Glassy dynamics in the isotropic phase of a smectogenic liquid crystalline compound

Sylwester J. Rzoska,[1,2,*] Sebastian Pawlus,[2] and Krzysztof Czupryński[3]

[1]*Institute of High Pressure Physics, Polish Academy of Sciences, ulica Sokołowska 27/39, PL-00-143 Warsaw, Poland*
[2]*Institute of Physics, University of Silesia, ul. Uniwersytecka 4, PL-40-007 Katowice, Poland*
[3]*Military University of Technology, ul. S. Kaliskiego 2, PL-00-908 Warszawa, Poland*

The temperature evolution of the primary relaxation time in the isotropic phase of 4-cyano-4′-tetradecylbiphenyl (14CB) above the isotropic-smectic A (I-SmA) transition is discussed. Based on the enthalpy space and distortion-sensitive analysis, the prevalence of the mode coupling theory (MCT) "critical" and "glassy" dynamics is shown. The obtained singular dependence is related to the MCT critical temperature located approximately 48 K below the clearing (I-SmA) temperature. However, a weak but detectable distortion in the immediate vicinity of the transition occurs. It is also shown that the value of the fragile strength coefficient D_T is characteristic of a very fragile glassy liquid whereas the steepness index m is typical of a strong one. Both magnitudes anomalously change on approaching the I-SmA phase transition. The static permittivity shows the pretransitional effect linked to the temperature of the hypothetical continuous phase transition located approximately 10.2 K below the I-SmA transition.

I. INTRODUCTION

In the past decade, significant research has been devoted to isotropic-mesophase transitions in rodlike thermotropic liquid crystalline (LC) materials [1–23] and references therein]. This can be associated with the fact that the dynamics of the isotropic phase of LC compounds may constitute a significant reference for the whole category of soft matter–complex liquid systems [24,25]. It is also worth recalling that four decades ago the Cotton-Mouton effect (CME) [26], Kerr effect (KE) [27], and light scattering (I_L) [28] studies in the isotropic phase of nematic liquid crystals established a base for the Landau–de Gennes (LdG) model [29], one of the most important and successful theoretical ideas of the physics of liquid crystals [30–34]. Recently, the ability of the modified, extended LdG approach to describe phase transitions from the isotropic to smectic mesophases was also shown [35–37]. One of key findings of the LdG model is the link of the strong increase of the mentioned properties to the appearance of orientationally ordered premesomorphic fluctuations, which correlate length (ξ) and time (τ_ξ) and are given by [29–34]

$$\xi = \xi_0 (T - T^*)^{-1/2} \text{ and } \tau_\xi = \tau_0^\xi (T - T^*)^{-1}, \quad (1)$$

where $T > T_C = T^* + \Delta T$, T_C is the melting ("clearing") temperature of the weakly discontinuous isotropic-nematic I-N phase transition, and ΔT is the measure of the discontinuity of the transition: In the case of the I-N transition, it is equal to 1–2 K. The temperature T^* denotes the extrapolated temperature of a hypothetical continuous phase transition.

It is noteworthy that theoretical models explaining the relatively small value of ΔT for the I-N transition appeared only recently [2]. The physical properties mentioned above are directly coupled to prenematic multimolecular fluctuations. The simple Arrhenius behavior was most often indicated for describing the temperature evolution of the single-molecule

primary relaxation time (τ_α), viscosity (η), diffusion coefficient (D), and electric conductivity (σ) [1,30,34]. Notwithstanding, a limited reference indicated a clearly non-Arrhenius evolution also existed. The latter results agreed with a growing evidence suggesting the similarity of dynamics in the isotropic phase of nematic liquid crystals and the complex dynamics in supercooled liquids approaching the glass transition. This issue is the key conclusion of the mode-coupling theory analysis in Refs. [3] and [6] and the Gay-Berne fluid modeling in Refs. [11], [15], and [16]. One can argue that if the "glass analogy" is applicable then the data should depend on the sample cooling rate, but such dependence takes place for the value of the glass temperature (T_g) and does not for the dynamics above T_g, in the supercooled liquid state. The isotropic phase is located not only well above T_g ($\tau_a = 100$ s) but also above the dynamic crossover temperature [$T > T_B$ ($\tau_a = 10^{-7 \pm 1}$ s)]. It is also noteworthy that the isotropic phase cannot be supercooled below the extrapolated temperature T^*, located very close to the isotropic-mesophase "melting" temperature, and then the real glass temperature (T_g) for the isotropic liquid phase cannot be reached [19].

As the key hallmark of the glassy dynamics, the parameterization of the non-Arrhenius behavior via the Vogel-Fulcher-Tammann (VFT) dependence is most often considered, namely [25], [38]:

$$\tau_\alpha = \tau_0 \exp \frac{D_T T_0}{T - T_0}, \quad (2)$$

where D_T is the fragility strength coefficient and T_0 denotes the VFT estimation of the ideal glass temperature. The VFT dependence is also expected to portray the evolution of $\eta(T)$, $D(T)$, or $\sigma(T)$.

The VFT equation can be derived from several basic theories for glass-forming liquids, such as Adam-Gibbs theory [38,39] or Turnbull free volume model [38], [40]. The latter is also the basis of Diogo-Martins (DM) dependence [41,42], which is very successful in parameterization of $\eta(T)$ and $D(T)$ data within the physics of liquid crystals. However, it mimes

*sylwester.rzoska@gmail.com

the VFT equation and introduces adjustable parameters such as T_0 temperature [41] and a "glass temperature" [42]. In the opinion of the authors, the DM concept can be also included in the discussed glassylike analogy for dynamics of the isotropic phase of liquid crystalline materials.

In recent years, a distortion-sensitive, derivative-based analysis of experimental data describing dynamics in complex liquid has been developed [23,43]. It made possible an ultimate verification of the validity of dynamic equations for $\tau_\alpha(T)$ and $\eta(T)$ evolution. This analysis, applied to the isotropic phase of n-pentylcyanobihenyl (5CB, I-N transitions, $\Delta T \approx 1.2$ K), showed the limited validity of the VFT parameterization [19]. The same type of treatment revealed the clear prevalence of the MCT-type "critical" relation [19], known to be valid in the high temperature domain of supercooled glass-forming liquids, namely [38]

$$\tau_\alpha(T) = \tau_0(T - T_X)^{-\phi}, \tag{3}$$

where T_X is the MCT critical temperature located approximately 30 K below the isotropic-nematic clearing temperature and the exponent $\phi = 2/4$. For supercooled liquids, T_X is linked to the ergodic-nonergodic crossover.

In classical supercooled liquids, this relation holds for $T > T_X + 20$ K [38].

The natural question at the present stage of research regards the dynamics of the transition from the isotropic liquid to more complex liquid crystalline mesophases. Results for the isotropic–chiral nematic (N*) transition [22,23] indicate no significant differences in the behavior observed for the I-N transition. For the isotropic-smectic transitions, the orientational ordering is supplemented by one-dimensional density modulation [29–34]. However, despite strongly revived interest in this transition, the existing experimental evidence is very puzzling and limited. Temperature studies of KE, CME, and I_L gave the behavior poorly related to the LdG model [9,44–47]. A decade ago, a novel method called the low-frequency nonlinear dielectric effect (LFNDE) was introduced [48–51]. In this technique, changes of the strong electric field induce a shift of dielectric permittivity that is detected for frequency at which the condition $f^{-1} \gg \tau_\xi$ is fulfilled, where f is the rf of the weak measuring field. It was shown that for I-N, I-N*, I-SmA, and I-SmE the same simple relation is valid, without any distortion [48–51]:

$$\varepsilon_{\text{NDE}} = \frac{C}{T - T^*} \tag{4}$$

where $T > T_C + \Delta T$, $\varepsilon_{\text{NDE}} = (\varepsilon^E - \varepsilon)/E^2$ is the measure of NDE, and ε^E and ε are dielectric permittivities in a weak and strong electric field E.

Based on this method, it was proved experimentally that for I-SmA and I-SmE transitions, the value of the discontinuity is essentially larger than for the I-N transition [48–51]. The obtained value of ΔT for smectogens range from 4 K to even 30 K. The value of discontinuity increases with the length of smectogenic LC molecules [51].

Very recent theoretical advances, based on the energy landscape analysis of a Gay-Berne model fluid, suggested the complex glassy pattern described by the VFT equation [11] for the primary relaxation time behavior $\tau_\alpha(T)$. In the opposition to this result, experimental evidence of $\tau_\alpha(T)$ and

$\eta(T)$ shows only simple Arrhenius behavior for the isotropic phase of smectogens [1,7,10,13]. However, in the opinion of the authors, these results are too limited in precision and temperature range for reliable conclusions.

This contribution presents the broadband dielectric spectroscopy (BDS) [38] studies of $\tau_\alpha(T)$ supported by distortion-sensitive analysis based on enthalpy space [23,43]. The target of the research was to establish clear experimental reference for theoretical models related to the I-SmA transition.

II. EXPERIMENTAL

Studies were carried out in the isotropic phase of 14CB, a particularly long and hardly tested member of the classical homologous series of rodlike liquid crystalline n-alkylcyanobiphenyls (nCBs) [29–34]. The high purity sample of 14CB was synthesized at the Technical Military University (WAT) in Warsaw, Poland, and showed I-SmA transition at $T_C = 336.4$ K. The sample was degassed immediately prior to measurements, which were carried out using a Novocontrol BDS 80 spectrometer with temperature control unit. The relaxation time was determined from the peak frequency of loss curves via $\tau_\alpha = 1/2\pi f_{\text{peak}}$ condition [38]. Analysis of data employed ORIGIN 7.0 software, which shows significant user-friendly advantages in fitting in comparison with its successors. Preliminary dielectric studies indicated a clear Arrhenius-type behavior of the relaxation time in the isotropic phase of 14CB [7]. LFNDE studies in the isotropic phase yielded $\Delta T = 10.2$ K [50].

III. RESULTS AND DISCUSSION

The obtained evolution of dielectric relaxation times in the isotropic phase of 14CB is presented in Fig. 1. The most characteristic feature is the presence of two relaxation processes. The low frequency one is associated with the relaxation around the short axis of the rodlike molecules. This
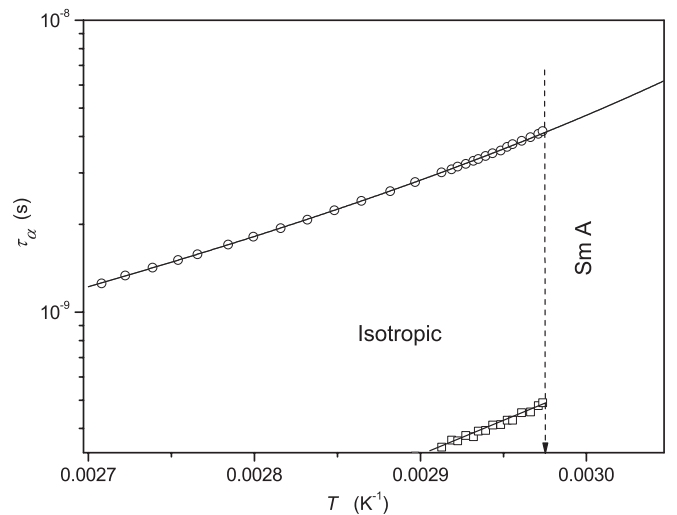

FIG. 1. Temperature evolution of the primary relaxation time (circles) and the tumbling mode relaxation (squares) in the Arrhenius scale. The upper solid curve represents the MCT "critical-like" equation [Eq. (3)] with parameters taken from the derivative-based analysis. Results are given in Fig. 3.

is the primary (τ_α) relaxation process. The high frequency process can be linked to the tumbling mode around the direction determined by the long axis of molecules.

In the isotropic phase of 5CB with the I-N transition, a single relaxation process is sufficient to describe the relaxation behavior, even in the immediate vicinity of the clearing temperature [19].

For the precise analysis of the temperature form of the evolution of the primary relaxation, the derivative, enthalpy space–based analysis introduced in Ref. [43] was used, namely,

$$\left[\frac{d \ln \tau_\alpha}{d(1/T)}\right] = \left[\frac{H_a(T)}{R}\right]^{-1/2} = (H_a')^{-1/2}$$
$$= [(D_T T_o)^{-1/2}] - \frac{[T_0(D_T T_0)^{-1/2}]}{T}$$
$$= A - \frac{B}{T}, \tag{5}$$

where $H_a(T)$ denotes the apparent activation enthalpy and R is the gas constant. The linear regression analysis yields $T_0 = B/A$ and $D_T = 1/AB$.

The above analysis resembles the transformation proposed by Hansen *et al.* [52] for supercooled glass-forming liquids, although they did not introduced explicitly the activation enthalpy and focused solely on detecting the so-called dynamical crossover temperature. Following Eq. (5), the domain of validity of the VFT equation at the plot $(H_a')^{-1/2}$ versus $1/T$ is visualized by a linear dependence for which the linear regression yields optimal values of T_0 and D_T coefficients. A similar reasoning can be used for the MCT critical-like Eq. (3), namely [43],

$$T^2/H_a'(T) = T_X/\phi - \phi^{-1}T = A - BT. \tag{6}$$

Experimental data presented in the plot $T^2/H_a'(T)$ versus T should exhibit linear behavior in the domain of validity of the critical-like MCT-based Eq. (3). The subsequent linear regression yields optimal values of parameters: $T_X = A/B$ and $\phi = 1/B$.

Results of the apparent enthalpy space analysis shown in Fig. 2 reveals that in the isotropic phase of 14CB there is no long-distance domains of the validity of the VFT description. Characteristic is the unusually small value of the coefficient D_T, which indicates extreme fragility related to definitively non-Arrhenius behavior [38,43]. Recalling the analogy with supercooled liquids [11], one can define also the steepness fragility index [15,16,38], which is the alternative measure of fragility, namely,

$$m = \frac{d \log_{10} \tau_\alpha(T)}{d(T^*/T)}. \tag{7}$$

The inset in Fig. 2 shows that $m(T)$ exhibits an unusually small, "strong glass former" type, value ($m \approx 5.4$), remote from T_X, which increases up to approximately $m = 16$ at the I-SmA transition. Generally values of $m < 30$ are considered typical for dynamics which is almost Arrhenius type (strong type). The fragile-type value of D_T [38] and strong-type value of m [8] occur in the isotropic phase of 14CB with the I-SmA transition. This can explain why tests carried out in the limited range of temperatures could be relatively well described by the Arrhenius approximation, particularly if the immediate
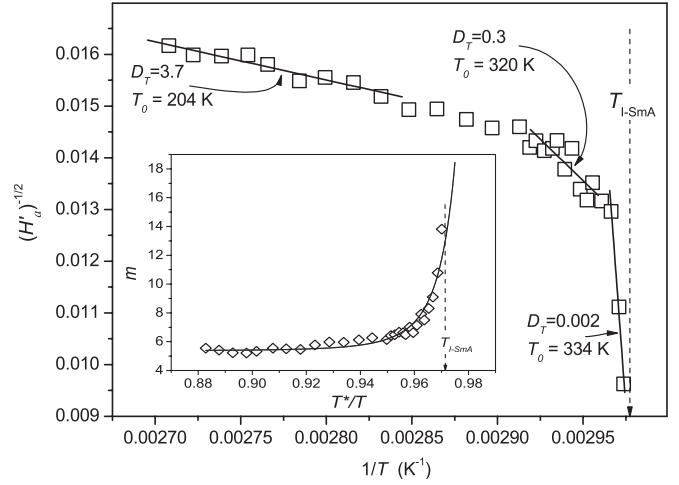

FIG. 2. Results of the derivative-based analysis via Eq. (5) focused on VFT [Eq. (2)]. Domains of the validity of the latter are indicated by straight lines. The inset shows the evolution of the steepness index defined by Eq. (7). The solid curve follows the empirical relation $m = 5.4 + 5.1 \times 10^{-6}(1 - T^*/T)^{-4}$.

vicinity of the I-SmA transition was not focused enough. The mentioned mismatching of fragility-related coefficients (m and D_T) is hardly, if at all, observed for the complex dynamics of classical supercooled glass-forming liquids [38].

Figure 3 shows that the MCT critical-type parameterization [Eq. (3)] offers a much better description of experimental data than the VFT equation, except in the immediate vicinity of the I-SmA transition. The solid curve for the low frequency primary process in Fig. 1 is based on coefficients obtained using Fig. 3. The relatively strong distortion in Fig. 3 in the immediate vicinity of the I-SmA transition is visibly weakly manifesting in the direct plot of $\tau_\alpha(T)$ in Fig. 1. This fact indicates that the direct fitting of $\tau_\alpha(T)$ or $\eta(T)$ data, without support of the derivative-based analysis, can easily erroneously estimate the range of validity of the given equation and give erroneous, "effective" values of parameters. The discussed distortion is negligible for the I-N transition
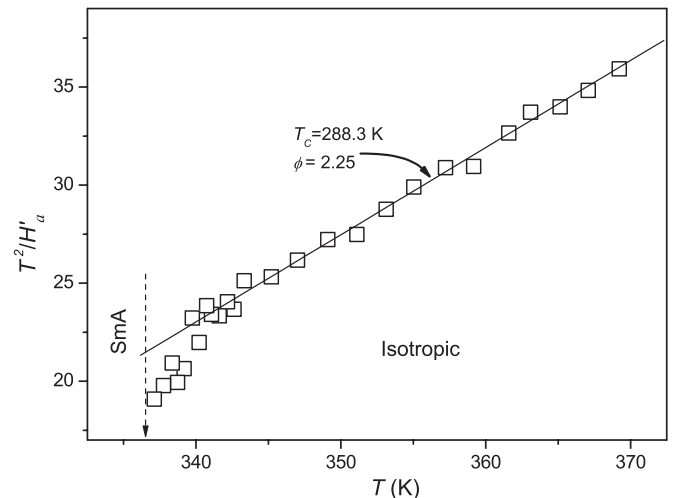

FIG. 3. Results of the derivative-based analysis via Eq. (6) focused on the validity of the MCT "critical-like" equation [Eq. (3)].
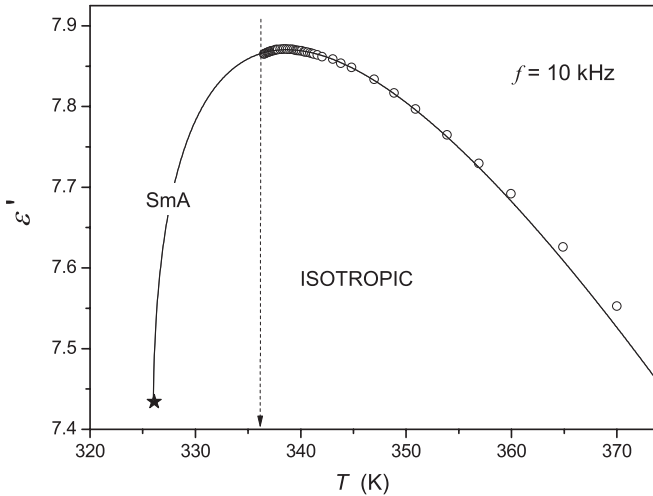
FIG. 4. Temperature evolution of the static dielectric permittivity in the isotropic phase of 14CB. The solid curve is related to Eq. (8) with $\varepsilon^* = 7.411$, $T^* = 326.0$ K, $A = -0.0363$ K^{-1}, and $B = 0.259$ K$^{1/2}$. The star indicates the locus of extrapolated hypothetical continuous phase transition.

in 5CB [12,19]. This distortion cannot be clearly associated with the proximity of the continuous phase transition, since in 14CB $\Delta T = 10.2$ K, whereas $\Delta T = 1.2$ K in 5CB [50].

Figure 4 shows the temperature evolution of the static dielectric permittivity ($f = 10$ kHz) in the isotropic phase of 14CB. It can be well portrayed by equation resembling one used for the homogeneous phase of critical mixtures of limited vicinity, namely [53,54],

$$\varepsilon'(T) = \varepsilon^* + A(T - T^*) + B(T - T^*)^{1/2}, \quad T > T_C, \quad (8)$$

where ε^* and T^* are coordinates of the extrapolated continuous phase transition.

The validity of the same equation was shown earlier for the isotropic phase of 5CB with the I-N transition in [54].

Following Mistura [55], one can link the above dependence to the critical behavior of the specific heat $d\varepsilon/dT \propto c_P \propto (T - T^*)^{-\alpha}$, where $\alpha = 1/2$ is the specific heat critical exponent within the mean field approximation. On the other hand, from the molecular point of view, the bending of $\varepsilon'(T)$ upon approaching the isotropic-mesophase transition may be associated with the decrease of the static dielectric permittivity due to the cancellation of ordered permanent dipole moments in an antiparallel way within pretransitional fluctuations.

This is possible due to the following facts: (i) The permanent dipole for nCB molecules is parallel to the long axis of the molecule, (ii) the equivalence $\vec{n}$ and $-\vec{n}$ for director vectors is a key feature of nematic ordering, and (iii) in presmectic fluctuations elements of the limited translational arrangement exist in addition to the "nematic" orientational ordering [34].

In 5CB this leads to the decrease of the Kirkwood factor down to approximately 1/2 at the I-N transition [56,57]. The clear relationship of the appearance of $\varepsilon'(T)$ anomaly with the angle between the long axis of the molecule and the permanent dipole moment is worth noting. In the isotropic phase, the

LC compound consisting of molecules with permanent dipole moment perpendicular to the long axis of the molecule $\varepsilon'(T)$ follows a linear dependence; that is, there is no pretransitional anomaly [58–60]. However, also for LC compounds with the transverse loci of the dipole moment, the evolution of $\tau_\alpha(T)$ is non-Arrhenius [60], similar to the one discussed in this paper. All these suggest that the relationship between the appearance of $\varepsilon'(T)$ anomaly and the non-Arrhenius evolution of $\tau_\alpha(T)$ is doubtful. The key artifact may be the domination of properties in the isotropic phase by premesomorphic fluctuations.

For the high frequency tumbling relaxation mode, the Arrhenius approximation delivers a reasonable description (Fig. 1). This can be associated with the limited range of temperatures and the experimental error.

In conclusion, the isotropic phase of the tested smectogenic liquid crystal exhibits both a critical behavior associated with the extrapolated phase transition at $T^* = T_C - 10.2$ K and the MCT critical characteristic for glass-forming liquid behavior for dynamics, linked to the extrapolated singularity at $T_X = T_C - 48$ K. Both features are hidden in the same BDS spectrum. It is noteworthy that the ultimate theory for the isotropic phase and isotropic-mesophase transitions is still lacking. Such a theory should describe experimental artifacts related both for pretransitional (precritical) anomalies and the complex dynamics.

Regarding dynamics, the same vales of D_T and m were obtained for 5CB ($\Delta T \approx 1.2$ K, I-N transition) and 14CB ($\Delta T \approx 10.2$ K, I-SmA transition) near the isotropic-mesophase transition. For the discussed glassy-type description of the complex dynamics in the isotropic phase of 14 CB, worth recalling is the analysis of the distribution of relaxation times related to the high frequency wing of the dielectric loss curve. It shows a behavior analogous to the universal pattern found by Dyre *et al.* [61,62] on approaching the real glass transition in supercooled glass-forming liquids. A similar coincidence was found earlier for surrounding the I-SmE transition in n-isothiocyanatobiphenyl (nBT) [63].

The obtained behaviors of static and dynamic dielectric properties in 5CB (I-N case) and 14CB (I-SmA case) are very similar, although for the latter a notable distortion from the critical-like dependence in the immediate vicinity of the I-SmA transition takes place. This occurs despite the large value of the discontinuity ΔT in 14CB; then it cannot be associated with the proximity of the continuous phase transition at T^*. The question arises if the glassy dynamics in the isotropic phase of the LC compound can be used as the argument for the heterogeneity and hidden phase transition–related hypothesis of a classical supercooled liquid, which does not exhibit any mesomorphic behavior, as suggested in Ref. [11]. Equally probable seems to be that the isotropic phase shows simply a complex dynamics reference for soft matter systems. We stress also the significance of the result obtained for the physics of liquid crystals.

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