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Mode coupling behavior in glass-forming liquid crystalline isopentylcyanobiphenyl

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Linear and nonlinear dielectric measurements of liquid crystalline chiral isopentylcyanobiphenyl (5*CB) and *n*-pentylcyanobiphenyl (5CB), combined with viscosity $\eta(T)$ data, are presented. The 5*CB compound glassifies on cooling in the cholesteric phase whereas 5CB crystallizes in the nematic phase. In both compounds the temperature evolution of dielectric relaxation times, the dc conductivity, and the viscosity are well described by the "critical-like" description from mode coupling theory (MCT). However, for 5*CB a unique coincidence of the MCT "critical" temperature and extrapolated temperature of the hypothetical continuous isotropic-cholesteric (T^*) phase transition was found. The temperature dependence of the strong electric-field-induced changes of the dielectric permittivity exhibits a strong anomaly in the direction of negative values on approaching T^*, not observed up to now. The anomaly is described by the susceptibility-related critical exponent $\gamma=1$. The divergence of the "nonlinear" dielectric relaxation follows a power dependence described by the exponent $y=1$. This paper recalls the recent discussions on the glassy dynamics of a "hard-ellipsoid" liquid and the possible relationship between the glass transition, critical phenomena, and isotropic-nematic transition.

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INTRODUCTION

Many studies of the dynamics of glass-forming liquids have shifted their focus to temperatures considerably higher than the glass temperature T_{glass} [1–30]. This challenging emphasis has been stimulated by mode coupling theory (MCT) [1,11]. One of its important predictions is the existence of a dynamic crossover between the ergodic and nonergodic regimes at the "critical" or crossover temperature $T_{\mathrm{MCT}}=(1.3\pm0.1)T_{\mathrm{glass}}$ [1–24]:

$$\tau_\alpha^{-1}, \eta, d \propto (T-T_{\mathrm{MCT}})^{-g}, \tag{1}$$

where τ_α is the structural (α) dielectric relaxation time, η the viscosity, and d the diffusion coefficient. In practice, the exponent $2<g<4$, in fair agreement with MCT.

MCT defines the singular temperature T_{MCT} as the point at which the dynamics of a liquid changes from the fluidlike regime to the solidlike one, via a qualitative change in the caging phenomenon [1,2,11,13,16–18]. This may be supported by recent studies in benzophenone, where the correspondence of T_{MCT} with the onset of possible nucleation and growth of a new phase was noted [24]. It is noteworthy that the critical-like relation (1) describes the experimental data only for $T>T_{\mathrm{MCT}}+(15-20\ \mathrm{K})$ [1,2,5,7,8,11,15,17]. However, in experiment the crossover between dynamic regimes on passing T_{MCT} is always gradual. In the full range of temperatures the $\tau_\alpha(T)$, $\eta(T)$, and $d(T)$ dependences can be portrayed by the VFT relation [1–23]

$$\tau_\sigma, \eta, d \propto \exp\left(\frac{DT_0}{T-T_0}\right), \tag{2}$$

where T_0 is the extrapolated ideal glass temperature and D is the parameter related to the fragility of the glass former.

The extended MCT took this experimental behavior into account by including the hopping diffusion to restore ergocidity even below T_{MCT} [11,23]. The significance of the MCT "critical temperature" supports the recent suggestion [17] that the value of the relaxation time $\tau_C=\tau_\alpha(T_{\mathrm{MCT}})\approx10^{-7}$ s may be "magic"—i.e., approximately the same for all glass-forming liquids. However, Casalini *et al.* [18,19] reasoned that the value of the relaxation time $\tau_C(P)=\tau_\alpha(P,T_{\mathrm{MCT}})$ is constant and independent from the pressure and T_{MCT} value, but only for a given class of glass formers.

The original MCT considers spheres and hence focuses on translational degrees of freedom [1,11,25]. Recently, the molecular MCT for a model system of hard ellipsoids, aiming at reaching insight into the interplay between translational and orientational degrees of freedom, was proposed by Schilling and co-workers [25–28]. It was found that for molecules with an aspect ratio greater than 2.5, an additional crossover temperature $T_{\mathrm{MCT}}^{\mathrm{upper}}=T_{\mathrm{MCT}}(\mathrm{orient})$ appears. It corresponds to the freezing of the orientational freedom while the translational degree of freedom remains still liquid like. This phenomenon was expected to appear near the nematic instability boundary—i.e., near the isotropic-nematic (*I*-*N*) transition in a real system of a rodlike liquid crystalline compound [26–28]. Very recently, the existence of $T_{\mathrm{MCT}}^{\mathrm{lower}}$ and $T_{\mathrm{MCT}}^{\mathrm{upper}}$ was shown in the isotropic phase of few rodlike nematogens with the *I*-*N* transition, including *n*-octylcyanobiphenyl (8CB) from *n*-cyanobiphenyls (*n*CB) homologous series, based on optical heterodyne Kerr effect (OHD-OKE) studies [29,30]. The temperature $T_{\mathrm{MCT}}^{\mathrm{upper}}$ was estimated slightly below the clearing temperature while the extrapolated value of $T_{\mathrm{MCT}}^{\mathrm{lower}}$ was located already in the solid phase, well below the *I*-*N* and isotropic-solid (*I*-*S*) phase transitions. For 8CB the obtained value of $T_{\mathrm{MCT}}^{\mathrm{lower}}$ was in agreement with the earlier estimation based on a multifrequency electric conductivity analysis [31]. Dielectric studies of isotropic *n*CB gave also clear evidence for canonical features for the "glassy dynamics" such as non-Arrhenius evolution relaxation times or the broadening of dielectric loss curves on cooling [31,32]. The dielectric relaxation time (τ_α) is a magnitude related to the two-point susceptibility [$\chi_2(t)$]. Recent simulations in a model supercooled liquid showed that the four-point susceptibility $\chi_4(T)$ and the related relaxation time t_4 also exhibit an anomaly on approaching T_{MCT} [33–37]:

$$\chi_4(T) \propto (T - T_{\mathrm{MCT}})^{-g_4}, \tag{3a}$$

$$t_4(T) \propto (T - T_{\mathrm{MCT}})^{-y_4}, \tag{3b}$$

where numerical analysis gave $g_4 = 0.5-1.2$ and $y_4 \approx 1-1.4$.

These results are particularly noteworthy due to the fact that $\chi_4(T)$ is a magnitude directly coupled to mesoscale heterogeneities [34–37]. Theoretical analysis in Refs. [33–37] enabled the identification of a growing dynamical length scale on approaching T_{MCT}, corresponding to fluctuations of the order parameter [34], as a source of anomalies of $\chi_4(T)$ and $t_4(T)$. The existence of spatially heterogeneous mesocale dynamics is well established experimentally close to T_{glass} [4,11–15,20–23]. There is also an experimental evidence for the existence of long-lived mesoscale heterogeneities at higher temperatures [6,11,12]. However, no experimental studies aiming at testing relations (3a) and (3b) are being conducted so far, to the best of the authors knowledge. The properties of the isotropic rodlike nematogens are very strongly influenced by well-defined prenematic fluctuations in the broad surrounding of the isotropic-nematic clearing temperature [29–32,38–43]. Hence their studies may be significant for a vivid discussion of the role of heterogeneities for supercooled liquids.

Here we discuss the validity of the MCT behavior for a liquid crystalline compound which glassifies on cooling. Results are presented based on a unique combination of "linear" and "nonlinear" dielectric studies together with shear viscosity measurements. Studies in 5*CB are compared with similar tests on *n*-pentylcyanobiphenyl (5CB), a "classical" nematogen showing the isotropic-nematic-crystal phase sequence.

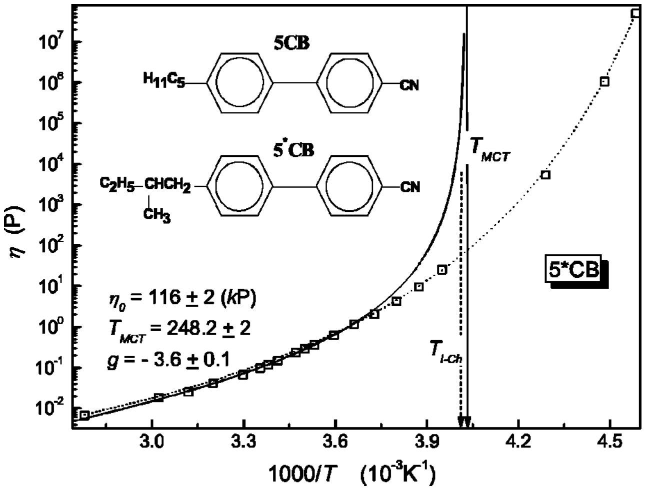

FIG. 1. The temperature evolution of shear viscosity $\eta(T)$ in 5*CB. The dashed and solid curves are portrayed by relation VFT (2) and MCT dependence (5), respectively. The inset shows structures of 5CB and 5*CB. Fitted parameters for the MCT dependence are given in the figure.

EXPERIMENT

Both tested compounds are rodlike mesogens, with a permanent dipole moment parallel to the long (main) axis of the molecule. 5*CB remains isotropic down to $T_{I\text{-Ch}} \approx 250$ K, at which the phase transition to the chiral nematic [cholesteric: N^*, Ch] phase occurs. On further cooling, the glassy state is attained at $T_g \approx 180$ K [38]. 5*CB is the isomer of *n*-pentylcyanobiphenyl. The latter forms on cooling the nematic phase at $T_{I\text{-}N} \approx 308$ K and next crystallizes at $T_{N\text{-}S} \approx 280$ K [32,39]. Structures of both compounds are shown in the inset in Fig. 1. A comprehensive discussion of broadband dielectric relaxation in 5*CB, both as a function of temperature and pressure, is given in Ref. [38]. A similar discussion for isotropic 5CB is given in Refs. [32,40]. For 5CB, this paper is based on data from Ref. [32]. For 5*CB novel BDS measurements were conducted, extending the range of tested temperatures in the isotropic phase up to $T \approx T_{I\text{-Ch}} + 150$ K, in comparison with Ref. [38]. Dielectric measurements were carried out using the Novocontrol BDS 80 spectrometer with Quattro temperature control unit, the same as applied in Refs. [32,38]. Steady-state and dynamic shear viscosities were measured using a Bohlin VOR rheometer with the parallel-plate geometry. Sample radii ranged from 3 to 20 mm with gaps ca. 1.5 mm. Viscosity data for the five highest temperatures in isotropic 5*CB were obtained using the Ubbelohde-type viscometer with the capillary of diameter of 0.6 mm and 120 mm long [41]. The temperature stability was at least ±0.1 K. For all measured temperatures, the steady-state and dynamic shear viscosities were equivalent. Nonlinear dielectric measurements are related to the shift of dielectric permittivity induced by a strong electric field [32,42]:

$$\varepsilon^E = \varepsilon + \Delta\varepsilon^E E^2 + \cdots, \tag{4}$$

where ε and ε^E are respective permittivities in a weak and strong electric field E. The measure of the nonlinearity, known as the nonlinear dielectric effect (NDE), is defined as $\mathcal{E}_{\mathrm{NDE}} = \Delta\varepsilon^E / E^2$.

In experiments the changes of electric capacitance ΔC^E, related to $\Delta\varepsilon^E$, are registered: $\Delta C^E = 1-10$ fF for a sample of $C = 100$ pF. This has to be detected with three-digit resolution during the action of a pulse of a strong electric field lasting $\Delta t_D = 1-4$ ms. A detailed description of the applied NDE spectrometer is given in Ref. [42]. It is based on the dual-field, single-generator, aperiodic principle with frequency-time direct measurements supported by the modulation domain analyzer HP 53 310A. For NDE measurements samples were placed in the flat-parallel capacitor made only from Invar and quartz (gap 0.5 mm, diameter 16 mm). The tested compounds were synthesized by Dąbrowski and

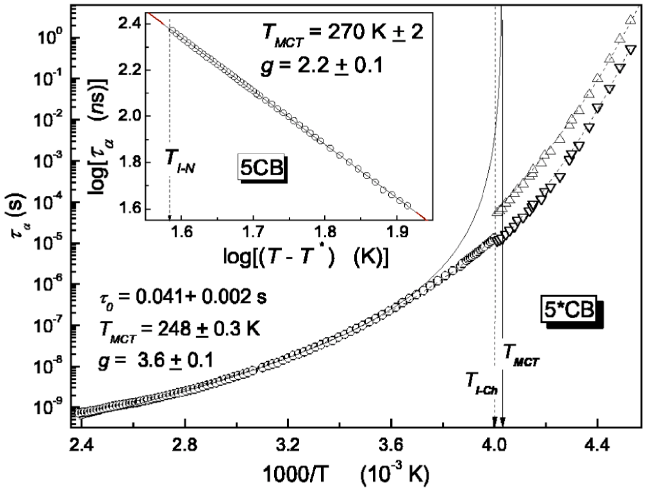

FIG. 2. The temperature evolution of dielectric relaxation time $\tau_\alpha(T)$ in 5*CB. The dashed and solid curves are portrayed by relation VFT (2) and MCT dependence (5), respectively. The inset shows the validity of the MCT dependence (2) for $\tau_\alpha(T)$ in isotropic 5CB, applying the log-log scale. Fitted parameters for the MCT dependence are given in the figure.

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RESULTS AND DISCUSSION

Figures 1–3 present Arrhenius plots of the shear viscosity, dielectric relaxation times, and dc conductivity in 5*CB, respectively. In each case the VFT dependence, with approximately the same values of T_0 and D parameters, can portray experimental data:

$$\eta_{\text{VFT}} = 355 \pm 10 \text{ (mP)}, \quad D = 5 \pm 0.2,$$

$$T_0 = 186 \pm 5 \text{ (K)} \quad \text{for } \eta(T),$$

$$\tau_{\text{VFT}} = 17 \pm 1 \text{ (ps)}, \quad D = 4.7 \pm 0.2,$$

$$T_0 = 186 \pm 3 \text{ (K)} \quad \text{for } \tau_\alpha(T),$$

$$\sigma_{\text{VFT}} = 84.6 \pm 0.3 \text{ (kS m}^{-1}), \quad D = 5.1 \pm 0.2,$$

$$T_0 = 187 \pm 3 \text{ (K)} \quad \text{for } \sigma(T).$$

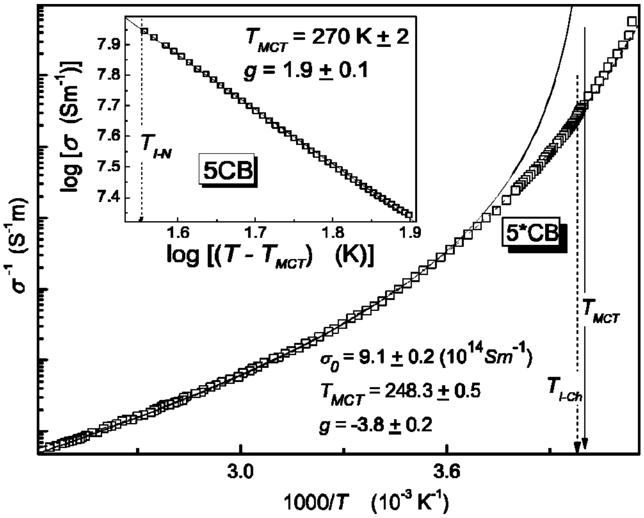

FIG. 3. The temperature evolution of dc conductivity $\sigma(T)$ in 5*CB. The dashed and solid curves are portrayed by relation VFT (2) and MCT dependence (5), respectively. The inset shows the validity of the MCT dependence (2) for $\sigma(T)$ in isotropic 5CB, applying the log-log scale. Fitted parameters for the MCT dependence are given in the figure.

For $\tau_\alpha(T)$ the relaxation is the cholesteric phase is clearly manifested by two processes, described by $\tau_{\text{VFT}}^{\text{upper}}(T)$ and $\tau_{\text{VFT}}^{\text{lower}}(T)$ relaxation times, which can be portrayed by VFT relations with the following parameters:

$$\tau_{\text{VFT}}^{\text{upper}} = 18.5 \pm 1 \text{ ps}, \quad D = 5.5 \pm 1, \quad T_0 = 182 \pm 5 \text{ K},$$

$$\tau_{\text{VFT}}^{\text{lower}} = 20 \pm 1 \text{ ps}, \quad D = 4.8 \pm 1, \quad T_0 = 186 \pm 5 \text{ K}.$$

The behavior of the dielectric relaxation time is in agreement with results discussed in Ref. [38]. The small differences may be explained by the broader range of temperature and significant increase of the number of tested temperatures in these studies. It is noteworthy that for $\eta(T)$, $\tau_\alpha(T)$, and $\sigma(T)$ experimental dependences passing of the I-Ch transition—i.e., the change in the symmetry of the system—seems to have no influence on T_0 and D values. The analysis presented in Figs. 1–3 shows that all the properties mentioned above can also be portrayed by the MCT "critical" relation (1): namely,

$$\sigma^{-1}(T), \tau_\alpha(T), \eta(T) \propto (T - T_{\text{MCT}})^{-g}, \quad T > T_{\text{MCT}} + 15 \text{ K}. \tag{5}$$

Values of the fitted parameters are given in Figs. 1–3. To the best of the authors's knowledge this is the first evidence showing the validity of the MCT "critical relation also for the dc conductivity. Although the single VFT dependence seems to deliver a fair description of experimental data, the distortion-sensitive analysis of experimental data proposed by Stickel *et al.* [43] confirms this only for the dc conductivity as shown in Figs. 4 and 5. The analysis presented in Fig. 4 reveals two VFT processes for $\tau_\alpha(T)$: starting from $T_B \approx T_{I\text{-Ch}} + 110 \text{ K} = 360 \text{ K}$, the fragility coefficient changes by ca. 20%. Moreover, a strong pretransitional distortion in the immediate vicinity of the I-N transition occurs. The insets in Figs. 4 and 5 present a log-log-plot-based analysis for isotropic 5*CB, to test further the validity of the MCT critical-like description [relation (5)]. In the opinion of the authors, such a plot, which is a standard for critical phenomena [44], is much more sensitive for possible distortions than the $(\tau_\alpha)^{1/g}(T)$ analysis, most often used in the physics of glassy liquids [2,11]. It is visible that for $\tau_\alpha(T)$ relation (5) is valid from $T_1 \approx T_{I\text{-Ch}} + 20 \text{ K} = 270 \text{ K}$ to $T_2 \approx T_{I\text{-Ch}} + 110 \text{ K} = 360 \text{ K}$. For $\sigma(T)$ the value of T_1 is the same, but there is no upper limit (T_2). Noteworthy is the fact that $T_2 \approx T_B$ for the $\tau_\alpha(T)$ dependence.

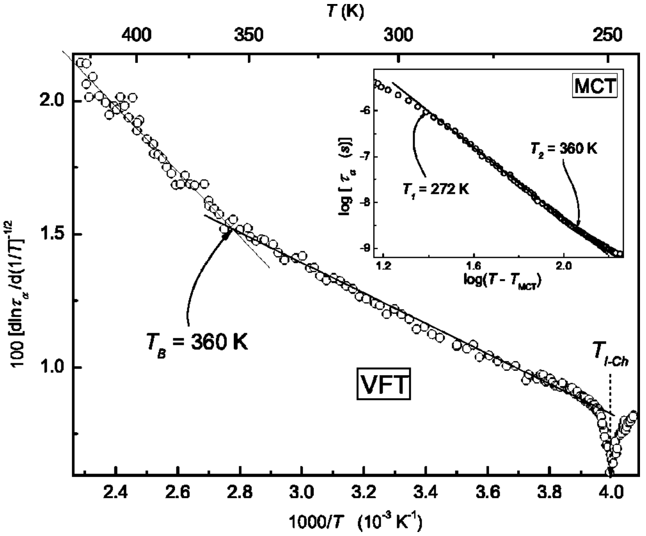

FIG. 4. The derivative analysis of the temperature dependence of dielectric relaxation times, showing whether the description via the VFT relation is possible in 5*CB. The inset presents the log-log plot of the MCT power relation for the same data. In both cases straight lines show regions of the validity of the VFT or MCT dependences, respectively. Characteristic temperatures appearing due to the applied analysis are given in the figure.

When discussing the analysis based on the MCT relation (5), noteworthy is a clear coincidence between T_{MCT} and T^*, describing the extrapolated temperature of the hypothetical isotropic-mesophase continuous phase transition. The latter can be estimated from the analysis pretransitional anomalies of the static dielectric permittivity $\varepsilon'(T)_{f=1\ \mathrm{kHz}}$ or maxima of loss curves $\varepsilon''(T)_{1\ \mathrm{MHz}<f_p<400\ \mathrm{MHz}}$: see Refs. [32,38] for 5CB and 5*CB, respectively. One of the most classical methods of the estimation of T^*, and hence the discontinuity $\Delta T = T_{I\text{-}N} - T^*$ of the *I-N* transition, employs the strong pretransitional anomalies of the Kerr effect, the Cotton-Mouton effect, or light scattering [39,44]. In the last decade it was shown that the same behavior shows the low-frequency, static NDE [32,40,45–47]. However, for the NDE the measurement field can be shifted over a range characteristic of the decay time of prenematic fluctuations [32,42], which is not possible for other methods mentioned above employing light. Figure 6 shows results of NDE measurements for a few frequencies in the isotropic 5*CB. For the lowest measurement frequency the NDE strongly increases in the direction of positive values on approaching the *I-N* clearing point. For higher measurement frequencies the negative-sign pretransitional anomaly in the isotropic phase occurs. This finding is in contradistinction to the existing claims that fluctuations always have to introduce a positive-sign contribution to the NDE [48–52]. In isotropic 5CB the NDE pretransitional anomaly in the isotropic phase remains always positive, although strong distortions from the linear dependence of $\mathcal{E}^{-1}_{\mathrm{NDE}}(T)$, not predicted by a simple mean-field analysis based on the Landau–de Gennes model, occur [32]. To parameterize the pretransitional anomaly in 5*CB one may apply the apparent amplitude analysis, successfully applied in the isotropic 5CB [32]:

$$\mathcal{E}_{\mathrm{NDE}} = \frac{A_{\mathrm{NDE}}}{T-T^*} \propto \chi_T(T)\langle \Delta M^0\rangle\langle \Delta M^f\rangle = \chi_0^* \frac{\langle|\Delta M^0|\rangle\langle|\Delta M^f|\rangle}{(T-T^*)^{\gamma}}, \tag{6}$$

$$A_{\mathrm{NDE}}(T)(T-T^*) = A^{\mathrm{LF}}_{\mathrm{NDE}} + \frac{A^{\mathrm{HF}}_{\mathrm{NDE}}}{1+\omega^2\tau^2}, \tag{7}$$

where the indices 0 and f are for the static limit, the given frequency values $\omega = 2\pi f$, $\langle \Delta M^0\rangle$, and $\langle \Delta M^f\rangle$ are deviations of the local order parameter, and $\gamma = 1$ is the critical exponent of susceptibility (compressibility): $\chi^*_T = \chi^*_0 / T - T^*$. The index

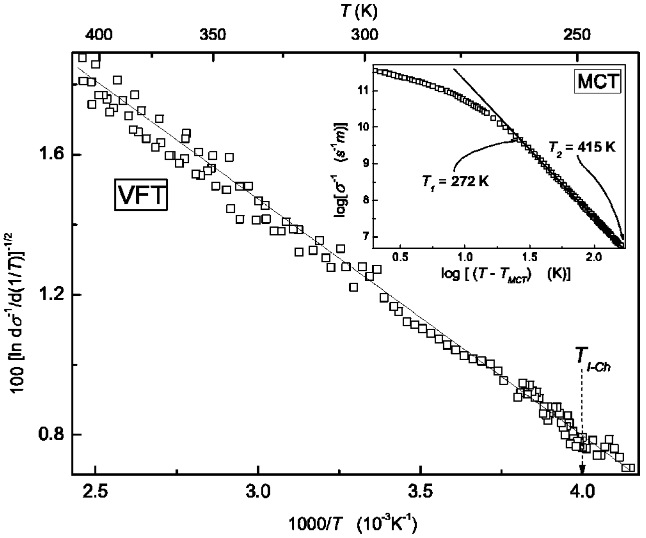

FIG. 5. The derivative analysis of the temperature dependence of dc conductivity showing whether the description via the VFT relation is possible in 5*CB. The inset presents the log-log plot of the MCT power relation for the same data. In both cases straight lines show regions of the validity of the VFT or MCT dependences, respectively. Characteristic temperatures appearing due to the applied analysis are given in the figure.

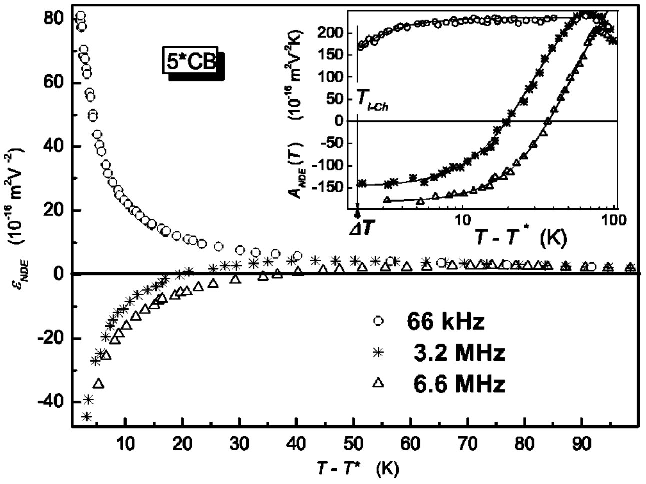

FIG. 6. Nonlinear changes of dielectric permittivity (NDE) in the isotropic phase of 5*CB, for selected measurement frequencies. The inset shows results of the apparent amplitude analysis.

"LF" refers to "low frequency"—i.e., the $\omega^{-1} \gg \tau$ limit—and "HF" to "high frequency"—$\omega^{-1} \ll \tau$. The relaxation time $\tau = \tau_0/(T-T^*)^y$, $y=1$. Regarding the amplitudes, $A_{\mathrm{NDE}}^{\mathrm{LF}} \propto \langle \Delta M_0 \rangle^2 \propto (\Delta\varepsilon^0)^2$ and $A_{\mathrm{NDE}}^{\mathrm{HF}} \propto \langle \Delta M^0 \rangle \langle \Delta M^f \rangle \propto \Delta\varepsilon^0 \Delta\varepsilon^f$, where $\Delta\varepsilon^0$ and $\Delta\varepsilon^f$ denote anisotropies in the dielectric permittivity of a perfectly ordered sample.

The inset in Fig. 6 clearly confirms the validity of the assumption that the unusual and unique behavior observed in isotropic 5*CB is indeed associated with the amplitude A_{NDE}. Distortions from the linear dependence of $\mathcal{E}_{\mathrm{NDE}}^{-1}(T)$ can be associated with the coincidence between two relevant time scales. The first one is related to the reciprocal of the measurement frequency ($\omega^{-1} = 1/2\pi f$), and the second one is associated with the relaxation time of premesomorphic fluctuations (τ). For higher frequencies, on approaching the clearing temperature, $\omega^{-1} \sim \tau$, and then $\langle \Delta M^f \rangle$ becomes related to the dielectric anisotropy of a single, prenematic fluctuation. For lower frequencies or remote from T^*, the condition $\omega^{-1} \gg \tau$ is fulfilled. In this domain the NDE measuring field can detect only an averaged response from a set of fluctuations and $\langle \Delta M^f \rangle$ is reduced to the dielectric anisotropy of a single molecule which is always positive. One of basic features of the nematic phase is the equivalence of $\vec{n}$ and $-\vec{n}$ vectors, known as "directors," showing the preferable orientational ordering direction. This causes, within the nematic phase, including prenematic fluctuations, projections of the permanent dipole moments on the director direction to be canceled. For 5CB this results in an almost perfect cancellation of the permanent dipole moments within the fluctuation, due to the rodlike structure of molecules. Hence, for 5CB, one may expect $A_{\mathrm{NDE}}^{\mathrm{HF}} \propto \langle \Delta M^f \rangle \langle \Delta M^0 \rangle \propto \Delta\varepsilon(\mu=0)\Delta\varepsilon^0 \approx 5.1 \times 11.2$ and $A_{\mathrm{NDE}}^{\mathrm{LF}} \propto \langle \Delta M^0 \rangle \propto (\Delta\varepsilon^0) \approx (11.2)^2$, where $\Delta\varepsilon^0$ denotes the dielectric anisotropy for a perfectly ordered mesophase in a zero-frequency limit. This reasoning gave a fair agreement between the experimental and expected ratios of the amplitudes, $A_{\mathrm{NDE}}^{\mathrm{LF}}/A_{\mathrm{NDE}}^{\mathrm{HF}}$, for 5CB [32]. However, for 5*CB the long molecular axis within premesomorphic fluctuations is less parallel to the director than in the case of 5CB. This is associated with different molecular structures of 5*CB and 5CB as shown in Fig. 1. For 5*CB there remains a nonvanishing component of the permanent dipole perpendicular to $\vec{n}$, practically absent for 5CB. Hence, for 5*CB, one may expect $\langle \Delta M^f \rangle = \langle M_{\parallel}^f - M_{\perp}^f \rangle < 0$ and hence $A_{\mathrm{NDE}} < 0$ for higher measurement frequencies. On moving away from T^* or for very low measurement frequencies, $\langle \Delta M^f \rangle = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$ and $A_{\mathrm{NDE}} > 0$. It is noteworthy that both in 5CB [32] and 5*CB the same values of the susceptibility-related exponent and the exponent related to the decay of premesomorphic fluctuations, $\gamma=1$ and $y=1$, have been obtained. As suggested in Ref. [32], the latter can be associated with the dynamical exponent for the nonconserved order parameter $z=2$.

Concluding, Cang *et al.* [29,30] experimentally showed the existence of the "lower" and "upper" MCT "critical" temperatures in the isotropic phase of classical rodlike nematogens, with the *I-N-S* phase sequence. The temperature $T_{\mathrm{MCT}}^{\mathrm{upper}}$ can be associated with the onset of orientational freezing and the temperature $T_{\mathrm{MCT}}^{\mathrm{lower}}$ with the onset of the possible loss of the translational degree of freedom. These results are in agreement with basic predictions of molecular MCT developed recently for a liquid consisting of hard-ellipsoid shape molecules [25–28]. As shown above, the MCT "critical-like" relation (5) perfectly describes the experimental data in the isotropic 5CB, for $T_{I\text{-}N}+50\ \mathrm{K} > T > T_{I\text{-}N}$, without any distortions. This can be explained by the fact that for 5CB the estimated value $T_{\mathrm{MCT}}^{\mathrm{lower}} = T_{I\text{-}N} - 35$ K is located already in the solid phase, whereas in glassy liquids relation (5) is valid for $T > T_{\mathrm{MCT}} + 20$ K [30]. Following Refs. [25–30] one may expect that $T_{\mathrm{MCT}}^{\mathrm{upper}}$ is close to the clearing temperature; hence, $T_{\mathrm{MCT}}^{\mathrm{upper}}$ and $T_{\mathrm{MCT}}^{\mathrm{lower}}$ are more than 35 K apart.

For glass-forming 5*CB, with the isotropic–chiral-nematic–glass phase sequence, a small distortion from the rodlike structure of 5CB caused that $T_{\mathrm{MCT}}^{\mathrm{upper}} = T_{\mathrm{MCT}}(\mathrm{orient}) \approx T_{\mathrm{MCT}}(\mathrm{trans}) = T_{\mathrm{MCT}}^{\mathrm{lower}}$ and these MCT "critical" temperatures coincide with the thermodynamic phase transition at $T=T^*$. It is noteworthy that for 5CB the extrapolated relaxation time $\tau_\alpha(T_{\mathrm{MCT}}^{\mathrm{lower}}) \approx \tau_\alpha(T_{\mathrm{MCT}}(\mathrm{trans})) \approx 2\times10^{-7}$ s is in fair agreement with the "magic, universal" relaxation time $\tau_\alpha(T_{\mathrm{MCT}}) \sim 10^{-7}$ s proposed by Novikov and Sokolov [17]. Regarding the upper relaxation time in isotropic 5CB, $\tau_\alpha(T_{\mathrm{MCT}}^{\mathrm{upper}}) = \tau_\alpha(T_{\mathrm{MCT}}(\mathrm{orient})) \approx 3\times10^{-9}$ s, assuming that $T_{\mathrm{MCT}}^{\mathrm{upper}} = T^* = T_{I\text{-}N} - \Delta T$ and $\Delta T \approx 1.1$ K [32]. For 5*CB, $\tau_\alpha(T_{\mathrm{MCT}}(\mathrm{orient})) \approx \tau_\alpha(T_{\mathrm{MCT}}(\mathrm{trans})) \approx 2\times10^{-5}$ s. In 5*CB this relaxation time drops with rising pressure, reaching the value $\tau_\alpha \approx 3\times10^{-9}$ s, characteristic for 5CB at the atmospheric pressure, for $P \approx 140$ MPa, as can be concluded from the results given in Ref. [38]. One of the still puzzling phenomena for supercooled liquids is the appearance of structural heterogeneities and their relationship to the observed experimental properties. The behavior of the isotropic liquid crystalline compounds is naturally dominated by well-defined heterogeneities—i.e., the premesomorphic fluctuations [28–32,45–47]. In the case of 5CB and 5*CB there are well-defined bond-ordering heterogeneities—i.e., ordered in an orientational way, "swarms" of rodlike molecules—in the liquidlike surrounding. They induce strong pretransitional anomalies of the NDE, associated with exponents $\gamma=1$ for susceptibility and $y=1$ for the relaxation time, which may be associated with the expected evolution of $\chi_4(T)$ and $t_4(T)$, mentioned in the Introduction.

It is noteworthy that when analyzing existing experimental data similar singular behavior associated with research methods directly coupled to mesoscale heterogeneities can be found also for "normal" glass-forming liquids such as *p*-terphenyl (PTP) [53] [transient grating optical Kerr effect (TG-OKE)] 2-biphenylmethenol (BPM) [optical-heterodyne-detected optical Kerr effect (OHD-OKE)] [29] and epoxy resin EPON 5 (NDE) [53,54]. When discussing the role of heterogeneities it is worth recalling the recent simulations on a polymer melt [34] which showed that density fluctuations remain short range whereas spatial correlations between monomers become long range on approaching T_{MCT}. In this way a growing dynamical correlation length and the bond-ordering order parameter were identified as the onset of a possible connection between critical phenomena and glass-forming liquids [34]. This behavior resembles the experimental findings of this paper and a recent proposal by Tanaka [55], who showed that the existence of both density and bond-ordering fluctuations may result in a general model for liquid-liquid transitions, covering supercooled liquids, liquids near the critical point, and the liquid-liquid transitions in a one-component liquid. In isotropic 5CB and $5*$CB dynamic and static properties are strongly influenced by ordered in a premesomorphic way as fluctuations and heterogeneities, even 100 K above the clearing point. There is strong evidence for the glassy the fluidlike, tricritical, and pseudospinodal description of the isotropic phase resembling the one observed for the liquid-liquid demixing in binary solutions [32,45,46,56]. A clear relationship between critical phenomena and the glassy behavior manifested via dynamical regimes and long-lived "glassy" heterogeneities, ordered in a positional and/or orientational way in a fluidlike surrounding, was also obtained in recent theoretical models by Berthier and Garrahan [57,58] and Bakai and Fischer [59]. For both tested compounds, $5*$CB and 5CB, the temperature evolution of dielectric relaxation times, the dc conductivity, and the viscosity are well described by the "critical-like" description from mode coupling theory. However, for $5*$CB a unique coincidence of the MCT "critical" temperature and extrapolated temperature of the hypothetical continuous isotropic-cholesteric (T^*) phase transition was found. The temperature dependence of the strong electric-field-induced changes of the dielectric permittivity exhibits a strong anomaly, described by the exponents $\gamma=1$ for susceptibility and $y=1$ for heterogeneity-related relaxation time. It is noteworthy that for the homogeneous phase of near-critical mixtures approximately the same critical exponent has been obtained [60–62]. Results presented above show a unique significance of studies of mesogenic compounds for a better insight into the dynamics of supercooled, glass-forming liquids. They also recall questions of the proper description of the isotropic phase and the *I*-*N* transition which in basic monographs on the physics of liquid crystals is most often presented as the best example of a simple mean-field description [39,44,62–65].

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