

Anisotropic light scattering spectra and fine wing structure in the isotropic phase of nematics

V. Yu. Lerman, L. M. Sabirov, and T. M. Utarova

A. Navoi State University, Samarkand

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The temperature behavior of the relaxation parameter R which relates the orientational and translational modes of motion as well as the orientational viscosity ν is determined on the basis of the anisotropic light scattering spectra in the isotropic phase of the nematics PAA and MBBA. Singular behavior of the parameter R and the viscosity ν is observed near the isotropic–nematic phase transition.

1. INTRODUCTION

The spectra of the Rayleigh scattering of light in liquid crystals provide valuable information on the static and dynamic properties near the isotropic liquid–nematic liquid crystal (IL–NLC) phase transition.^{1,2} Since fluctuations in the order parameter near the IL–NLC transition are fluctuations in the distribution of the axes of the anisotropic molecules, the halfwidth of the depolarization component of the scattered light, that is to say, the halfwidth of the Rayleigh line wing (RLW)

$$\Gamma = 1/\tau = \pi c \Delta \nu \quad (1)$$

is related to the rate of decay of these fluctuations. Here τ is the relaxation time of the order parameter, c is the speed of light, and $\Delta \nu$ is the RLW halfwidth in cm^{-1} .

De Gennes predicted the existence of fine structure of the wing (WFS) in the component $I_{xx}(\omega)$ of the RLW spectrum in the isotropic phase of liquid crystals. In Refs. 3 and 4 expressions were obtained for the translational–rotational parameter R associated with the viscosity coefficients η , μ , and ν , which were introduced by de Gennes to describe the isotropic phase of a liquid crystal:

$$R = 2\mu^2/\eta\nu.$$

Growth of the relaxation time τ (or, what is the same, decrease of the RLW halfwidth) was explained in Ref. 5 by the growth of the susceptibility χ :

$$\tau = \nu \chi. \quad (2)$$

By measuring τ , χ , and R simultaneously it is possible to uniquely determine whether the viscosity coefficients ν and μ have any singularities near the IL–NLC transition.

A few experimental studies of the shape and halfwidth of the RLW in the isotropic phase of a NLC (Ref. 6) have shown that the latter are very narrow in comparison with the RLW halfwidth in ordinary liquids. Whereas $\tau \sim 10^{-12}$ – 10^{-10} sec holds in ordinary liquids, we have $\tau \sim 10^{-8}$ – 10^{-7} sec in liquid crystals. This requires a high degree of resolution from the experimental setup, and this evidently explains the clear inadequacy of the experimental data in this region.

Since the aim of the present study was to determine the temperature kinetics of the RLW halfwidth in the region of the IL–NLC phase transition, we used a spherical Fabry–Perot interferometer. From the temperature dependence of the total intensity of the depolarized scattering we obtained information on the susceptibility χ , and from the RLW halfwidths, information on the relaxation time τ of the order

parameter. From the shapes of the spectra we also determined the values of the translational–rotational parameter R , and on the basis of all these data we concluded that a singularity does exist in the viscosity coefficient ν . The line shape of the depolarized scattering in the isotropic phase in the liquid crystals PAA and MBBA was compared with that predicted by de Gennes's theory³ and with the results of a theoretical analysis of the shapes of the spectra of liquids with anisotropic molecules.⁷

2. THEORY

The susceptibility χ can be found from measurements of the total intensity (the scattering coefficients R_{ij})¹

$$R_{xx} = \frac{2}{3} (\omega_0/c)^4 (\Delta \epsilon / 4\pi)^2 kT \chi, \quad (3)$$

$$R_{zz} = \frac{8}{27} (\omega_0/c)^4 (\Delta \epsilon / 4\pi)^2 kT \chi.$$

Here ω_0 is the frequency of the exciting light, c is the speed of light, $\Delta \epsilon$ is the anisotropy of the dielectric constant for the state in which the molecules of the NLC are oriented parallel to each other, k is the Boltzmann constant, and T is the absolute temperature.

For the distribution of the intensity of the light scattered by the fluctuations of the order parameter Q_{ab} , de Gennes obtained the following expressions:

$$I_{zz}(\omega) = \frac{16(\Delta \epsilon)^2 kT}{27A} \frac{\Gamma}{\Gamma^2 + \omega^2}, \quad (4)$$

$$I_{xx}(\omega) = \frac{4(\Delta \epsilon)^2 kT}{9A} \left\{ \frac{\Gamma}{\Gamma^2 + \omega^2} \sin^2 \frac{\theta}{2} + \frac{\Gamma[\omega^2 + (1 - 2\mu^2/\eta\nu)\eta^2 q^4/\rho^2] \cos^2(\theta/2)}{(\omega^2 - \Gamma\eta q^2/\rho)^2 + \omega^2[\Gamma + (1 - 2\mu^2/\eta\nu)\eta q^2/\rho]^2} \right\}. \quad (5)$$

Here $\Gamma = A/\nu$, $A = a(T - T_c^*)$ is the coefficient in the Landau free energy expansion,⁸ θ is the scattering angle, ω is the difference of the frequencies of the exciting and scattered light, η , μ , and ν are the viscosity coefficients, ρ is the density, and $q = 2k_i \sin(\theta/2)$, where k_i is the wave vector of the exciting light.

Allowing for the relation $R = 2\mu^2/\eta\nu$ and making some simple transformations, we can rewrite Eq. (5) in a form more suitable for analysis:

$$I_{xx}(\omega) = \frac{4(\Delta \epsilon)^2 kT}{9A} \left\{ \frac{1/\Gamma}{1 + \omega^2/\Gamma^2} \sin^2 \frac{\theta}{2} + \frac{(1/\Gamma)[\omega^2/\Gamma^2 + (1-R)q^4\eta^2/\rho^2\Gamma^2] \cos^2(\theta/2)}{(\omega^2/\Gamma^2 - q^2\eta/\rho\Gamma)^2 + (\omega^2/\Gamma^2)[1 + (1-R)\eta q^2/\rho\Gamma]^2} \right\}. \quad (6)$$

It can be seen from Eq. (6) that the spectrum of the component $I_{zx}(\omega)$ of the scattered light consists of two parts: a Lorentzian with halfwidth Γ , which is due to the rotational motions of molecules that do not interact via their translational motions, and a second part, whose line shape is a function of the two dimensionless parameters R and $q^2\eta/\rho\Gamma$. The first component, as has already been stated, expresses the coupling between the translational and the rotational modes of the motion, and the second is the ratio of the two characteristic times $\tau = 1/\Gamma$ and $\rho/q^2\eta$ associated, respectively, with the relaxation time of the order parameter and the re-sorption times of the viscous flows.

A theoretical analysis of the line shape as a function of $q^2\eta/\rho\Gamma$ and R was carried out in Ref. 7. There four characteristic regions were considered, for which the following conditions are fulfilled, respectively:

- 1) $q^2\eta/\rho\Gamma \ll 1$, 2) $q^2\eta/\rho\Gamma \leq 1$,
- 3) $q^2\eta/\rho\Gamma \geq 1$, 4) $q^2\eta/\rho\Gamma \gg 1$.

The theoretical predictions for the first three characteristics were validated by the experimental study of the shape of the component $I_{zx}(\omega)$ in pure liquids.⁷ The fourth condition can be achieved in pure liquids only by supercooling, i.e., for $R = 1$.

In liquid crystals condition 4) is attained for $R \sim 0.4 - 0.5$ in conjunction with a huge relaxation time $\tau = 1/\Gamma$ in comparison with ordinary liquids, which, moreover, increases as the transition temperature T_c is approached. This paper represents the first effort to verify the theoretical predictions of the line shape of the component $I_{zx}(\omega)$ under condition 4) in the isotropic phase of the nematics PAA and MBBA. For this case the theory predicts the observation of a Lorentzian of width $\Gamma/(1-R)$ and that the spectrum of the component $I_{zx}(\omega)$ can be represented in the form

$$I_{zx}(\omega) \propto \frac{\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{\Gamma}{1-R} \left[\frac{\Gamma^2}{(1-R)^2} + \omega^2 \right]^{-1} \cos^2 \frac{\theta}{2}. \quad (7)$$

3. EXPERIMENT

To investigate the RLW spectra in the liquid-crystal isotropic phase, we used a high-resolution spherical interferometer, and scanning was achieved by varying the pressure. The dispersion region of the interferometer was 0.0156 cm^{-1} , and the definition of the interference picture was of order 40. Thus, the halfwidth of the apparatus function was $\approx 5 \text{ MHz}$. A block diagram of the experimental setup is shown in Fig. 1. As the source of the exciting light we used a single-frequency stabilized LG-77 He-Ne laser with power 0.5 mW ($\lambda = 6328 \text{ \AA}$). After first removing any dust present in the liquid crystal sample by forcing it through a teflon filter with pore diameter $0.22 \mu\text{m}$, we sealed it in a cylindrical cuvette under vacuum. The cuvette was then placed in an electronic thermostat⁹ in which the temperature was kept constant to within 0.01°C .

The total intensity and the scattering spectra were investigated for two cases—for the polarizations with indices zx and zz , where the first index indicates the polarization of the incident light and the second, that of the scattered light. In addition, the RLW spectra were investigated at three

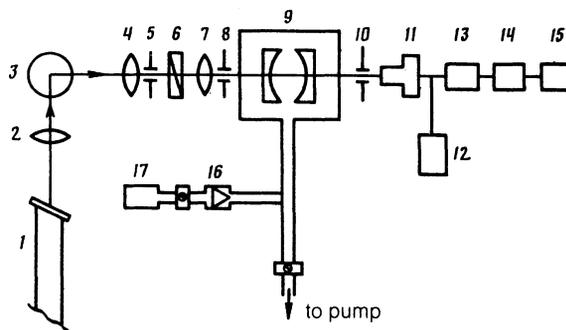


FIG. 1. Diagram of the experimental setup for recording RLW spectra in the isotropic phase of a NLC: 1) laser, 2) focusing lens, 3) thermostat with sample, 4) collimating lens, 5, 8, and 10) diaphragms, 6) polarizer, 7) matching lens, 9) spherical Fabry-Perot interferometer in pressure chamber, 11) photomultiplier, 12) emitter repeater, 14) intensimeter, 15) recorder, 16) flow regulator, and 17) nitrogen cylinder.

scattering angles: for PAA— 13° , 90° , and 167° , and for MBBA— 20° , 90° , and 160° . Typical RLW spectra in PAA for the two scattering polarizations, obtained at the scattering angle 13° , are shown in Fig. 2. The relaxation time τ was determined from the halfwidth of the spectrum for the zz polarization $(1/2)\Delta_{zz}$. To determine the true halfwidth of the RLW spectra, the apparatus function, which was of Voigt type, was taken into account in the same way as in Ref. 10. The temperature kinetics of the values of τ for the two scattering angles in the liquid crystal PAA are shown in Table I. Here also are given the values of the parameter R , calculated according to the formula

$$R = (1 - 4I_{zx}(0)/3I_{zz}(0)) \cos^2(\theta/2). \quad (8)$$

Equation (8) can be obtained by taking the ratio of expression (6) to expression (4) at $\omega = 0$. To calculate the quantity $q^2\eta/\rho$, we used the values of the viscosity η and the density ρ which were measured for PAA in Ref. 11. As was stated above, we measured the temperature dependence of the total intensity of depolarized light scattering in PAA and MBBA. The measurements were carried out by comparing with scattering in benzene. As the scattering constant R_u in

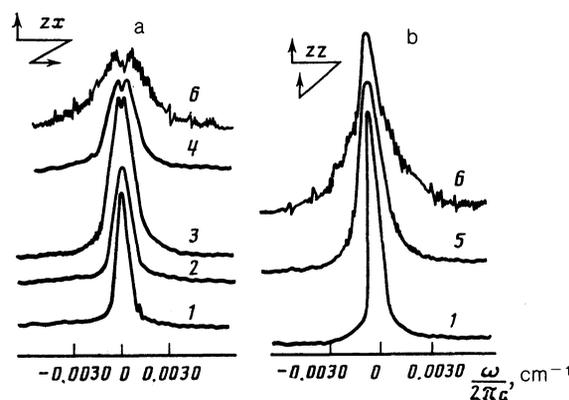


FIG. 2. Rayleigh line wing spectra in the isotropic phase of the NLC PAA, recorded at an angle of 13° for ΔT equal to 1) 0.1 K , 2) 0.65 K , 3) 2.6 K , 4) 4.7 K , 5) 5.0 K , and 6) 11 K .

TABLE I.

T, K	$1/2\Delta\nu_{zz}\cdot 10^4$, cm^{-1}	$\tau\cdot 10^8$, sec	R	$q^2\eta\tau/\rho$	$1/2\Delta\nu_{I_z}\cdot 10^4$, cm^{-1}	$\frac{1/2\Delta\nu_{zz}\cdot 10^4}{1-R}$, cm^{-1}
Scattering angle 13°						
406.40	2.0	2.50	0.20	1.15	NLS*	—
406.50	1.8	2.90	0.22	1.12	»	—
406.60	1.9	2.80	0.20	1.07	»	—
406.75	2.2	2.44	0.22	0.93	»	—
406.95	2.2	2.40	0.24	0.89	»	—
407.57	3.2	1.64	0.25	0.61	»	—
408.00	3.4	1.50	0.32	0.58	»	—
408.90	5.1	1.10	0.33	0.38	WFS	—
410.10	5.6	0.92	0.37	0.33	»	—
411.05	7.0	0.76	0.34	0.26	»	—
412.75	8.3	0.64	0.44	0.22	»	—
414.20	11.0	0.49	0.39	0.17	»	—
417.20	15.0	0.35	0.46	0.11	»	—
420.20	20.0	0.27	0.44	0.084	»	—
424.50	24.0	0.22	0.48	0.063	»	—
Scattering angle 90°						
406.50	1.8	3.000	0.25	22.00	2.4	2.4
406.55	1.9	2.950	0.20	21.40	2.8	2.4
406.70	2.0	2.700	0.35	20.30	3.7	3.1
406.85	2.3	2.360	0.31	17.60	3.9	3.6
407.00	2.6	2.000	0.33	15.00	4.3	3.9
407.50	3.3	1.620	0.33	12.20	4.9	4.9
408.40	4.3	1.230	0.36	9.00	6.9	6.7
409.45	5.5	0.960	0.33	7.10	7.9	8.2
410.65	7.3	0.730	0.45	5.10	NLS	—
412.70	10.1	0.530	0.48	3.60	»	—
415.55	13.4	0.400	0.48	2.32	»	—
418.30	16.5	0.320	0.48	1.90	»	—
423.30	22.0	0.250	0.50	1.42	»	—
425.50	28.0	0.190	0.53	1.30	»	—
432.00	39.0	0.140	0.50	0.60	»	—
440.00	52.5	0.100	0.50	0.30	WFS	—
443.00	72.0	0.073	0.50	0.22	»	—
449.50	72.0	0.073	0.50	0.20	»	—
453.00	83.0	0.064	0.06	0.15	»	—

*NLS—non-Lorentzian shape.

benzene, we took the value $40\cdot 10^{-6}\text{cm}^{-1}$ at $\lambda = 4360\text{ \AA}$ and $T = 293\text{ K}$, which is used to calibrate nephelometers.¹²

To calculate χ , we used our own measurements of the scattering constants R_{zz} and R_{zx} and the quantity $\Delta\varepsilon = (n_{\parallel}^2 - n_{\perp}^2)/S$. The values of the refractive indices n_{\parallel} and n_{\perp} and the order parameter S for the investigated NLC's were taken from Ref. 13. The dependence of χ and χ^{-1} on temperature is shown in Fig. 3 for PAA.

4. DISCUSSION

It can be seen from Eqs. (4) and (6) that the relaxation time of the order parameter τ can be determined directly only from the halfwidth of the component $I_{zz}(\omega)$ of the scattered light since the distribution of the intensity in the zx polarization $I_{zx}(\omega)$ is the sum of two distributions:

$$I_{zx}(\omega) = I_1 \sin^2(\theta/2) + I_2 \cos^2(\theta/2). \tag{9}$$

Here I_1 and I_2 are the factors of $\sin^2(\theta/2)$ and $\cos^2(\theta/2)$ in Eqs. (4) and (6). The intensity distribution I_1 coincides with that of $I_{zz}(\omega)$, which presents the practical opportunity of distinguishing the intensity distribution I_2 from the total intensity distribution over frequency of the component $I_{zx}(\omega)$. We carried out this operation of separating the intensity distributions in the scattering spectra of both samples. The contour $I_1 = (3/4)I_{zz}(\omega)\sin^2(\theta/2)$ was placed alongside of the contour $I_{zx}(\omega)$, and after subtracting it

point-by-point from the contour $I_{zx}(\omega)$, the distribution I_2 was obtained. Analysis of the contour I_2 showed that the doublet or wing fine structure (WFS) is clearly visible at the small scattering angles (13° and 20°). At the scattering angle 90°, to observe the WFS it is necessary to heat the liquid crystals to higher temperatures. In exact agreement with Eq. (9), at $\theta = 180^\circ$ we do not observe any WFS, since $\cos^2\theta/2 \rightarrow 0$ as $\sin^2\theta/2 \rightarrow 1$.

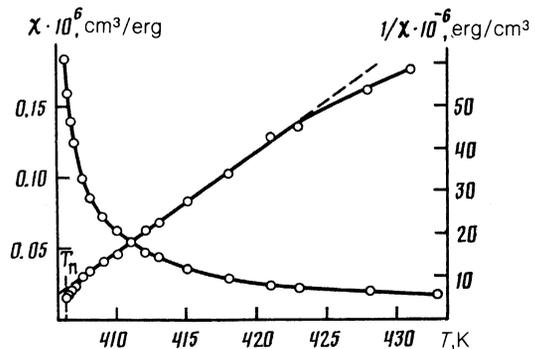


FIG. 3. Temperature dependence of the susceptibility χ and the inverse susceptibility χ^{-1} in the isotropic phase of PAA. The solid line is the result of smoothing the data.

As was also predicted by theory,⁷ WFS is observed for $q^2\eta/\rho\Gamma < 0.5$, i.e., in the second region (see Sec. 2) at the angles 13° and 90° in PAA. For these same angles the dip in the spectral lines is not visually observed for $q^2\eta/\rho\Gamma > 0.5$. In MBBA the picture is similar with the difference that the RLW halfwidth here is significantly smaller than in PAA and the resolving power of our setup allowed us to observe WFS only down to a value of $q^2\eta/\rho\Gamma \approx 0.05$. For $q^2\eta/\rho\Gamma \geq 1$, our analysis of the shape of the contour I_2 both for MBBA as well as PAA gave a non-Lorentzian line without a dip in the center, which is also in agreement with theoretical predictions. As has already been said, in the isotropic phase of a nematic it is possible to experimentally reach the region $q^2\eta/\rho\Gamma \gg 1$ for moderate viscosities. As can be seen from Table I, for PAA at the scattering angle of 90° the value of this parameter near the transition temperature becomes greater than 20. For MBBA near the transition temperature T_c we have $q^2\eta/\rho\Gamma \approx 1000$. Under these conditions the theory predicts that the intensity distribution I_2 will again be Lorentzian with halfwidth

$$\Delta v_{1z} = \Gamma / (1 - R) = \Delta v_{zz} \pi c / (1 - R).$$

Analysis of the line shape I_2 at the scattering angle $\theta = 90^\circ$ in the temperature interval 406.5–409.4 K (eight points in all) confirmed the theoretical predictions. The values of the halfwidth $(1/2)\Delta v_{1z}$ are given in Table I. They can be compared with the values of $(1/2)\Delta v_{zz} / (1 - R)$, given in the last column of the table. One can check that there is satisfactory agreement between experiment and theory. Analysis of the intensity distribution I_2 for $q^2\eta/\rho\Gamma \gg 1$ in MBBA also gave agreement of experiment and theory.

The temperature dependence of the parameter R for PAA is shown in Fig. 4. As can be seen from the figure, far from the transition temperature the value of R is constant and close to those found for pure liquids, i.e., $R = 0.4$ – 0.5 . The value of the parameter R was observed to decrease as T_c was approached both in the sample of MBBA and in the sample of PAA—in PAA R decreased, starting at $\Delta T = 4$ K; in MBBA, starting at $\Delta T = 13$ K. This is the first time that this behavior of R has been observed. In de Gennes's theory R is a dimensionless parameter connected with the transport coefficients μ , η , and ν , which have the dimensions of viscosity. A singularity in R should be associated with singularities in these coefficients. A singularity in ν in MBBA and BMOAB was indicated in Ref. 14, but since the relaxation time used in the calculation in Ref. 14 was taken from ultrasound experiments⁵ and the susceptibility was taken from light scattering experiments, the result obtained there was not unique.

In our experiment the susceptibility χ and the relaxation time τ were measured in the same cuvette by the light scattering method, which allowed us to calculate the value of ν with an accuracy of not worse than 10%. Figure 4 shows values of ν calculated according to formula (2). As can be seen from the figure, the magnitude of ν near T_c has a singularity of the order of 30%. It can also be seen from the figure that the temperature regions in which the singularities of R

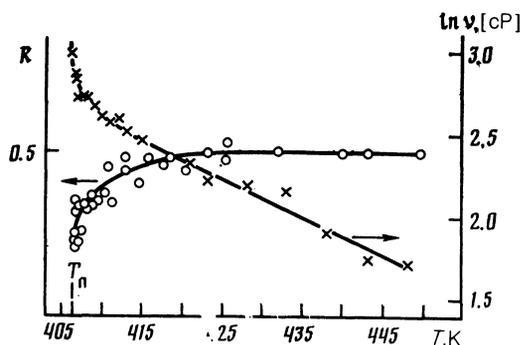


FIG. 4. Temperature dependence of the parameter R and the viscosity coefficient ν of PAA in the isotropic phase. Solid lines are the results of smoothing the data.

and ν are observed coincide. Since $R = 2\mu^2/\nu\eta$, its decrease with approach to T_c is in good agreement with the increase of ν in the same temperature interval and all the more so since the viscosity coefficient η is identical with the shear viscosity and has no singularities near T_c . We obtained similar results for MBBA.

The viscosity coefficient ν is usually associated with the orientational modes of motion,¹ and since fluctuations near the IL–NLC transition are fluctuations of the orientation of the axes of the molecules, a singularity of the viscosity ν was completely to be expected in analogy with the singularity of the viscosity η in binary critical mixtures.¹⁵

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