be a Lorentzian line centered about the incident laser frequency. If $\Gamma/2\pi$ is the half-width at half height (in Hz) for the scattered spectrum, the Orsay theory predicts:

$$\Gamma_a = K_{33} q_3^2/\eta_B \tag{7a}$$

$$\Gamma_b = K_{33} q_3^2/\eta_B \tag{7b}$$

$$\Gamma_c = K_{11} q_1^2/[\gamma_1 - (\gamma_1+\gamma_2)\alpha_3/\alpha_s] \tag{7c}$$

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where the notation of Ref. 3 has been used for the viscosity coefficients.

From the MPS model, we calculate:

$$\Gamma_a = M_5 q_3^2/\eta_5 \tag{8a}$$

$$\Gamma_b = M_5 q_3^2/\eta_5 \tag{8b}$$

$$\Gamma_c = L_5 q_1^2/\eta_5 \tag{8c}$$

using the notation of Ref. 6.

We give the measured linewidths as a function of temperature in Fig. 2. The Orsay theory is consistent with our experimental results

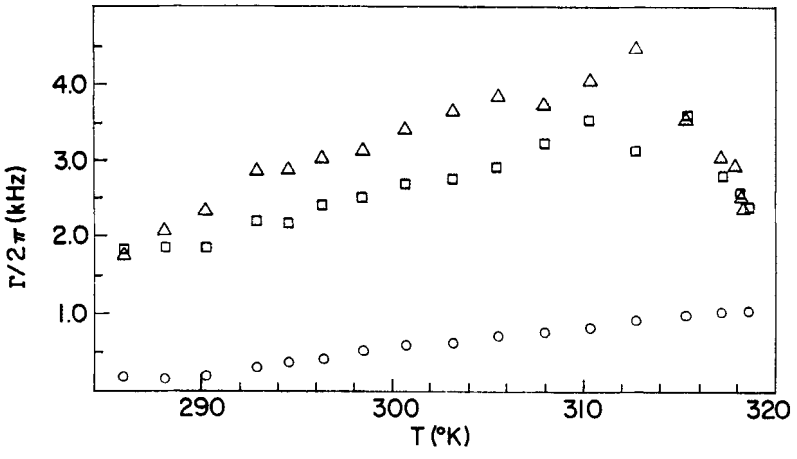

Figure 2. Linewidth of the Lorentzian spectrum of light scattered by fluctuations in the nematic phase of MBBA. The squares, triangles, and circles correspond to experimental configurations *a*, *b* and *c* discussed in the text.

within experimental errors and allows evaluation of the temperature dependence of the viscosity coefficients (Fig. 3). From the different temperature dependences of Γ_a and Γ_c, however, we see the MPS model is consistent with our data only if M_5 and L_5 have different temperature dependences. Our intensity measurements then show that the coefficients A and B must vary differently with temperature.

Equation 3 permits rotation of the optic axis by both the symmetric and the anti-symmetric part of the displacement gradient. The anti-symmetric part is pure rotation and might naively be thought of as the unique or predominant contributor to optic axis

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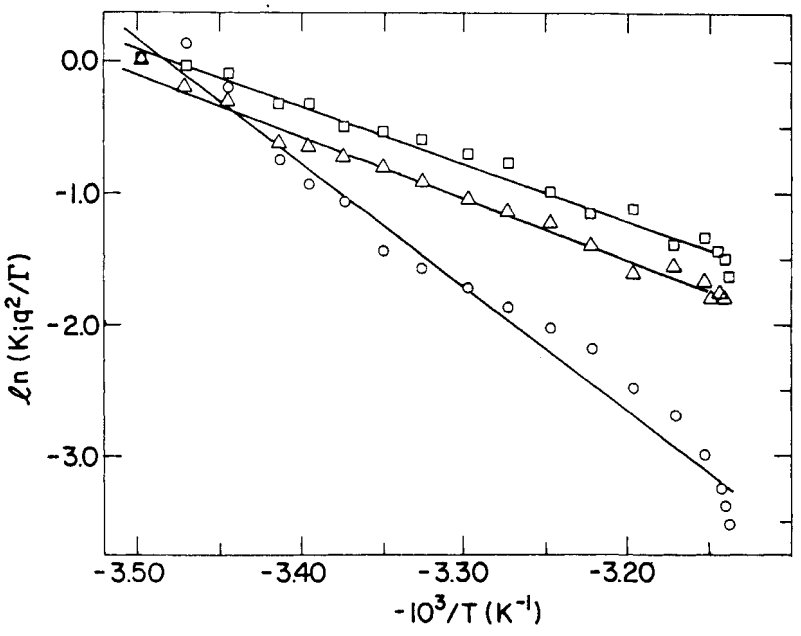

Figure 3. Temperature dependence of the viscosity coefficients for damping of director motions in the Orsay model. The squares, triangles, and circles correspond to η_a, η_b, and η_c, respectively.

rotation. If in the strained medium the optic axis merely rotated according to the rotational part of the strain, then we should have $A = -B = 1$ at all temperatures. This, however, is ruled out by our experiments.

Discussion

It is interesting to speculate on the mechanism by which the strains u_{ij} cause re-orientations of the optic axis. Since the strains u_{ij} are thermally excited fluctuations, they are not static distortions. A plausible mechanism which might result in different temperature dependences for A and B would be flow alignment[10] of the molecular axes.

The anisotropy of the diamagnetic susceptibility enables one, however, to study the elastic constants under static conditions, by using magnetic fields to exert torques on the liquid crystal molecules. For certain experimental configurations the applied magnetic field

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has no effect until a critical field has been reached.[11] The Frank theory can be used to treat finite distortions and hence to obtain the rotation of the molecular axis as a function of field. A detailed theoretical discussion may be found in a paper by Saupe.[12]

The critical field at which distortion can first occur, is given[12] in terms of the Frank theory by

$$H_{c\perp} = (\pi/d)(K_{33}/Q\Delta\chi)^{1/2}$$

for the perpendicular configuration and by

$$H_{c\parallel} = (\pi/d)(K_{11}/Q\Delta\chi)^{1/2}$$

for the parallel configuration. In the perpendicular configuration the nematic sample of thickness d is enclosed by plane parallel plates which have been pretreated such that the optic axis in the absence of a magnetic field is perpendicular to the boundary, and the field is applied in the plane. In the parallel configuration the nematic liquid is aligned in a direction parallel to and the field is applied perpendicular to the plates.

Assuming Eq. (4) also relates the optic axis displacement to static strains, an analogous derivation of critical fields using the MPS theory yields

$$H_{c\perp} = (\pi/d)(M_5/Q\Delta\chi A^2)^{1/2},$$

and

$$H_{c\parallel} = (\pi/d)(L_5/Q\Delta\chi B^2)^{1/2}$$

The temperature dependence of the critical field has been studied by Saupe[12] for p-azoxyanisole (PAA). He found that K_{33}/Q^2 and K_{11}/Q^2 were independent of temperature. This is in agreement with our light scattering intensity results for MBBA and means that Eq. (4) relating the optic axis rotation to static strains provides consistency between experiment and the MPS model. Since the magnetic field exerts a steady torque on the optic axis and a steady restoring torque is supplied by the elastic constants M_5 and L_5 under static conditions, it is clear that flow alignment cannot be the mechanism for the coupling of the optic axis to the strains.

We have seen that our measurements of the temperature dependence of the intensity and spectrum of the light scattered in the nematic phase of MBBA may be interpreted with either the Orsay model or the MPS model for liquid crystals. For the MPS model to be consistent with our data it is necessary to postulate a rather

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involved temperature dependent relation between the strain variables u_{ij} of the model and the motion of the optic axis of the liquid crystal. Comparision with static experiments in a magnetic field suggest that the coupling between the director orientation and the strains is the same for static strains or thermally excited time dependent ones; this rules out flow alignment as a possible mechanism for this coupling. It appears that the strains consist of a mixture of center of mass translation and axial realignment of the liquid crystal molecules; the relative amount of each type of molecular motion for a given strain seems to depend on temperature. In the Orsay model restoring forces are produced only for reorientations of the molecular axis, but it seems that in the MPS model there must also be restoring forces resulting from displacements of the molecules.

A complete version of the MPS model will require the introduction of an equation of motion for the director in order to determine the temperature and frequency dependence of the coupling constants A, and B. The model then loses the attractive simplicity which distinguished it from earlier approaches.

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Appendix: Experimental and Computational Details

The spectrum of the scattered light was measured with the technique of self-beating spectroscopy. The 6328 Å light from a Spectra Physics model 119 He–Ne laser was focused on the aligned MBBA sample contained between two Pyrex microscope slides 25 mm square. The sample thickness of 50 μ was maintained by a Teflon gasket. To obtain good alignment, the slides were cleaned in chrome-sulfuric acid and rubbed repeatedly on cheesecloth: the extinction ratio between crossed and parallel polars was better than

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100. The sample assembly was mounted in an aluminum block whose temperature was controlled to better than 8 mdeg. Temperatures were measured with a platinum resistance thermometer. Parallel light scattered by the sample was focused on an EMI 9558B photomultiplier tube. The spectrum of the photo-current was analyzed with a Hewlett Packard 310A wave analyzer.

The MBBA was purified by vacuum distillation. To minimize decomposition, the scattering chamber was purged with dry nitrogen. The nematic–isotropic transition temperature of the sample was frequently checked and observed to stay in the range $45.45 \pm 0.15\,^{\circ}\mathrm{C}$.

We studied light scattered in three configurations: (a) **n**, **i**, and **f** in the scattering plane; (b) **n** and **f** in the scattering plane with **i** normal to them; (c) **i** parallel to **n** and normal to the scattering plane with **f** in the scattering plane. Light entered perpendicular to the glass slides, and the laboratory scattering angle, θ_1 was fixed at 45.0°. The corresponding internal scattering angles, θ, varied from 24.0° to 25.3° in configurations (a) and (b), and from 27.2° to 26.8° in configuration (c) over the temperature range from 12.8 °C to the clearing point.

In configuration (c) f_2 vanishes only at a single, temperature-dependent scattering angle. The ratio f_2^2/f_1^2 is easily computed, however, from trigonometric relations and was shown to be smaller than 0.0086 under the conditions of our experiments.

The dielectric constant fluctuations appearing in Eq. (5) and (6) relate the electric displacement associated with the scattered wave to the incident electric field, within the liquid crystal medium. To obtain them from the intensities measured in air, the temperature dependent reflectivities of the two glass-MBBA interfaces need to be taken into account. The multiplicative coefficients C_a, C_b, and C_c, for configuration (a), (b) and (c), respectively, were obtained from the Fresnel coefficients for uniaxial bodies. They are listed, along with relations used for other temperature dependent quantities below:

Configuration (a):

$$\sin\theta = (1/n_f)\sin\theta_1$$
$$n_f = [n_e^2 - (n_e^2/n_0^2 - 1)\sin^2\theta_1]^{1/2}$$
$$q_1^2 = (2\pi/\lambda_0)^2(n_f\cos\theta - n_0)^2$$

$$q_3^2 = (2\pi/\lambda_0)^2 \sin^2\theta_1$$
$$f_1 = \sin\theta$$
$$C_a = [(n_f n_g \cos\theta + n_e^2 \cos\theta_g)(n_0 + n_g)/4n_g \cos\theta]^2$$

Configuration (b):

$$n_f = [n_e^2 - (n_e^2/n_0^2 - 1) \sin^2\theta_1]^{1/2}$$
$$q_1^2 = (2\pi/\lambda_0)^2 (n_f \cos\theta - n_e)^2$$
$$q_3^2 = (2\pi/\lambda_0)^2 \sin^2\theta_1$$
$$f_3 = \cos\theta$$
$$C_b = [(n_f n_g \cos\theta + n_e^2 \cos\theta_g)(n_0 + n_g)/4n_g \cos\theta]^2$$

Configuration (c):

$$n_f = n_0$$
$$q_1^2 = (2\pi/\lambda_0)^2 (n_e^2 + n_0^2 - 2n_e n_0 \cos\theta)$$
$$q_3 = 0$$
$$f_1 = n_e \sin\theta/(n_e^2 + n_0^2 - 2n_e n_0 \cos\theta)^{1/2}$$
$$f_2 = (1 - f_1^2)^{1/2}$$
$$C_c = [n_0(n_g \cos\theta + n_0 \cos\theta_g)(n_e + n_g)/4n_g \cos\theta]^2$$

Here n_e and n_0 are extraordinary and ordinary indices of refraction and n_f the effective index for the scattered light in MBBA. $n_g = 1.473$ is the refractive index of glass, and

$$\cos\theta_g = [1 - (1/n_g)^2 \sin^2\theta_1]^{1/2}.$$

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