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Universal pattern for the distribution of relaxation times in the isotropic phase of liquid crystalline *n*-cyanobiphenyls

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A universal pattern emerging from the analysis of the distribution of relaxation times in the isotropic phase of liquid crystalline *n*-alkylcyanobiphenyls (*n*CB) from 4CB to 14CB is presented. The increase of the length of *n*CB molecules causes the high-frequency (short-time) branch of the primary relaxation loss curve to approach the form $\varepsilon(f>f_{peak})\sim\omega^{-n}$, with $n\to 1/2$ in frequency ($\omega=2\pi f$) or $\sim\sqrt{t}$ in time on cooling toward the isotropic-mesophase "clearing" phase-transition temperature (T^C). Recently, such behavior was suggested as a hypothetical universal pattern for diverse glass forming organic liquids on approaching the glass temperature [A. I. Nielsen, T. Christensen, B. Jakobsen, K. Niss, N. B. Olsen, R. Richert, and J. C. Dyre, J. Chem. Phys. **130**, 154508 (2009)]. The isotropic phase of rodlike liquid crystalline compounds is considered to be an important experimental model system for studying glassy dynamics since it constitutes a link with the model fluid of hard ellipsoids of revolution.

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Universal patterns in dynamics of viscous liquids are particularly important in searching for a solution of the puzzling glass transition behavior [1–3]. Recently, it was suggested that on approaching glass temperature ($T\to T_g$), a fundamental universality associated with the time-temperatures superposition (TTS) may exist, namely, $\varepsilon''(f>f_{peak})\propto\omega^{-n}$ with $n\to 1/2$, where $\omega=2\pi f$ and f_{peak} is the peak frequency of the primary relaxation loss curve [4–6]. These studies were summarized as follows in Ref. [6]: "*The data consisting of 347 spectra for 53 liquids show prevalence of minimum slopes close to* −1/2 (in the log-log plot), *corresponding to the square-root-time dependence of dielectric relaxation function at short times.*"

This result seems to be in an agreement with earlier studies by Careri *et al.* [7] based on $1/f$ noise method in selected spin-, relaxor-, and molecular liquid-glass formers for $T\to T_g$. Noteworthy is also the clear evidence for $n\to 1/2$ in supercooled liquid crystalline isopentylcyanobiphenyl (5*CB) [8,9] and an orientionally disordered crystal (ODIC) $[(CH_3)_3C(CH_2OH)]_{0.70}[(CH_3)_2C(CH_2OH)_2]_{0.30}$ [10,11], both for the temperature and pressure paths of approaching the glass transition. Recently, a similar tendency was shown for ten selected pressurized molecular liquids [12]. It is noteworthy that some distortions from $1/\sqrt{\omega}$ or $\sqrt{t}$ patterns were also reported in Ref. [6]. They were explained by the interference biasing factors such as the secondary β relaxation or other, yet unknown, generic properties. The search for the correlation between the mentioned universal pattern and such fundamental artifacts as fragility, TTS, or half width of the loss curve has been indicated as inconclusive. Finally it was stated [6] that "*If* $\sqrt{t}$ *relaxation is confirmed by other groups as being generic for the a-process (excluding high-loss liquids), the dynamics of glass-forming organic liquids is simpler than presently generally believed*…"

For instance, such universality may appear to be important for the Ngai coupling model [13], which links primary and secondary relaxations using a parameter describing the distribution of relaxation times. It seems that further studies on this hypothetical universality should focus on investigations in systems which (i) are as simple as possible, (ii) enable extraction of some basic mechanisms, and (iii) are closely related to a theoretical model system. Recently, the isotropic phase of rodlike nematic liquid crystalline compounds has been promoted as an experimental model fluid whose dynamics can be paralleled by a hard ellipsoid fluid within the mode-coupling theory (MCT) approximation [14,15]. Particularly noteworthy is the decoupling between the orientational (OR) and translational (TR) degrees of freedom, leading to two ergodic-nonergodic crossover temperatures. The first one (T_{OR}) is associated with orientational freezing. It is located in the immediate vicinity of the isotropic-nematic (I-N) transition [15–20]. This transition has a weakly discontinuous character, namely, the hypothetical continuous phase transition is placed at $T^*=T_{I\text{-}N}-\Delta T$, where ΔT is the measure of the discontinuity of the I-N transition [21]. The second crossover temperature (T_{TR}) is placed well below $T_{I\text{-}N}$ [15–20]. It can be determined from the analysis of the temperature evolution of the primary (dielectric) relaxation time in the isotropic phase, namely, [22–24], namely,

$$\tau(T)=\tau_0^{MCT}(T-T_{TR})^{-\phi'}, \tag{1}$$

where $\phi'=1.5-3$ is the MCT power exponent.

Studies in the isotropic phase of *n*-pentylcyanobiphenyl (5CB) showed the validity of Eq. (1) even up to $\sim T_{I\text{-}N}+100$ K, with the extrapolated "critical" temperature $T_{TR}\approx T_{I\text{-}N}-35$ K [22,23]. A weak distortion from Eq. (1) was found only in the immediate vicinity of $T_{I\text{-}N}$ [22].

When discussing the glassy dynamics in the isotropic phase studies based on optical heterodyne detected optical Kerr effect (OHD OKE) should be recalled [16–20]. This is a unique experimental method enabling an insight from ~1 ps to over 100 ns in time. OHD OKE studies gave a clear evidence for the existence of two mode-coupling crossover "critical-like" temperatures for the isotropic phase of nematic rodlike liquid crystals (LCs). They also revealed a set of common features of the isotropic phase of rodlike nematic LC for $T \to T_{\text{I-N}}$ and "classical," nonmesogenic, molecular liquids for $T \to T_g$ [16–20,25,26].

Most often for describing the non-Arrhenius dynamics in viscous fluids the Vogel-Fulcher-Tammann (VFT) is used, namely [1–3],

$$\tau(T) = \tau_0^{\text{VFT}} \exp\left(\frac{D_T T_0}{T - T_0}\right), \tag{2}$$

where D_T is the fragility strength coefficient and $T_0 \ll T_g$ is the VFT estimate of the ideal glass temperature.

In classical, nonmesogenic, supercooled molecular liquids, there are two dynamical domains with the crossover at $T_g < T_B(\tau \sim 10^{-7\pm 1}\ \text{s}) < T_m$ [27,28], where the latter denotes the melting temperature. Each dynamical domain is associated with different set of (T_0, D_T) values. Only the set for the low-temperature dynamical domain $(T < T_B)$ can be linked to the real glass transition at $T_g(\tau \sim 100\ \text{s})$ [29,30]. For the given dynamical domain, the value of D_T is constant, whereas the steepness index $m(T) = d \log_{10}\tau / d(T_g/T)$ [31] continuously increases, finally reaching the value $m = m(T \to T_g)$ [29,30]. Both D_T and m are considered as basic metrics of fragility, one of the most important properties for the glass transition physics ([1–3,29–31] and references therein). For the isotropic phase of 5CB, it was shown that $D_T \to 0.05$ for $T \to T_{\text{I-N}}$, i.e., it decreases to a value indicating an anomalously fragile system. This can be associated with a set of virtual temperature dependent values of $T_0 \to 295$ K for $T \to T_{\text{I-N}}$. However, the value of the steepness index $m(T = T_{\text{I-N}}) \sim 10$ [22,24], i.e., it is typical for strong, (nonfragile) glass-forming systems [1,2,27–31]. In the opinion of the author, this inconsistency may be associated with the influence of prenematic fluctuations-heterogeneities, associated with the weakly discontinuous character of the I-N transition.

This report presents results of the analysis of the dielectric relaxation times distribution in the series of n-alkylcyanobiphenyls (nCB), from $n=4$ to 14CB. 4CB is a monotropic liquid crystalline compound which crystallizes in the isotropic phase well above $T_{\text{I-N}}$ on cooling [21]. However, the nematic phase can be reached for a well-purified and degassed sample [32]. For 5CB, 6CB, and 7CB, the isotropic-nematic-solid mesomorphism takes place. For 8CB, 9CB, and 11CB the isotropic–nematic–smectic–A–solid phase sequence is reported [21,33]. It is worth stressing that for 9CB and 11CB, the range of the nematic phase is reduced solely to ~1.5 and ~0.5 K, respectively. For 10CB, 12CB, and 14CB, the isotropic–smectic A–solid mesomorphism occurs [21,33]. Reference results for 14CB are very limited so far [34,35]. To the best of the author's knowledge, there no reports for nCB with $n \geq 15$. High-purity samples of tested liquid crystalline (LC) compounds were obtained from the Military Technical University (Warsaw) due to Roman Dąbrowski's courtesy. Always prior to measurements, they were carefully degassed. Investigations were conducted with the use of Novocontrol BDS 80 impedance analyzer (BDS is the broad band dielectric spectroscopy) with Quattro temperature unit. A gold-covered flat-parallel measurement capacitor with $d = 100\ \mu$m gap was used. The analysis presented below employs data from author's earlier studies, namely, 4CB [32], 5CB [22], and 8CB, 9CB, and 10 CB [23]. The full set of data for 14CB will be discussed in a further report.

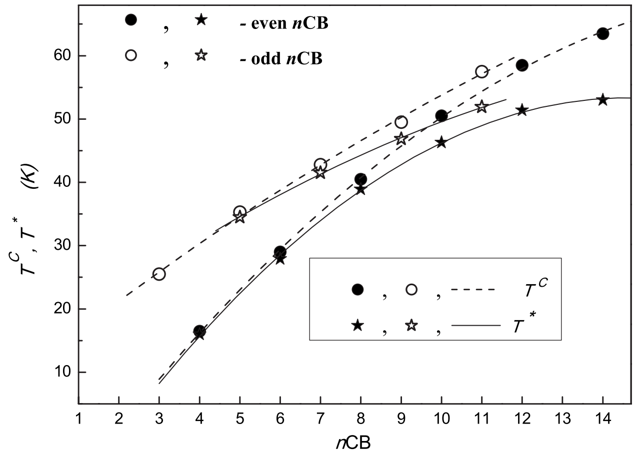

FIG. 1. The evolution of the clearing temperature ($T^C = T_{\text{I-N}}$, $T_{I\text{-}SmA}$) and the temperature of the hypothetical "virtual" continuous phase transition (T^*) in the homologous series of n-cyanobiphenyls. Dashed and solid curves are guides for eyes. Values of $T^*(n)$ were determined via LF NDE measurements [36,37].

The evolutions of the isotropic-mesophase clearing temperatures ($T^C = T^{\text{I-N}}$, $T^{I\text{-}SmA}$) and the extrapolated temperature of the virtual continuous phase transition ($T^* = T^C - \Delta T$) in nCB homologous series are shown in Fig. 1. Values of $T^*(n)$ were determined using low-frequency nonlinear dielectric effect measurements. This is a unique, fluctuation-sensitive, method which enables simple and reliable estimation of T^* and then ΔT for the case of both isotropic to nematic and isotropic to smectic phase transitions [36,37]. Noteworthy are different evolutions of $T^C(n)$ and $T^*(n)$ for even and odd nCBs. There have been no reports of such odd-even effect for $T^*(n)$ so far. Results presented in Fig. 1 also show the increase of the discontinuity of the isotropic-mesophase transitions when increasing the length of nCB molecule, from $\Delta T \approx 0.7$ K (4CB) to $\Delta T \approx 11$ K (14CB).

Studies of the distribution of dielectric relaxation times in the isotropic phase of rodlike liquid crystalline compounds have a long history [[8,9,22–24,38–50] and references therein]. The analysis was carried out using Cole-Cole (CC), Cole-Davidson (CD) [38–42,45,50], and Havriliak-Negami (HN) functions [43–48]. Results presented below indicate the latter as the most optimal, since broadening of dielectric loss curves on cooling is asymmetric. Studies of distribution related parameters in a broad range of temperatures with a careful insight in the immediate vicinity of the clearing temperature are reported only recently [8,9,22–24,45,50,51].

In this report, to minimize the uncertainty associated with a multiparameter fitting, the distribution dependence introduced by Jonscher [51] was used. In the log-log, it can be presented as follows:

$$\log_{10}[\varepsilon''(f)] \propto m \log_{10} f \quad f < f_{peak}, \tag{3}$$

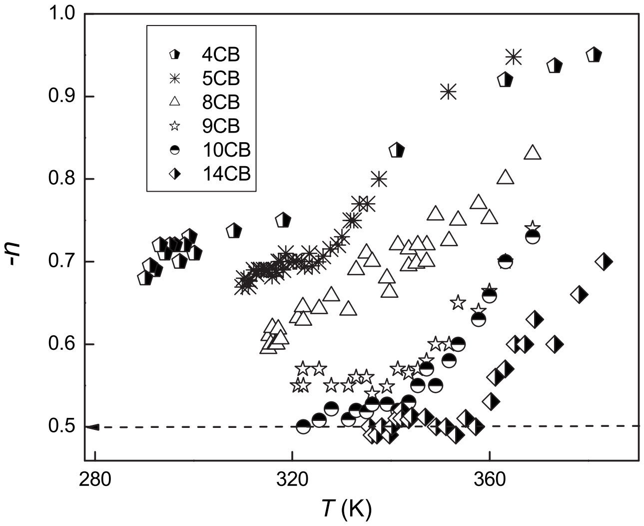

FIG. 2. The evolution of the coefficient n describing the high-frequency distribution of relaxation times. Results are for the isotropic phase, beginning from ca. 0.02 K above the clearing temperature.

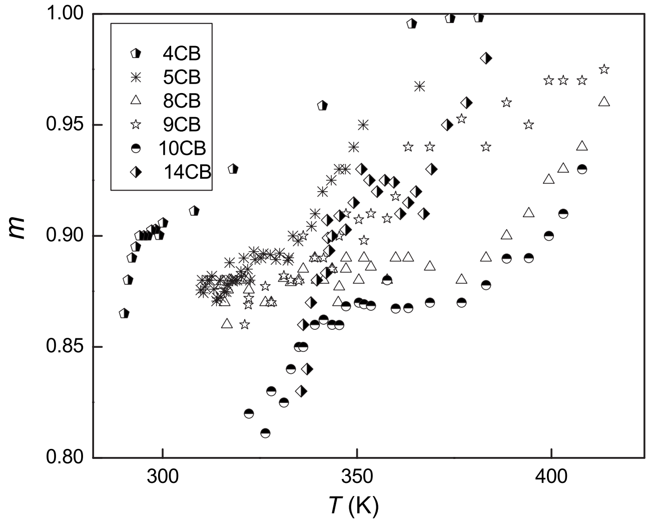

FIG. 3. The evolution of the coefficient m reflecting the low-frequency distribution of relaxation times. Results are for the isotropic phase, beginning from ca. 0.02 K above the clearing temperature.

$$\log_{10}[\varepsilon''(f)] \propto -n \log_{10} f \quad f > f_{peak}, \qquad (4)$$

where m and n coefficients describe the low- and high-frequency domains of the distribution of relaxation times. For the simplest Debye distribution $m=n=1$.

With the use of the derivative-based analysis, the range of the validity of Eqs. (3) and (4) can be identified as horizontal linear dependences [9,23,49]. This enables a reliable estimation of m and n coefficients.

Figure 2 presents the temperature evolution of the low-frequency (m) and high-frequency (n) distribution coefficients in the isotropic phase of nCB homologous series. It is visible that the high-frequency wing of the loss curve parameter $n \to 1/2$ for $T \to T^C$ on shifting from 4CB to 14CB. For the latter, such "universal" behavior occurs even well above the clearing temperature, namely, for $T_{I\text{-}SmA} < T < T_{I\text{-}SmA} + 25$ K. Hence, in this domain a clear TTS behavior for the high-frequency wing of $\varepsilon''(f)$ is possible. The emerging universal value of the high-frequency part of the distribution of relaxation times in Fig. 2 coincides with the universal, "generic" value for $T \to T_g$ [6]. Figure 3 shows the evolution of the power exponent characterizing the low-frequency domain of relaxation times. It is visible that also this part of $\varepsilon''(f)$ curves becomes more "non-Debye" for $T \to T^C$: $m \to 0.85-0.8$ for longer members of nCB series. It is noteworthy that $m \to 0.8$ as well as $n \to 1/2$ can be noted in epoxy resins (DGEBA is the epoxy resin diglycidyl ether of bisphenol-A) for $T \to T_g$ if dominated linear, "elongated," structures appear [52].

In the opinion of the author, the emerging universal behavior of the distribution of relaxation times may be associated with following artifacts: (i) premesomorphic fluctuations-heterogeneities in the isotropic, *fluidlike* surrounding [22], (ii) the change in the structure of fluctuations on increase of the length of nCB molecule ordering, or (iii) the increase of uniaxiality of nCB molecules from 4CB to 14CB. Regarding the isotropic phase of liquid crystals worth recalling is the mentioned shift of $D_T(T)$ and $T_0(T)$ on approaching the isotropic-nematic temperature in 5CB [22,24].

On the basis of these results and the condition $\tau(T_g) = 100$ s, a set of virtual glass temperatures, $T_g^{virtual} \to 300$ K for $T \to T_{\text{I-N}}$ can be estimated [24]. It seems that such a behavior may be associated with the increase of the length and time scales of premesomorphic fluctuations on cooling in the isotropic phase. However, the distance from the temperature of the hypothetical continuous phase transition (T^*) is much larger for 14CB than for other tested nCB (see Fig. 1). This may indicate a possible significance of the increasing uniaxiality when shifting from 4CB to 14CB. The importance of this factor on glassy dynamics was shown recently in Ref. [53].

Concluding, this report shows that the distribution of the relaxation times for the isotropic phase of the homologous series of liquid crystalline n-cyanobiphenyls for $T \to T^C (\tau \ll 10^{-7}$ s) may coincide with the hypothetical universal time scale $\omega^{-1/2}$ or $\sqrt{t}$ for $T \to T_g (\tau \approx 100$ s). Therefore, studies in longer members of nCBs ($n=15,16,\ldots$) can be recommended. Unfortunately such compounds are extremely difficult to obtain and untested so far. When discussing glassy dynamics in the isotropic phase, studies-based results based on OHD OHE should be recalled [16–20]. For longer time scales detected in such studies, the exponential decay with the evolution relaxation time well described by the Landau–de Gennes (LdG) theory of the randomization of pseudonematic domains was detected [16–21]. This result agrees well with a set of earlier studies based on Kerr effect, light scattering, Cotton-Mouton effect, or nonlinear dielectric effect studies [9,21–24]. At very short times, a power-law decay in time, in 5CB associated with the exponent $p \approx 0.65$, was found [16]. It was also suggested that this exponent should increase with the rise of the aspect ratio (length/width) of the molecule, which for 5CB is equal to 3.98. In this respect noteworthy is the coincidence between the value of $p \approx 0.65$ and $n(T \rightarrow T^{\text{I-N}}) \rightarrow 0.65$ as well the smaller values of $n(T \rightarrow T^{C})$ for longer nCB, i.e., with larger values of the aspect ratio. It seems that studies employing both OHD OKE [16,20] and BDS techniques [8,9,22–24], eventually supported by nonlinear dielectric spectroscopy (NDE) [9,22], may be fundamental for further insight into dynamics of the isotropic phase of liquid crystals.

Over the last decade, the dynamics of the isotropic phase of rodlike liquid crystalline compounds have been widely explored as an experimental model system for resolving some puzzling issues of dynamics in vitrifying liquids [9,16–20,22–26,53]. However, these studies have focused solely on nematogenic n-cyanobiphenyls and similar compounds. This paper points to possibilities in these studies which can appear on testing homologous series of LC compounds.

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