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Heterogeneity-related dynamics in isotropic *n*-pentylcyanobiphenyl

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The evolution of the dielectric relaxation time $\tau(T)$ and its strong electric field related counterpart $\tau_{fluct.}(T)$ in the isotropic phase of rodlike liquid crystalline *n*-pentylcyanobiphenyl (5CB) is discussed. For the $\tau_{fluct.}(T)$ a strong pretransitional increase on approaching the virtual critical point located at $\Delta T = 1.1$ K below isotropic nematic clearing temperature T_{IN} is shown. The linearized derivative analysis applied to test the evolution of $\tau(T)$ revealed a sequence of Vogel-Fulcher-Tammann based dynamical domains, for which the fragility increases enormously on approaching T_{IN}. The similar analysis focused on testing the "critical" mode-coupling theory behavior showed superior features of such description. A strong asymmetric broadening of the dielectric loss curves is also discussed.

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INTRODUCTION

Defining the role of heterogeneities appearing in the supercooled liquid on cooling is recognized as one of the possible milestones in understanding the vitrification phenomenon [1]. Their existence near the glass temperature T_g seems to be experimentally well established [1–4]. However, the question of their persistence well above T_g and their influence on the complex dynamics remains still unclear [1,5,6]. Hence different experimental results in systems hardly explored up to now may be of particular importance here. The isotropic phase of rodlike, liquid crystalline compounds with the isotropic-nematic (I-N) transition is naturally dominated by structural, prenematic, heterogeneities appearing in the isotropic, fluidlike, surrounding [7–18]. For compounds with the permanent dipole moment parallel to the main molecular axis the cancellation of the dipole moments within fluctuations leads to a strong pretransitional anomaly of the static dielectric permittivity $\varepsilon'(T)$ [9–11], confirmed by $d\varepsilon'(T)/dT$ distortion-sensitive analysis [9,11]. This phenomenon is associated with the fact that the number of molecules within prenematic fluctuations increases on approaching the virtual temperature of the continuous phase transition (T^*) due to the singular behavior of the correlation length [7]:

$$\xi(T) = \xi_0\left(\frac{T - T^*}{T^*}\right)^{-\nu}, \tag{1}$$

where $T > T_{IN}$, $T^* = T_{IN} - \Delta T$, T_{IN} is the clearing temperature, i.e., the temperature of the weakly discontinuous phase transition, ΔT denotes the measure of the discontinuity of the I-N transition. The exponent $\nu = 1/2$. Also the lifetime of fluctuations exhibits a singular behavior [7,9]:

$$\tau_{fluct.}(T) \propto \frac{1}{(T - T^*)^{y}}. \tag{2}$$

Relations (1) and (2) can be derived from the simply mean-field Landau–de Gennes (LdG) model which yields $y = \gamma = 1$, where γ denotes the critical exponent for the compressibility $\chi(T)$ [7]. However, recently the possible validity of relation $y = z\nu = 1$, where $z = 2$ is the dynamical exponent for the nonconserved order parameter, was suggested [9]. Recent broad-band dielectric spectroscopy (BDS) [9,12] and optical-heterodyne-detected optical Kerr effect (OHDOKE) [13,14] studies clearly show the existence of the canonical features of the glassy dynamics even well above the orientational "melting" temperature, i.e., the I-N clearing point. These results coincide with the analysis for a model fluid of hard ellipsoids of revolution given in Refs. [15,16] where also the unique existence of two ergodic-nonergodic mode coupling theory (MCT) crossovers related to the translational freezing and orientational freezing was indicated. These conclusions seems to be supported by the mentioned OHDOKE [13,14] and BDS [12] tests on isotropic *n*-octylcyanobiphenyl (8CB).

This contribution shows the evidence of the significant influence of prenematic heterogeneities on the dynamics of the isotropic phase. It recalls authors' earlier tests on isopentylcyanobiphenyl (5^*CB) [17] and *n*-butyl-cyanobiphenyl (4CB) [18]. However, none of these papers took into account different possibilities of analysis related to the application of the linearized derivative analysis [19–21], up to now applied only for "classical," nonmesogenic supercooled liquids. Results presented are based on BDS and its strong electric related counterpart, NDE [22], measurements. The latter was used for determining the evolution of prenematic fluctuation relaxation time. Studies were conducted in *n*-pentylcyanobiphenyl (5CB), a rodlike compound with longitudinal permanent dipole moment and isotropic ↔ (35 °C) ↔ nematic ↔ (20 °C) ↔ solid phase sequence [7]. Measurements were conducted up to $T_{IN}+90$ K. It is noteworthy that for 5CB a unique detailed insight into the evolution of prenematic fluctuations due to transient grating optical Kerr effect (TGOKE) studies is available [8].

RESULTS AND DISCUSSION

The tested compound was purchased from the Military Technical University (Warsaw, Poland) and carefully degassed prior to measurements. BDS measurements were carried out via Novocontrol BDS 80 spectrometer with Quattro temperature units. Nonlinear dielectric effect (NDE) describes changes of dielectric permittivity due to the applica-

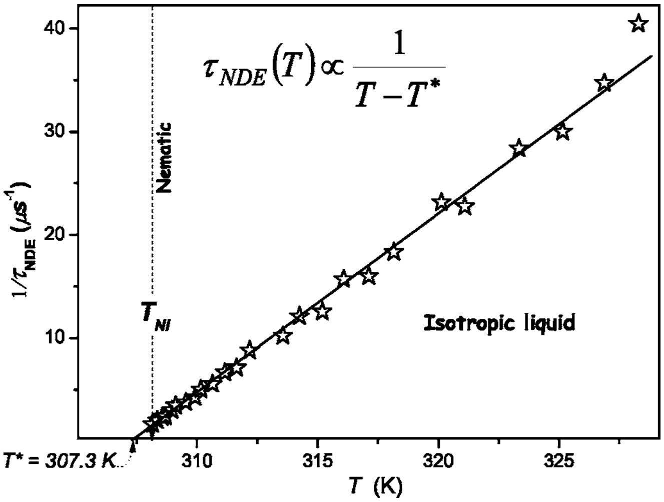

FIG. 1. The temperature dependence of the nonlinear dielectric relaxation time related to the lifetime evolution of prenematic fluctuation heterogeneities. The solid line is portrayed by the quasicritical dependence given in the figure. The dashed arrow shows the I-N discontinuous transition. The value of T^* is also indicated.

tion of a strong electric field, namely [22] $\mathrm{NDE}=\Delta\varepsilon/E^2=[\varepsilon(E)-\varepsilon(E\to 0)]/E^2$. The applied dual-field, aperiodic high voltage excitation and modulation domain analysis based NDE spectrometer is described in Ref. [22]. The principle of measurements is based on the application of few ms lasting dc pulse of a strong electric field ($V_{\mathrm{dc}}=500-1000$ V) which induced the anisotropy in the sample. The obtained changes of dielectric permittivity were scanned via radio-frequency weak electric field ($V_{meas.}=0.3$ V) with frequency scanned from $f_{meas.}=20$ kHz to $f_{meas.}=20$ MHz. The sample was placed in a measurement capacitor with $d=0.5$ mm gap, made solely from Invar and quartz [22].

Figure 1 shows results of the temperature dependence of the NDE relaxation times, reflecting the evolution of the lifetime of fluctuation heterogeneities [9]. They were determined from the inflection frequency of $\varepsilon'(f_{meas.})$ [9]. The obtained dependence presented in Fig. 1 is in fair agreement with earlier optical Kerr effect studies [8,23]. As shown in Refs. [7–9,13,14] in the isotropic phase the distribution of the fluctuation-related relaxation time of fluctuations follow the Debye pattern. Results presented in Fig. 1 are well portrayed by the quasicritical relation (2) with a singularity at $T^*=307.3$ K, located approximately $\Delta T=1.1$ K below T_{IN}. It is noteworthy that on approaching the continuous or weakly discontinuous phase transition $\mathrm{NDE}\propto\langle\Delta M^2\rangle_V\chi$, where $\langle\Delta M^2\rangle_V$, denotes the mean of the square of the local order parameter fluctuation [9]. This shows the coupling of $\tau_{fluct.}(T)$ to the lifetime evolution of fluctuation heterogeneities in the isotropic phase.

Dielectric relaxation time $\tau(T)$ detected in BDS measurements is associated with the relaxation of the single permanent dipole moment distorted by the averaged local structural ordering [9,12,15–19]. Its evolution in the isotropic 5CB is shown in Fig. 2. At first sight the $\tau(T)$ dependence seems to be well portrayed by a single Vogel-Fulcher-Tammann (VFT) dependence, namely [1]

$$\tau(T) = \tau_0^{VFT} \exp\left(\frac{D_T T_0}{T - T_0}\right). \qquad (3)$$

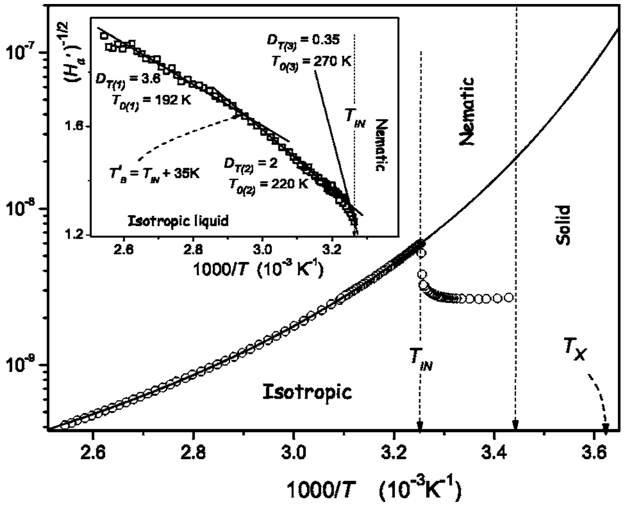

FIG. 2. The temperature dependence of the dielectric relaxation time. The solid curve is portrayed by the single VFT dependence with parameters given in the text. The dashed arrow indicates the I-N clearing temperature. The inset shows the linearized derivative plot of the same data aimed at the testing regions of the validity of VFT relations [relation (5)]. Following dynamical domains are portrayed by linear dependences with parameters given in the figure.

In glassy liquids the extrapolated temperature T_0 is associated with the ideal glass transformation and D_T is the fragility strength coefficient [1]. For $D_T<10$ the glassy liquid can be recognized as a fragile one, i.e., strongly non-Arrhenius [1,22]. Results given in Fig. 2 show that the isotropic 5CB can be encountered to this category. Comparing Figs. 1 and 2, it is worth stressing that $\tau_{fluct.}(T_{IN})=0.65$ μs for the fluctuation-related relaxation time and $\tau(T_{IN})=6$ ns for the single permanent dipole moment related relaxation time.

Although the single VFT relation seems to portray fairly well experimental data (see the main part of Fig. 2), the linearized, distortion-sensitive, derivative analysis presented in the inset in Fig. 2 clearly contradicts such a conclusion. It explores the fact that the non-Arrhenius temperature evolution of a dynamic property can be alternatively described by the Arrhenius-like relation but with an apparent activation energy $E_a(T)$, namely [1,19–21]

$$\tau(T) = \tau_0 \exp\left(\frac{E_a(T)}{RT}\right). \qquad (4)$$

The derivative of relations (3) and (4) yields [19]

$$H_a'(T) = \frac{H_a(T)}{R} = \frac{d\ln\tau}{d(1/T)} = D_T T_0\left(\frac{T}{T-T_0}\right)^2, \qquad (5)$$

where $H_a(T)$ denotes the apparent activation enthalpy.

Consequently for a given "dynamical domain" [19–21], i.e., the region of validity of the VFT relation with the given set of parameters, the plot $[H_a']^{-1/2}$ vs $1/T$ should yield a linear dependence from which values of T_0 and D_T can be deduced [19]. As shown in Fig. 2, values of D_T decrease on

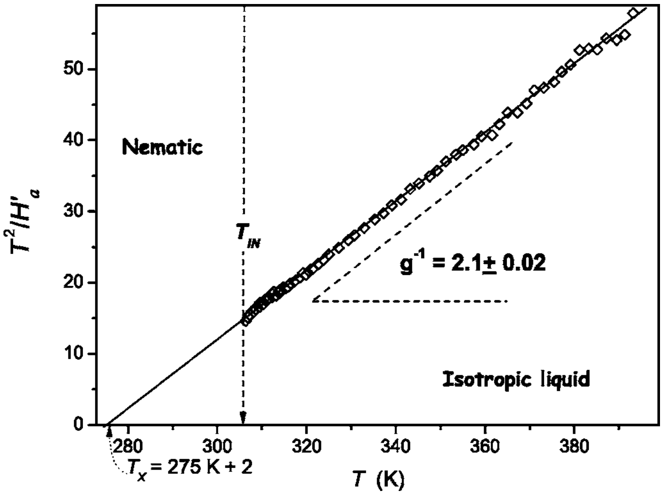

FIG. 3. Linearized derivative plot of dielectric relaxation time aimed at the testing regions of the validity of the MCT critical-like relation, coupled with the evolution of the apparent activation enthalpy $H'_a(T)$. The solid line shows the region of validity of relations (6) and (7). Fitted parameters are given in the figure. The application of relation (6) with parameters from Fig. 4 yields $\tau_0^{\mathrm{MCT}}=0.7\times10^{-10}$ s.

cooling, i.e., the isotropic phase becomes more fragile on approaching T_{IN}. The intersection of the lines describing following dynamical domains indicate dynamic crossovers [19–21]. Note the coincidence between T'_B and $T_{fluct.}$. The analysis of experimental data in "classical" glassformers showed that $T_B \approx T_X$, where T_X is the ergodic-nonergodic crossover temperature predicted by the MCT [1]. This temperature can be estimated from the analysis of dielectric relaxation time data, via [1]

$$\tau_{\mathrm{MCT}}(T)=\tau_0^{\mathrm{MCT}}\left(\frac{T-T_X}{T_X}\right)^{-g}. \tag{6}$$

Such dependence follows experimental data only in the high temperature region for $T>T_X+20$ K, where $T_X \approx 1.2T_g$ [1]. In practice T_X and g are determined from $[\tau_{\mathrm{MCT}}(T)]^{-1/g}$ vs T [1,24] $\ln[\tau_{\mathrm{MCT}}(T)]$ vs $\ln(T-T_X)$ [12,17] plots. For such analysis the exponent g or the temperature T_X are adjusted until they reach the best linear regression fit possible. In practice, this has to led to an enormous uncertainty in the estimation of T_X and g, due to the extremely large "discontinuity" $T-T_X \approx 20$ K. However, recalling the derivative analysis one can see from relation (6) [19]

$$\left(\frac{d\ln\tau}{d(1/T)}\right)=\frac{gT^2}{T-T_X}, \tag{7}$$

which yields a linear dependence $T^2/[d\ln\tau/d(1/T)]=T^2/H'_a=A+BT$ with $T_X=B/A$ and $g=A^{-1}$. Results of analysis based on the latter relation are shown in Fig. 3. It is worth noting that only the linear regression, without any hidden coefficients, can yield desired parameters. Figure 3 also shows that the MCT description remains valid up to $T_{IN}+90$ K, without distortions near T_{IN}. This may be associated with the fact that the MCT "critical-like" relation is expected to follow the experimental data for $T>T_X+20$ K whereas the isotropic phase extends for $T>T_{IN}=T_X+33$ K. It is noteworthy that the extrapolation of the effective VFT dependence from Fig. 2 up to $T=T_X$ yields 2×10^{-7} s, which is in fair agreement with the "magic" (universal) relaxation time expected for $T_B \approx T_X$ dynamic crossover temperature [25] for glassy liquids. Hence the crossover occurring at $T=T'_B$ cannot be associated with the crossover usually observed in supercooled liquids.

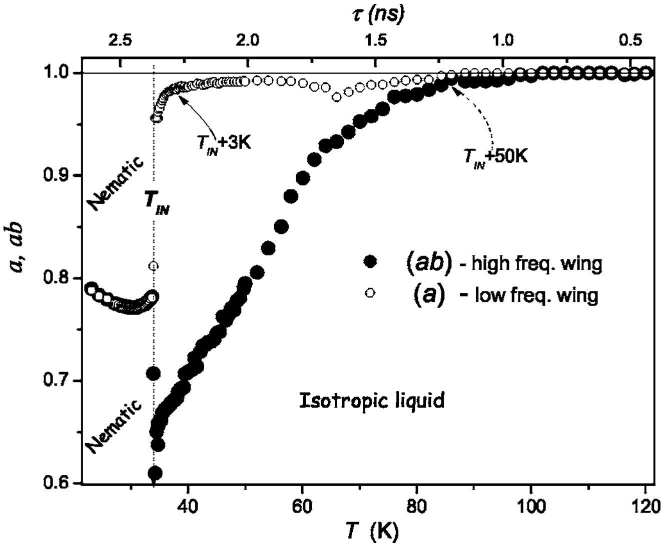

FIG. 4. The temperature evolution of Havriliak-Negami shape parameters in isotropic 5CB for the high and low frequency wings of dielectric loss curve. The temperature of the crossover into the single relaxation time pattern is indicated in the figure.

The evolution of the Havriliak-Negami parameters characterizing the distribution of dielectric relaxation times [1] is shown in Fig. 4. It is noteworthy that although the temperature evolution of the relaxation time remains permanently non-Arrhenius, the distribution of relaxation times changes from the Debye pattern remote from T_{IN} to the strongly non-Debye, asymmetric distribution for $T \to T_{IN}$. In the opinion of the authors the decrease of the high frequency wing related parameter $n \approx ab \to 0.6$ for $T=T_{IN}$ is of some importance since in Ref. [26] the value $n \approx 0.5$ was postulated as the possible universal one for glassy liquids on $T \to T_g$. The value of T_{IN} is definitely well above the real T_g in 5CB [27]. However, in supercooled glassy liquids the glass temperature is often estimated from the extrapolation of the evolution of dielectric relaxation time times via $\tau_{VFT}(T_g)=100$ s [1]. For following dynamical domains indicated in Fig. 2 this yields set of fictive, nonreal values T_g: 215, 240, and 274 K for following domains on approaching T_{IN}. Consequently the question arises whether this fact may correlate with the hypothesis given in Ref. [26].

Concluding, results presented above show a strong dependence of the evolution and distribution of dielectric relaxation time on the distance from the clearing temperature (T_{IN}). On cooling the correlation length of prenematic fluctuations strongly increases reaching $\xi \approx 3\xi_0$, i.e., two to three molecules in a fluctuation, at $T_{fluct.} \approx 40$ K and $\xi \approx 120\xi_0$ at $T=T_{IN}$ [21]. Below the temperature $T_{fluct.}$ fluctuationsensitive properties start to follow a quasicritical description with a singularity at T^*. The obtained coincidence of $T_{fluct.}$ and dynamic crossover temperature T'_B (Fig. 2) supports the hypothesis of the relationship between growing-up heterogeneities-fluctuations and the rapidly increasing fragility. Figure 2 may suggest that the Arrhenius behavior may eventually appear for $T > T_{IN} + 80$ K which coincides with $\xi \approx \xi_0$ fluctuation heterogeneity. This coincides with the region of the Debye distribution of relaxation time shown in Fig. 4.

Results presented above and those of Refs. [9,12–18] stress the significance of the isotropic phase of rodlike nematogens, giving a different insight into glassy dynamics. They also recall the question of the nature of the I-N transition which until recently was presented as the most successful example of the simple mean-field description [7,28].

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