Fluctuations in a nematic liquid crystal in a light-scattering experiment; correlations at the thermal phase transition to isotropic liquid

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The results of measurements of the scattering intensity and of the coherence times (in the direction of an incident laser beam) are presented for three types of fluctuations (transverse, biaxial, and longitudinal) in thin oriented specimens of MBBA in the nematic and isotropic phases, and also in the phase-transition region. The experimental data are interpreted by introducing several additional assumptions regarding the influence of the forces that couple the molecules with the walls and regarding the fluctuation-stabilizing effect of the laser field. From the data obtained, values are estimated for the parameters that characterize the phase transition in MBBA. The specificity of a phase transition in thin oriented specimens, as compared with thick cells, is demonstrated. A possible explanation of the tricritical nature of the phase transition in MBBA is given for the first time.

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1. INTRODUCTION

Experimental investigation of the statistical properties of laser radiation transmitted through nematic liquid crystals (NLC), especially near the phase transition (PT) to isotropic liquid, is important both for the physics of PT and for NLC themselves; and there are now a number of papers devoted to this problem. In particular, measurements have been made of the intensity and linewidth of the scattered light, and also of the temperature behavior of the parameters of the NLC[1-7] and of the spatial coherence of the transmitted light in the region of the NLC PT.[8] Of greatest interest are direct measurements of the correlations of the light scattered into the NLC in the immediate vicinity of the PT. Experiments on scattering are usually interpreted from the point of view of fluctuations of the orientation of the director, which are the principal cause of anomalously strong scattering of light in NLC.[9] But under certain conditions, in addition to these (transverse uniaxial) fluctuations, there may show up in the experiment fluctuations of the NLC order parameter of another type, longitudinal and transverse biaxial[10,11]: the first are due to fluctuations of the modulus of the order parameter, the second to fluctuations that disturb the uniaxiality of the order parameter. In longitudinal fluctuations in NLC, for visible light, the so-called singular longitudinal fluctuations should dominate; they originate as a result of strong transverse fluctuations, in distinction to the nonsingular.[11,12]

The present paper presents the results of measurements on the intensities of various types of scattering and on the temporal correlation functions of the intensity (TCFI) of the scattered light, $\langle I(t+\tau)I(t)\rangle$, in oriented thin specimens of the NLC N–p-methoxybenzlylidene–p-butylaniline (MBBA), including measurements in the immediate vicinity of the PT region, by use of a correlation technique of recording. The scattered radiation was recorded near zero angle by optical subtraction; the TCFI was measured with a many-channel analyzer. An experimental geometry was achieved in which the various types of fluctuations should show up whose contribution is being discussed. Estimates were obtained for the parameters that characterize the PT. Attention was paid to the role of external fields and in particular, for the first time, to the role of the laser field itself. The increase of the coherence time τ_c of the recorded radiation in the region of the PT was observed. An attempt was made to interpret the results from the point of view of an explanation of the nature of the PT in NLC, in particular of its recently discussed tricritical behavior.[13-15] This is the first time that this has been done in light-scattering experiments. An explanation is also offered of the possible reasons for the tricritical character of the PT, resulting from the structure of oriented thin specimens of NLC. While important assumptions are made here for NLC, they make it possible to explain in a unified manner the experimental results obtained.

2. ARRANGEMENT OF THE APPARATUS AND METHOD OF MEASUREMENT

The experimental setup, partially explained by us earlier,[8,16] is represented in Fig. 1. Its principal elements are: 1, a stabilized single-mode, single-frequency He-Ne laser ($\lambda = 0.633\ \mu$m) with linearly polarized radiation, with radiation power of the order of several milli-watts; 2, an electronic system for stabilization and control of the temperature in the thermostat in which the cell containing the NLC is located; 3, a polarization interferometer[17]; 4, a system for recording radiation by count of photons; 5, a multichannel pulse-height analyzer AI-4096V with output of the data to a digital printer. The apparatus also had a reference arm for control of the laser power. The stabilization of the temperature over the time of the experiment was of the order of several thousandths of a degree. For recording of the light radiation, an FÉU-79 was used, with photocathode cooled by an electronic system; the threshold of sensitivity of the recorded power, for red light, was of the order of 10^{-18} W for measurement time t_{meas}

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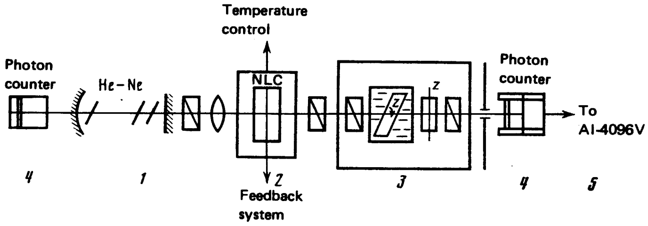

FIG. 1. Block diagram of the experimental setup.

$=10$ sec. Used in the work were planarly and homeotropically oriented (by rubbing with diamond paste in the first case and by a special treatment in the second), freshly prepared cells containing purified NLC MBBA (Mark KhCh), of thickness $d=30$ μm. The separation of the various types of fluctuations and the control of the orientation of the specimens were carried out by means of polarizers located before and after the cell containing the NLC. The laser beam was incident in a direction perpendicular to the glass surfaces of the specimens. The radius of the laser beam was $r_0=0.8$ mm.

The laser radiation was focused on the cell containing the NLC by a lens of focal length $f=11$ cm. The recorded scattered light was cut out by a diaphragm of size ~20 μm, located at a distance of 1 m from the scattering volume. Thus the experiment accomplished a local probing of the process of nucleation of a new phase during the PT, and thereby diminished both the role of inhomogeneities of orientation of the NLC specimen, and also the role of structural inhomogeneities that occur during the PT in NLC near the heterogeneous-state region.[18] Furthermore, the localness of the scattering volume decreased the influence of various secondary factors (temperature gradients, multiple scattering, gravitational effects, etc.).

The measurement method included two stages and consisted of the following.

1. In the first stage, the light scattered at zero angle was separated and its intensity was measured. The laser beam transmitted through the NLC fell on a polarization interferometer, which was adjusted for measurement of the minimum $I_{\min}$ of the interference picture in the direction of the incident beam and thereby, in essence, produced an optical subtraction (heterodyning) of the spatially coherent component of the transmitted light.[16] The method of measurement in this stage was tested by measurement of the absolute value of the intensity of Rayleigh scattering in nitrobenzene,[16] and also by comparison of the intensity of scattering by transverse fluctuations in MBBA, as obtained by us, with values calculated by known formulas.[11]

2. In the second stage, direct measurements were made of the TCFI $\langle I(t+\tau)I(t)\rangle$ of the light I_{scat} scattered at zero angle, by means of a multichannel analyzer that measured the statistics of the sequence intervals $W(\tau)$ of the pulses of photo-counts. It can be shown[19,20] that if the mean number of pulses recorded within the limits of the coherence time τ_c is appreciably smaller than unity, then the distribution function of the time intervals is

$$W(\tau)\sim\langle I(t+\tau)I(t)\rangle. \tag{1}$$

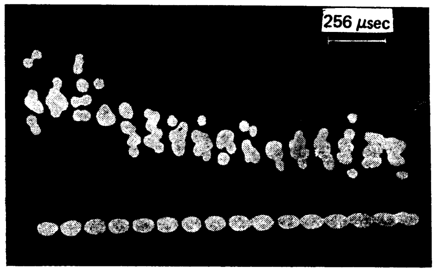

FIG. 2. Typical photograph for TCFI, obtained on the screen of the AI-4096V.

Thus under these conditions, we obtained directly on the screen of the AI-4096V the TCFI of the light transmitted through the NLC; one of the typical photographs is shown in Fig. 2.

The operation of the whole system and the method of measurement were tested with a calibration light source with variable τ_c, namely laser radiation scattered by a rotating dull disk. Our values for τ_c agreed with accuracy no worse than 10% with calculated values. The values of τ_c that could be measured with the AI-4096V comprised an interval from several microseconds to one hundred milliseconds. Formula (1) was well satisfied at low counting rates, no higher than 0.2 pulses during the coherence time. This also determined the time of the information collection in the experiment during each measurement of the TCFI; it was usually of the order of 20–30 min.

The value of τ_c that we obtained directly for the laser beam, with the same measurement procedure, was of the order of several milli-seconds over a wide range of values of its intensity, and exceeded by more than an order of magnitude the values obtained for the light scattered by the NLC. We note also that although the measured values in the method considered are of the TCFI, which usually convey no information about phase fluctuations, the optical subtraction used leads to an a actual dependence of the TCFI on a constant phase shift between the interfering beams. This makes it possible in principle to separate the spectra of amplitude and of phase fluctuations (compare with the so-called method of optical synchronous detection[21]).

3. EXPERIMENT

It is well known that during the PT in NLC, there is a heterogeneous-state region in which the two phases, nematic and isotropic, coexist. This complicates the obtaining of direct information about the behavior of the parameters of the NLC in the PT region. Such effects show up most strongly in thin oriented cells.[8,18] Therefore the measurements of the temperature dependence of I_{scat} and τ_c for MBBA during the phase transition, in our experiments, were made by cooling from the isotropic phase to the temperature T_1 corresponding to the upper bound of the heterogeneous region, and by heating of the nematic phase to T_2, corresponding to the lower bound of this region. The temperature interval T_1-T_2 of its existence was ~0.5 K in the experiment. But in the measurements of the values of I_{scat} and τ_c, both for the nematic and for the isotropic phase, the tempera-

TABLE I.

Phase of NLC	Orientation	Experimental geometry number	Angle (in degrees) between: p & n	p & p′	Type of scattering	$I^{rel}_{scat} = I^{(i)}_{scat}/I^{(3)}_{scat}$	τ_c, 10^{-6} sec
Nematic	Planar	1	0	0	Longitudinal	0.73	312
		2	0	90	Transverse	0.02	229
		3	90	0	Longitudinal + biaxial	1.00	405
	Homeotropic	4	90	90	Transverse	0.02	246
		5	90	90	Biaxial	0.03	240
		6	90	0	Longitudinal + biaxial	2.27	282
Isotropic		7	–	0	Longitudinal + biaxial	3.54	507
		8	–	90	Biaxial	0.03	243

ture was fixed and differed from the value T_2 (below and above, respectively) by about 10 K. These data, for various experimental geometries, are presented in Table I (the values of I_{scat} have been normalized to the scattering intensity in geometry 3: $I^{rel}_{scat} = I^{(i)}_{scat}/I^{(3)}_{scat}$, where $i = 1$ to 8). The data presented are averages over several measurements (five to seven) on different cells containing MBBA. The reproducibility of the results was on the average of the order of 30%. The values for I^{rel}_{scat} correspond to the experimentally recorded intensity of the light transmitted through the NLC, with subtraction of the background noise of the laser, measured for an empty cell without NLC.

Figure 3 shows the dependences of $I^{(3)}_{scat}$ and of τ_c on ΔT obtained for light transmitted through MBBA in experimental geometry 1, when the polarization vectors **p** of the incident light and **p′** of the scattered were parallel to the direction **n** of the director in the NLC cell (scattering by longitudinal fluctuations). The vertical lines isolate the heterogeneous-state region. The value of ΔT is measured from the temperature T_2 ($\Delta T = T - T_2$). We also measured the temperature dependence of $I^{(2)}_{scat}$ (geometry 2, scattering by transverse fluctuations) and of $I^{(5)}_{scat}$ (geometry 5, scattering by biaxial fluctuations) during rise of temperature in the nematic phase. In these cases, the values of $I^{(2),(5)}_{scat}$ are tens of times

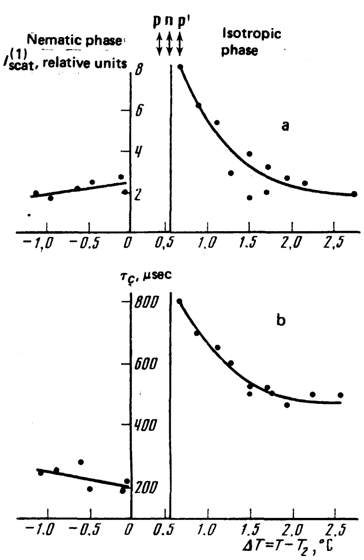

FIG. 3. Experimental relations for intensity (a) and temporal coherence (b) as functions of temperature, for longitudinal scattering.

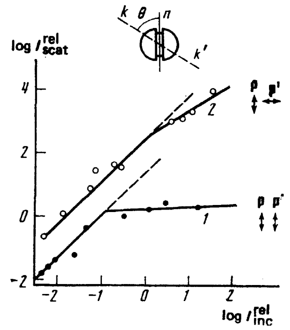

FIG. 4. Scattering intensity in the nematic phase of MBBA as a function of the value of the power of the incident light, for two experimental geometries (on a log-log scale).

smaller than $I^{(1)}_{scat}$ (see Table I) and are close to the level of noise from the laser. Therefore it was not possible to obtain a sure quantitative behavior of the $I^{(2),(5)}_{scat}$ (ΔT) relation. But qualitatively, the value of $I^{(5)}_{scat}$ decreased in the immediate vicinity of the region of PT to isotropic liquid [$\Delta T \sim (-1)°$], and $I^{(2)}_{scat}$ remained practically constant. The relation represented in Fig. 4 will be discussed in numbered part 4 of Section 4. Part 8 of the same section gives data on the scattering of light in the isotropic phase as a function of the cell thickness.

4. DISCUSSION

1. We shall first discuss the contribution of various types of fluctuations of the order parameter during scattering of light in NLC.[10-12] Upon change of the relative orientation of the vectors **p**, **p′**, and **n**, different fluctuations will express themselves differently (for the isotropic phase, the vector **k** must be considered instead of the vector **n**), as is shown in the fourth and fifth columns of Table I. Usually the strongest are the transverse uniaxial fluctuations; the intensity of the scattering by them is proportional to $1/Kq^2$, where K is the elastic constant of the NLC. Excitation of biaxial transverse fluctuations requires surmounting of an energy barrier Δ, whose magnitude is determined by the relation between the coefficients B and C in the expansion of the free-energy density in the Landau theory of PT[22]:

$$\Phi - \Phi_0 = {}^1/_2 AS^2 - {}^1/_3 BS^3 + {}^1/_4 CS^4 + \ldots, \quad A = a(T - T_{cr}) \qquad (2)$$

[for simplicity, tensorial indices have been omitted in (2)]; $\Delta = 20B^2/9|C|$, and the scattering intensity $\sim 1/(Kq^2 + |\Delta|)$, i.e., it is determined by the nature of the PT in the NLC. If the PT is a transition of the first kind, for example near isolated singular or tricritical points, at which $B = 0$, then the intensity of the scattering by biaxial fluctuations increases (Δ is small in this case) and becomes comparable with the scattering by transverse fluctuations (here biaxial static configurations in the NLC should occur interchangeably with uniaxial[11]).

For values $\Delta \neq 0$, scattering by biaxial fluctuations will be appreciable only in the range of sufficiently short wavelengths ($\lambda \leq 3 \times 10^{-6}$ cm).[11] But even in this case, it may show up also in an experiment with visible light in the immediate neighborhood of the transition between isotropic liquid and nematic phase. As was shown by

Korzhenevskiĭ and Shalaev,[12] if the near-continuity of the PT is due to the specific character, for the NLC, of the interaction of the fluctuations, then $|\Delta| \sim [(T - T_{cr})/T_{cr}]^{\gamma}$, where $\gamma = 1.0$ (T_{cr} is the critical temperature). Thus in this case, $\Delta \to 0$ when $T \to T_{cr}$ (but when the PT is near an isolated singular point, Δ is practically independent of temperature).

Longitudinal (singular) fluctuations show up for waves of visible light and dominate in the region of small values of the scattering vector $\mathbf{q} = \mathbf{k} - \mathbf{k}'$; the intensity of scattering by them $\sim 1/q$, i.e. their role increases for scattering at zero angle (we note that for zero scattering angle, the value of q need not tend to zero when $\mathbf{p} \perp \mathbf{p}'$, since in this case the moduli of the wave vectors of the incident and scattered light, $\mathbf{k}$ and $\mathbf{k}'$, are different because of the anisotropy of the medium[9]; this case occurs for scattering by transverse fluctuations in the nematic phase).

The intensity of scattering by longitudinal nonsingular fluctuations $\sim 1/|\Delta|$, and for visible light it is usually less than the intensity of singular scattering.[11] But here one must keep two points in mind: first, allowance for an additional term in the expansion (2), involving the spatial derivatives of the order parameter: $\frac{1}{2}D \times |\nabla S|^2$ for an isotropic medium.[23]

Thus in the experiment, manifestation of scattering by all types of fluctuations is possible for various geometries. But it is not always easy to separate them from each other. The possible difficulties (the principal ones are evidently due to the influence of defects[23]) are discussed in Ref. 24; there it is shown that they do not have an important effect in our experiment.

2. We proceed directly to consideration of our experimental results for I_{scat} and τ_c and comparison of them with theoretical estimates.

In the case of zero-angle scattering, the experimental geometry is important for the value of q. Estimates show that in our experiment, $q \approx 80$ cm^{-1} for geometries 1, 3, and 5–8, and $q \approx 2 \times 10^4$ cm^{-1} for geometries 2 and 4 (with allowance for the finite dimensions of the receiving diaphragm). This also determines the intensity of the scattering in the various experimental geometries; in particular, the fact that the usually most effective uniaxial transverse fluctuations (fluctuations of the orientation of the NLC director) in the present case manifest themselves weakly. Analysis of the data of Table I shows that for geometries 3 and 6, the scattering proceeds principally because of longitudinal fluctuations. Similar suppositions may be made also for geometry 7.

It is interesting to compare our data for the scattering intensity with theoretical estimates. Exact expressions for the differential cross section of scattering by various types of fluctuations, per unit volume, unit solid angle, and unit angular frequency, $d\sigma/d\omega d\Omega$, have been given in a number of papers.[10-12] By comparing the expressions given by Korzhenskii and Shalaev[12] with the experimental data from Table I, one can estimate the values of the parameters that characterize the scattering for MBBA. In particular, from the results for geometries 4 and 5 the value of Δ is estimated as

$$\Delta \approx 320 \text{ cgs.} \tag{3}$$

But the estimation of S leads to an extremely small value, close to zero (the intensity of singular longitudinal scattering is about twice as large as the intensity of nonsingular scattering).

3. The results of part 2 can be explained if attention is paid to the effect of the surfaces of the glass plates between which the NLC layer is located. Their orienting effect is equivalent to the presence of an external field (acting along the long axis of the molecules), which, as is well known, stabilizes the fluctuations, diminishing their amplitude and accelerating their relaxation[9,25] (compare with Ref. 26). The role of the external field here is analogous to a temperature factor in the PT: in the latter case, the fluctuation-suppressing factor is the distance $T - T_{cr}$ to the PT point, while here this role is played by a temperature-independent factor, the external field.[1),22] Modification in this manner of the relations for $d\sigma/d\omega d\Omega$ with allowance for the external field substantially changes the relation of the intensities for the singular and nonsingular scattering; the latter becomes appreciably preponderant, a consequence of the absence of an energy barrier in the excitation of longitudinal singular fluctuations.

Thus the longitudinal scattering is determined in this case by nonsingular scattering, and what must be compared with experiment is the intensities, normalized to it, of scattering by transverse and biaxial fluctuations. Then from the data of Table I (geometries 3–5) one can obtain the following relations (for $T \approx 300$ K):

$$\Delta \approx (101 - 0.8u_1) \text{ cgs}, \quad u_2 \approx (1.8u_1 + 460) \text{ cgs}, \tag{4}$$

where u_1 and u_2 are the coupling energies in planar and homeotropic cells. The requirement of stability of the state of the NLC in the specimen leads to the inequality $\Delta + u > 0$.[11] If we suppose that $\Delta > 0$, then we get from (4) the following inequalities: $u_1 < 126$, $\Delta < 101$, $u_2 < 687$ cgs. Thus according to the estimates (3) and (4), the value of Δ in our experiments, for the nematic phase of MBBA, should not exceed several hundred cgs units.

Anisimov *et al.*[13] assumed that the PT in MBBA is near the region of transition from tricritical behavior to critical. Tricritical behavior of the PT under consideration has now been corroborated in a number of new experiments.[14,15] Our estimates for Δ can also provide confirmation of the proximity of the PT to a tricritical point. We note that the small value of Δ itself leads to an excess of the intensity of longitudinal scattering over the intensity of transverse. This result can be understood if we recall the above-discussed influence of an external field (the glass plates in the present case), which leads to the possibility of occurrence of a tricritical point, originating, as is well known, as a result of the interaction of two different order parameters.[25,27] In our experiment, one of these is due to the nematic order in the NLC; the other may appear because of the influence of the external field,[2)] the role of which is played by the orienting influence of the glass plates (and perhaps also the laser field itself; see below, and cf.

Ref. 28).

4. For full explanation of our experimental results for the nematic phase (cf. geometries 1, 3, and 6), it is necessary to make some additional assumptions, in particular about the orienting influence of the focused incident laser radiation (for example, via the Kerr effect). The laser field then fulfills the role of an additional force, directed along the polarization of the incident light, tending to align the NLC molecules in this direction (for MBBA, $n_e > n_0$). Its influence must be taken into account at values of the electromagnetic field intensity $E \gtrsim 10^3$ V/cm, which is comparable with the continuous laser fields in which the MBBA was located in our experiment.

With such transverse reorientation, the action of the laser field in geometry 1 should stabilize the fluctuations, i.e. diminish the intensity of the scattering, and in geometries 3 and 6 should increase it. In all cases of influence of the field, the value of τ_c should decrease. Therefore the scattering intensity in geometry 1 ($I^{(1)}_{\rm scat}$) is only a fraction 0.7 of its value in geometry 3 ($I^{(3)}_{\rm scat}$) (according to the theoretical estimates given above, $I^{(1)}_{\rm scat}/I^{(3)}_{\rm scat} \approx 3.5$), which is close to the experimental data obtained by us in weak unfocused fields, and the coherence time of the transmitted light is appreciably smaller in the first case than in the second. The large value of the scattering intensity in geometry 6, with a relatively small value of τ_c, also becomes comprehensible.

We especially tested the effect of the laser field on the orientation in MBBA for an oblique experimental geometry (see Ref. 29). Figure 4 shows the experimentally obtained variation of the power of the scattered light with the power of the incident light $I_{\rm inc}$ (the maximum power density in the specimen was of the order 1 kW/cm^2) for two experimental geometries, $\mathbf{p} \parallel \mathbf{p}'$ (1) and $\mathbf{p} \perp \mathbf{p}'$ (2), with an angle of 53° between **k** and **n**. It is evident that in the first case (extraordinary polarization of the scattered wave), strong saturation occurs at large values of $I_{\rm inc}$ because of stabilization of the fluctuations of the MBBA in the laser field. In the second case, this effect of the laser radiation shows up only slightly: a scattered o-wave. Thus the laser field exerts a more strongly stabilizing effect on fluctuations that occur in the vertical plane formed by the vectors **k** and **n**; these show up in longitudinal scattering. The mechanism of this effect must be connected with longitudinal reorientation. For transverse scattering, however, the role of the transverse mechanism of stabilization of fluctuations is increased.

We note also that because an o-wave during its propagation in an inhomogeneous medium does not feel the phase fluctuations of the index of refraction, the appearance of an anomalous transparency is possible for a plane, unoriented layer of NLC during propagation of light with o-polarization in this plane.

5. For scattering in the isotropic phase, it can be shown[24] that comparison of the data for the scattering intensities in the isotropic and nematic phases, with allowance for the influence of an external field, leads to a small value (not larger than a few hundred cgs units) of the parameter $A - u_{\rm isotr}$ in (2). It is interesting that from this one can estimate the order of the temperature interval ΔT of smoothing out of the PT because of the presence of an external field[22]; the result is close to the experimental interval $T_1 - T_2$. Furthermore, our results lead to the relation $\Delta_{\rm isotr} > \Delta$.

6. We shall consider briefly our results for τ_c. As was shown in Ref. 24, the relations between the values of τ_c for the different experimental geometries, shown in Table I, agree qualitatively with theoretical estimates. For example, for the isotropic phase, in fact, the relaxation of the fluctuations should be faster for biaxial scattering than for longitudinal (cf. geometries 7 and 8), and the value of the relaxation time for biaxial scattering should be smaller by about a factor 2 than for longitudinal scattering.

7. We pass on to the temperature dependences. Qualitatively, the theoretical formulas give the following picture.[24] During a PT from the side of the isotropic phase, for longitudinal (nonsingular) scattering, $I_{\rm scat}$ varies little with temperature. From Fig. 3a one can get the result that $I_{\rm scat} \sim (T - T_2)^{\psi}$, where for ψ one gets the estimate $\psi \approx 1.3 \pm 0.1$ at $T - T_2 \approx 3°$. The value $\psi \approx 1.3$ differs from the value of ψ for the tricritical point, for which $\psi \approx 1$, and is close to its scaling value $\psi = 1.28$. But this is apparently an accidental coincidence, caused by the smallness of the temperature interval within which we are determining the value of ψ (cf. Ref. 14). We note that the value $\psi = 1$ for the isotropic phase of MBBA was observed earlier experimentally[5,9] and was interpreted as a substantiation of the classical nature of the PT in NLC because of accidental coincidence of the values of ψ for critical and for tricritical character of the PT.

Biaxial fluctuations also behave similarly in the nematic phase (in the immediate vicinity of the PT, at $T \approx T_2$, $I_{\rm scat\,bi}$ may decrease), but $I_{\rm scat\,bi}$ should be constant also in the isotropic phase near the PT.

Temperature effects are weakly expressed also for transverse scattering in the nematic phase; they are related to a practically constant value of the parameter u_1 ($I_{\rm scat\,transv} \sim 1/u_1$). This result was observed earlier[7,9] but was explained in another manner. We note that in

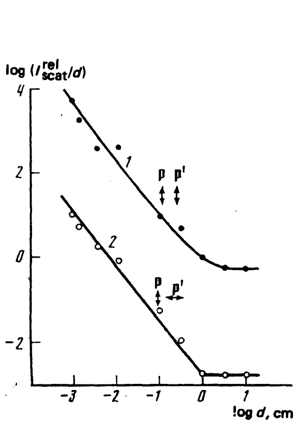

FIG. 5. Effectiveness of scattering $I_{\rm scat}/d$ for various cell thicknesses d in the isotropic phase of MBBA for two experimental geometries (on a log-log scale), for scattering by longitudinal (1) and biaxial (2) fluctuations.

the absence of an external field, $I_{scat\ transv} \sim 1/S^2$ and should increase in the PT region.

The increase of τ_c that we observed for longitudinal scattering at the PT in the isotropic phase (see Fig. 3b) may be due to a discontinuity of the viscosity ν at the PT.[7,9] If we assume, as is usually done, that here $\nu \sim S^2$, then the increase of τ_c is due just to the proximity of the PT in MBBA to the tricritical point, for which $\tau \sim (\Delta T)^{-\varphi}$ with $\varphi = 0.5$ (in the critical region, τ should remain constant). Our data lead to the relation $\tau_c \sim (T - T_2)^{-\varphi}$ with the estimate $\varphi \approx 0.6 \pm 0.1$ at $T - T_2 \approx 3°$. In the nematic phase, for increasing distance from T_{cr} the temperature effects should be weakly expressed.

8. We measured the effectiveness of the light scattering in the isotropic phase of MBBA as a function of the thickness d of the cell, over the range 8 μm to 10 cm. Figure 5 shows the variations obtained for I_{scat}/d. A substantial influence of the boundary layers on the value of I_{scat} is seen in thin cells; it is evidently due to residual orientation of the molecules in them (cf. Ref. 30) and leads to greater effectiveness of the scattering. Approximation of the graph for thin specimens with a straight line leads to a dependence of I_{scat} on the thickness of the form $I_{scat} \sim d^{1-k}$ with $k \sim 1.25$. Only beginning with thicknesses ~1 cm is proportionality of I_{scat} to the thickness of the scattering layer (emergence of the plotted relations to a plateau) actually observed. Analysis shows that in this case the values of the parameters that describe the PT in thick cells increase and approach the values known from the literature. It follows from a comparison of our data with theoretical formulas (see Ref. 24) that the principal influence on the intensity of the scattered light in the isotropic phase, for thick cells, is exerted by the coefficient a in the expansion (2); this agrees with estimates of the values of a and of $\Delta = 20B^2/9C$ from the paper of Anisimov *et al.*[13] for this expansion ($a \gg \Delta$).

9. As follows from what has been presented, at present the tricritical behavior of the PT in MBBA may be considered proved; thus the traditional ideas about the reasons for the similarity of the PT in NLC to a PT of the second kind have been reconsidered, but the reason for such tricritical character of the PT is considered unclear.[13-15] Some explanations for our case have already been presented above. We shall now discuss this specifically.

Analysis shows[24] that the large values of τ_c that we measured in the PT region of MBBA are due to formation of local correlated regions (clusters). They may exert a large influence on the character of the PT in NLC (cf. Ref. 23). In fact, the ordering in these regions must be described not solely by means of the parameter S that is traditional for NLC and describes the nematic order, but also by introduction of some parameter that describes the mean attraction between molecules, as is usually accepted for smectic A.[9 3)] This latter parameter actually plays the role of a second order parameter and interacts with S. The presence of two parameters leads to a tricritical point[25, 27] (see also Ref. 31). Interesting in this connection is the paper of Hardouin,[32] where it is shown that the PT between nematic and smectic A actually reveals tricritical behavior (see also Ref. 33). Thus the tricritical nature of the PT in MBBA can be understood from this point of view.

Another explanation, related to the symmetry of oriented specimens of NLC, is also possible. There are now already a number of experimental demonstrations of the noncentrosymmetric character and optical biaxiality of the oriented nematic phase of MBBA.[34] The nature of the PT in MBBA can then be understood from the point of view of this strong physical assertion for NLC. In fact, the noncentrosymmetric character of the medium during the PT must lead to the vanishing identically of terms of odd degree in the expansion (2) for the free energy[35 4)] (cf. Ref. 36). Thus we at once obtain an explanation of the small value of the coefficient B (and therefore also of Δ) measured in our experiments, and also a necessity for taking account of u_{isotr} in (2) (see Ref. 24). But biaxiality of these specimens leads to a tricritical point, that is to smallness also of the coefficient C.[14] Since these properties of MBBA show up only in thin oriented specimens, it may be stated that orientation of NLC makes the PT in them more nearly continuous; in particular, it enhances its tricritical character, which must be only weakly expressed in experiments with large unoriented volumes of NLC. Furthermore, a definite role in the character of the PT may be played by the microscopically inhomogeneous structure of the NLC; this actually has to do with the local symmetry of the structure at distances larger than the scale of the intermolecular interactions, but smaller than λ (cf. crystals with incommensurable superstructure[37]).

We note that the large values of τ_c that we measured may also serve as an indirect manifestation of noncentral symmetry, and also apparently of biaxiality, in MBBA.[24]

In conclusion, we remark that the last assumptions about the structure of NLC, which have far-reaching physical consequences, actually go beyond the framework of the theoretical approach that is used in the description of fluctuations in NLC, and therefore a more systematic analysis is necessary.

5. CONCLUSION

We shall summarize the main results obtained in this paper.

Values were obtained experimentally for the scattering intensity I_{scat} in the direction of the incident beam and for the coherence time τ_c, for three types of fluctuations in thin oriented specimens of the NLC MBBA: transverse, biaxial, and longitudinal. The contribution of each of these is analyzed with introduction of several additional assumptions (about the effect of the coupling of the molecules with the walls and about the action of the laser radiation). Large values of τ_c, of the order of hundreds of microseconds, were obtained.

The temperature dependences for I_{scat} and τ_c were measured for MBBA in the PT region in the isotropic liquid. An increase of the values of I_{scat} and τ_c was recorded for the first time for longitudinal scattering in the PT region, on the isotropic-phase side.

From the experimental data, estimates were made of the coefficients in the Landau expansion of the thermodynamic potential, which have anomalously small values and lead to a large value of the intensity of longitudinal scattering.

The nature of the PT in NLC and the possible reasons for its tricritical behavior are analyzed from the point of view of untraditional assumptions about the structure of NLC, which have far-reaching consequences for the physics of NLC and lead to small values of the coefficients in the Landau expansion. The smallness of B may be due to noncentral symmetry of oriented thin specimens of NLC; the nearness to a tricritical point (smallness of B and C) may be due to the influence of external forces, leading in particular to the formation of clusters (local regions in the NLC with correlation both in the orientations and in the positions of the centers of gravity of the molecules) or to the appearance of biaxiality in the NLC. Both these causes are characteristic specifically of thin oriented specimens of NLC. In thick cells, the values of the parameters that describe the PT are close to those known from the literature.

These conclusions already follow from a qualitative interpretation of the results obtained. To obtain more exact quantitative results and to confirm the important assumptions made in this paper about the nature of the liquid-crystal state, additional independent investigations are necessary.

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[1)]Then there appears in the expression (2) an additional term, linear in the order parameter, $-Su/3$.

[2)]We note that the presence of walls is equivalent to the presence of impurities in the MBBA. The occurrence of two order parameters in the NLC is most obvious in this latter case.

[3)]Cf. the cybotactic clusters that occur in the nematic phase above the temperature of the PT between nematic and smectic.[9]

[4)]Here additional noncentrosymmetric terms[9] must be added to the expression (2); in particular, along with quadrupolar order for the NLC when the order parameter $S_2 \sim \langle P_2(\cos\theta)\rangle \neq 0$, one must consider also dipolar order $S_1 \sim \langle P_1(\cos\theta)\rangle \neq 0$. Thus here also two order parameters occur.

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