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Complex dynamics of supercooling *n*-butylcyanobiphenyl (4CB)

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Results of broadband dielectric spectroscopy (BDS) studies, for a remarkable temperature range (130 K), in supercooled rodlike liquid crystalline *n*-butylcyanobiphenyl (4CB) are shown. They are supplemented by static nonlinear dielectric effect (NDE) measurements in 4CB and 3CB (*n*-propylcyanobiphenyl), giving unequivocal estimations of the hypothetical isotropic-nematic (*I-N*) continuous phase transition temperature T^* and of the discontinuity of this transition ΔT. The distribution of relaxation times becomes strongly non-Debye on approaching the *I-N* transition and follows the Debye pattern for $T > T_{I\text{-}N}+75$ K. The temperature evolution of relaxation times $[\tau(T)]$ and dc conductivity $[\sigma(T)]$ remain non-Arrhenius in the tested temperature range. Their descriptions via the Vogel-Fulcher-Tammann (VFT), Cohen-Grest (CG), and mode coupling theory (MCT) based relations are discussed. The derivative analysis of $\tau(T)$ and $\sigma(T)$ experimental data enabled the detection of dynamic crossovers and the insight into the behavior of the apparent activation energy which follows the relations $E_A^\tau, E_A^\sigma(\sigma) \propto (T/T-T_0)^2$, with a small distortion in the immediate vicinity of the *I-N* transition. The glassy dynamics coexist with the critical-like behavior of temperature dependences of the static dielectric permittivity, maximum of the loss curves and strong pretransitional NDE pretransitional anomaly. These results indicate the significant role of prenematic fluctuations-heterogeneities in the isotropic, fluidlike, surrounding regarding both static and dynamic properties.

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INTRODUCTION

Despite the enormous progress over the last decade the dynamics of glassy liquids remains one of the most puzzling and challenging problems of condensed matter physics (Refs. [1–3] and references therein). One of the possible ways of reaching a detailed insight into this phenomenon is the comparison of a model-based theoretical analysis with experimental results in a system which can mime the given model. In this respect the successful feedback between the mode coupling theory (MCT) based analysis on the hard-spheres model and the experimental studies on colloidal glass formers is worth noting [4–6]. Unfortunately, a molecular glass former can hardly if at all be matched with the hard sphere approximation. Recently it has been suggested that a wide variety of additional structures in the dynamics of molecular glass formers can be the result of the interplay between translational and orientational degrees of freedom [7]. Following this statement a mode coupling analysis was applied to a fluid of hard ellipsoids of revolution which is claimed to be the simplest possible system keeping to the mentioned mechanism [7–11]. As a result, a clear glassy dynamics in the isotropic, fluidlike phase influenced by quasinematic fluctuations-heterogeneities was found. Next an unusual two mode-coupling ergodic–nonergodic crossovers, the upper one associated with orientational freezing ($T_{\mathrm{MCT}}^{\mathrm{orient}}$) and the lower one with translational ($T_{\mathrm{MCT}}^{\mathrm{transl}}$) solidification were obtained. The singular temperature $T_{\mathrm{MCT}}^{\mathrm{orient}}$ was located near the isotropic-nematic (*I-N*) phase transition [8–13].

Rodlike nematogens in the isotropic phase above the *I-N* transition, can be considered as a natural experimental mirror of the hard ellipsoid model fluid [8,10,14–16]. In this respect worth recalling are the "canonical" features of glassy dynamics [1–3,17], namely (i) the non-Arrhenius evolution of dielectric relaxation time (ii) its non-Debye distribution, often temperature dependent.

However, experimental evidence from broadband dielectric spectroscopy (BDS) studies in rodlike nematogens is really puzzling. The big part of experimental results suggest the simple Arrhenius temperature or pressure behavior of relaxation times and their almost Debye distribution. Most often this behavior coincides with the lack of the pretransitional anomaly of the static dielectric permittivity $[\varepsilon'(T)]$ near the *I-N* transition (Refs. [17–31] and references therein). However, a reliable reference to a completely opposite behavior was already noted in the early 1980s [32–40] but rarely cited since. Already in 1981 Bradshow and Raynes [32] followed by Thoen and Menu [33] proved the occurrence of a strong pretransitional anomaly for $\varepsilon'(T)$ in some *n*-cyanobiphenyls (*n*CB), in which the permanent dipole moment is located along the main molecular axis ("rod"). The violation of the Arrhenius dependence was clearly shown by Johari [34,35], Zeller [36–38], and Benguigi [39,40] also in the early 1980s, although their tests focused mainly on liquid-crystal (LC) mesophases. These results have been clearly confirmed in a recent set of studies on rodlike isotropic liquid crystals with the *I-N* transition, including *n*-cyanobiphenyls (*n*CB from $n=5$ to 8) [41–48]. Namely it was shown that

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

$$\varepsilon''_{\mathrm{peak}}(T) = \varepsilon''^* + a''(T-T^*) + b''(T-T^*)^{1-\alpha}, \tag{2}$$

where $\varepsilon'(T)$ was measured for $f=10$ kHz (static domain) and $\varepsilon''_{\mathrm{peak}}(f_{\mathrm{peak}})$ for 20 MHz $< f_{\mathrm{peak}} <$ 200 MHz (dielectric relaxation domain), The $\alpha=0.5\pm0.02$ is the specific heat or inter-

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nal energy related exponent, $T^{*}=T_{I\text{-}N}-\Delta T$ is for the hypothetical, extrapolated continuous transition, ΔT is the measure of the discontinuity of the *I-N* transition.

The validity of the above dependencies was next confirmed by the distortion-sensitive derivative analysis, which gave [43,44,46]

$$\frac{d\varepsilon'(T)}{dT},\frac{d\varepsilon''_{\text{peak}}}{dT} \propto \text{const} + (T+T^{*})^{-\alpha}. \tag{3}$$

Relations (1) and (3) for $\varepsilon'(T)$ can be considered as the consequence of the dominant influence of prenematic fluctuations on the isotropic phase. Due to the equivalence of $\vec{n}$ and $-\vec{n}$ directors, indicating the local nematic ordering, the cancellation of permanent dipole moments positioned in an antiparallel way within the fluctuations, occurs. Consequently, the static dielectric permittivity of fluctuations is qualitatively smaller than the one for the isotropic surrounding, and $\varepsilon'(T)$ starts to decrease on approaching $T_{I\text{-}N}$, in agreement with relations (1) and (3). The behavior of $\varepsilon'_{p}(T)$ may be related to the validity of Kramer-Kronig relations for the pretransitional phenomenon [46].

The above critical-like behavior was coupled with the non-Debye distribution of dielectric relaxation times and their non-Arrhenius temperature dependence. For the latter the validity of the Vogel-Fulcher-Tammann (VFT) relation up to $T_{I\text{-}N}+50$ K was shown [45,46,48–52],

$$\tau(T) = \frac{1}{2\pi f_{\text{peak}}} = \tau_0^{\text{VFT}} \exp\left(\frac{DT_0}{T-T_0}\right). \tag{4}$$

For supercooled liquids T_0 is associated with the extrapolated ideal glass transition and the coefficient D is the measure of fragility, i.e., it is the measure of the distortion from the simple Arrhenius dependence [1–3].

Moreover, in Refs. [45,48] the validity of the alternative, MCT-based parametrization was also shown,

$$\tau(T) = \tau_0^{\text{MCT}}(T-T_X)^{-g} \tag{5}$$

where T_X is the extrapolated ergodic-nonergodic crossover temperature. In Refs. [45,48] T_X was located in the solid phase (*S*), well below the *I-N* and *N-S* transitions.

In the supercooled, nonliquid crystalline, molecular liquids the above relation is valid for $T>T_X+20$ K and the exponent $g=1.5-5$ (Refs. [1,3] and references therein).

The glassy dynamics, particularly the appearance of the two MCT "critical" crossover temperatures predicted in Refs. [8–11] was explicitly shown in the optical heterodyne detected optical Kerr effect (OHD OKE) studies in isotropic 8CB [12,13]. Comparison of OHD OKE [12,13] and BDS [45,48] results indicated that $T_X=T_{\text{MCT}}^{\text{trans}}=T_{\text{MCT}}^{\text{lower}}$.

The results above suggest that rodlike nematogens can be considered as one of the experimental model systems for studying unusual glassy dynamics. This can be related to their relationship with the model fluid of hard ellipsoids [7–13] and to the domination of the isotropic phase by well-defined fluctuation heterogeneities [8,10,12,13,41–48]. Hence, experimental results in this field may be of particular importance, regarding also existing contradictions in literature.

This paper presents the results of BDS ($f<1$ GHz) and nonlinear dielectric effect (NDE) studies in *n*-butylcyanobiphenyl (4CB), a rodlike liquid crystalline compound supercooled well below the *I-N* transition. Up to now it was suggested that members of *n*CB series for $n\leqslant 4$ on normal cooling crystallize in the isotropic phase, well above the *I-N* transition [53]. Probably this fact led Jadżyn *et al.* [47] to claim that isotropic 4CB exhibits unusual behavior, namely that prenematic fluctuations do not affect dielectric properties in the isotropic liquid, contrary to the behavior noted for 5CB [42,44,46–48]. Results presented below show a clear coexistence of the glassy and critical-like behavior. The low value of the *I-N* temperature made it possible to carry out BDS studies up to $T_{I\text{-}N}+120$ K, i.e., well above the range of temperatures reached in similar studies. This made it possible to test the validity of the Vogel-Fulcher-Tammann equation, Cohen-Grest model, mode coupling theory, and the apparent activation energy related relation [3] regarding both relaxation time and dc conductivity. The dynamical crossovers [3] obtained due to the distortion-sensitive derivative analysis are compared with ranges of validity of the pretransitional behavior, related to prenematic fluctuations-heterogeneities within the isotropic, fluidlike surrounding.

EXPERIMENT

The tested compound belongs to the *n*-cyano-alkylbiphenyls (*n*CB) homologous series of liquid crystalline compounds (C_nH_{2n+1}PhPhCN, *n*CB), where Ph denotes the phenyl ring, which has attracted broad interest since its discovery in 1973 [53]. From 5CB to 7CB the show isotropic-nematic-solid (*I-N-S*) sequence of phases. For higher homologous the smectic *A* phase appears. For "shorter" *n*CB compounds ($n\leqslant 4$) in equilibrium thermodynamic conditions the isotropic-nematic phase transition is not observed [53]. In this paper we present the experimental results of dielectric relaxation studies and nonlinear dielectric effect measurements for 4CB and 3CB. Broadband dielectric spectroscopy (BDS) studies were conducted using the Novocontrol Concept 80 broadband dielectric spectrometer with the Quatro temperature control system, applied in the authors earlier studies [46,48]. The masterplot which measured the imaginary part of the complex dielectric permittivity data is presented in Fig. 1. Noteworthy is the extremely large temperature range, up to 120 K above the clearing temperature, covered. Worth stressing is also the large number of experimental points, which density per decade increases on approaching the *I-N* transition to facilitate analysis of possible pretransitional phenomena in the imaginary part.

Nonlinear dielectric effect describes the shift of dielectric permittivity induced by the strong electric field in liquids [54],

$$\varepsilon_{\text{NDE}} = \frac{\varepsilon'_E - \varepsilon'}{E^2}, \tag{6}$$

where ε'_E and ε' denotes dielectric permittivities in a strong and weak electric field.

NDE measurements were carried out using aperiodic, dual field, modulation domain analysis based spectrometer which

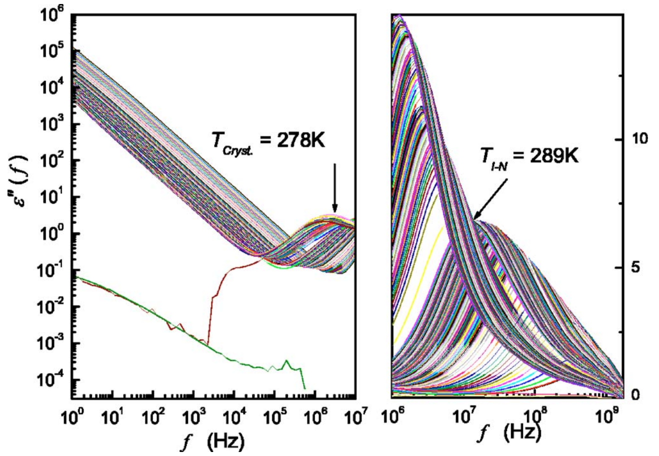

FIG. 1. (Color online) Dielectric loss curves in isotropic and nematic supercooled 4CB.

design is given in Ref. [54]. Tested compounds 4CB and 3CB were purchased from the Merck Comp. They were carefully degassed prior to measurements. Due to this procedure measurements could be continued well below melting temperatures declared in Refs. [47,53], i.e., in the supercooled state. Weakly degassed 4CB crystallized 10–20 K above the clearing temperature. Deeply degassed 4CB crystallized well below the *I*-*N* transition. Results were analyzed using ORIGIN 7.0 software. All errors are given as three standard deviations. The majority of the value of fitted parameters are given in the figures.

RESULTS AND DISCUSSION

Figure 2 shows reciprocals of NDE values for isotropic 4CB and 3CB. For both compounds pretransitional anomalies are portrayed by the relation [43,46]

$$\varepsilon_{\mathrm{NDE}}^{-1} = A_{\mathrm{NDE}}^{-1}(T - T^{*}) \tag{7}$$

which can be obtained from the dependence derived for the homogeneous phase of critical mixtures, namely [46]

$$\varepsilon_{\mathrm{NDE}}^{-1} = \chi\langle\Delta M^2\rangle_V \propto \chi(\Delta\varepsilon^0\Delta\varepsilon^f), \tag{8}$$

where A_{NDE} denotes the amplitude of the NDE pretransitional effect, T^* the temperature of the virtual continuous phase transition, $\langle\Delta M^2\rangle_V$ denotes the mean square of the order parameter fluctuation, $\chi=\chi_0/(T-T^*)$ is the compressibility, and $\Delta\varepsilon^0$ and $\Delta\varepsilon^f$ are the anisotropies of the dielectric permittivity within the static limit and for the given measurement frequency f, respectively.

The above relation shows that NDE is a magnitude directly coupled to the mesoscale heterogeneities but unlike the Kerr effect or light scattering [22,53]. For the static NDE, applied in this research, $f_{\mathrm{NDE}}^{-1} \gg \tau_{\mathrm{fluct.}}$ and consequently $A_{\mathrm{NDE}}=(2\varepsilon_0/3\chi_0)(\Delta\varepsilon^0)^2=\mathrm{const.}$ It is noteworthy that the static NDE does not exhibit any deviations in the immediate vicinity of the clearing temperature [41–46].

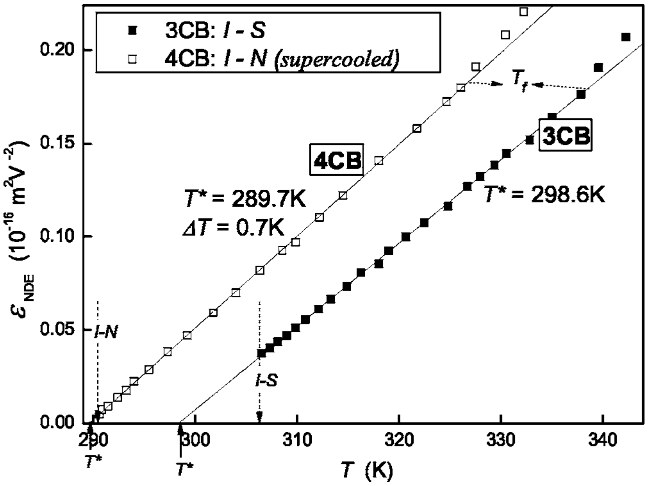

FIG. 2. The evolution of the static NDE in isotropic phase of supercooled nematogens 3CB and 4CB. Independently whether the sample crystallized in the isotropic phase or reached the *I*-*N* transition the same NDE values were obtained. Results presented are for deeply degassed 3CB and 4CB samples. Dashed arrows show the isotropic-nematic (*I*-*N*, 4CB) and isotropic-solid (*I*-*S*, 3CB) transitions. Solid arrows indicate hypothetical continuous phase transition temperature (T^*) in tested compounds.

Relation (7) parametrizes experimental data up to $T_{\mathrm{fluct.}} \approx T^*+40$ K, at which prenematic fluctuations shrink to 2–3 molecules, i.e., the correlation length decreases to $3\xi_0$, where ξ_0 denotes the correlation length of prenematic fluctuations (Ref. [46] and references therein). Such a validity of relation (7) permits a simple estimation of T^* for 4CB and 3CB. It is noteworthy that owing to the careful degassing also 3CB was supercooled down to 8 K above T^*, ca. 20 K below the temperature reached previously [53,55]. Three decades ago Rizi and Ghosh [55] already obtained an analogous result for 3CB and 4CB based on time resolved optical Kerr effect studies, although their samples crystallized always well above $T_{I\text{-}N}$. Similar result was obtained for NDE ($f_{\mathrm{NDE}}=300$ kHz) in 4CB in the mid-1990s [42]. Values of temperature T^* given in Fig. 2 and those from Refs. [42,55] are in fair agreement. In the case of 4CB the estimation of the discontinuity $\Delta T=0.6\ \mathrm{K}\pm0.05$ was also possible. The above results clearly show the basic influence of heterogeneities-fluctuations on properties of the isotropic phase.

The cancellation of permanent dipole moments within prenematic fluctuations, whose dimensions increase upon approaching T^*, also leads to the pretransitional decrease of the static dielectric permittivity $\varepsilon'(T)$ ($f=10$ kHz) as mentioned in the Introduction. Such behavior is clearly manifested for isotropic 4CB as shown in Fig. 3. Similar anomaly occurs for the temperature dependence of maxima of dielectric loss curves $\varepsilon_p''(T)$ (20 MHz$<f<$250 MHz), also given in Fig. 3. Both $\varepsilon'(T)$ and $\varepsilon_p''(T)$ dependences can be well portrayed by isomorphic relations (1) and (2), with approximately the same value of the exponent $\alpha\approx0.5$. However, due to the number of fitted parameters, a reliable fit was only possible if the value of T^* from NDE measurements (Fig. 2) was assumed.

The validity of such parametrization confirms the distortion-sensitive derivative analysis $d\varepsilon'(T)/dT$ and $d\varepsilon_p''(T)/dT$ presented in Fig. 4. It is noteworthy that three

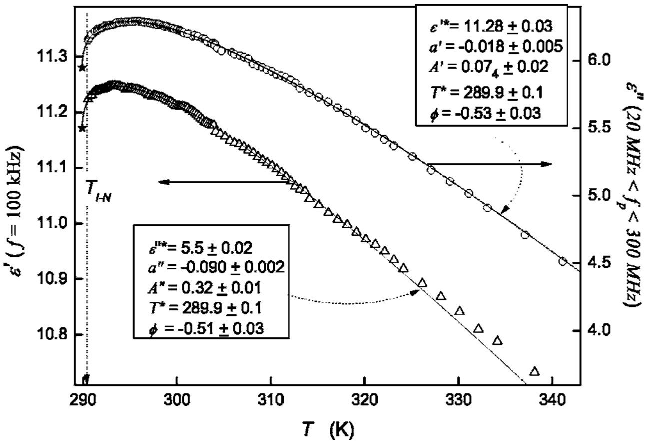

FIG. 3. Temperature dependences of the static dielectric permittivity and the maximum of the loss curves in isotropic 4CB. Solid curves are parametrized by relations (1) and (2), respectively. Fitted parameters are given in the figure. Solid stars denote the temperature of the hypothetical continuous phase transition.

decades ago Mistura [56] showed the equivalence of the pretransitional behavior of the specific heat and $d\varepsilon'/dT$, although his reasoning was only limited to the homogeneous phase of critical mixtures. Results presented in Figs. 3 and 4 may be considered as an experimental argument for extending Mistura's reasoning to the case of the *I-N* transition. It is noteworthy that relations (1) and (3), which parametrize $\varepsilon'(T)$ and $d\varepsilon'(T)/dT$, remain valid up to $T_{I-N}+120$ K. This may suggest that there is no difference in the formation of prenematic ordering below and above $T_{\text{fluct.}}$, although above this temperature fluctuations cannot be recognized by methods directly coupled to fluctuation [NDE, relation (8)]. However, for $\varepsilon''_p(T)$ and $d\varepsilon''_P(T)/dT$ relations (2) and (4) are valid only for $T < T_{\text{fluct.}}$, i.e., in the same temperature range as NDE in Fig. 2.

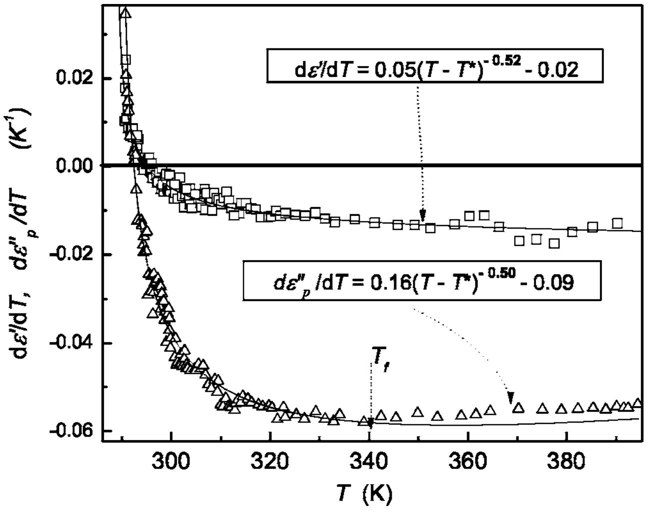

FIG. 4. Temperature dependences of derivative of experimental data for $\varepsilon'(T)$ and $\varepsilon''_{\text{peak}}(T)$. Solid curves are parametrized by relation (3). Fitted parameters are given in the figure. The error of the exponent, α, ±0.06.

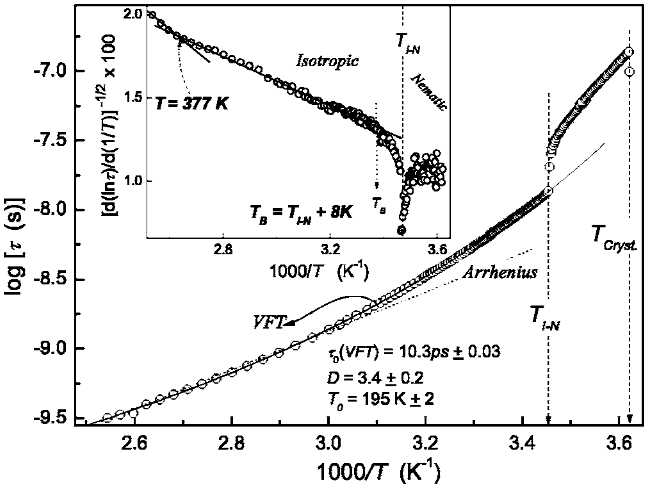

FIG. 5. The temperature dependence of dielectric relaxation time in isotropic and nematic 4CB. The inset shows Stickel's [57,58] derivative analysis in which the region of the validity of the VFT relation appears as the sloped solid line. The solid curve in the main part of the figure portrays the CG relation (9).

Figure 5 presents the Arrhenius plot of dielectric relaxation time. The linear dependence, expected for the simple Arrhenius behavior of $\ln\tau$ vs $1/T$ may eventually appear only remote from T_{I-N}. However, results of the linearized derivative analysis of experimental data given in the inset in Fig. 5, originally introduced by Stickel *et al.* [57,58] for glassforming liquids, clearly shows that even far away from T_{I-N} the Arrhenius temperature dependence is not adequate. For the Stickel's plot [57,58] the region of validity of the VFT function is described by a linear dependence of transformed experimental data, with a nonzero slope while the Arrhenius region is characterized by the zero-sloped linear dependence. It is visible that at $T \approx T_{I-N}+377$ K and at $T_B \approx T_{I-N}+8$ K dynamical crossovers occurs. The VFT based fit of experimental data for $T_B < T < T_{I-N}+377$ K yielded $T_0 = 196$ K and $D = 1.5$. The latter value is characteristic for very "fragile" glassformers, with particularly strong distortions from the simply Arrhenius behavior [3,17]. The obtained VFT dependence allowed for the estimation of the hypothetical, extrapolated glass temperature $T_g \approx 222$ K, from the condition $\tau(T_g) = 100$ s [3,17]. In "classical" glassforming liquids a crossover between two dynamic regimes, described by two different VFT dependences seems to be a common phenomenon. Cohen and Grest (CG) [59] developed a model resulting in a single, four-parameter relation covering the region beyond the single VFT dependence, namely [59,60],

$$\tau(T) = \tau_0^{\text{CG}} \exp\left(\frac{B}{T - T_{\text{CG}} + [(T - T_{\text{CG}})^2 + CT]^2}\right). \tag{9}$$

In the CG model the system is divided into liquidlike and solidlike cells, only the latter having a free volume responsible for the dynamics [59]. Experimental analysis pointed to a possible coincidence of T_{CG} characteristic temperature with T_0, T_g, or T_B (crossover between two VFT regimes) temperatures (Ref. [60] and references therein). The analysis presented in Fig. 5 shows that relation (9) can parametrize experimental data also in the whole tested temperature range in

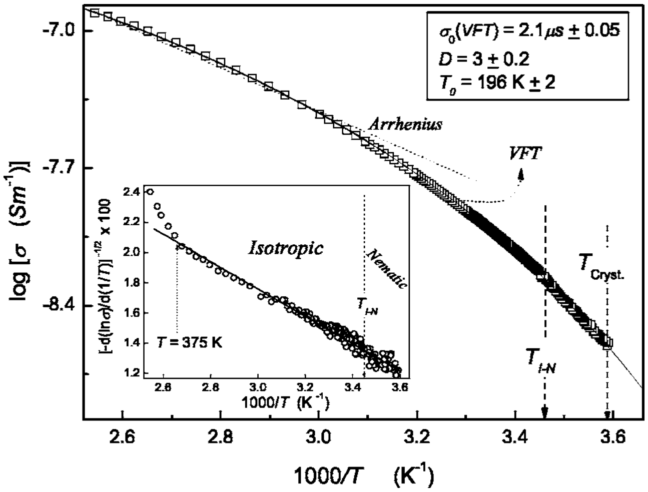

FIG. 6. The temperature dependence of dc conductivity in isotropic and nematic 4CB. The inset shows Stickel's derivative analysis [57,58] presenting the real region of the validity of the VFT relation (solid line). The VFT dependence (4) parametrizes also the solid curve in the main plot, in the region indicated in the inset.

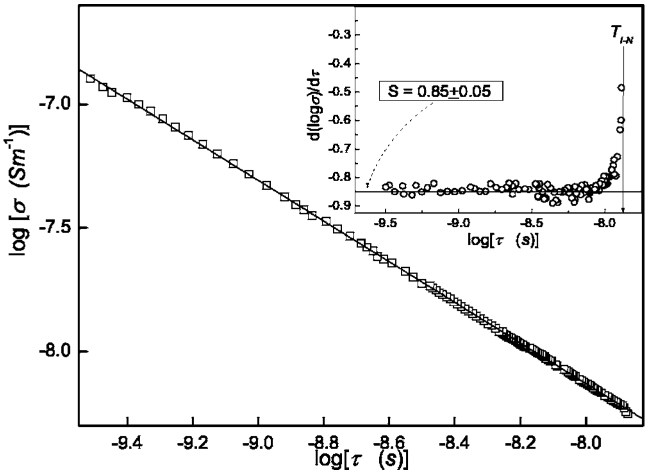

FIG. 8. The plot showing the distortion from the validity of the fractional Debye-Stokes-Einstein law [relation (11)]. The inset shows the derivative analysis from the main plot. Solid line in the inset confirms the validity of the fractional DSE law.

the isotropic phase. It is noteworthy that the obtained value of $T_{\mathrm{CG}} \approx 222$ K is in fair agreement with the value of $T_g \approx 220$ K mentioned above.

In supercooled glassforming liquids the non-Arrhenius behavior of $\tau(T)$ coincides with a similar evolution of the dc conductivity $[\sigma(T)]$ [3,17]. This is also the case of 4CB (Fig. 6). It is noteworthy that $\sigma(T)$ dependence can be portrayed by a single VFT relation up to $T=375$ K. However, the Stickel's transformation derivative based analysis given in the inset of Fig. 6 reveals no distortions from the single VFT parametrization of $\sigma(T)$ near $T_{I\text{-}N}$, contrary to the behavior of $\tau(T)$ (see the inset in Fig. 5).

Mode coupling theory (MCT) is one of the most successful theoretical models in the physics of glassy liquids, particularly regarding the high temperature behavior (Refs. [1,3,48] and references therein). Figure 7 shows that for 4CB both the MCT critical-like relation (5) for $\tau(T)$ dependence and its analog for dc conductivity are valid,

$$\sigma(T) = \sigma_0^{\mathrm{MCT}}(T - T_X)^{-g'}. \tag{10}$$

Analysis given in Fig. 7 yielded the following parameters $T_X=250$ K±2, $g=2.8\pm0.1$, and $g'=2.4\pm0.1$. It is noteworthy that relation (10) also describes the experimental data in the nematic phase down to ca. T_X+20 K, in fair agreement with "classical," nonmesogenic, glass formers (Refs. [3,48] and references therein). This can be recognized as the reason for the lack of distortions from relations (5) and (10) near the clearing point, due to the fact that $T_{I\text{-}N} \approx T_X+40$ K. However, MCT relations (5) and (10) cease to be valid for $T \approx 375$ K, i.e., in the range of validity of the VFT relation (Figs. 5 and 6). There is a small difference in the value of the exponents g and g' describing the behavior of $\tau(T)$ and $\sigma(T)$, respectively. This can be related to the failure of the Debye-Stokes-Einstein (DSE) relation, often occurring for glassforming liquids [3], namely,

$$\sigma(T)\tau(T)^S = 1. \tag{11}$$

The validity of the above relation, known as the fractional DSE law, is shown in Fig. 8. The inset shows the derivative analysis of DSE dependence, based on data from the main part of Fig. 8. It gives clearly the value of the exponent S in the given temperature/time domain and additionally reveals the distortion from relation (11) in the immediate vicinity of $T_{I\text{-}N}$. It is noteworthy that dividing MCT critical-like $\tau(T)$ and $\sigma(T)$ dependences given by relations (5) and (11) one can obtain $S=gg' \approx 0.88\pm0.05$, in fair agreement with the result value of $S \approx 0.85$ obtained in Fig. 8.

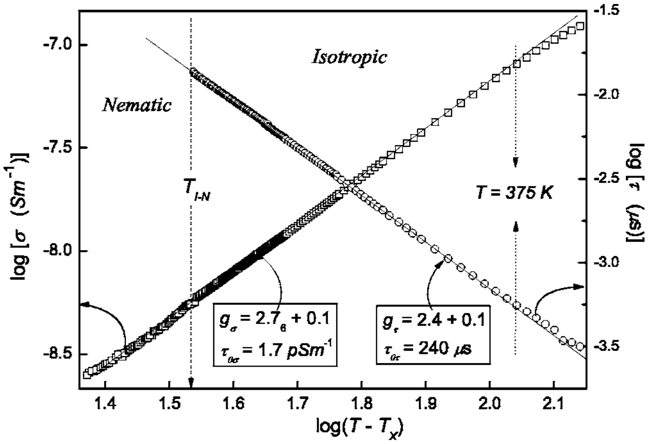

FIG. 7. The log-log plot testing the validity of the MCT based "critical-like" dependences (5) and (10).

When discussing the temperature dependence of the primary relaxation in glassforming liquids one may also assume the validity of the Arrhenius-type dependence with the apparent (temperature-dependent) activation energy $E_a(T)$ [3,61]. Applying this to dielectric relaxation time and dielectric conductivity one can obtain

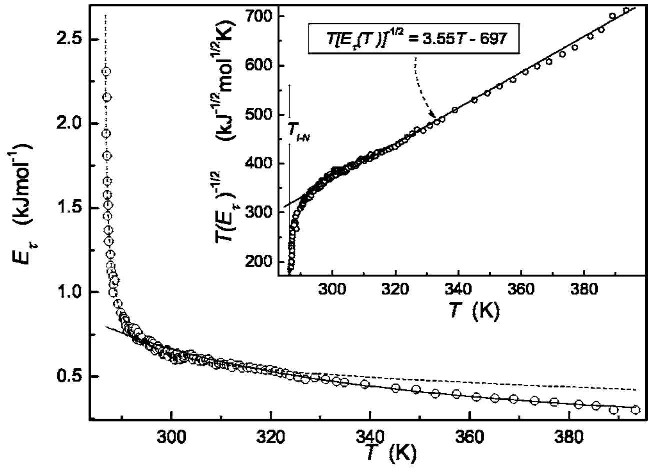

FIG. 9. The temperature dependence of the apparent activation energy related to dielectric relaxation time. The linear dependence in the inset shows the validity of relations (14) and (15). The temperature dependence obtained in this way is additionally given as the solid curve in the main part of the figure. The dashed curve shows results of the analysis via the power relation (13) with C =const.

$$\tau(T),\sigma(T) \propto \exp\left(\frac{E_a(T)}{RT}\right), \qquad (12)$$

where $E_a=E_\tau$ for $\tau(T)$ and $E_a=E_\sigma$ for $\sigma(T)$.

The derivative analysis of ln τ vs $1/T$ constitutes a simple way of obtaining $E_a(T)$ values. Recently, Jadżyn *et al.* [47,62] suggested that the orientational apparent activation energy $E_\tau(T)$ exhibits a critical-like dependence,

$$E_\tau(T) = A_E(T-T^*)^{-\lambda_\tau} + C. \qquad (13)$$

Basing on the analysis of isotropic 5CB up to $T_{I\text{-}N}+40$ K they obtained $\lambda_\tau=0.5$ [47]. The coincidence of this exponent with the specific heat exponent α or the order parameter exponent β was suggested [47,62]. However, the analysis presented in the insets of Figs. 9 and 11 clearly shows that both activation energies $E_\tau(T)$ and $E_\sigma(T)$ up to $T_{I\text{-}N}+120$ K can be well portrayed by the relation originally developed for glassforming liquids [61],

$$E_a(T) = R\left(\frac{d\ln\tau}{d(1/T)}\right) = RDT\left(\frac{T}{T-T_0}\right)^2, \qquad (14)$$

which yields the linear dependence shown in the insets of Figs. 9 and 11, namely,

$$T/(E_a)^{-1/2} = (RDT_0)^{-1/2}(T-T_0). \qquad (15)$$

The solid line in the inset of Fig. 9 is given by $T[E_\tau(T)]^{-1/2}=3.55_{\pm0.02}T-697_{\pm5}$ yielding $T_0=697/355$ $=196\pm3$ K, in fair agreement with T_0 value obtained directly from the VFT fit, supported by Stickel's derivative analysis (Fig. 5). The visible distortions in the immediate vicinity of $T_{I\text{-}N}$ are only possible for the analysis in the case of $E_\tau(T)$ if $C=RDT_0T/(T-T_0)^2$ is taken as the nonpretransitional background term, i.e., by extending relation (15) up to $T_{I\text{-}N}$. This gave$\lambda_\tau=1.5\pm0.1$, as shown in Fig. 10. A similar analysis for ionic transport related electric conductivity apparent activation energy is given in Fig. 11. The inset in Fig. 11 shows the validity of description via the analog of relation (16) and gives $T[E_\sigma(T)]^{-1/2}=4.15_{\pm0.02}T-823_{\pm5}$ yielding T_0 $=823/4.15=198\pm3$ K, also in fair agreement with T_0 value obtained above (Fig. 6). Unfortunately, the distortion from dependence obtained in the inset was too weak for a reliable qualitative analysis.

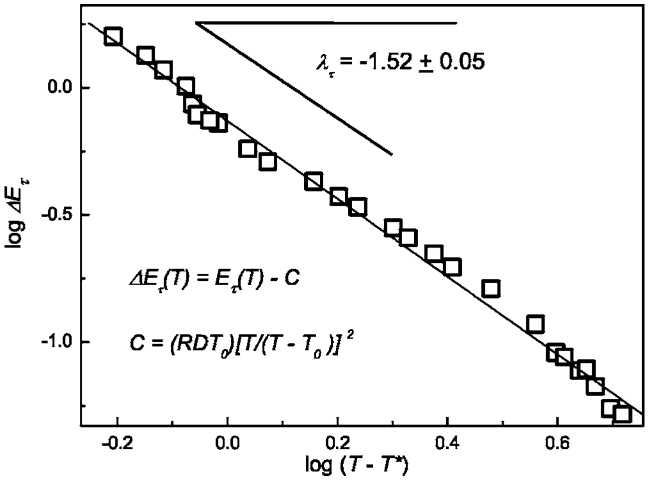

FIG. 10. The pretransitional excess of the apparent activation energy related to orientational processes (dielectric relaxation time) in the log-log scale to illustrate the powerlike dependence. The form of the fitted function and the obtained value of the quasicritical exponent are given in the figure.

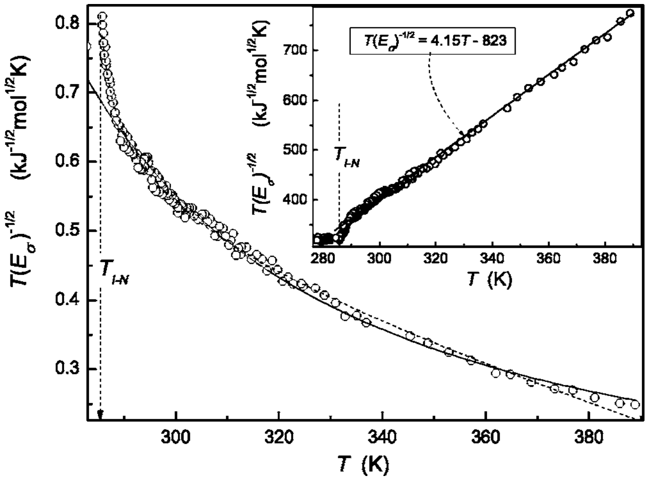

FIG. 11. The temperature dependence of the apparent activation energy related to the dc electric conductivity. The linear dependence in the inset shows the validity of relation (14) and (15). The temperature dependence obtained in this way is additionally given as the solid curve in the main part of the figure. The dashed curve shows results of the analysis via the power relation (13) with C =const.

The alternative proposal of analysis of $E_\tau(T)$ dependence from Ref. [47], basing solely on relation (13) with C =const, only enables the parametrization in a limited range of temperatures, as shown in Figs. 9 and next in Fig. 11 via dashed curves. For $E_\tau(T)$ dependence such parametrization

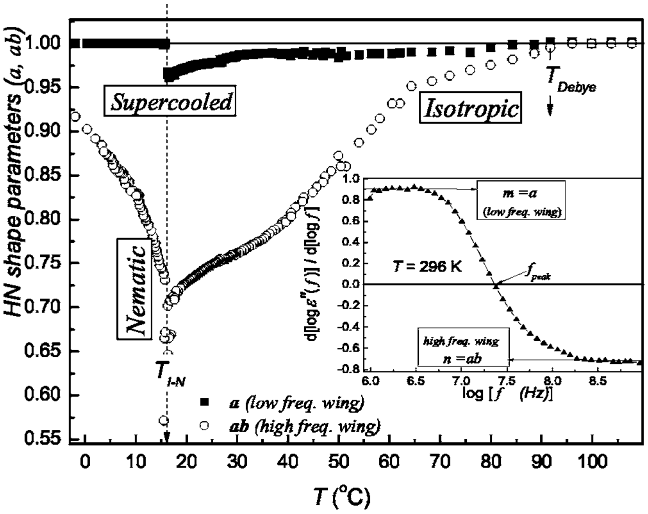

FIG. 12. The temperature dependence of Havriliak-Negami-Jonsher [relations (16) and (17)] shape parameters for the low- ($m=ab$) and high- ($n=a$) frequency wings of the loss curve, respectively. The inset shows results of the derivative analysis $d\ln\varepsilon''/d\ln f$ for a selected loss curve.

follows the activation energy dependence only up to ca. $T_{I\text{-}N}+30$ K. Moreover the shift of λ_τ from 0.3 to 0.7 and $T^*\pm 1$ K does not significantly change the fit quality in this case. For $E_\sigma(T)$ such parametrization is possible in the whole temperature range although also in this case the shift of the exponent λ_σ from 0.03 to 0.12 (!) and $T^*\pm 1$ K does not significantly change the fit quality.

Regarding the distribution of relaxation times the analysis was conducted in terms of the Havriliak-Negami (HN) dependence to encompass the asymmetry of loss curves, namely [3,17],

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau_{\mathrm{HN}})^a]^b}, \tag{16}$$

where ε_∞ represents the asymptotic value of permittivity at high frequencies, and ε_s is the value of the opposite limit. The power exponents are responsible for the shape of the loss curve.

Exponents a and b in the HN function can be related to Jonsher [3,63] "universal law" which relates the distribution of the relaxation times to the high- and low-frequency wings of the loss curve via relations

$$\varepsilon''_{T=\mathrm{const}} \propto \left(\frac{f}{f_p}\right)^{m} \quad \text{for } f \ll f_p \text{ and } \varepsilon''_{T=\mathrm{const}} \propto \left(\frac{f}{f_p}\right)^{-n} \quad \text{for } f \gg f_p, \tag{17}$$

where parameters $0\leqslant m \leqslant 1$, $0 \leqslant n \leqslant 1$, and $n=ab$, $m=a$ characterize the shape of the loss curve, $m=n=1$ for the single relaxation time in the Debye process.

The validity of the parametrization of loss curves by means of a single HN function, as well as validity of relations (17), clearly shows the derivative analysis of $d(\ln\tau)/d\ln f$ presented in the inset in Fig. 12. It is noteworthy that the distribution of relaxation times in isotropic *n*CBs is often discussed as the sum of two Cole-Cole (CC) functions [17–31]. This is also the case applied in Ref. [47], although the existence of the second (CC) relaxation process was only claimed there. Moreover, for higher temperatures in Ref. [47] the high frequency wing must be practically absent owing to the limited range of frequencies ($f<100$ MHz) that in our opinion make the declared fit unreliable. We found that the application of two CC functions does allow for a reliable result due to the large number of parameters, both for isotropic 4CB (this research) and 5CB [46]. It is visible in Fig. 12 that on moving away from the clearing point, for $T>T_{I\text{-}N}+70$ K, exponent $m,n\rightarrow 1$, i.e., the distribution approaches the single relaxation time, Debye-type form. On the other hand, the exponent for the high frequency part of the loss curve approaches $n\rightarrow 1/2$ for $T\rightarrow T_{I\text{-}N}$. It is noteworthy that in Ref. [64] such value was suggested as the universal one for glass forming liquids when $T\rightarrow T_g$. In 4CB the temperature $T_{I\text{-}N}$ is located well above the hypothetical extrapolated glass temperature ($T_g\approx 220$ K) but one may expect that $T_{I\text{-}N}$ coincides with $T_{\mathrm{MCT}}^{\mathrm{orient}}=T_{\mathrm{MCT}}^{\mathrm{upper}}$ [8,12,13].

CONCLUSIONS

Results presented above show coexistence between the pretransitional and the glassy properties in supercooled isotropic 4CB. There are strong pretransitional anomalies of NDE, $\varepsilon'(T)$, $\varepsilon''_P(T)$, $d\varepsilon'(T)/dT$, $d\varepsilon''_P(T)/dT$, clearly related to prenematic fluctuations-heterogeneities in the fluidlike, isotropic surrounding. Regarding dynamics, the distribution of dielectric relaxation time is clearly non-Debye and non-Arrhenius for $T<T_{I\text{-}N}+85$ K, i.e., it exhibits canonical glassy features [1–3,17]. For the $T>T_{I\text{-}N}+85$ K the temperature behavior remains non-Arrhenius whereas the distribution approaches the Debye pattern. In the opinion of the authors, interesting for future studies would be matching the values detected in Figs. 5 and 6 for the dynamic crossover with size of the correlation length of prenematic fluctuations-heterogeneities. It is noteworthy that in the immediate vicinity of $T_{I\text{-}N}$ a strong influence of prenematic fluctuation on dynamics is much more pronounced for dielectric relaxation time related properties (Figs. 5, 8–10, and 12) than for the dc conductivity related behavior (Figs. 6, 8, and 11). These results clearly contradict the statement in Ref. [47] that no influence of prenematic heterogeneities in isotropic 4CB occurs.

When discussing the theoretical background of the above experimental evidence, the recent general model of a liquid-liquid phase transition by Tanaka [2], including the vitrification on cooling, is worth noting. One of the characteristic features of his scheme is the existence of the liquid-liquid spinodal curve terminating at the critical point. In the case of the postulated liquid-liquid transition in water or the glass transition, this spinodal curve is hidden in experimentally inaccessible or hardly accessible regions. In the opinion of the authors the results above suggest that *I-N* transition may fit Tanaka's scheme [2]. The glassy dynamics discussed agrees well with the molecular MCT (MMCT) for a system of hard ellipsoids of revolution introduced in Refs. [7–11]. Results presented in this paper recall also the question on the nature of the isotropic phase and the *I-N* transition, until recently considered as an example of a successful simple mean-field description [53].

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