Complex dynamics of isotropic 4-cyano-4-*n*-pentylbiphenyl (5CB) in linear and nonlinear dielectric relaxation studies

A. Drozd-Rzoska and S. J. Rzoska

Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

A comprehensive presentation of the temperature evolution of ''linear'' and ''nonlinear'' dielectric relaxation in the isotropic phase of nematic liquid crystalline compound 5CB (4-cyano-4-*n*-pentylbiphenyl) is given. The ''nonlinear'' relaxation is related to the strong pretransitional rise in the lifetime of prenematic fluctuations. The ''linear'' relaxation has a clear non-Debye and non-Arrhenius form. In the immediate vicinity of the nematic clearing point it shows a weak pretransitional anomaly. Results obtained coincide with the complex liquid relaxation pattern found in transient grating optical Kerr effect studies [A. Sengupta and M. D. Fayer, J. Chem. Phys. **102**, 4193 (1995); R. Torre *et al.*, Philos. Mag. A **77**, 645 (1997)]. The striking similarity to the behavior found in critical, binary mixtures suggests the extension of the ''fluidlike'' hypothesis for the isotropic-nematic transition to dynamic phenomena in the isotropic phase [P. K. Mukherjee. J. Phys.: Condens. Matter **10**, 9191 (1998)]. The presence of both glassy and fluidlike features in isotropic 5CB coincides with the recent results of simulation analysis for the system of hard ellipsoids by Latz *et al.* [Phys. Rev. E **62**, 5173 (2000)] and with the novel general picture for liquid-liquid transitions proposed by Tanaka [Phys. Rev. E **62**, 6968 (2000)].

I. INTRODUCTION

The dynamics of complex liquids is one of the challenges of modern condensed matter physics [1–4]. Its commonly recognized features are the complex pattern of relaxation [1–8], the unusual increase of relaxation times on cooling [1–4] or pressuring [5–7], and the significance of mesoscale structures [1,2,8,9]. Studies of complex liquid dynamics may be particularly interesting near the phase transition where the influence of universal, system-independent behavior occurs [1,8–10]. In the 1990s transient grating optical Kerr effect (TG-OKE) studies [11–18] revealed the complex, three-stage relaxation in isotropic nematogens. The first, slow relaxation showed a strong pretransitional anomaly on approaching the isotropic-nematic (*I-N*) clearing temperature [11–18],

$$\tau_{\text{slow}} = \frac{\tau_0^{\text{slow}}}{T - T^*}, \tag{1}$$

where the τ_0^{slow} is the amplitude, T^* is the extrapolated virtual critical temperature, and $\Delta T = T_{I\text{-}N} - T^*$ denotes the discontinuity of the isotropic-nematic (*I-N*) transition. $T_{I\text{-}N}$ is the nematic clearing temperature and T^* is the extrapolated virtual critical temperature.

This relaxation was already known from dynamic light scattering or time-resolved Kerr effect studies ([19–25] and references therein). However, TG-OKE studies in *n*-cyano-*n*-pentylbiphenyl (5CB), *n*-*p*-methoxybenzylidene-*p*′-butylaniline (MBBA) [11–16], and nematic mixture ZLI 1167 [17,18] showed that relation (1) may be valid up to $T_X \approx T_{I\text{-}N} + (35\text{–}40\text{ K})$, where fluctuations shrink to two or three molecules and practically cease to exist. The value of τ_{slow} changes from about 1 ms at $T_{I\text{-}N}$ to less than 1 ns at T_x [11–18]. Relation (1) can be derived from the mean-field Landau–de Gennes (LdG) model [19].

In the intermediate time scale TG-OKE studies revealed a weak temperature-dependent relaxation [17,18],

$$\frac{\tau_{\text{int.}}}{\eta} = \frac{\tau_0^{\text{int.}}}{T}, \tag{2}$$

where the shear viscosity η was described using the Arrhenius temperature dependence.

The intermediate relaxation time reached a few nanoseconds for $T \rightarrow T_{I\text{-}N}$. It is noteworthy that no pretransitional effects were observed. However, experimental data in Refs. [17,18] were not conclusive near $T_{I\text{-}N}$. The Debye-Stokes-Einstein (DSE) form of relation (2) suggested that $\tau_{\text{int.}}$, corresponds to the diffusive reorientational motions of the long axis of rodlike molecules [17,18].

In the picosecond domain a fast relaxation, described by the universal decay function, was found to be [12–18]

$$G(t) \propto t^{-\vartheta}, \tag{3}$$

where t is the elapse time at a given temperature and the exponent $\vartheta \approx 0.63$.

In 5CB, the temperature dependence remained almost constant at about 300 ps for $T < T_x$ [16]. Sengupta and Fayer [16] showed that analysis based on the LdG model gives the value $\vartheta = \frac{1}{2}$ [16]. Their novel theoretical approach, employing the Ising model for critical systems and the mode-coupling theory (MCT) [16], made it possible to reproduce the slow and the fast relaxations. The non-mean-field behavior appearing in relation (3) was also obtained in the molecular dynamics simulation for a single particle relaxation [26,27]. It is noteworthy that the complex relaxation in isotropic 5CB given by Eqs. (1)–(3) was also found in the stimulated gain-phase dynamic light scattering studies [28].

Dielectric relaxation is one of the basic tools for studying dynamics in complex liquids [1–9]. Regarding the isotropic phase, the vast majority of dielectric relaxation studies sug-

gest the validity of the Arrhenius temperature dependence and the almost-Debye spectrum of relaxation times [24,29–37] and references therein], which agrees with the mean-field description for the *I-N* transition. In 1977 Druon and Wacrenier [29] and Lippens, Parneix, and Chapoton [30] tested nematic *n*-cyanobiphenyls (7CB, 8CB) and compared Cole-Cole plots in the nematic and in the isotropic phase. For the latter they reported a strong asymmetric deformation. In 1985 Buka and Price [31] suggested that for rodlike molecules as *n*-cyanobiphenyls this behavior may be a result of two single relaxation time, Debye, processes. In 1987 Bose *et al.* [32] for 8CB and 7CB pointed to the possible validity of the Martin-Maier-Saupe mean-field model. Recently, Jadzyn *et al.* [36,37] summarized the molecular interpretation of dielectric relaxation of nematic liquid crystals basing on measurements in 4-(trans-4-*n*-hexylcyclohexyl)-isothiocyanatobenzene. The resolution into elementary spectra contributions of the Cole-Cole plot was performed by using the Cole-Cole formula [37]

$$\varepsilon^* = \varepsilon_\infty + \sum_i \frac{\Delta\varepsilon_i}{1 + (i\omega\tau_i)^{1-k_i}}, \tag{4}$$

where k_i is the parameter that refers the distribution of relaxation times of the *i*th reorientational process, $\Delta\varepsilon_i$ and τ_i denote the relaxation strength and relaxation time, respectively. The ε_∞ is the high-frequency value of the permittivity, $\omega = 2\pi f$, and f is the measurement frequency.

Regarding the isotropic phase Jadzyn *et al.* [37] obtained the parametrization using two terms in Eq. (3), which corresponded to the rotation of the rodlike molecule around the short and the long axes. For the nematic phase he suggested three modes of reorientation. Values of parameters k_i about 10^{-2} were reported, i.e., the almost Debye distribution of two relaxation processes associated with the rotation of the rodlike molecule around the short and long axes. Regarding the important temperature evolution of relaxation times the application of the simple Arrhenius dependence is strongly recommended [24,39–37]. However, as for the isotropic phase such a statement is based on the analysis of not more than ten temperatures chosen up to (5–20 K) above the clearing temperature. Moreover, the analysis of the distribution of dielectric relaxation time were conducted for one or two temperatures remote from the nematic clearing temperature [24,29–37]. Recently, Massalska-Arodz *et al.* [38] and Urban, Gestblom, and Dabrowski [39] tested isopentylcyanobiphenyl (5*CB), a compound resembling the structure of 5CB, which can be supercooled down to 230 K in the isotropic phase. They obtained a clear non-Arrhenius temperature behavior and a strong broadening of loss curves on cooling. A similar behavior was noted in the nematic phase of liquid crystalline mixture *E*7 [40]. In the immediate vicinity a "singular" broadening of loss curves was found. The broad nematic phase in *E*7 enabled studies in a large range of temperatures and gave the evidence for a clear non-Arrhenius temperature evolution of relaxation times [40]. The non-Arrhenius and non-Debye dependences were also noted in preliminary tests for the isotropic phase of 8CB [41]. It is noteworthy that for 5CB the non-Arrhenius tem-

perature behavior was already found by Zeller [42] in 1982 although his data only covered a limited range of temperatures in the isotropic phase.

In basic monographs the simple mean-field description is still the only proposal for the *I-N* transition [19,24,25,33,43–45]. This is mainly based on the success of the LdG model in the parametrization of pretransitional static anomalies in the isotropic phase of the electro-optic Kerr effect, the optical Kerr effect (OKE), the Cotton-Mouton effect (CME), and the intensity of the scattered light (*I*) [19,24,25,43–52] and references therein. However, discrepancies between the mean-field-based predictions and the experimental results for static and thermodynamic properties of the *I-N* transition piled up since the mid-1970s ([53–55], and references therein). It seems that for the static properties the agreement between the theory and the experiment can be reached by the *fluidlike* hypothesis [54,56,57] which assumes that T_{I-N} lies on a branch of the hypothetical coexistence curve (binodal) [54,56]. Studies of the static *linear* and *nonlinear* dielectric permittivity provided a particularly strong support for the *fluidlike* hypothesis. The most important studies here are the precise experimental estimations of the discontinuity ΔT and the specific-heat critical exponent $\alpha = 0.5 \pm 0.02$ [55,57–60].

This paper presents a comprehensive analysis of temperature behavior of *linear* and *nonlinear* dielectric relaxation of in the isotropic phase of 4-cyano-4-*n*-pentylbiphenyl (5CB, $T_{I-N} = 35.1\,^\circ$C and $T_{N\text{-Cryst.}} = 21\,^\circ$C), often treated as a model liquid crystalline compound [24]. The first aim of the presented studies was the comparison of the relaxation patterns obtained for the TG-OKE measurements and for the dielectric relaxation tests. The second aim was to test the possible extension of the *fluidlike* hypothesis for dynamic phenomena in the isotropic phase of nematic liquid crystals. The obtained coexistence of *glassy* and *fluidlike* features in the isotropic phase correlate with the recent results of the simulation analysis for hard ellipsoids by Latz, Schilling, and Latz [61] and the novel model for liquid-liquid transitions proposed by Tanaka [62].

II. EXPERIMENT

Dielectric relaxation studies were conducted using the Novocontrol Concept 80 broadband dielectric spectrometer with the Quatro temperature control system. Studies were conducted from $f = 1$ MHz to $f = 1$ GHz, the range usually applied in dielectric relaxation tests in similar compounds [36,37]. Measurements were conducted with the five-digit resolution and ± 0.02 K temperature stabilization.

In liquids, changes of dielectric permittivity induced by the strong electric field are described by the nonlinear dielectric effect (NDE). It is defined as $\varepsilon_{\text{NDE}} = (\varepsilon^E - \varepsilon)/E^2$, where ε^E and ε are dielectric permittivities in a strong and weak (measuring) electric field. The strong electric field was applied in the form of dc pulses: length $\Delta t_D = 2$–16 ms and voltage $U = 200$–1200 V. The application of rectangular high-voltage pulses made the the heating of the sample unnecessary. The validity of the condition $\varepsilon^E - \varepsilon \propto E^2$ was always tested. Measurements were conducted for frequencies ranging from $f = 34$ kHz (the lowest frequency ever used in
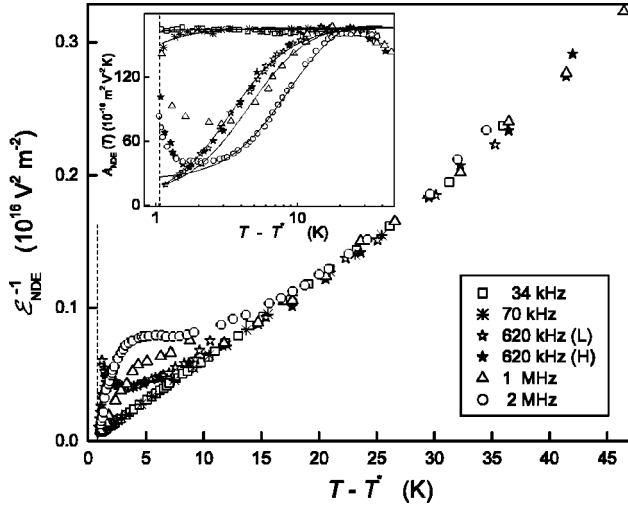
FIG. 1. Reciprocals of measured NDE values for frequencies given in the figure. For $f = 620$ kHz results are presented for the measuring field $U = 2$ V mm^{-1} (L) and $U = 20$ V mm^{-1} (H). The inset shows results of apparent amplitude analysis of data from the main part of figure. The arrow shows the clearing point.

NDE tests) up to $f = 2.0$ MHz. The strong electric field induced a change in the capacitance of the measurement capacitor containing the sample: about 1 fF for $C_{\text{sample}} \approx 100$ pF. This caused a shift in frequency of the generator including the measurement capacitor [63], which was registered with the use of the modulation domain analyzer HP 53310A. This measurement technique essentially differs from the two-generator technique used up to now [64]. Only this novel technique made measurements of frequencies as low as $f = 34$ kHz possible. Due to this novel measurement technique the frequency and the intensity of the weak measuring field can be changed. The apparatus was designed and built in our lab by Michal Gorny. The sample was placed in a flat-parallel measurement capacitor made of Invar with a gap of 0.5 mm and the diameter of 20 mm. The capacitor was surrounded by a special jacket fed by the Julabo HD 45SP circulating thermostat. The temperature was measured using a miniature platinum resistor (DIN 43 260) placed in one of the capacitor covers. The tested 5CB was purchased from the BDH company and carefully degassed immediately prior to measurements. Data were analyzed using the ORIGIN 6.1 software. All errors are given as three standard deviations.

III. RESULTS AND DISCUSSION

Figure 1 shows reciprocals of measured NDE values for a series of frequencies of the weak measuring field. For the lowest tested frequency ($f = 34$ kHz) experimental data up to $T_X = T_{I-N} + 35$ K, without any distortions near T_{I-N}, are described by the linear dependence [57]

$$\varepsilon_{\text{NDE}}^{-1} = A_{\text{NDE}}^{-1}(T - T^*), \tag{5}$$

where $A_{\text{NDE}} = (2\varepsilon_0/3a)(\Delta\varepsilon^0)^2$ denotes the amplitude of the pretransitional effect in the static limit, $\Delta\varepsilon^0$ denotes the an-

isotropy of static dielectric permittivity for a perfectly ordered sample. The coefficient a is the constant amplitude of the second-rank term in the LdG expansion [19].

For 5CB the collective relaxation time $\tau_{\text{slow}}(T_{I-N}) = 0.6$ μs [20–22] and hence for $f = 34$ kHz the static condition $f\tau_{\text{slow}} \gg 1$ is well satisfied. The experiment gave $A_{\text{NDE}} = 168$ (10^{-16} m^2 V^{-2} K). Taking the value $\Delta\varepsilon^0 = 11$ [22] one may get $a = 0.043$ (10^{-6} J mol^{-1} K^{-1}) [22] in a fair agreement with earlier data [22–25]. The obtained value of discontinuity of the transition, $\Delta T = (1.1 \pm 0.05)$ K, agrees well with results of earlier studies [55,58]. Noteworthy is the lack of the "background term" in relation (5) often taken into account in KE or CME studies [21–25]. The application of the novel NDE experimental technique showed that even for the frequency $f \approx 100$ kHz, taken as the static one in earlier tests [55,58–60], deviations from Eq. (5) in the immediate vicinity occur. This is particularly visible for the distortion-sensitive apparent amplitude analysis (the inset in Fig. 1). The appearance of distortions near T_{I-N} can be associated with the coincidence between the time scale of the NDE response ($1/f$) and the time scale of the tested (τ) system occurring on the rise of the measurement frequency. For an arbitrary frequency the application of the LdG model gives: $A_{\text{NDE}} = (2\varepsilon_0/3a)(\Delta\varepsilon^0\Delta\varepsilon^f)$ [57], where $\Delta\varepsilon^f$ denotes the anisotropy of dielectric permittivity for the given measurement frequency f. Hence, for 5CB the amplitude A_{NDE} should be frequency and temperature independent. This is in clear disagreement with the results presented in Fig. 1. The obtained behavior can be explained by recalling the *fluidlike* hypothesis. In the homogeneous phase of critical mixtures [65],

$$\varepsilon_{\text{NDE}} = C\chi\langle\Delta M^2\rangle_V, \tag{6}$$

where C is a constant parameter, $\chi = \chi_0(T - T_C)^{-\gamma}$ denotes susceptibility, T_C is the critical consolute temperature and $\langle\Delta M^2\rangle_V$ is the mean-square of the order parameter fluctuations.

Critical mixtures belong to the same universality class as the Ising model and the one-component fluids for which $d = 3$ and $n = 1$, where d and n denote dimensionalities of the system and of the order parameter, respectively. In this universality class properties are described by nonclassical critical exponents, for instance for the susceptibility $\gamma = 1.23$, for the correlation length $\nu \approx 0.63$, and for the specific heat $\alpha \approx 0.12$ [44]. However, it was argued in Ref. [65] that in a strong electric field the correlation length may become anisotropic: $\xi(E) = (\xi_{\parallel}, \xi_{\perp}, \xi_{\perp})$. The component $\xi_{\parallel}$ remains nonclassical whereas the component $\xi_{\perp}$ crosses over the Ginzburg criterion and is described by the classical (mean field) exponent $\nu = \frac{1}{2}$. The quasinematic structure induced by a strong electric field makes the susceptibility exponent almost classical ($\gamma \approx 1$). This made the explanation of unusual critical anomalies of NDE [65,66] and EKE [67] possible. For naturally anisotropic, prenematic fluctuations, the relation (6) takes the form [57]

$$\varepsilon_{\text{NDE}} = C\chi\langle|\Delta M|\rangle_V^{f\to 0}\langle|\Delta M|\rangle_V^f, \tag{7}$$

where the susceptibility $\chi^* = \chi_0^*(T-T^*)^\gamma$, $\gamma = 1$.

Hence, one may expect that the amplitude of NDE describes the properties of mesoscale pretransitional fluctuations. The influence of the measurement frequency on the stationary NDE response may be shown using the apparent amplitude analysis results of which are presented in the inset in Fig. 1,

$$A_{NDE}(T) = \varepsilon_{NDE}(T-T^*) = A_{NDE}^{HF} + \frac{A_{NDE}^{LF}}{1+\omega^2\tau_{slow}^2}, \quad (8)$$

where τ_{slow} is given by relation (1).

The simultaneous fitting for all tested frequencies gave $A_{NDE}^{LF} = 164 \pm 2(10^{-16}\ m^2\ V^{-2}\ K)$, $A_{NDE}^{HF} = 7 \pm 2(10^{-16}\ m^2\ V^{-2}\ K)$ and $\tau_0^{slow} = (0.55 \pm 0.05)\ \mu s\ K$. The latter value agrees with the ones obtained in time-resolved OKE [20–22] or TG OKE [12–18] studies. In the static limit, NDE registers an average response of several fluctuations but does not detect a single fluctuation: $\langle|\Delta M|\rangle_V^{f\to 0} \propto \Delta\varepsilon^0$. This is the case of the static NDE. On increasing the frequency, the coincidence between the system and the measurement time scales occurs. Hence, the response from a single prenematic fluctuation can be detected. But within the fluctuation the prenematic order causes the cancellation of permanent dipole moments (μ) ordered in the antiparallel way. For higher frequency near T_{I-N} the anisotropy of dielectric permittivity associated with the permanent dipole moment is almost negligible and so $\langle|\Delta M|\rangle_V^f \propto \Delta\varepsilon^0$ ($\mu = 0$). This may explain the unusual negative sign of NDE near T_{I-N} obtained in some nematogens for higher measurement frequencies [68–71]. The above hypothesis is supported by the comparison of the experimental ratio of amplitudes with those resulting from Eqs. (7) and (8): $(A_{NDE}^{LF}/A_{NDE}^{HF})_{exp.} = 23 \pm 1$ and $(A_{NDE}^{LF}/A_{NDE}^{HF})_{Eqs.\ (6,7)} = (\Delta\varepsilon^0)^2/(\Delta\varepsilon^0\Delta\varepsilon_{\mu=0}^0) = 22.4$ where $\Delta\varepsilon^0 = 11$ [22] and $\Delta\varepsilon_{\mu=0}^0 = 0.49$ [72]. For the novel NDE technique a test of the effect of the weak measuring field intensity on the pretransitional behavior was also possible. No influence of this factor was found on the static limit. However, already for $f = 620\ kHz$ the pretransitional behavior is strongly affected by the intensity of the measuring field (Fig. 1). This factor may be responsible for deviations from relation (8) occurring in the immediate vicinity of T_{I-N}.

Considering the validity of the *fluidlike* hypothesis the question arises whether the dependence for the relaxation time applied in Eqs. (1) and (8) can be found in systems belonging to the Ising universality class for critical phenomena. Dynamic light scattering and sound attenuation experiments showed that in critical binary mixtures the evolution of the relaxation time is given by [44]

$$\tau_{flukt.} \propto (T-T_C)^{-y}, \quad (9)$$

where $y = z\nu$, z is the critical dynamic exponent and T_C is the critical consolute temperature. Light scattering or sound attenuation experiments gave $y \approx 1.9$ in agreement with relation (8) for $\nu = 0.63$ and $z \approx 3$ (the value for the conserved order parameter) [44].
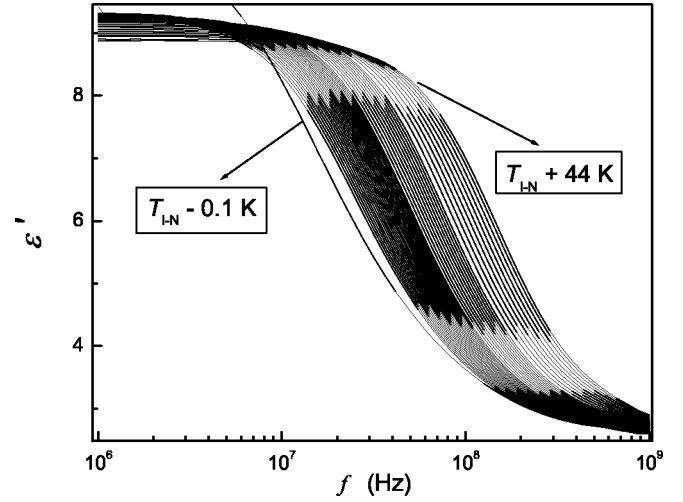

FIG. 2. Results of measurements of the real part of dielectric permittivity in the isotropic phase of 5CB.

However, these experiments were associated with isotropic fluctuations. In the opinion of the authors the dynamics of prenematic fluctuations should be compared with the decay of elongated, anisotropic fluctuations. This may happen in a critical mixture under a strong external field, for instance, under shear flow [73,74] or under strong electric field [66,75,76]. The recent analysis of the shear viscosity anomaly [77] and the decay of NDE after switching-off the strong electric field [66] suggests that in both cases the quasinematic structure in the immediate vicinity of T_C may appear. This yielded $y \approx 1$ and hence $\nu = 1/2$ and $z = 2$ (the value for the nonconserved order parameter) in agreement with relations (1) and (7).

Let us now consider the *linear* dielectric relaxation behavior. Measurements were conducted for 51 temperatures ranging from T_{I-N} to $T_{I-N} + 44$ K. Results of measurements of the real and imaginary parts of dielectric permittivity are presented in Figs. 2 and 3. It is clearly visible that the number of tested temperatures per decade increases on approaching the clearing temperature. Basing on these data Fig. 4 shows the Cole-Cole plot for the immediate vicinity of the nematic
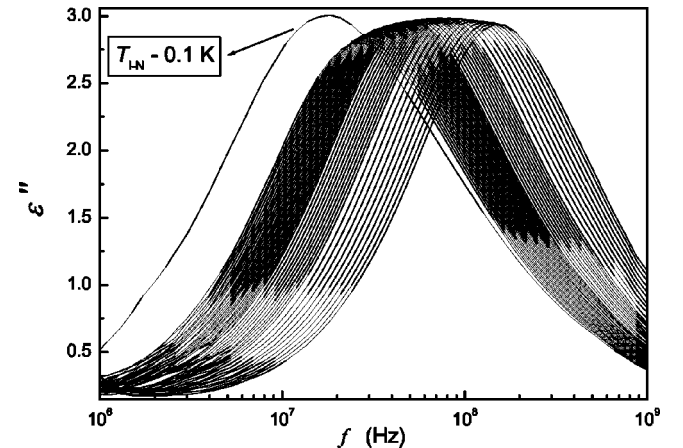

FIG. 3. Results of measurements of the imaginary part of dielectric permittivity in the isotropic phase of 5CB.
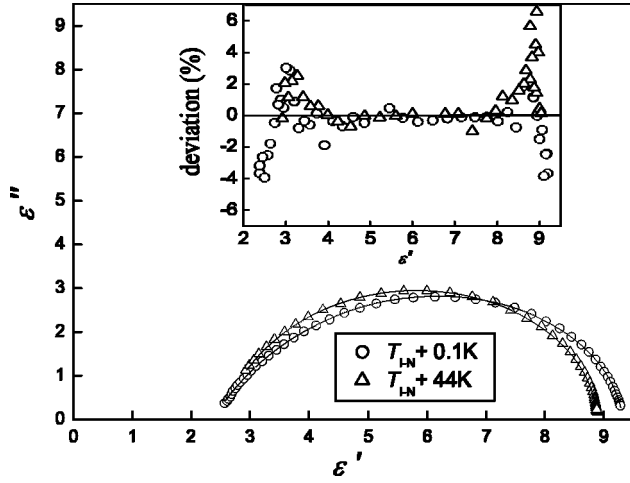
FIG. 4. Cole-Cole plot of data from Figs. 2 and 3 for the immediate vicinity and for the largest tested distance from the clearing point. The maximal values of ε'' are related to $f = 25.5$ MHz for $T = (T_{I\text{-}N} + 0.1 \text{ K})$ and $f = 155$ MHz for $T = (T_{I\text{-}N} + 44)$ K. The solid curves are parametrized by the HN relation (9) with the following parameters: $a = 0.74 \pm 0.02$, $b = 0.93 \pm 0.02$, $\tau_{\text{HN}} = 7.4$ ns ± 0.03, $\Delta \varepsilon = 6.92 \pm 0.05$, $\tau_\infty = 2.52 \pm 0.03$ for $T = (T_{I\text{-}N} + 0.1)$ K and $a = 0.83 \pm 0.02$, $b = 1 \pm 0.01$, $\tau_{\text{HN}} = 1.2$ ns ± 0.01, $\Delta \varepsilon = 6.47 \pm 0.02$, $\tau_\infty = 2.46 \pm 0.06$ for $T = (T_{I\text{-}N} + 44)$ K. The inset shows the relative deviation of the HN fit from experimental data given in Fig. 4.

clearing temperature and for the greatest tested distance from $T_{I\text{-}N}$. An attempt to parametrize the Cole-Cole dependence in Fig. 4 by means of the sum of two Cole-Cole equations [37] failed for the immediate vicinity of $T_{I\text{-}N}$. A parametrization with a reliable error of fitting both near and remote from the clearing temperature was possible when applying the Havrilliak-Negami (HN) function [78] that is often used in complex liquids,

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta \varepsilon}{[1 + (i \omega \tau_{\text{HN}})^a]^b}. \tag{10}$$

The obtained parameters are given in Fig. 4. It is noteworthy that similar singular behavior of the distribution of relaxation times was recently obtained also in high-resolution tests in the nematic phase of 5CB that included the immediate vicinity of $T_{I\text{-}N}$ [79].

Figure 5 shows the normalized superposition of a few chosen experimental loss curves, known as the time-temperature superposition in the glass transition physics [78,80]. The validity of the dependences found for amorphous materials by Jonsher [81] can be seen in Fig. 1,

$$\varepsilon''_{T = \text{const}} \propto \left(\frac{f}{f_p} \right)^m \quad \text{for} \quad f < f_p$$

and

$$\varepsilon''_{T = \text{const}} \propto \left(\frac{f}{f_p} \right)^{-n} \quad \text{for} \quad f > f_p, \tag{11}$$
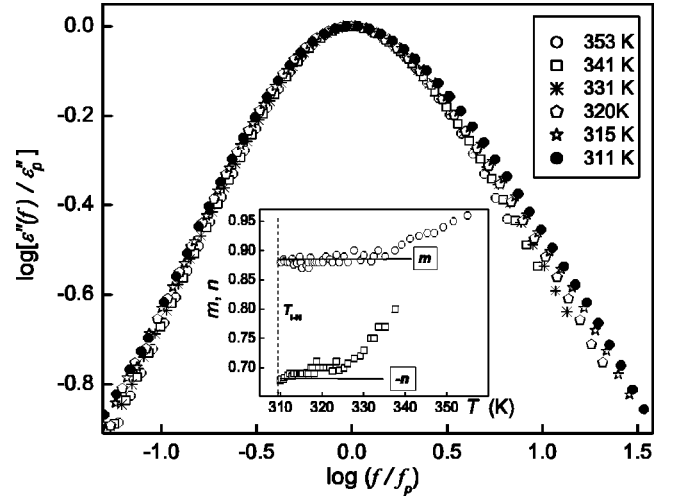

FIG. 5. Normalized superposition of chosen dielectric loss curves in the tested range of temperatures. The inset shows the temperature evolution of m and n power coefficients [see Eq. (11)] determined from the derivative analysis $d(\ln \varepsilon'')/(\ln f)$ as constant-value horizontal lines [38].

where parameters $0 \leqslant m \leqslant 1$ and $0 \leqslant n \leqslant 1$ characterize the shape of the loss curve; Values $m = n = 1$ are for the single relaxation time in the Debye process. Parameters in relation (11) are associated with HN relation (10) by $m = a$ and $n = ab$ [78]. Values of coefficient m and n presented in the inset were determined using the derivative analysis of the loss curves: $(d \ln \varepsilon'')/d \ln f$. The constant values of the obtained dependence determine parameters m (for $f < f_p$) and n (for $f > f_p$). The obtained temperature evolution of these parameters is shown in the inset to Fig. 5. It is noteworthy that for $T < T_X$ the low-frequency wing power exponent remains constant at $m \approx 0.88$. The same value of m, within the limit of experimental error, was recently found for the ethanol-dodecane critical mixture [82]. Regarding the high-frequency wing, the value of the coefficient n decreases gradually to about 0.6.

Figure 6 shows the temperature evolution of dielectric relaxation times, taken as $\tau = 1/f_p$. Value of f_P were determined from the condition $(d \ln \varepsilon'')/(d \ln f) = 0$. It is clearly visible that the simple Arrhenius description is valid only in a narrow range of temperatures. To parametrize the non-Arrhenius behavior the Vogel-Fulcher-Tamman (VFT) function is often applied to complex liquids [1–8]. It also portrays the data presented in Fig. 3,

$$\tau = \tau_0^{\text{VFT}} \exp\left(\frac{D T_0}{T - T_0} \right), \tag{12}$$

where $\tau_0^{\text{VFT}} = 0.172$ ns, the ideal glass temperature $T_0 = 218 \pm 5$ and $D = 2.26 \pm 0.2$ the parameter classifying the fragility of glass-forming materials. The latter value is typical of fragile glass formers [3,4].

Recently, the Eyring-type equation was successfully applied to portray the dependence of dielectric relaxation times remote from T_C for the ethanol-dodecane critical mixture [82]. It is worth recalling that such a dependence was already
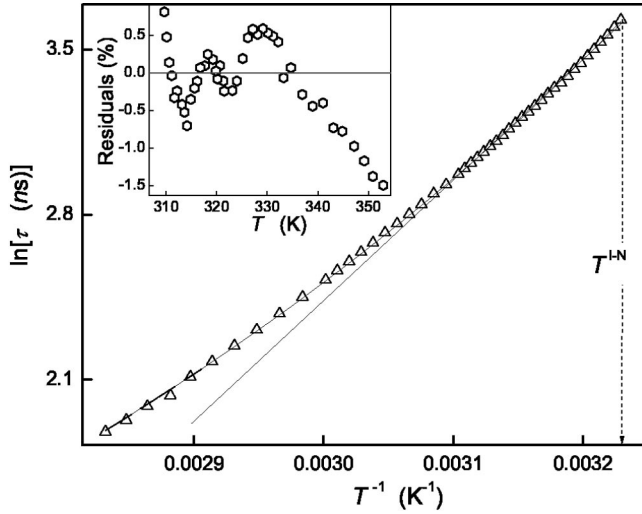
FIG. 6. Temperature evolution of dielectric relaxation times, taken as reciprocals of loss curve peaks, in the isotropic phase of 5CB. The solid curve is parametrized by the VFT Eq. (12). The line shows the limited validity of the Arrhenius dependence for portraying $\tau(T)$ experimental dependence. The inset shows the residual analysis of the VFT relation fit quality.

used for the intermediate relaxation time in TG-OKE studies [relation (2)]. The distortion sensitive analysis of experimental data applied in Fig. 7 shows that except for the vicinity of $T_{I\text{-}N}$ this dependence also portrays dielectric relaxation times in isotropic 5CB,

$$\tau_{\text{Eyring}} = \left(\frac{A}{T}\right)\exp\left(\frac{B}{T}\right), \tag{13}$$
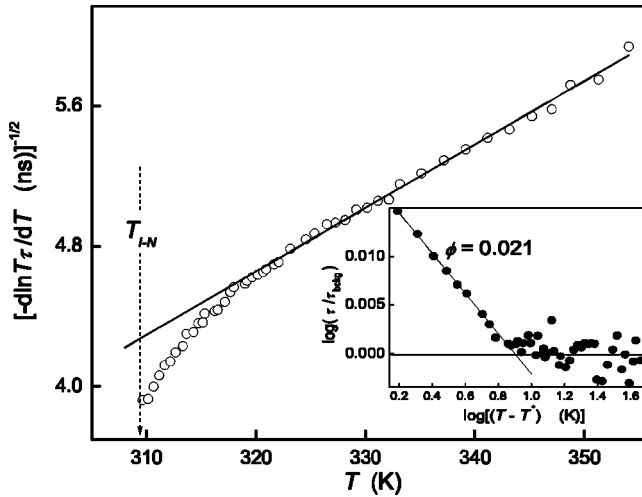

FIG. 7. Plot of the derivative analysis of the temperature dependence of dielectric relaxation times. It shows the possible validity of the Eyring-type dependence [relation (13)] remote from the clearing point (straight line) and the pretransitional effect in the immediate vicinity of $T_{I\text{-}N}$ (the deviation from the straight line). The inset shows the proposal of parametrization of this pretransitional effect by relation (14). The horizontal dashed line shows the "background" behavior remote from $T_{I\text{-}N}$ (straight line in the main part of the figure).

where $A = (0.36 \pm 0.05)$ ns K and $B = (2102 \pm 10)$ K.

Near $T_{I\text{-}N}$ the discrepancy from this behavior is clearly visible. The inset in Fig. 7 shows that it can be portrayed by

$$\tau = \tau_{\text{Eyring}}(T - T^*)^{-\phi}, \tag{14}$$

where $\phi = 0.021 \pm 0.04$.

It is noteworthy that the obtained value of the discontinuity of the *I-N* transition (ΔT) is once more the same as the one presented in NDE studies. Similar pretransitional behavior of dielectric relaxation time was also obtained for the ethanol-dodecane critical mixture [82]. However, in the isotropic 5CB the detection of the anomaly was only possible owing to the derivative analysis (Fig. 7). This can be associated with the principal weakness of the obtained anomaly caused by the discontinuity of the *I-N* transition and the fact that *linear* dielectric permittivity is not directly coupled to fluctuations as it is in the case of NDE. For dielectric permittivity the registered response is the average from the isotropic and prenematic regions. The influence of prenematic fluctuations is more significant on approaching T^* due to the increase of their size and lifetime (ξ, τ). Hence, the pretransitional discrepancy from relation (12) may be related to the local viscosity within fluctuations and to the changes of the number of molecules in them. Noteworthy is the recent proposal of a novel analysis of the viscosity anomaly in critical mixtures [77]. In the immediate vicinity of the critical point the appearance of classical (mean-field) quasinematic structure described by the MCT critical exponent $\phi = 0.042$ was suggested. Assuming that such a dependence also occurs for the viscosity within the prenematic fluctuations that are associated with the number of molecules changing according to the relation $(T - T^*)^{-0.5}$ [83], one may obtain the value of the exponent from Eq. (14).

It was found that the temperature evolution of loss curve maxima is described by the same function as the static dielectric permittivity [55,57,58]. A similar behavior was also observed for the ethanol-dodecane critical mixture [82]. Solid lines in Fig. 8 are parametrized by

$$\varepsilon_p''(T) = \varepsilon''^* + a''(T - T^*) + A''(T - T^*)^{1-\alpha}$$

for

$$T_{I\text{-}N} + T_x > T > T_{I\text{-}N}, \tag{15}$$

where $\varepsilon''^* = 1.93 \pm 0.01$, $\alpha = 0.49 \pm 0.04$, $a'' = -0.00122 \pm 0.0006$, $A'' = 0.121 \pm 0.005$, and $\Delta T = 1.1 \pm 0.1$. Values of $\varepsilon_p''(T)$ are for 20 MHz$< f_p <$1 GHz.

For the static dielectric permittivity it was found in Ref. [55] that

$$\varepsilon'(T) = \varepsilon'^* + a'(T - T^*) + A'(T - T^*)^{1-\alpha}$$

for

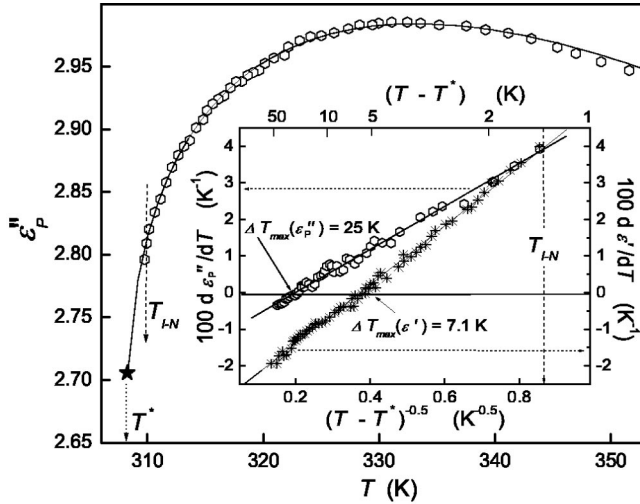$$T_{I\text{-}N} + 100 \text{ K} > T > T_{I\text{-}N}, \tag{16}$$

FIG. 8. Evolution of maxima of dielectric loss curves in the isotropic phase of 5CB. The solid curve is parametrized by Eq. (15). The star shows the extrapolated value of the virtual critical (*tricritical*) point. The arrow indicates the clearing point. The inset shows results of the derivative analysis of experimental data maxima of peaks and static dielectric permittivity (data from Ref. [55]) in the linearized scale giving evidence for the critical exponent $\alpha = 1/2$. The intersection with the horizontal line determines the place at which ε_p'' and ε' change their temperature behavior on approaching $T_{I\text{-}N}$.

where results are for constant frequency $f = 10$ kHz, $\varepsilon'^* = 10.741 \pm 0.03$, $\alpha = 0.50 \pm 0.04$, $a' = -0.0277 \pm 0.002$, $A' = 0.144 \pm 0.003$, and $\Delta T = 1.1 \pm 0.1$.

In both cases, the same values of the exponent $\alpha \approx 0.5$ and the discontinuity $\Delta T \approx 1.1$ were obtained. It is noteworthy that the validity of relation (16) for portraying both the static and ionic domains down to 20 Hz in *n*-cyanobiphenyls was shown in Ref. [83]. The validity of relations (15) and (16) is supported by the distortion-sensitive derivative analysis presented in the inset in Fig. 8. For $\varepsilon_P''(T)$ relation (15) describes the experimental data up to $T \approx T_x$, i.e., in the fluctuation region. For $\varepsilon'(T)$ relation (16) is valid for the whole tested range of temperatures, up to $T = (T_{I\text{-}N} + 100)$ K. The static dielectric permittivity registers the cancellation of permanent dipole moments due to the antiparallel ordering and this process does not react to the passing through T_X. The anomaly of $\varepsilon_P''(T)$ may be associated with the energy accompanying this process. The inset in Fig. 8 shows that the temperature at which the pretransitional effects bend down (antiparallel ordering dominates) for ε_P'' occurs at $(T_{I\text{-}N} + 27)$ K and for ε' already at $(T_{I\text{-}N} + 7)$ K.

IV. CONCLUSIONS

Results are presented of an experimental attempt at a comprehensive presentation of the temperature dependence of *linear* and *nonlinear* dielectric relaxation in the isotropic phase of nematogens. Results obtained coincide with the complex liquid relaxation pattern found in TG-OKE studies [12–18]. Noteworthy is the similarity of the obtained properties with those found in the homogeneous phase of a criti-

cal mixture [73]. This suggests that the *fluidlike* hypothesis [54–60] may be also valid for the dynamic phenomena in the isotropic phase of nematogens. Dynamic processes registered by the NDE are associated with the slow, collective relaxation [Eq. (1)]. In the immediate vicinity of $T_{I\text{-}N}$ the sensitivity to the intensity of the weak measuring field occurs. One may associate this fact with the increase of size and lifetime of pretransitional fluctuation as well as with the increase of the susceptibility to external disturbances (χ^*). The *linear* dielectric relaxation can be associated with the intermediate relaxation found in TG-OKE studies. The temperature dependence of the linear dielectric relaxation time shows a weak pretransitional anomaly, not detected in TG-OKE experiments [12–18]. Dielectric relaxation studies also provide information on the distribution of relaxation times. Particularly noteworthy is the universal, temperature-independent value of the exponent describing the low-frequency wing of the loss curves: $m \approx 0.88$. All the mentioned features of the linear dielectric relaxation were also found in similar studies of the ethanol-dodecane critical mixture [82]. This may suggest that the structure created by the prenematic fluctuations may have a vital influence on the behavior of the isotropic phase as it was suggested for the low-frequency, ionic-dominated behavior of dielectric permittivity [83].

Results of TG-OKE studies and the discussed dielectric measurements may suggest that in the isotropic phase of liquid crystalline materials apart from the *fluidlike* behavior some *glassy* features appear, such as the complex relaxation pattern, the non-Debye form of loss curves and their broadening on cooling, and the possible validity of the VFT equation [78]. The *fluidlike* behavior dominates the NDE pretransitional anomaly, manifested in $\varepsilon_P''(T)$ and $\varepsilon'(T)$ dependences. The universal, system-independent behavior also influences the form of the low-frequency wing of loss curves. The *fluidlike* behavior in isotropic nematogens may be associated with the *pseudospinodal* and *tricritical* behavior [57]. This is supported by the fact that the application of Josephson's scaling law [44] gives the dimensionality $d = 3$ for the experimental values of the critical exponents for specific heat $\alpha \approx 0.5$, susceptibility $\gamma = 1$, and the correlation length $\nu = 0.5$. These values point to the pseudospinodal fluidlike and *tricritical behavior*. Recently, Marinelli and Mercuri [84] conducted precise photopyroelectric measurements of anisotropy in the thermal conductivity for the nematic phase of 5CB. Rzoska *et al.* [85] analyzed the anisotropy of the static dielectric permittivity in 6OCB and 7OCB using high-resolution data. Both tests gave clear evidence for the tricritical value of the order parameter exponent $\beta = 0.25$ in the nematic phase.

Regarding the appearance of *glassy* properties Latz, Schilling, and Latz [61] showed that for the hard ellipsoid system with prenematic, orientational fluctuation dynamic properties, the behavior typical of the ideal glass transition should be expected. Also, recently Tanaka proposed [62] a novel model of liquid-liquid transitions suggesting the basic significance of cooperative medium-range local structures appearing in a sea of a "normal liquid." One of the interesting results of this model is the proposal of explaining the appearance of the so called "Fisher clusters" [78,86]. Tanaka

associated this phenomenon with the existence of a hidden, critical (spinodal) point below the glass temperature, to be expected in the negative pressure region [87]. The lifetime of his "pretransitional fluctuations" should be described within the mean-field limit by $\tau \propto (T - T_{Sp})^{-1}$, where T_{Sp} is the (pseudo)spinodal temperature. Tanaka [62] also suggested that the postulated local bond ordering should be associated with the nonconserved order parameter, in contrast to the "normal liquid" dominated by density changes. Pressure should decrease the manifestation of this pretransitional effect. For the *fluidlike* description of the *I-N* transition T^* is the (pseudo)spinodal temperature. The pretransitional behavior is strongly influenced by the mean-field properties as discussed above. Pressure increases the discontinuity of the I-N transition and hence pretransitional anomalies are smaller for higher pressures [58]. The evolution of prenematic fluctuations is given by relations (1) and (7) and may be associated with nonconserved order parameter. Basing on data from Refs. [55,58] one may estimate the pressure evolution of the discontinuity of the *I-N* transition for 5CB: $\Delta T = 1.1 + 0.0093P$, where P is in MPa and T is in K. Hence, the hypothetical "hidden" critical (tricritical) point may be placed at $P = (-115 \pm 20)$, MPa, i.e., for a stretched 5CB.

[1] R. G. Larson, *The Structure and Rheology of Complex Liquids* (Oxford University Press, New York, 1999).

[2] *Micelles, Membranes, Microemulsions and Monolayers*, edited by W. M. Gelbart, A. Ben-Shaul, and D. Roux, Springer Series on Partially Ordered Systems (Springer-Verlag, New York, 1994).

[3] W. Goetze and L. Sjoegren, Rep. Prog. Phys. **55**, 214 (1992).

[4] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, Contemp. Phys. **41**, 15 (2000).

[5] M. Paluch, J. Ziolo, S. J. Rzoska, and P. Habdas, Phys. Rev. E **54**, 4008 (1996).

[6] M. Paluch, S. J. Rzoska, and J. Ziolo, J. Phys.: Condens. Matter **10**, 4131 (1998).

[7] S. J. Rzoska, A. Drozd-Rzoska, M. Paluch, and J. Ziolo, J. Phys.: Condens. Matter **11**, L451 (1999).

[8] *The Physics of Complex Liquids*, Proceedings of the International Symposium on Complex Liquids, Nagoya, Japan, 1997, edited by F. Yonezawa, K. Tsuji, K. Kaji, M. Doi, and F. Fujiwara (World Science, Singapore, 1998).

[9] P. Pincus, in *Phase Transition in Soft Matter*, NATO Advanced Study Institute Series: Physics, edited by T. Riste (Springer, New York, 1991).

[10] A. Drozd-Rzoska, S. J. Rzoska, J. Ziolo, and K. Czuprynski, J. Phys.: Condens. Matter **43**, L473 (1999).

[11] F. W. Deeg, J. J. Stankus, S. R. Greenfiled, V. J. Newell, and M. D. Fayer, J. Chem. Phys. **90**, 6893 (1989).

[12] F. W. Deeg, S. R. Greenfield, J. J. Stankus, V. J. Newell, and M. D. Fayer, J. Chem. Phys. **93**, 3503 (1990).

[13] J. J. Stankus, R. Torre, C. D. Marshall, S. R. Greenfield, A. Sengupta, A. Tokmakoff, and M. D. Fayer, Chem. Phys. Lett. **193**, 213 (1992).

[14] R. Torre, I. Santa, and A. Righini, Chem. Phys. Lett. **212**, 90 (1993).

[15] J. J. Stankus, R. Torre, and M. D. Fayer, J. Phys. Chem. **97**, 9480 (1993).

[16] A. Sengupta and M. D. Fayer, J. Chem. Phys. **102**, 4193 (1995).

[17] R. Torre and S. Califano, J. Chim. Phys. Phys.-Chim. Biol. **93**, 1843 (1996).

[18] R. Torre, F. Tempestini, P. Bartolini, and R. Righini, Philos. Mag. A **77**, 645 (1997).

[19] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1972); P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[20] H. J. Coles, Mol. Cryst. Liq. Cryst. **49**, 67 (1978).

[21] P. V. Kolinsky and B. R. Jennings, Mol. Phys. **40**, 979 (1980).

[22] R. Yamamoto, S. Isihara, S. S. Hayakawa, and K. Morimoto K, Phys. Lett. **69A**, 276 (1978).

[23] T. Ueno, K. Sakai, and K. Takagi, Phys. Rev. E **54**, 6457 (1996).

[24] *Handbook of Liquid Crystals, Vol. 1 Fundamentals*, edited by G. D. Demus, J. Goodby, G. W. Gray, H. W. Spies, and V. Vill (Wiley-VCH, New York, 1998).

[25] S. Singh, Phys. Rep. **324**, 107 (2000).

[26] A. Perera, S. Ravichandran, M. Moreau, and B. Bagchi, J. Chem. Phys. **106**, 1280 (1997).

[27] S. Ravichadran, A. Perera, M. Moreau, and B. Bagchi, J. Chem. Phys. **109**, 7349 (1998).

[28] R. S. Miller and R. A. MacPhail, Chem. Phys. Lett. **241**, 121 (1995).

[29] C. Druon and J. M. Wacrenier, J. Phys. (France) **38**, 47 (1977).

[30] D. Lippens, J. P. Parneix, and A. Chapoton, J. Phys. (France) **38**, 1645 (1977).

[31] A. Buka and A. K. Price, Mol. Cryst. Liq. Cryst. **116**, 187 (1985).

[32] T. K. Bose, B. Campbell, S. Yagihara, and J. Thoen, Phys. Rev. A **36**, 5767 (1987).

[33] G. Vertogen and V. W. H. De Jeu, in *Thermotropic Liquid Crystals, Fundamentals*, Springer Series in Chemical Physics Vol. 45 (Springer-Verlag, Berlin, 1988).

[34] S. Urban and A. Wuerflinger, in *Advances in Chemical Physics*, edited by I. Pregogine and S. A. Rice (Wiley, New York, 1997), Vol. XCVIII, p. 143.

[35] A. Shoenhals, H. L. Zubova, R. Fricke, S. Frunza, L. Frunza, and R. Moldovan, Cryst. Res. Technol. **34**, 1309 (1999).

[36] J. Jadzyn, G. Czechowski, R. Douali, and C. Legrand, Liq. Cryst. **26**, 1591 (1999).

[37] J. Jadzyn, L. Hellemans, G. Czechowski, C. Legrand, and R. Douali, Liq. Cryst. **27**, 613 (2000).

[38] M. Massalska-Arodz, G. Williams, I. K. Smith, C. Conolly, G. A. Aldridge, and R. Dabrowski, J. Chem. Soc., Faraday Trans. **94**, 387 (1998).

[39] S. Urban, B. Gestblom, and R. Dabrowski, Phys. Chem. Chem. Phys. **1**, 4843 (1999).

[40] M. Paluch, S. J. Rzoska, and N. Gogibus, presented at the *4th International Discussion Meeting on Relaxation in Complex Liquids, Hersonissos, Greece, June, 2001* (unpublished).

[41] S. J. Rzoska, M. Paluch, A. Drozd-Rzoska, P. Janik, and K. Czuprynski (unpublished).

[42] H. R. Zeller, Phys. Rev. Lett. **48**, 334 (1982).

[43] F. H. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. **135**, 195 (1986).

[44] M. A. Anisimov, *Critical Phenomena in Liquid and Liquid Crystals* (Gordon and Breach, Philadelphia, 1993).

[45] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, U.K., 1994).

[46] T. W. Stinson and J. D. Litster, Phys. Rev. Lett. **30**, 688 (1973).

[47] H. Zink and W. H. de Jeu, Mol. Cryst. Liq. Cryst. **124**, 287 (1985).

[48] K.-I. Muta, H. Takezoe, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys. **8**, 2073 (1979).

[49] D. A. Dunmurr and E. Tomes, Mol. Cryst. Liq. Cryst. **76**, 231 (1981).

[50] W. Fuchs and W. Burchard, J. Phys. II **4**, 1451 (1994).

[51] L. Schneider and J. H. Wendorff, Liq. Cryst. **22**, 29 (1997).

[52] N. Blachnik, H. Kneppe, and F. Schneider, Liq. Cryst. **27**, 1219 (2000).

[53] L. Senbetu and Chia-Wei Woo, Mol. Cryst. Liq. Cryst. **84**, 101 (1982).

[54] P. K. Mukherjee, J. Phys.: Condens. Matter **10**, 9191 (1998).

[55] A. Drozd-Rzoska, S. J. Rzoska, and J. Ziolo, Acta Phys. Pol. A **98**, 637 (2000).

[56] P. K. Mukherjee and M. Saha, Phys. Rev. E **51**, 5745 (1995).

[57] A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999).

[58] A. Drozd-Rzoska, S. J. Rzoska, and K. Czuprynski, Phys. Rev. E **61**, 5355 (2000).

[59] A. Drozd-Rzoska, Liq. Cryst. **24**, 835 (1998).

[60] A. Drozd-Rzoska and S. J. Rzoska, Mol. Cryst. Liq. Cryst. **330**, 29 (1999).

[61] M. Latz, R. Schilling, and A. Latz, Phys. Rev. E **62**, 5173 (2000).

[62] H. Tanaka, Phys. Rev. E **62**, 6968 (2000).

[63] M. Górny, J. Ziolo and S. J. Rzoska, Rev. Sci. Instrum. **67**, 4290 (1996).

[64] S. J. Rzoska, A. Drozd-Rzoska, M. Górny, J. Jadzyn, and J. Ziolo, in Proceedings of the 4th International Discussion on Complex Liquids, Hersonissos, Greece, 2001, edited by K. Ngai [J. Non-Cryst. Solids (to be published)].

[65] S. J. Rzoska, Phys. Rev. E **48**, 1136 (1993).

[66] S. J. Rzoska, A. Drozd-Rzoska, and J. Ziolo, Phys. Rev. E **61**, 960 (2000).

[67] S. J. Rzoska, V. Degiorgio, and M. Giardini, Phys. Rev. E **49**, 5234 (1994).

[68] S. J. Rzoska, J. Ziolo, and W. Pyzuk, Chem. Phys. Lett. **197**, 277 (1992).

[69] A. Drozd-Rzoska, S. J. Rzoska, M. Górny, and J. Ziolo, Mol. Cryst. Liq. Cryst. **260**, 443 (1995).

[70] J. Malecki and J. Nowak, J. Mol. Liq. **71**, 11 (1997).

[71] J. Malecki and J. Nowak, Polish J. Chem. (to be published 2001).

[72] D. Demus and T. Inukai, Liq. Cryst. **9**, 1257 (1999).

[73] A. Onuki and K. Kawasaki, Ann. Phys. (N.Y.) **121**, 456 (1979).

[74] D. Beysens, M. Gdabamassi, and B. Momcef-Bouanz, Phys. Rev. A **28**, 2491 (1983).

[75] S. J. Rzoska, J. Ziolo, and A. Drozd-Rzoska, Phys. Rev. E **56**, 2578 (1997).

[76] D. Wirtz, K. Berend, and G. G. Fuller, Macromolecules **25**, 7234 (1992).

[77] A. Drozd-Rzoska, Phys. Rev. E **62**, 8071 (2000).

[78] E. Donth, *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials* (Springer-Verlag, Berlin, 2001).

[79] G. Czechowski, J. Jadzyn, J. Ziolo, S. J. Rzoska, and M. Paluch, J. Phys.: Condens. Matter (to be published).

[80] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. Lett. **86**, 1271 (2001).

[81] A. K. Jonscher, Nature (London) **267**, 673 (1977).

[82] S. J. Rzoska, K. Orzechowski, and A. Drozd-Rzoska, Phys. Rev. E. **65**, 042501 (2002).

[83] A. Drozd Rzoska, S. J. Rzoska, J. Ziolo, and J. Jadzyn, Phys. Rev. E **63**, 052701 (2001).

[84] M. Marinelli and F. Mercuri, Phys. Rev. E **61**, 1616 (2000).

[85] S. J. Rzoska, J. Ziolo, W. Sulkowski, J. Jadzyn, and G. Czechowski, Phys. Rev. E **64**, 052701 (2001).

[86] E. W. Fisher, Physica A **210**, 183 (1993).

[87] A. R. Imre, K. Martinas, and L. P. N. Rebelo, J. Non-Equilib. Thermodyn. **23**, 351 (1998).