Origin of glassy dynamics in a liquid crystal studied by broadband dielectric and specific heat spectroscopy

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A combination of broadband dielectric (10^{-2} Hz $- 10^9$ Hz) and specific heat (10^{-3} Hz $- 2 \times 10^3$ Hz) spectroscopy is employed to study the molecular dynamics of the glass-forming nematic liquid crystal $E7$ in a wide temperature range. In the region of the nematic phase the dielectric spectra show two relaxation processes which are expected theoretically: The δ relaxation which corresponds to rotational fluctuations of the molecules around its short axis and the tumbling mode at higher frequencies than the former one. For both processes the temperature dependence of the relaxation rates follows the Vogel-Fulcher-Tammann formula which is characteristic for glassy dynamics. By applying a detailed data analysis, it is shown that close to the glass transition the tumbling mode has a much steeper temperature dependence than the δ process. The former has a Vogel temperature which is by 30 K higher than that of the δ relaxation. Specific heat spectroscopy gives one relaxation process in its temperature and frequency dependence which has to be assigned to the α relaxation (dynamic glass transition). The unique and detailed comparison of the temperature dependence of the dielectric and the thermal relaxation rates delivers unambiguously that the dielectric tumbling mode has to be related to the dynamic glass transition.

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I. INTRODUCTION

The glass transition is an actual problem of soft matter physics (see, for instance [1–3]). It is not known up today whether a glass-forming system freezes into the glassy state instead of solidifying as a crystal. If a glass-forming liquid cools down, a dramatic increase of both the viscosity and the structural relaxation time, τ is observed. When decreasing the temperature by a factor of 2, τ may increases by more than 14 orders of magnitude. This bridge microscopic and macroscopic time scales. As a well accepted explanation, this occurs because in the neighborhood of a given molecule, others have to rearrange cooperatively to reach the minimum of a complex energy landscape. The underlying relaxation process is called α relaxation (structural relaxation) or dynamic glass transition.

The glass transition phenomenon is not only observed for low molecular weight liquids, silica glasses, polymers, but also for plastic crystals and other systems with partial order and restricted mobility (see, for instance [4,5] and references therein). For plastic crystals this was reported by Seki and Suga [6]. Especially in systems with partial order and restricted mobility it is controversially discussed which molecular fluctuations give rise to glassy dynamics. An example for that is the molecular dynamics in associated alcohols [7]. Studies on such systems like liquid crystals might be useful to shine light on the glass transition phenomena in general.

Thermotropic liquid crystals (LC) are materials which have structures between the crystalline and the isotropic state [8,9]. They are formed for instance by molecules which have a stiff, rodlike mesogenic unit in their structure [10]. In crystals, the molecules have maximal (positional and translational) order and minimal mobility, while in liquids the reverse is the case. In LC's aspects of both states are combined and mesomorphic phases are formed in which order and mobility compete. The most important liquid crystalline structures are the nematic and the smectic mesophases. The nematic phase is the liquid crystalline state with the lowest order. The molecules have all translational degrees of freedom and therefore no long range positional order. Their long axes are preferentially aligned with respect to a common unit vector, the nematic director. The degree of orientation of the molecules is described by an order parameter S [9].

Broadband dielectric spectroscopy is a suitable tool to study the molecular dynamics in liquid crystalline materials (for reviews, see for instance [11–13]). Liquid crystals are anisotropic systems. Therefore the dielectric properties are also anisotropic and the complex dielectric function $\varepsilon^*(\omega)$ (ω-represents angular frequency) has to be described by a tensor. For uniaxial nematic phases this tensor has two main components, $\varepsilon_\parallel^*(\omega)$ and $\varepsilon_\perp^*(\omega)$, respectively parallel and perpendicular to the nematic director. The theory of dielectric relaxation of LC's is shortly outlined in [11]. A more refined discussion can be found in [14,15]. Starting point is that a mesogenic unit has two components of the molecular dipole vector which are oriented longitudinal (L) and transverse (T) to its long axis. The dielectric response is due to correlation functions of the polarization fluctuations parallel and perpendicular to the nematic director. In that semimicroscopic treatment the measured dielectric function parallel $\varepsilon_\parallel^*(\omega)$ and perpendicular $\varepsilon_\perp^*(\omega)$ to the director comprises different weighted sums of four underlying relaxation modes depending on the macroscopic orientation of the sample. The relaxation mode with the lowest frequencies is due to rotational fluctuations of the molecule around its short axis. This pro-

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cess determines mainly $\varepsilon_{\parallel}^{*}$ and is called δ relaxation. The other three relaxation modes (different tumbling fluctuations of the molecules around their long axis) have nearly the same relaxation rate and form one broad relaxation process, which is mostly related to $\varepsilon_{\perp}^{*}(\omega)$. This process is observed at higher frequencies than the δ process. The intensity or the dielectric strength of the δ relaxation relative to that of the tumbling mode, depends on the order parameter S of the sample [11]. In detail

$$\varepsilon_{\parallel}^{*}(\omega) = \varepsilon_{\infty,\parallel} + \frac{G}{3k_BT}[(1+2S)\mu_L^2 C_{\parallel}^L(\omega) + (1-S)\mu_T^2 C_{\parallel}^T(\omega)],$$

(1a)

$$\varepsilon_{\perp}^{*}(\omega) = \varepsilon_{\infty,\perp} + \frac{G}{3k_BT}\left[(1-S)\mu_L^2 C_{\perp}^L(\omega) + \left(1+\frac{S}{2}\right)\mu_T^2 C_{\perp}^T(\omega)\right]$$

(1b)

is obtained. $\varepsilon_{\infty,\parallel}$ and $\varepsilon_{\infty,\perp}$ are the limiting high frequency permittivities parallel and perpendicular to the local director and G is a constant. $C_j^i(\omega)$ ($i=L, T; j=\parallel, \perp$) denote the one-sided Fourier transformations of the correlation functions of the longitudinal and transverse component of the dipole moment vector of the mesogenic unit projected parallel $\vec{\mu}_L$ and perpendicular $\vec{\mu}_T$ to the nematic director [11].

According to this theoretical approach the temperature dependence of the relaxation rate f_p [$f_p = 1/(2\pi\tau)$] should obey the Arrhenius law: $f_p = f_\infty \exp(-E_A/k_BT)$ (E_A, activation energy; f_∞, preexponential factor; k_B, Boltzman's constant; T, temperature) for both the δ relaxation and the tumbling mode as well. Due to the nematic potential [9,16] the activation energy for δ should be higher than that for tumbling process. This behavior is experimentally found in a limited temperature regime ([11,17–19] and references cited herein). However, careful measurements performed over a large temperature interval, especially in the isotropic state, and a more detailed analysis have shown that the temperature dependence can be better described by the Vogel-Fulcher-Tammann (VFT) law which reads [20–22]

$$\log_{10}f_p = \log_{10}f_\infty - \frac{A}{T-T_0} = \log_{10}f_\infty - \frac{\ln(10)DT_0}{T-T_0}.$$

(2)

f_∞ and A are constants and T_0 is the so-called Vogel temperature. Generally a temperature dependence of the relaxation rates or times according to the VFT equation is regarded as a sign of glassy dynamics. The degree of deviation from an Arrhenius-type temperature dependence provides a useful classification of glass formers [4,5]. Materials are called "fragile" if their $f_p(T)$ dependence deviates strongly from an Arrhenius-type behavior and "strong" if $f_p(T)$ is close to the latter. Despite of other possibilities the parameter $D = A/T_0 \ln(10)$ in Eq. (2) can be used as quantitative measure of "fragility" [4,5]. Recently optical Kerr effect measurements have been employed to study the molecular dynamics of liquid crystals including cyanobiphenyls from pico seconds to more than 100 ns [23–27]. The temperature dependence of the relaxation times is also found to be VFT-like. This was explained by the critical growing of preordered

nematic structures in the frame of the Laudau–de Gennes theory [23,24]. More recently the mode coupling theory to glass transition was also applied to interpret these results [26,27]. To be complete, molecular dynamic simulations on calamitic model systems give also evidence for glassy dynamics in an energy landscape [28,29].

Deviations from the theoretically predicted Arrhenius-like dependence of the temperature dependence of the relaxation rates of the δ and the tumbling mode, in the range of liquid crystalline mesophases, have been already reported for cyanobiphenyl systems and other nematics [30–39]. Diogo and Martins applied the free volume concept to describe the VFT-like temperature dependence of the relaxation rate of the δ-process [32]. Because the glass transition is not completely understood in general also the molecular origin of the glassy dynamics in liquid crystals is hardly explored up to now. Especially it is not known whether the δ or the tumbling mode corresponds to the α or structural relaxation in conventional glass-forming liquids which has also a signature in the thermal response.

In this contribution a combination of broadband dielectric and specific heat spectroscopy is applied to investigate the molecular dynamics of the nematic liquid crystal $E7$. While dielectric spectroscopy is sensitive to dipole reorientations, thermal spectroscopy sense entropy or enthalpy fluctuations. Therefore both methods provide different insights in the molecular dynamics of the nematic liquid crystal. The molecular assignment of the different relaxation modes in liquid crystals is provided by the theory of dielectric relaxation. So the comparison of the results obtained by both methods delivers which molecular fluctuations corresponds to glassy dynamics. A similar combination of methods has been applied to a polymeric side chain liquid crystal [40]. Recently dielectric and specific heat spectroscopy was also to study the molecular dynamics in an alcohol [41].

II. EXPERIMENT

The nematic liquid crystal $E7$ was purchased from Merk (Darmstadt, Germany) and used without further purification. It is a mixture of four components [4-cyano-4′-pentyl-1, 1′-biphenyl (51 wt. %), 4-n-heptyl-4′-cyanobiphenyl (25 wt. %), 4,4′-n-octyloxycyanobiphenyl (16 wt. %) and 4′-n-pentyl-4-cyanoterphenyl (8 wt. %);see [34,42]] and has the well known phase transition from the nematic to the isotropic state at $T_{I/N}=333$ K. It undergoes a glass transition with a glass transition temperature $T_g=211$ K measured by DSC [35,39]. Because the mixtures consist mainly of cyanobiphenyls the mean dipole moment is oriented along to the long axis of the molecules. Therefore $E7$ is a liquid crystal with a positive dielectric anisotropy [11]. Dielectric studies for $E7$ in a limited frequency range were already reported by [33–39]. Not al dielectric active processes are considered in [38].

The equipment to measure the complex dielectric function $\varepsilon^{*}(f) = \varepsilon'(f) - i\varepsilon''(f)$ (f, frequency; ε; real part; ε'', loss part) from 10^{-2} Hz to 10^9 Hz is described in detail elsewhere [43]. From 10^{-2} Hz to 10^7 Hz a high resolution ALPHA analyzer (Novocontrol®, Hundsangen, Germany) with an active
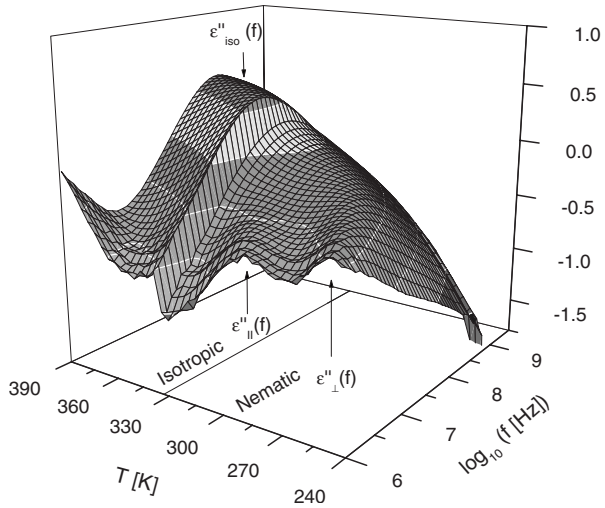
FIG. 1. Dielectric loss vs frequency and temperature for an unaligned sample of $E7$ in the high frequency range.

FIG. 2. Dielectric loss vs frequency for $E7$ at different temperatures and mesophases. *Nematic state*: □, $T=214.2$ K; ○, $T=220.1$ K; ◇, $T=252.2$ K; △, $T=274.2$ K. *Isotropic state*: ☆, $T=363.7$ K. Lines are guides to the eyes. Because the dielectric properties in the low and in the high frequency range are measured using different samples their order parameter can be also slightly different. The inset gives an example for the decomposition of the relaxation spectra at $T=320.1$ K in to the δ and the tumbling mode by fitting three HN functions and one conductivity contribution to the data: Solid line, whole fit function; dashed line, contribution δ relaxation; dashed-dotted line, contribution tumbling relaxation; dotted line, contribution third relaxation process.

sample head was used. From 10^6 Hz to 10^9 Hz a coaxial line reflectometer was employed based on the impedance analyser HP 4191A. Samples were prepared in parallel plate geometry between two gold-plated electrodes of 20 mm and 6 mm diameters, respectively. For both setups isothermal frequency scans were carried out on a series of temperatures with a stability better than 0.05 K.Two samples with different orientations were measured, one with a preferential orientation of the nematic director parallel to the electrical field and a second one with a preferential orientation of the nematic director perpendicular to it.

Specific heat spectroscopy was carried out by a combination of temperature modulated DSC (TMDSC) and ac calorimetry. These measurements result in a complex heat capacity $c^*(f)=c'(f)-ic''(f)$ (c', real part; c'', loss part) [44]. $\tan\delta=c''(f)/c'(f)$ is the part of the phase angle which is due to time dependent processes in the sample. It must be corrected for heat transfer processes [45]. At low frequencies TMDSC measurements were carried out by a Perkin Elmer Pyris1 DSC. The frequency f of the temperature oscillation is varied from 10^{-3} Hz to 0.1 Hz. All data were taken from the heating runs where the corresponding rates were chosen between 1 K min^{-1} and 3 K h^{-1} to meet stationary conditions. Details can be found elsewhere [46]. The ac calorimetric measurements were done using the chip sensor X-3974 from Xensor Integrations, NL. Frequency sweeps from 20 Hz to 2000 Hz are performed and the temperature is changed stepwise from 193 to293 K in steps of 2 K. The maximum in the phase angle is used to determine the dynamic glass transition temperature at the given frequency. A detailed description of the method and the data evaluation is given in [47].

III. RESULTS

Figure 1 gives the dielectric loss of an unaligned sample of $E7$ versus frequency and temperature in a 3D representation in the high frequency range. In the nematic state two
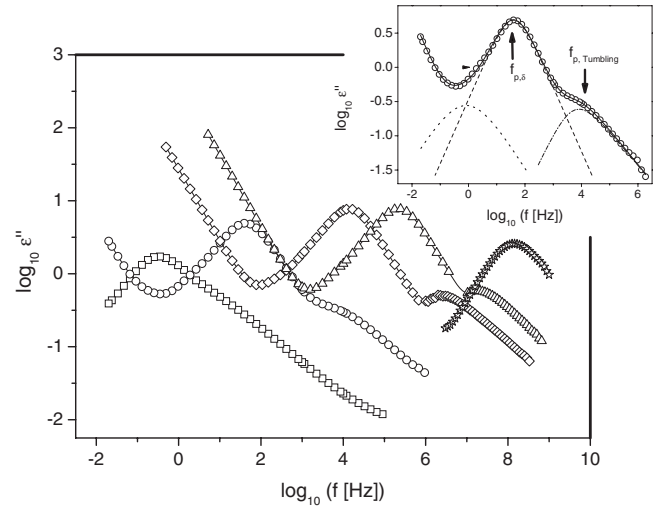
relaxation processes indicated by peaks in ε'' can be observed which are assigned to the tensorial components of the complex dielectric function parallel and perpendicular to the director. The process at lower frequencies corresponds to the δ relaxation where the peak at higher ones is the tumbling mode. Above the clearing temperature the two processes collapse into one broadened relaxation. Figure 2 gives the dielectric loss of $E7$ in the available frequency range at the labelled temperatures. A careful analysis of the measurements shows that there is in addition to the processes discussed above, a third relaxation mode at frequencies lower than that of the δ process also reported in references [39,48]. Its molecular assignment is still under discussion in the literature.

With increasing temperature the loss peaks shifts to higher frequencies as expected and the dielectric strength of the δ relaxation increases. According to the relative intensities of the δ and tumbling mode one has to conclude that this sample has a preferential parallel alignment for frequencies lower than 10^6 Hz.

The dielectric measurements are analzsed by fitting the model function of Havriliak-Negami (HN function) [49] to the data which reads

$$\varepsilon^*(f) - \varepsilon_\infty = \frac{\Delta\varepsilon}{[1 + (if/f_0)^{\beta_{HN}}]^{\gamma_{HN}}}. \tag{3}$$

f_0 is a characteristic frequency related to the frequency of maximal loss f_p (relaxation rate) and ε_∞ describes the value
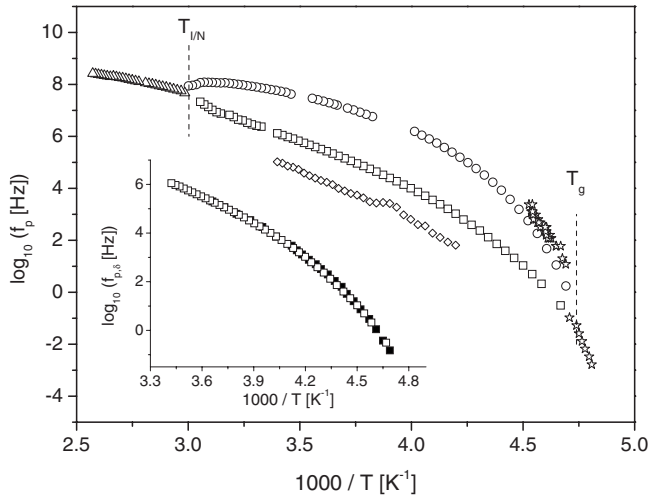
FIG. 3. Relaxation rates f_p versus inverse temperature obtained by dielectric spectroscopy for the different processes ($\square$, δ relaxation; $\bigcirc$, tumbling mode; $\triangle$, isotropic state) and specific heat spectroscopy ($\star$). The inset compares the temperature dependence of the relaxation rates of the δ process reported here ($\square$) with data taken from [39] ($\blacksquare$). Note also that the relaxation rates measured for the both samples with the different orientation collapses into one chart with regard to its absolute values and its temperature dependence for both the δ and the tumbling mode.

of the real part ε' for $f \gg f_0$. β_{HN} and γ_{HN} are fractional parameters ($0 < \beta_{HN} \leq 1$ and $0 < \beta_{HN}\gamma_{HN} \leq 1$) characterizing the shape of the relaxation time spectra. $\Delta\varepsilon$ denotes the dielectric strength. Conduction effects are treated in the usual way by adding the contribution $\sigma_0/\varepsilon_0(2\pi f)^s$ to the dielectric loss where σ_0 is related to the dc conductivity of the sample and ε_0 is the dielectric permittivity of vacuum. The parameter s ($0 < s \leq 1$) describes for $s = 1$ Ohmic and for $s < 1$ non-Ohmic effects in the conductivity. The results of the theory of dielectric relaxation of nematic liquid crystals are summarized by Eq. (1) which comprises a sum of different relaxation modes. This is proves that the different modes are statistically independent. Therefore if more than one relaxation process is observed in the experimental frequency window a sum of HN functions is fitted to the data. For details, see Ref. [50]. The inset of Fig. 2 gives an example of a fit of three HN functions to the dielectric spectrum at 320 K. From this analysis the relaxation rates f_p and the dielectric strength is taken for each relaxation process for further discussions.

In Fig. 3 the relaxation rates f_p for each relaxation process are plotted versus reciprocal temperature. The absolute values and the temperature dependence of the relaxation rates do not dependent on the macroscopic orientation of the sample. This is further confirmed by the data presented in the inset of Fig. 3 which agree in the low frequency range with those published recently in [39]. These data were measured on a different sample having a different order parameter. This proves that dielectric strengths of the δ and tumbling mode depend on the orientation of the sample but not the relaxation rates including its temperature dependence.

The temperature dependencies of relaxation rates for the observed processes are essential different. This will be discussed in detail now. The third process, located at the lowest
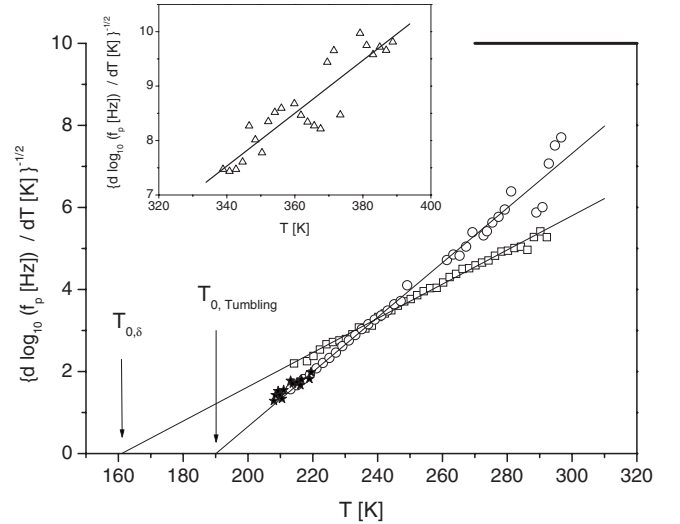

FIG. 4. $(d \log_{10} f_p/dT)^{-1/2}$ vs temperature for dielectric spectroscopy for the different processes ($\square$, δ relaxation; $\bigcirc$, tumbling mode) and specific heat spectroscopy ($\star$). The lines are linear regressions to the dielectric data for the different processes. The inset shows $(d \log_{10} f_p/dT)^{-1/2}$ versus temperature for the dielectric data in the isotropic range for temperatures above the phase transition. The line is a linear regression to the data.

frequencies, seems to follow an Arrhenius behavior. Further discussions by several of us can be found in [39]. The temperature dependence of f_p of both the δ and the tumbling mode is curved in the Arrhenius plot. At high temperatures, close to the phase transition from the nematic to the isotropic state, both modes show a pronounced pretransition behavior (see Fig. 3). At low temperatures, approaching the glass transition these two modes seem to follow a VFT dependence. It looks as if they merge at T_g.

For a more detailed analysis of the temperature dependence of the relaxation rates a derivative method is used [11,51]. This method is sensitive to the functional form of $f_p(T)$ irrespective of the prefactor. For a dependency according to the VFT equation one gets

$$\left[\frac{d \log_{10} f_p}{dT} \right]^{-1/2} = A^{-1/2}(T - T_0). \qquad (4)$$

In a plot $[d \log_{10} f_p/dT]^{-1/2}$ versus T a VFT behavior shows up as a straight line.

Taking the dielectric data this analysis shows (see Fig. 4) that indeed the temperature dependence of the relaxation rates of both the δ relaxation and the tumbling mode follows a VFT dependence. For the first time it is shown that both processes have different Vogel temperatures and so different temperature dependencies. The estimated VFT parameters are summarized in Table I. Close to T_g the temperature dependence of the tumbling mode is much steeper than that of the δ relaxation. Consequently, the fragility measured by the D parameter [see Eq. (2)] is much smaller for the tumbling mode that that for the δ relaxation (see Table I). The difference in the Vogel temperatures is about 30 K. A similar phenomenon is observed for the α relaxation and the chain dynamics of polymers (see for instance [52] and references

TABLE I. Estimated VFT parameters for the different processes. The Vogel temperature and the A parameter were taken from the derivative technique. The prefactors were obtained by a fit of the VFT equation to the relaxation rates keeping T_0 and A fixed. D was calculated according to Eq. (2).

Process	$\log_{10}[f_\infty \text{ (Hz)}]$	T_0 (K)	A (K)	D
δ relaxation	10.4	161.0	576	8.2
Tumbling mode	10.0	190.1	225	2.7
Isotropic	10.5	184.9	424	5.3

quoted) and for the α and δ relaxation in liquid crystalline side group polymers [11,40,53]. To be more general a decoupling of the temperature dependence of the rotational and translatorial diffusion in low molecular weight glass forming liquids has also reported (see, for instance [54]) and can be regarded as characteristic for glassy dynamics.

The most commonly method used to detect the transition from the liquid to a glass are heat capacity measurements. Therefore to study which dielectric active mode corresponds to glassy dynamics specific heat spectroscopy was employed. In difference to dielectric spectroscopy this method is sensitive to enthalpy (entropy) fluctuations and only one relaxation process related to glassy dynamics is expected. Figure 5 gives an example for ac calorimetry data measured at 640 Hz.

The maximum in the phase angle is used to determine the dynamic glass transition temperature at the given frequency. From these measurements the relaxation rate related to enthalpy (entropy) fluctuations can be extracted and compared directly to those measured by dielectric spectroscopy (see Fig. 3). The ac calorimetry data agree with that obtained for the dielectric tumbling mode with regard to both their absolute values and their temperature dependence. This becomes even more convincing applying the derivative technique also to the thermal data (full stars in Fig. 4). The temperature
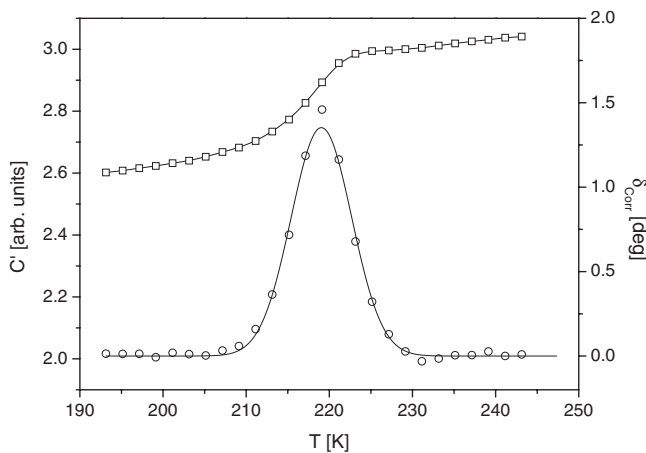

FIG. 5. Real part of the complex heat capacity C' ($\square$) and phase angle δ_{corr} ($\bigcirc$) versus temperature of an ac calorimetry measurement at 640 Hz. The phase angle is corrected for heat transfer processes. The solid line is a guide for the eyes. The dashed line is a fit of a Gaussian to the data of the phase angle to estimate its maximum position.
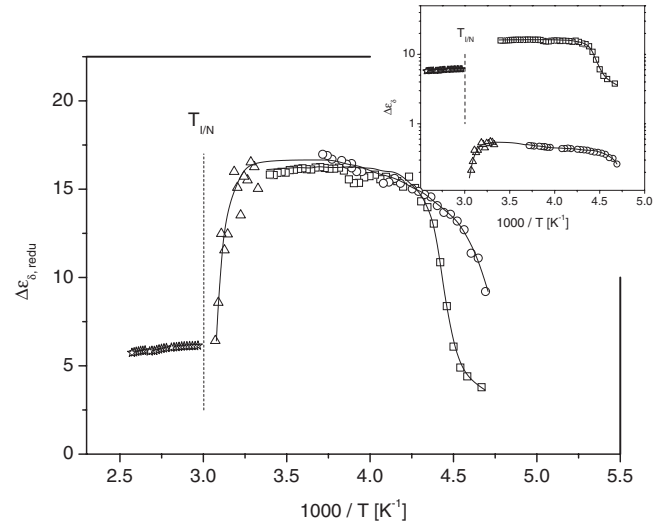

FIG. 6. Dielectric strength $\Delta\varepsilon_\delta$ of the δ relaxation vs reciprocal temperature: $\square$, parallel oriented sample; $\bigcirc$, perpendicular oriented sample at low frequencies scaled by a factor of 35; $\triangle$, perpendicular oriented sample at high frequencies scaled by a factor of 35; $\Rightarrow$, isotropic state. Lines are guides for the eyes. The inset show the unscaled data: $\square$, parallel oriented sample; $\bigcirc$, perpendicular oriented sample at low frequencies; $\triangle$, perpendicular oriented sample at high frequencies. $\star$, isotropic state. Lines are guides for the eyes.

dependence of the relaxation rates measured by both ac and TMDSC follow exactly the linear regression obtained using only the dielectric tumbling mode data. Therefore one has to conclude that the molecular process that determines the glassy dynamics in this nematic liquid crystal is the tumbling mode. In other words, the tumbling mode in $E7$ corresponds to the α or structural relaxation in conventional glassforming systems. This statement is achieved unambiguously only by the direct combination of broadband dielectric and specific heat spectroscopy without any sophisticated data treatment.

To be complete, the temperature dependence of the dielectric strengths of the δ and the tumbling process will be discussed briefly (for a literature overview see [11]). The Debye theory of dielectric relaxation generalized by Kirkwood and Fröhlich [55] predicts for the temperature dependence of the dielectric relaxation strength

$$\Delta\varepsilon = \frac{1}{3\varepsilon_0} g \frac{\mu^2}{k_B T} \frac{N}{V} \qquad (5)$$

were μ is the mean dipole moment of the process under consideration and N/V is the number density of dipoles involved. g is the so-called Kirkwood-Fröhlich correlation factor which describes static correlation between the dipoles. The Onsager factor describing internal field effects is omitted for sake of simplicity.

According to Eq. (1) the relative dielectric strengths of the both process should dependent on the macroscopic orientation of the sample. This is demonstrated in the inset of Fig. 6.

This figure compares the temperature dependence of the dielectric relaxation strength of the δ process, $\Delta\varepsilon_\delta$, for a
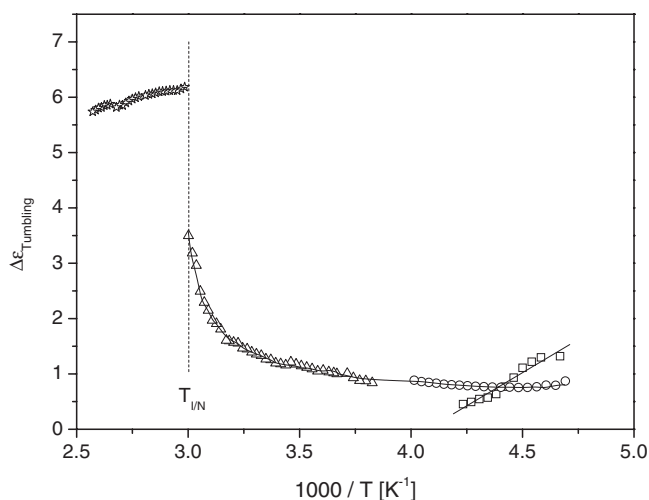
FIG. 7. Dielectric strength $\Delta\varepsilon_{\text{tumbling}}$ of the tumbling relaxation vs reciprocal temperature: □, parallel oriented sample; ○, perpendicular oriented sample at low frequencies, △, perpendicular oriented sample at high frequencies. ☆, isotropic state. Lines are guides for the eyes.

sample with a preferential parallel orientation of the nematic director (circles) with respect to the electrical field with one which is preferentially perpendicular oriented (squares). The corresponding dielectric strengths differ by more than one order of magnitude (see inset of Fig. 6). By a simple scaling, $\Delta\varepsilon_\delta$ for the sample with the perpendicular orientation can be matched to that measured for parallel oriented sample. As it can be seen already from the raw data (see Fig. 2), $\Delta\varepsilon_\delta$ for the δ relaxation increases with increasing temperature and reaches a plateau for temperatures higher than about 238 K. Moreover, there seems to be a slight difference in the temperature dependence of $\Delta\varepsilon_\delta$ for the two different main orientations. Close to the phase transition to the isotropic state $\Delta\varepsilon_\delta$ drops down. This can be also seen directly from Fig. 1. Such a behavior is expected for a liquid crystal with a positive dielectric anisotropy [11]. Near to the phase transition the orientation of the sample is lost.

The reason for this temperature dependence of $\Delta\varepsilon_\delta$ is not clear now and needs further investigation. Because the dipole moment is constant using Eq. (5), this can be understood either by an increase of the number density of fluctuating dipoles or by an increase of the correlation factor g. The latter explanation seems to be more likely because it is known that the order parameter changes with temperature. This will change the dielectric strength of the δ process [see Eq. (1)].

The dielectric strength for the tumbling mode, $\Delta\varepsilon_{\text{tumbling}}$, is given in Fig. 7 The difference between the samples with the different orientations seems to be small. At low temperatures, far from the phase transition, $\Delta\varepsilon_{\text{tumbling}}$ is approximately constant but increases strongly close to $T_{I/N}$.

To be complete, also the temperature dependence of the relaxation rate in the isotropic phase shows a VFT-like behavior (see inset of Fig. 4). This is expected because for

temperatures above the clearing temperature the system should behave as a normal glass-forming system. The corresponding VFT parameters are given in Table I. The fragility of this relaxation process is in-between the values obtained for the δ and tumbling mode. It is planned to carry out high frequency measurements on 4-cyano-4′-pentyl-1,1′-biphenyl (5CB) and 4-cyano-4′-octyl-1,1′-biphenyl (8CB) including a detail comparison of the temperature dependence of the relaxation times with that obtained by optical Kerr effect studies [23,24,27].

Also the relaxation strength of the process in the isotropic state decreases with increasing temperature as expected.

IV. CONCLUSION

It was shown by several authors that the nematic liquid crystal *E*7 undergoes a glass transition [33,35–39] characterized by a glass transition temperature T_g. Up to know the molecular origin of glassy dynamics in constrained systems with partial order and restricted mobility is under strong discussion in the literature. To study the glassy dynamics in *E*7 as model case, broadband specific heat spectroscopy was combined with dielectric spectroscopy. The theory of dielectric relaxation of liquid crystals predicts for the nematic state two relaxation processes. The δ relaxation is observed at low frequencies and corresponds to rotational fluctuations of the molecule around its short axis. The tumbling mode is related to different tumbling fluctuations of the molecules with regard to its long axis and is observed at higher frequencies than the former one. The broadband dielectric measurements give that the temperature dependence of the relaxation rates of both the δ process and the tumbling mode follows the Vogel-Fulcher-Tammann behavior, which is regarded as a proof of glassy dynamics. By employing a derivative technique it is shown for the first time that Vogel temperatures of both processes are different by about 30 K. Close to T_g, the temperature dependence of the tumbling mode is much steeper having a higher Vogel temperature than the δ relaxation. A similar behavior is for the temperature dependencies of rotational and translatorial diffusion of simple glass forming liquids [54] and seems to be characteristic for glassy dynamics. This phenomenon can be understood on the basis of the cooperative character of the underlying fluctuations and their heterogeneity [54].

So the assignment which dielectric active relaxation process corresponds to the structural α-relaxation can not be done using dielectric data alone. Specific heat spectroscopy provides complementary information to dielectric studies and is sensitive to entropy (enthalpy) fluctuations. Only one relaxation process is observed which has to be assigned to the dynamic glass transition, to the structural or α relaxation. A detailed comparison of the temperature dependence of the observed dielectric active relaxation process with that sensed by specific heat spectroscopy results in the conclusion that the dielectric tumbling mode has to be linked to the α relaxation which is responsible for glassy dynamics in the nematic liquid crystal *E*7.

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