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Anomalous temperature behavior of nonlinear dielectric effect in supercooled nitrobenzene

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Studies of the nonlinear dielectric effect (NDE), describing changes of the dielectric permittivity induced by a strong electric field, in normal and supercooled liquid nitrobenzene are presented. An unusual increase of the stationary NDE, portrayed by the critical-like relation $\sim(T-T^{+})^{-1}$, was obtained. Nitrobenzene samples solidified at $T_S\approx T^{+}+2$ K, approximately 10 K below the reported melting temperature $T_m\approx 278$ K. The anomalous increase of the NDE coincided with a slow relaxation process, detected in time-resolved measurements. The results presented offer a reinterpretation of the classical description by Piekara and Piekara [A. Piekara and B. Piekara, C. R. Hebd. Seances Acad. Sci. **203**, 852 (1936)] of a positive sign contribution to the NDE in liquids. It is suggested that the obtained anomaly may be associated with the appearance of local quasinematic structures. This is supported by a speculative link to a general model for liquid-liquid transitions [H. Tanaka, Phys. Rev. E **62**, 6968 (2000)] and a phenomenological model originally developed for the self-focusing of laser beams [J. Hanus, Phys. Rev. **178**, 420 (1969)]. The case of the isotropic-nematic transition in liquid crystalline materials is also recalled. The NDE results reported here are related neither to the glass transition phenomenon nor to the recently developed concept of a second liquid-liquid transition.

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I. INTRODUCTION

Recently, nonlinear dielectric spectroscopy has been strongly recommended as a possible successor to broadband dielectric spectroscopy (BDS) for studying fundamental properties of liquids [1–3]. However, this property under the name the "nonlinear dielectric effect" (NDE), has been studied for several decades [4–16]. Experimentally, NDE values are determined as small changes of the dielectric permittivity, $\Delta\varepsilon^{E}/\varepsilon\sim 10^{-6}$, induced by a pulse of a strong electric field and detected by a weak radio-frequency field, namely [4–16],

$$\varepsilon^{E}=\varepsilon_1+\varepsilon_3E^2+\cdots \quad \text{and} \quad \mathcal{E}_{\text{NDE}}=\varepsilon_3=\frac{\varepsilon^{E}-\varepsilon}{E^2}=\frac{\Delta\varepsilon^{E}}{E^2}, \tag{1}$$

where $\mathcal{E}_{\text{NDE}}$ is the experimentally measured NDE, and ε and ε^{E} are the dielectric permittivities for the weak (measuring) field and for the strong electric field E, respectively. Usually, in low-molecular-weight liquids, changes of dielectric permittivity $\sim E^4$ are not observed [7,12].

The first successful NDE measurements were carried out by Herweg in diethyl ether [4], where a negative sign of the NDE was noted. This result was explained by the application of the Langevin-Debye model, yielding [4–7]

$$\mathcal{E}_{\text{NDE}}=-f\frac{N\mu^4}{45k_B^3T^3}R_S, \tag{2}$$

where N denotes the number of permanent dipole moments (μ) linked to the given molecule per unit volume, k_B is the Boltzmann constant, f is a factor related to the local field model, and $R_S\approx 1$ describes the dipole-dipole correlation.

Equation (2) links the NDE with the orientation of noncoupled or weakly coupled permanent dipole moments in a strong electric field. In subsequent decades it was found that the NDE is sensitive to inter- and intramolecular interactions, and statistical fluctuations of the polarizability ([6–12] and references therein). The strong influence of pretransitional fluctuations in critical mixtures [7,9,10,12,13] and in the isotropic phase of nematic liquid crystals (NLCs) [7,12–16] was also noted. Until recently, the orientational effect was commonly considered to be the only source of a negative sign of the NDE ([4–12] and references therein). However, in Ref. [16], the negative-sign contribution to the NDE from pretransitional fluctuations in the isotropic phase of chiral isopentylcyanobiphenyl was found.

The first evidence for a positive and nonorientational NDE was obtained in nitrobenzene by Piekara and Piekara seven decades ago [8]. He attributed this phenomenon to the intermolecular coupling, leading to a "scissorslike" arrangement of permanent dipole moments of neighboring nitrobenzene molecules [7–11]. Piekara also observed an anomalous positive increase of the NDE near the critical consolute point in nitrobenzene-hexane mixtures [9,10]. The origin of this anomaly was explained relatively recently, on the basis of a model which assumed the elongation of critical fluctuations under a strong electric field. This yielded [12,13]

$$\mathcal{E}_{\text{NDE}}(T)-(\mathcal{E}_{\text{NDE}})_{\text{bckg}}=C\langle\Delta M^2\rangle_V\chi=\frac{A_{\text{NDE}}}{(T-T_C)^{\psi}}, \tag{3}$$

where $\mathcal{E}_{\text{NDE}}(T)$ is for the total, measured NDE, $(\mathcal{E}_{\text{NDE}})_{\text{bckg}}$ denotes the noncritical background effect, C is a constant coefficient, $\langle\Delta M^2\rangle_V=(T-T_C)^{2\beta}$ is the mean of the square of the order parameter fluctuations, $\beta\approx 0.33$ is the critical exponent for the order parameter, and $\chi\propto(T-T_C)^{-\gamma}$ is for the critical anomaly of the compressibility. (susceptibility). A_{NDE} is the NDE critical amplitude and $\psi=\gamma-2\beta$ denotes the NDE critical exponent.

It was suggested in Refs. [12,13] that the elongation of critical fluctuations may lead to the classical-nonclassical anisotropy of the correlation length, $\xi(E\to 0)\to\xi(E\gg 0)=(\xi_{\parallel},\xi_{\perp},\xi_{\perp})$ for $\xi(E\to 0)$, $\xi_{\parallel}(E\gg 0)\propto(T-T_C)^{-0.63}$, and

$\xi_\perp(E \gg 0) \propto (T - T_C)^{-1/2}$. This behavior induces the almost classical value of the susceptibility exponent $\gamma \approx 1$ and $\psi \approx 0.37$ for the NDE critical exponent [12,13].

For weakly interacting fluctuations in the isotropic phase of rodlike nematic liquid crystalline compounds the above relation is reduced to [12–14]

$$\mathcal{E}_{\mathrm{NDE}}(T) = \frac{2}{3}\varepsilon_0 \chi_0^* \frac{(\Delta\varepsilon^0)^2}{(T - T^*)^\gamma} \propto \langle \Delta M \rangle^2 \chi^*, \qquad (4)$$

where $\chi^*(T) = \chi_0^*(T - T^*)^{-\gamma}$ with the exponent $\gamma = 1$, $\Delta\varepsilon^0$ is the dielectric anisotropy of the perfectly ordered LC sample, and T^* is the temperature of the virtual critical point. In the isotropic phase of NLCs, measurements can be carried out for $T > T_{IN} = T^* + \Delta T$, where T_{IN} denotes the temperature of the discontinuous phase transition and ΔT is the measure of the discontinuity: usually $\Delta T = 1-2$ K.

Basing on the same model, in Refs. [13,17] a common description of the NDE and the transient electric birefringence (TEB)–electro-optic Kerr effect (EKE) in the homogeneous phase of near-critical binary mixtures and in the isotropic phase of NLCs was proposed.

This paper presents evidence that in a one-component liquid, such as nitrobenzene, a NDE pretransitional anomaly associated with a singularity hidden below the melting temperature may exist. Subsequently, a speculative common description of NDE behavior in nitrobenzene, in the homogeneous phase of critical mixtures, and in the isotropic phase of NLCs is proposed.

It is noteworthy that nitrobenzene is often considered as a model system for studying molecular interactions and fundamental properties of nitroaromatic compounds [7,11,18–22]. The properties of nitrobenzene and related compounds are also important for manufacture of explosives and some other chemicals [23–25].

II. EXPERIMENT

The results presented below are based on nonlinear and linear dielectric measurements, in normal and in supercooled liquid nitrobenzene. To the best of the authors' knowledge no results in supercooled nitrobenzene have been reported so far. The linear dielectric measurements were conducted using a broadband dielectric spectrometer Novocontrol Concept 80 (model 2005) equipped with a Quattro temperature control system. A quartz ring was applied as a spacer in a flat, parallel, gold-coated capacitor with $d = 100$ μm gap.

There are two basic principles for NDE measurements. For the first one, a single sine-wave strong electric field is applied. The NDE is determined from the charge-related distortions of the output signal via selective [12,26] or broadband [12,27] detection. In practice, this method is focused on samples characterized by very large values of $\Delta\varepsilon^E$. This can be obtained for very high intensities of the electric field, most often reached by a very small gap of the measurement capacitor, namely, $5 < d < 100$ μm. Technical restrictions also suggest small values of the electric conductivity of samples [12,26,27]. For this method such parasitic artifacts as surface-related effects, electrostriction, deformation of the plates of the measurement capacitor, ion-related heating, or dissolved gas minibubbles have to be carefully considered [12]. These artifacts are particularly important because the strong electric field is continually applied [12]. Successful NDE measurements based on this principle have been reported for ferroelectric liquid crystals and polymeric films ([12,26,27] and references therein).

For the second principle of NDE measurements a strong electric field induces anisotropy in a liquid or in a soft matter sample. This causes changes of electric capacitance of the sample detected via a capacitance meter. The latter introduces a second, weak measuring field of a radio frequency [7–12]. This dual-field method was used already by Herweg [4], Piekara and Piekara [8,9], and in all subsequent studies recalled in the Introduction [6,7,11–16]. The advantages of this method are [7,12] (i) high sensitivity, since the capacitor with the sample is usually placed within a resonant circuit; (ii) much weaker intensities of the electric field needed than for the single-field method; (iii) a large gap of the measurement capacitor, reaching even $d = 2$ mm, which reduces the parasitic influence of gas minibubbles; (iv) application of the strong electric field in the form of very short ac or dc pulses, which significantly reduces the ionic heating; (v) detection of parasitic heating and the presence of gas minibubbles on line during measurements. Until recently, only the superheterodyne-based method was used for selective detection of the output signal in this method [7,11,12]. However, the authors' experience in NDE studies indicates significant problems with grounding for this design. This problem is absent for the NDE apparatus design applied in this paper. We would like to stress the similarity between NDE and TEB measurements. It is noteworthy that both NDE and TEB measurements yield directly $\Delta\varepsilon^E \sim E^2$ or $\Delta n^E \sim E^2$ as the experimental output [13,17], although the frequencies of the weak measuring field are qualitatively different for these methods.

Recently Weinstein and Richert [2,3] estimated NDE values in supercooled glycerol and propylene glycol via BDS measurements, using a strong ($E_{\mathrm{strong}} = 284$ kV/cm) and a weak ($E_{\mathrm{weak}} = 14$ kV/cm) measuring field. Subsequently NDE values were calculated, namely, $\Delta\varepsilon^E / E^2 = \varepsilon(E_{\mathrm{strong}}) - \varepsilon(E_{\mathrm{weak}}) / E^2$. Measurements were conducted by applying a Solartron SI 1260 impedance analyzer supplemented by a high-voltage amplifier and a flat parallel capacitor with $d = 10$ μm gap. A significant advantage of this method of measurement is the possibility of a frequency scan.

The results presented in this paper were obtained using the dual-field NDE apparatus whose scheme is shown in Fig. 1. The weak measuring field was characterized by $f_{\mathrm{weak}} = 5$ MHz and $U_{\mathrm{weak}}^{\mathrm{peak\text{-}peak}} = 1$ V, which yielded $E_{\mathrm{weak}} = 10$ V/cm. The pulse was equal to $U_{\mathrm{strong}} = 200-600$ V, which gave $E_{\mathrm{strong}} = 2-6$ kV/cm. The strong electric field was applied for $\Delta t_D = 0.5-5$ ms. The sample was placed in a flat parallel capacitor with a $d = 1$ mm gap and $2r = 20$ mm diameter. The capacitor was made from Invar and a quartz ring was used as spacer. Such experimental conditions made it possible to minimize the influence of gas minibubbles and the heating associated with residual ionic contamination.

When studying the NDE or the Kerr effect (TEB), the question of the validity of the condition $\Delta n, \Delta\varepsilon^E \propto E^2$ always arises. It can be noted from Refs. [7,11,12,15] that in low-

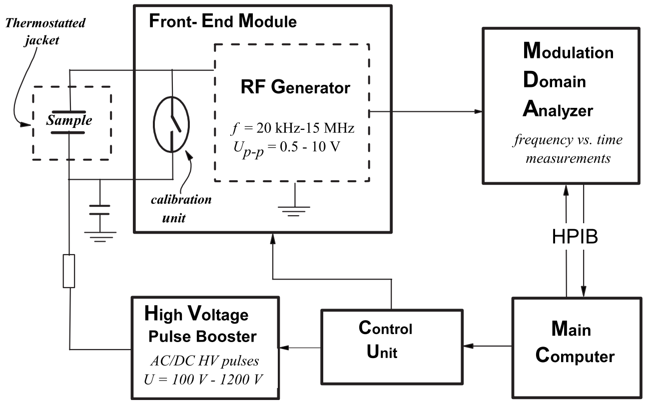

FIG. 1. Scheme of the dual-field, single-generator, and modulation-domain-based nonlinear dielectric effect apparatus. The switch-relay-based calibration unit is directly linked to the measurement capacitor. Its detailed description is given in Ref. [12].

molecular-weight dipolar liquids this condition is satisfied up to at least 5×10^{6} V m^{-1}. For nondipolar liquids it is valid even for $E>10^{7}$ V m^{-1}, within the limit of the experimental error [7]. A significant influence of the higher-order harmonic terms was observed in the immediate vicinity of the critical consolute temperature in binary mixtures for $T-T_C<0.1$ K [28]. We would like to stress that for each tested temperature the NDE measurements were carried out for four different intensities of the electric field and violation of the $\Delta\varepsilon^{E}\propto E^{2}$ condition was not noted. Higher-order harmonics ($\sim E^{4},E^{6},\ldots$) are often detected for the single-field periodic NDE technique [12,26,27]. In this case electric fields above 10^{7} V m^{-1} define the typical measurement conditions.

The tested sample of nitrobenzene was purchased from Fluka and subsequently twice distilled under reduced pressure and carefully degassed immediately prior to measurements. The conductivity of the tested samples was about 10^{-11} Ω^{-1} m^{-1}.

III. RESULTS

Figure 2 presents results of isothermal measurements in mixtures composed of a dipolar component and a nondipolar solvent (hexane, hexene). It shows basic molecular mechanisms which can contribute to NDE in molecular liquids [6–12]. For pure nondipolar solvents the NDE is positive and extremely small, $\sim10^{-19}$ m^{2} V^{-2}. This value results from the density and the polarization fluctuations [7]. For 1-nitropropane mixtures the NDE changes linearly with increase of the dipolar component concentration, in agreement with the Langevin-Debye-Herweg equation (2). For o-nitrotoluene and nitrobenzene mixtures, the sign of the NDE changes from initially negative values to positive ones for concentration $x\rightarrow1$. For a nitrobenzene-hexane mixture an additional positive NDE, with the peak at $x\approx0.43$ mole fraction of nitrobenzene, appears. This value reflects the critical concentration of the nitrobenzene-hexane solution of limited miscibility, which shows a two-phase region below the critical temperature $T_C=19.5$ °C [29]. The evolution of the NDE in a nitrobenzene-hexene mixture can be considered as the noncritical reference, the so-called background effect [13,29], for the nitrobenzene-hexane critical mixture. For the nitrobenzene-hexene background mixture of perfect solubility only the negative, orientational effect is present. The molecular geometry of hexene parallels the structure of hexane much better than those of carbon tetrachloride or benzene applied up to now [13,29]. The results given in Fig. 2 can be considered as the summary of the main experimental NDE results discussed in the Introduction

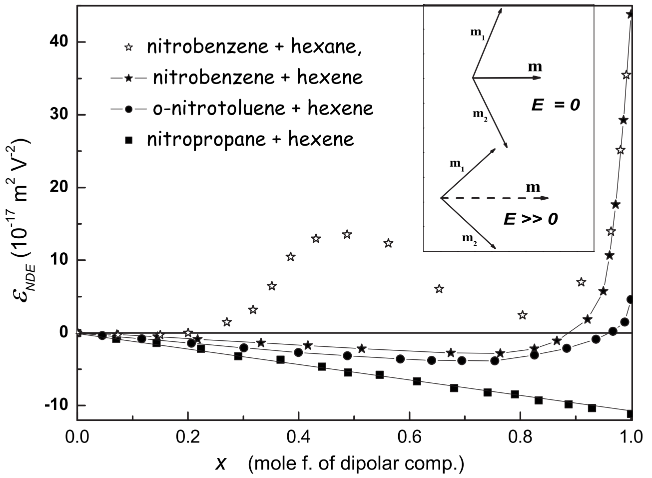

FIG. 2. Isothermal behavior ($T=20$ °C) of nonlinear dielectric effect in mixtures of a dipolar component (nitrobenzene, o-nitrotoluene, and 1-nitropropane) in nondipolar solvents (hexene and hexane). For the nitrobenzene-hexane mixture a double phase region below $T_C=19.5$ °C, associated with the critical consolute concentration $x_C=0.43$ mole fraction of nitrobenzene, exists. Curves and lines in the figure are solely guides for the eyes. The inset shows the molecular mechanism applied by Piekara and Piekara for explaining the anomalous positive NDE in nitrobenzene [7–10]. Permanent dipole moments m_1,m_2 are for coupled nitrobenzene molecules and m is the effective dipole moment.

To the best of the authors' knowledge, no reliable attempts to parametrize the temperature evolution of the NDE in pure nitrobenzene have been reported so far ([7,11,30] and references therein). In practice Eq. (2) can only be used to portray experimental data for isothermic, concentration dependences of the NDE [6,7,11]. Moreover, for nitrobenzene the available results of dielectric studies refer to the region above the melting temperature $T_m\approx5$ °C ([7,30] and references therein). Probably due to the careful preparation of the nitrobenzene samples, we succeeded in carrying out dielectric measurements also below T_m. The results of NDE measurements in normal and supercooled nitrobenzene are shown in Fig. 3. We found an anomalous increase of NDE on cooling, which may be portrayed by a "critical-like" dependence, namely,

$$\mathcal{E}_{\mathrm{NDE}}(T)=a+bT+A(T-T^{+})^{-\varphi}. \qquad (5a)$$

For the reliable estimation of the parameters in Eq. (5a), a derivative analysis, reducing the number of parameters, was also used, namely,

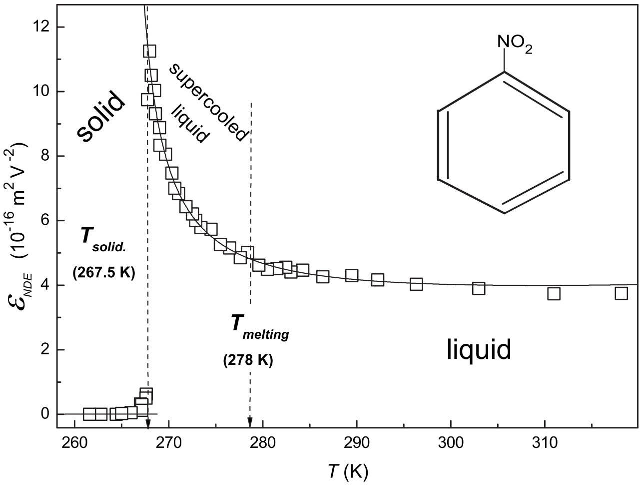

FIG. 3. Temperature behavior of the nonlinear dielectric effect in the liquid, supercooled, and solid states of nitrobenzene. Solid line is parametrized by relation (5a). The form of the nitrobenzene molecule is also presented.

$$\frac{d\mathcal{E}_{\mathrm{NDE}}(T)}{dT} = b - A'(T-T^{+})^{-\varphi-1}, \tag{5b}$$

where $\varphi = 1 \pm 0.05$, $A = (24 \pm 3) \times 10^{-16}$ m^2 V^{-2} K, $T^{+} = 265$ K ± 0.5, and $b = (0.02 \pm 0.005) \times 10^{-16}$ m^2 V were the fitting parameters. These parameters substituted in Eq. (5a) yielded the solid curve portraying the experimental data in Fig. 3. In our studies nitrobenzene always solidified at T_S, well below the suggested melting temperature T_m. The parametrization applied in Fig. 3 may explain the linear temperature dependence of the NDE given in Refs. [7,30], which can be considered as the "high-temperature tail" of an anomaly hidden in the high temperature region. The results discussed above concern the stationary NDE, i.e., that observed for the duration of the pulse of the strong electric field $\Delta t_D \gg \tau_f$, where τ_f is the relaxation time of a hypothetical slow relaxation process. The time-resolved NDE analysis made it possible to detect relaxation times of processes above the threshold time of the internal dynamics of the NDE spectrometer, i.e., for $\tau_f > 0.05$ ms. The time-resolved NDE responses to a rectangular pulse of a strong electric field in normal and supercooled nitrobenzene are shown in the insets in Fig. 4. For supercooled nitrobenzene a clear deformation of the NDE response occurs. It can be portrayed by the stretched-exponential (SE) dependence [12,31]

$$R(t) = \frac{\mathcal{E}_{\mathrm{NDE}}(t)}{\mathcal{E}_{\mathrm{NDE}}^{\mathrm{saturation}}} = \exp\left[-\left(\frac{t}{\tau_f}\right)^{X}\right], \tag{6}$$

where $R(t)$ is the response function, t is the elapsed time after the strong electric field is switched off, $\varepsilon_{\mathrm{NDE}}^{\mathrm{saturation}}$ is for the stationary, saturated NDE, i.e., for $t = \Delta t_D \gg \tau_f$. The SE exponent $x < 1$ indicates a non-Debye distribution of relaxation times.

The deformation of the NDE response was observed for $T < 275$ K. The analysis presented in the main part of Fig. 4 reveals its almost single-exponential, i.e., Debye-type, characteristic, namely, $x = 0.94 \pm 0.1$ for $\tau_f = 1.4$ ms at $T = 269$ K. In supercooled nitrobenzene the intensity of the electric field was decreased down to $E_{\mathrm{strong}} = 2$ kV/cm, to reduce the ionic heating. The same artifact limited the duration of the strong electric pulses to $\Delta t_D < 5$ ms.

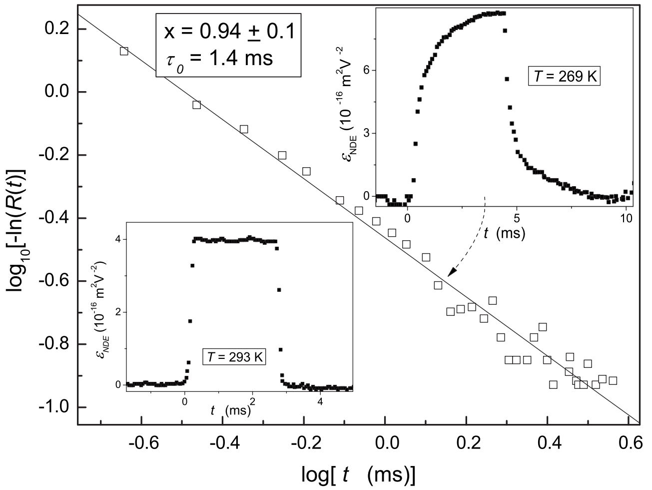

FIG. 4. Stretched-exponential evolution of NDE response after switching off a strong dc electric field in supercooled nitrobenzene. The solid line indicates the validity of the SE relation (6) with parameters given in the figure. The upper inset shows experimental decay applied for the analysis in the main part of the figure. The lower inset presents the time-resolved NDE response at room temperature, well above the melting temperature.

The linear relaxation time in supercooled nitrobenzene can be estimated from the peak frequency of the loss curve determined in the BDS measurements presented in Fig. 5, via the condition $\tau = 1/2\pi f_{\mathrm{peak}}$ [32]. Noteworthy is the qualita-

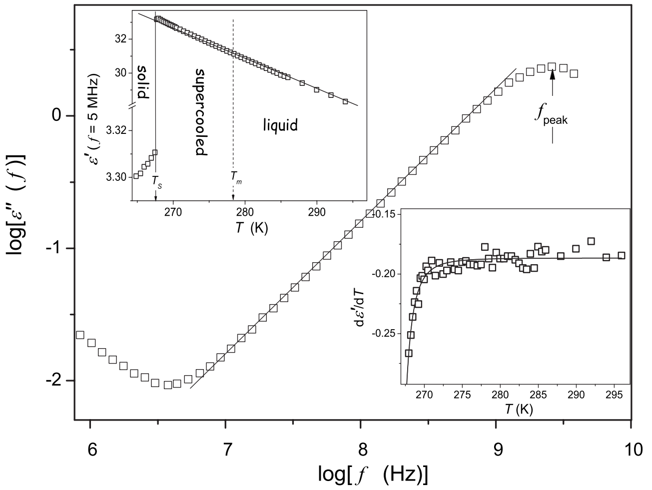

FIG. 5. Dielectric relaxation process manifested for the $\varepsilon''(f)$ plot on a log-log scale in supercooled nitrobenzene at $T = 268$ K. The arrow indicates the peak frequency related to the dielectric relaxation time via $\tau = 1/2\pi f_{\mathrm{peak}} \approx 70$ ps. The slope of the solid line $m = 1.00_2 \pm 0.02$ indicates the distribution of relaxation times described via the Debye or Cole-Davidson function [32]. The upper inset shows the temperature evolution of the static dielectric permittivity $\varepsilon'(T)$ and the lower inset is for the derivative of the experimental data from the upper inset.

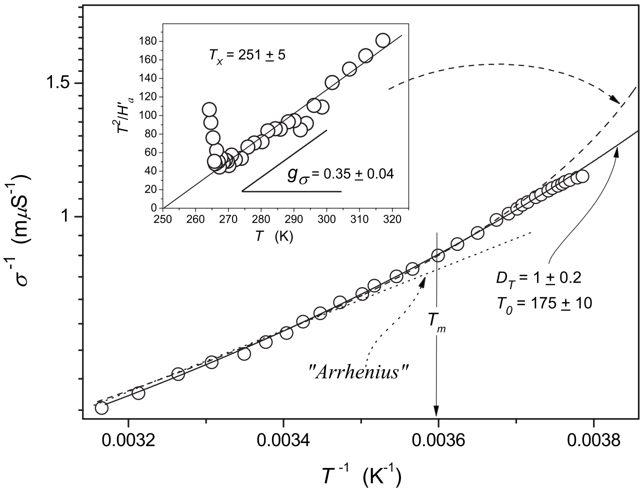

FIG. 6. Arrhenius plot of the temperature evolution of electric conductivity in normal and supercooled nitrobenzene. The solid curve is linked to the VFT equation (7) and the dashed curve is for the critical-like relation (8). The latter is supported by parameters from the derivative-based transformation in the inset where the apparent activation enthalpy $H'_a = d \ln \tau/(1/T)$ [33,45]. The derived exponents do not support a direct link to the physics of the glass transition.

tive distance between the nonlinear and the linear dielectric relaxation times, namely, $\tau_f/\tau \approx 2 \times 10^7$, near the solidification temperature. It is worth recalling that the linear dielectric relaxation time is linked to the dynamics of a single, average, permanent dipole moment. The nonlinear dielectric relaxation time may be associated with multimolecular bond-ordering structures, for instance pretransitional fluctuations as shown by Eq. (3) [12–16].

The upper inset in Fig. 5 presents the behavior of the static dielectric permittivity $[\varepsilon'(T)]$. It shows an almost linear increase of $\varepsilon'(T)$ on cooling, with a very small distortion near the solidification temperature. This evolution is particularly visible for the derivative analysis presented in the lower inset in Fig. 5, although the scatter of the transformed data made quantitative analysis of $\varepsilon'(T)$ near T_S impossible. For both the static dielectric permittivity and the NDE a small pretransitional effect seems to be visible also in the solid, hypothetically crystalline, phase.

In supercooled liquids the temperature evolution of dielectric relaxation times and electric conductivity can be portrayed by the Vogel-Fulcher-Tammann (VFT) equations associated with the same values of key parameters in the high-temperature domain, namely [32],

$$\sigma^{-1} = \sigma_\infty \exp\left(\frac{D_T T_0}{T - T_0}\right), \tag{7}$$

where T_0 is the VFT singular temperature, often linked to the ideal glass temperature, D_T is the fragility strength coefficient for the given temperature domain, and the prefactor σ_∞ is related to the high-temperature behavior.

Figure 6 shows the non-Arrhenius evolution of the electric conductivity, confirming the validity of the parameterization via Eq. (7). However, the same data can also be portrayed by a critical-like dependence, namely [32,33],

$$\sigma^{-1}(T) \propto (T - T_X)^{-g_\sigma}. \tag{8}$$

The supporting derivative-based analysis, $T^2/H'_a = g_\sigma^{-1}(T - T_X) = A + BT$ and $H'_a = d \ln \sigma^{-1}/d(1/T)$, enables a reliable estimation of basic parameters solely from the linear regression fit, namely, $g_\sigma = B^{-1}$ and $T_X = -A/B$ [33]. The results shown in the inset in Fig. 6 gave $g_\sigma \approx 0.35$ and the critical-like temperature T_X, located well below the singular temperature manifested in NDE studies (Fig. 3). It is noteworthy that for glass-forming liquids the critical-like behavior is observed for dielectric relaxation time $\tau(T) \propto (T - T_C)^{-g}$ for $T > T_C + 20$ K and $g = 1.5 - 4$, in agreement with the mode coupling theory (MCT) predictions [32–35]. Recalling the Debye-Stokes-Einstein (DSE) relation $\sigma(T)\tau(T) = \text{const}$ [32], one should expect similar values of the g and g_σ exponents. Consequently, the results presented in Fig. 6 do not support a direct link to the physics of the glass transition for the reported phenomenon.

IV. DISCUSSION

One of the great problems of condensed matter physics is the possible "heterogeneous" nature of supercooled and maybe also normal liquids [32,35]. This is associated with hypothetical dynamic, locally ordered structures [36]. Their existence seems to be proved for supercooled liquids, particularly near the glass transition temperature ([32,35,36] and references therein). However, experimental studies of their basic properties are still a challenge. Dynamical heterogeneities, associated with a time scale comparable to the linear dielectric relaxation time τ, were noted in nonlinear dielectric studies by Weinstein and Richert (WR) in supercooled glycerol [2] and propylene glycol [3]. Similar results were obtained earlier by nonresonant hole-burning spectroscopy (NHBR) [37–39]. It is noteworthy that the results of both WR [2,3] and NHBR [37–39] were carried out in a similar, BDS-based, way. Consequently, they can yield a single dipole response in the environment modified by hypothetical heterogeneities, in the opinion of the authors. On the other hand, photon-correlation spectroscopy studies by Patkowski *et al.* [40,41] in glassy liquids detected heterogeneities with the time scale $\tau_f/\tau > 10^6$. A similar time scale was observed in NDE studies in the epoxy resin EPON 828 [31]. In the opinion of the authors both photon-correlation spectroscopy and NDE yield an experimental output directly coupled to nano- and microscale heterogeneities. This seems to be also supported by results of measurements in near-critical liquids [12–17].

A few years ago, Tanaka in Ref. [36] gave a "general view of a liquid-liquid transition," in which he suggested a possible common description of (i) the liquid-liquid transition in a one-component liquid, (ii) the liquid-gas critical point, and (iii) the glass transition phenomena. The key assumption was the existence of unique, locally favored, structures appearing in any liquid and characterized by two order parameters linked to the density (ρ) and bond-ordering (S) changes. The short-range ordering was associated with the symmetry-selective nature of the molecules or atoms, originating mainly from the shape and intermolecular interactions. The competition between ρ and S led to the formation of different locally favored structures. The inconsistency between short-range bond ordering and long-range crystalline ordering was suggested as the key prerequisite for vitrification. It was characterized by the so-called frustration. In Tanaka's model the size and lifetime of local bond-ordering structures should increase on cooling, eventually yielding a liquid-liquid transition above or below the glass transition line in the pressure-temperature plane. For the glass transition strong frustration is essential. In the case of critical-like phenomena the coupling between fluctuations of ρ and S was basic [36,42].

We would like to consider first the isotropic-nematic transition in rodlike compounds, not included in Tanaka's pattern. One of the most "classical" NLCs is *n*-pentylcyanobiphenyl (5CB), from the *n*-alkylcyanobiphenyl (*n*CB) homologous series. 5CB remains in the isotropic phase down to about $T_{IN} \approx 35$ °C, where the isotropic to nematic (I-N) transition occurs. At the temperature $T_{NS} \approx 15$ °C it crystallizes [43]. Shorter members of the *n*CB series usually crystallize on cooling in the isotropic phase, well above the I-N transition. However, *n*-butylcyanobiphenyl (4CB) can be supercooled well below the usual crystallization temperature T_{IS}, reaching at least the I-N transition [44]. Starting from *n*-propylcyanobiphenyl (3CB) the sample always crystallized well above the I-N transition, in practice [43,44]. It is noteworthy that all these compounds exhibit a similar non-Arrhenius and non-Debye dynamics in the isotropic phase, as shown in BDS-based studies [14,15]. The application of the derivative-based analysis for $\tau(T)$ evolution revealed an enormous increase of fragility on approaching T_{IN} [45]. On the other hand, the dynamics of prenematic fluctuations is clearly of single-exponential (Debye) type, with the anomalous increase of relaxation time $\sim (T-T^*)^{-1}$, as detected in NDE [15,16], Kerr effect, or light scattering studies [43,46,47].

Tanaka suggested that van der Waals interactions favor denser packing and hence there is a density-related component of the order parameter [36,42]. However, for *n*CB molecules the denser packing ought to coincide with orientational ordering due to the rodlike symmetry of molecules. The orientational ordering within local structures (fluctuations) increases on cooling. Hence, the increase of the coupling between ρ and S fluctuations should be expected. The increasing coincidence of the symmetry of local structures and the preferred crystalline symmetry is linked to a decrease of frustration and an increase of fragility. This makes spontaneous crystallization more and more probable on cooling. In fact in 5CB the fragility increases enormously on approaching T_{IN} [45,48]. Finally, orientational freezing at the I-N transition occurs. Hence, it seems that the isotropic phase can be located within Tanaka's model.

Regarding nitrobenzene, it is worth recalling that Tanaka [36] predicted the existence of local structures for any liquid. It is noteworthy that stringlike structures are often suggested for heterogeneities in supercooled liquids [49,50]. For nitrobenzene this may lead to the appearance of nematic quasimolecules, resembling *n*CB molecules. In fact, in nitrobenzene the appearance of at least molecular dimers near room temperature seems to be a proved fact [7,11,19,20]. On cooling, feedback between the ρ and S components of Tanaka's order parameter may eventually occur in nitrobenzene, as in the case of the isotropic *n*CB. However, the hypothetical quasinematic local structures appearing on cooling may also facilitate benzene ring couplings, suggested for benzene-ring-based molecules [18–21]. Consequently, tetragonal structures within quasinematic fluctuations, coinciding with the ones appearing for solid crystalline nitrobenzene [51], may appear. Hence, the growth of heterogeneities can finally lead to a decrease of frustration and then to crystallization, based on the model of Tanaka [36,42]. This speculation is also supported by (i) the similar dynamics in nitrobenzene and in isotropic 5CB for linear and nonlinear dielectric studies; (ii) the weak or even negligible influence of a strong electric field on the range of supercooling in nitrobenzene; (iii) the emergence of a slow relaxation process in supercooled nitrobenzene, suggesting a collective, multimolecular process. In the opinion of the authors, a similar reasoning may explain the mentioned preferable crystallization well above the I-N transition for shorter *n*CB molecules.

The question arises whether any other experimental or theoretical indications for hypothetical quasinematic structures in liquid nitrobenzene exist. We recall here the model by Freiser and de Joenk [52], finally formulated by Hanus [53], which was developed four decades ago to elucidate the relationship between the phenomenon of self-focusing of intense laser beams and the optical Kerr effect (OKE). In Ref. [53], based on the semiphenomenological Maier-Saupe mean-field model, it was suggested that for molecular liquids which do not exhibit a liquid crystalline polymorphism a phase transition to a partially aligned nematiclike mesophase may occur under a strong electric field. The possible appearance of such a phenomenon was suggested for molecular liquids with interacting molecules and a relatively high melting temperature, such as nitrobenzene [53]. Although Refs. [52,53] focused on the OKE, the parallel relation for NDE can be easily derived, namely,

$$\frac{\Delta n}{E^2}, \frac{\Delta \varepsilon^E}{E^2} \propto f'(\varepsilon) C \frac{\Delta\alpha \Delta\alpha'}{T-T_i} \propto (T-T_i)^{-1},$$

$$1.05 T_K \geq T > T_K, \tag{9}$$

where $f'(\varepsilon)$ is the local field factor. Within the Onsager model $f'(\varepsilon)=\varepsilon(\varepsilon+2)/(2\varepsilon+1)$, and C denotes the constant amplitude. For the NDE $C=16\pi/45k_B$; $\Delta\alpha$ and $\Delta\alpha'$ are the anisotropies of dielectric polarizabilities for presumably prolate molecules, linked to the strong electric field inducing anisotropy and to the weak measuring field, respectively. T_i denotes the lowest temperature to which a given liquid can be hypothetically supercooled; T_K is the one-dimensional freezing temperature at which a discontinuous transition occurs.

In Ref. [53], the appearance of a cooperative relaxation time, anomalously increasing on approaching T_i, was also postulated. For molecular liquids with anisotropic and interacting molecules a modified, "anomalous," temperature dependence was suggested even for electric fields near 10^{-6} V m^{-1}. Nitrobenzene was indicated as a candidate for this phenomenon [53]. Hanus [53] also noted that in the isotropic phase on nematic liquid crystals the relation OKE $\sim(T-T_i)^{-1}$ should appear even for relatively weak electric fields, because of the natural uniaxial symmetry of rodlike molecules. Indeed, in subsequent years this behavior of the OKE as well as of the light scattering or Cotton-Mouton effect (CME) became one of the most classical results presented in monographs on liquid crystals [43,46,47]. In Ref. [54], this behavior was first reported for the NDE. These anomalies are usually considered within the Landau–de Gennes (LdG) model [46,55]. However, relations derived in this way are parallel to Eq. (9).

We found only two published experimental reports that pointed to the induction of quasi-liquid-crystalline structures in nitrobenzene or similar liquids. The pretransitional anomaly of pure nitrobenzene was indicated for a liquid embedded in a porous medium [56,57]. It was associated with a hypothetical hexatic phase. A more precise analysis was only given for aniline and carbon tetrachloride [57]. However, the authors of Ref. [57] did not comment on the extremely large and negative values of the NDE ($\sim10^{-14}$ m^2 V^{-2}). It is worth recalling that for carbon tetrachloride a positive NDE of the order of 10^{-19} m^2 V^{-2} is an established experimental fact [7]. Moreover, in the opinion of the authors the experimental data in Ref [57]. do not allow for a reliable numerical analysis. An anomalous increase of dielectric permittivity in nitrobenzene was also noted in Ref. [58] as a result of the orientationally ordered wall-adjacent liquid layer near the metallic substrate. The appearance of a so-called epitropic liquid crystal was claimed to influence the value of the static dielectric permittivity even at a distance of 0.3 mm from the wall [58]. Unfortunately, the description of the relevant details of the experimental technique is not clear.

V. CONCLUSIONS

Nonlinear dielectric spectroscopy (NDS) is suggested as one of the most promising tools for resolving the mystery of supercooled glassy liquids [1–3,38,59,60]. This is due to its direct coupling with cooperative phenomena, hardly possible for BDS-based tests. It is expected that NDS- and hence NDE-linked physical properties may exhibit strong anomalies on approaching some fictitious temperatures, estimated on the basis of BDS measurements [59,60]. The results presented in this paper show that for some one-component nonmesogenic molecular liquids, such as nitrobenzene, the NDE may reveal heterogeneity-related anomalous behavior in the weakly supercooled state, related neither to glass transition phenomena [35] nor to the recently developed concept of the second liquid-liquid critical point [61,62].

Employing the general model for liquid-liquid transition phenomena by Tanaka [36,42] and the Hanus [53] model, developed for the self-focusing of intense laser beams, we speculatively linked the obtained NDE behavior to the appearance of quasinematic fluctuation heterogeneities. This paper also presents supplementary experimental evidence and interpretation for the classical, seven-decade-old finding by Piekara and Piekara [8,9] of a positive nonlinear dielectric effect in nitrobenzene.

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