

Pretransitional behavior of the nonlinear dielectric effect for the liquid-solid transition in nitrobenzene

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The nonlinear dielectric effect describes changes of dielectric permittivity induced by the strong electric field. This report shows the evidence for the critical-like pretransitional behavior for the liquid-solid transition in the supercooled nitrobenzene. Hallmarks of such behavior extend even above the melting temperature. A method for the analysis of pretransitional effects, avoiding the biasing impact of the noncritical background contribution, is proposed.

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I. INTRODUCTION

For the liquid-to-crystal discontinuous phase transition, sharp changes of various physical properties without pretransitional hallmarks occur. The continuous phase transition has already been approached away from the critical point [1]. There are also intermediate weakly discontinuous phase transitions where both pretransitional effects and discontinuous changes of physical properties take place. This is the common case in liquid-crystal materials where phase transitions are limited to select elements of symmetry [2,3]. For the most classical example of the isotropic liquid to nematic transition the freezing and melting are restricted to the orientation of rodlike liquid-crystal (LC) molecules. The most well known feature of this transition are strong pretransitional anomalies of the Kerr effect (KE), light scattering I_L , the Cotton-Mouton effect (CME), or the nonlinear dielectric effect (NDE), which are described by the same functional form [2–4]

$$\Delta n^E/E^2, \quad \Delta n^B/B^2, \quad \Delta \varepsilon^E/E^2, \quad I_L \propto \frac{A}{(T - T^*)^\psi},$$

$$T > T_{\text{IN}}, \quad \psi = \gamma = 1, \quad (1)$$

where $\Delta n^E/E^2$, $\Delta n^B/B^2$, and $\Delta \varepsilon^E/E^2$ are experimental metrics of the KE, CME, and NDE, respectively, $\Delta n^{E,B}$ are for the birefringence (optical frequencies $\sim 700\text{--}400$ THz) induced by the electric E or magnetic B fields, and $\Delta \varepsilon^E = \varepsilon(E) - \varepsilon(E \rightarrow 0)$ is for the strong electric-field-induced changes of dielectric permittivity (frequency domain ~ 1 kHz to 10 MHz). In addition, $T^* = T_{\text{IN}} - \Delta T$ is temperature of the hypothetical continuous phase transition, determined from the extrapolation of pretransitional effects below the isotropic-nematic discontinuous phase transition temperature T_{IN} , and ΔT is the measure of the discontinuity. The exponent γ is related to the precritical behavior of compressibility.

The amplitude A is related to molecular anisotropies of physical properties detected by the given method. For instance, for the electro-optic Kerr effect (EKE) $A \propto \chi_0 \Delta n \Delta \varepsilon^0$, for the optical Kerr effect $A \propto \chi_0 (\Delta n)^2$, for the NDE $A \propto \chi_0 \Delta \varepsilon \Delta \varepsilon^f$, etc., where χ_0 is the amplitude for the pretransitional anomaly of susceptibility (compressibility) and Δn , $\Delta \varepsilon^0$, and $\Delta \varepsilon^f$ are anisotropies of perfectly ordered samples in the nematic

phase for the refractive index and dielectric constant in the zero-frequency limit and for the measurement radio frequency [2–4]. The evidence related to the CME and KE constituted the inspiration for the Landau–de Gennes (LdG) model, one of the most successful approaches in the physics of liquid crystals [2,3] and soft matter physics [5]. It is notable that the striking similarity of the KE, I_L , or the NDE pretransitional effect is absent when approaching, for instance, the gas–liquid-critical point or on approaching the critical consolute point in binary mixtures of limited miscibility [1,6–10]. In this case the power exponent $\psi = \gamma \approx 1.2$ for $I_L(T)$ [1,6], $\psi \approx 0.85$ for the EKE [7,8], and $\psi \approx 0.4$ or $\psi \approx 0.6$ for the NDE [9–11]. It is notable that, at least for the KE and NDE, a common description in LCs, critical mixtures, and the gas-liquid supercritical domain seems to be possible. As shown in Ref. [11], it can result from the general dependence

$$\Delta n^E/E^2, \quad \Delta \varepsilon^E/E^2 \propto \langle \Delta M^2 \rangle_V \chi_T, \quad (2)$$

where $\langle \Delta M^2 \rangle_V$ denotes the mean of the square of the local order parameter distortion and $\chi_T(T) = \chi_0 (T - T^*)^{-\gamma}$ is for the pretransitional evolution of susceptibility (compressibility). In the case of critical mixtures of limited miscibility or the gas-liquid critical point $T^* = T_C$.

The NDE describes changes of dielectric permittivity ε due to the action of the strong electric field E : $\Delta \varepsilon^E/E^2 = [\varepsilon(E) - \varepsilon]/E^2$ [12,13]. For the NDE the shift of the measurement frequency f covering two significant regimes is possible: $f \tau_{\text{fluct}} > 1$ and $f \tau_{\text{fluct}} < 1$, where $1/f$ estimates the measurement time scale and $\tau_{\text{fluct}} = \tau_0 (T - T_C)^{-\nu}$ is for the lifetime of pretransitional fluctuations, defining the relevant process time scale [9,13]. For $f \tau_{\text{fluct}} < 1$ (the case of the low-frequency NDE) the relation (1) is valid also for isotropic liquid on approaching smectic- A , smectic- E , or N^* (cholesteric) mesophases [13–17]. For the KE, CME, and I_L only the condition $f \tau_{\text{fluct}} \gg 1$ is always fulfilled. In liquid-crystal materials melting and freezing are associated with select elements of symmetry [2,3,6]. For the classical melting from the liquid to the crystalline network there are (almost) no pretransitional anomalies reported experimentally [1,5,6]. There are two exceptions from this basic behavior. Torre *et al.* [18] reported an optical Kerr effect measurement in p -terphenyl, showing a clear pretransitional behavior

described by Eq. (1) from $T = 568$ K down to freezing at $T_m = 485$ K. The extrapolated temperature $T^* = 460$ K for the hypothetical continuous phase transition was obtained. Recently, the anomalous increase of the NDE in the supercooled nitrobenzene crystallization was reported in Ref. [19]. The preliminary analysis suggested the parametrization described via

$$(\Delta\epsilon^E/E^2)(T) = \frac{A}{T - T^*} + (a + bT). \quad (3)$$

In addition to the first, critical-like, term, the notable noncritical background contribution ($a + bT$) was detected. However, the analysis was notably influenced by the scatter associated with the preliminary character of measurements and the multiparameter nonlinear fitting.

This paper shows results of NDE studies in the normal liquid and supercooled nitrobenzene with improved resolution and in an extended range of temperatures. Here a derivative method for determining parameters of the critical effect without the biasing impact of the background term is proposed.

II. EXPERIMENT

Nonlinear dielectric effect studies were conducted via the dual-field method, whose design and description is given in Refs. [20,21]. There are two basic modes of NDE measurements in which the strong electric field is switched on for a few milliseconds (the ac mode) or a strong electric field is applied permanently and switched off for a few milliseconds [12,13]. The latter was commonly used three to five decades ago when the possibilities of sampling a single NDE pulse were very limited. It enabled the reduction of the parasitic heating caused by the electric conductivity associated with ionic contaminations. The effectiveness of the dc mode in the NDE measurement has been proved for liquid dielectrics where the electric conductivity is associated with a limited number of ionic impurities. The parasitic heating is manifested by the shift between baselines prior to and after switching on and off the strong electric field. This leads also to undesired deformations of the output NDE signal ($\sim \Delta\epsilon^E$). The application of the dc mode of NDE measurements enabled the qualitative reduction of the undesired electric conductivity related heating of samples [12]. It is notable that NDE measurements in ac and dc modes yield the same NDE values [12]. Also worth mentioning are extremely small values of NDE-related changes of dielectric permittivity $\Delta\epsilon^E/\epsilon \sim 10^{-6}$ [12,13]. This shows that estimations of the NDE or more generally nonlinear dielectric spectroscopy dielectric directly from broadband dielectric spectroscopy via $\epsilon(E)$ and $\epsilon(E \rightarrow 0)$ measurement to estimate $\Delta\epsilon^E$ requires extreme values of intensities of the electric field ($E \sim 80$ kV/cm) [13]. In the given report the dc mode NDE measurements ($V = 500\text{--}1000$ V) were applied: The strong electric field was switched off for $\Delta t = 1\text{--}5$ ms. The influence of the parasitic heating was visible already for $\Delta t > 10$ ms. The resulting changes of dielectric permittivity were registered by the weak measurement field: frequency $f = 5$ MHz and $V_{\text{peak-peak}} = 1$ V. The frequency shift between 20 kHz and 12 MHz had no influence on detected values. For the frequency $f = 5$ MHz the system had the optimal sensitivity. The sample of nitrobenzene was placed in the flat

parallel capacitor made from Invar, with a quartz ring as the spacer. The diameter of the flat capacitor $2r = 30$ mm and the distance between plates $d = 1$ mm. Hence, in the given experiment $E_{\text{strong}} = 5\text{--}10$ kV/cm and $E_{\text{meas}} = 10$ V/cm. The measurement capacitor was placed in a special oven linked to the thermostat with the external circulation (volume of the cooling-heating medium $V = 20$ L) enabling temperature control ± 0.01 K. The temperature was monitored via sensors placed within plates of the capacitor. Nitrobenzene (Fluka) was three times distilled and subsequently degassed prior to measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows results of NDE measurements in nitrobenzene on cooling from 350 K in the liquid state down to 250 K in the solid state. On heating from the solid state only a sharp increase of the NDE at the melting temperature $T_m \approx 280$ K was observed.

Eight decades ago there was a strong conviction for the general validity of the negative NDE sign in liquids, i.e., $\Delta\epsilon^E = \epsilon(E) - \epsilon(E \rightarrow 0) < 0$, supported by state-of-the-art experiments by Herweg and Potsch [22,23] and the inclusion of this result by Debye into his Nobel Prize lecture [24]. Based on measurements in nitrobenzene, Piekara and Piekara showed that in liquids with strong intermolecular interactions, $\Delta\epsilon^E > 0$ is possible [25–27]. The phenomenon was explained as the consequence of the intermolecular coupling between nitrobenzene molecules, leading to the scissorslike arrangement of the permanent dipole moment within the $\text{C}_6\text{H}_5\text{NO}_2$ molecule. Under the strong electric field the angle between dipole moments decreases, increasing the effective dipole moment [25–27]. This leads to an increase of the dielectric permittivity of the sample and then $\Delta\epsilon^E = \epsilon(E) - \epsilon(E \rightarrow 0) > 0$.

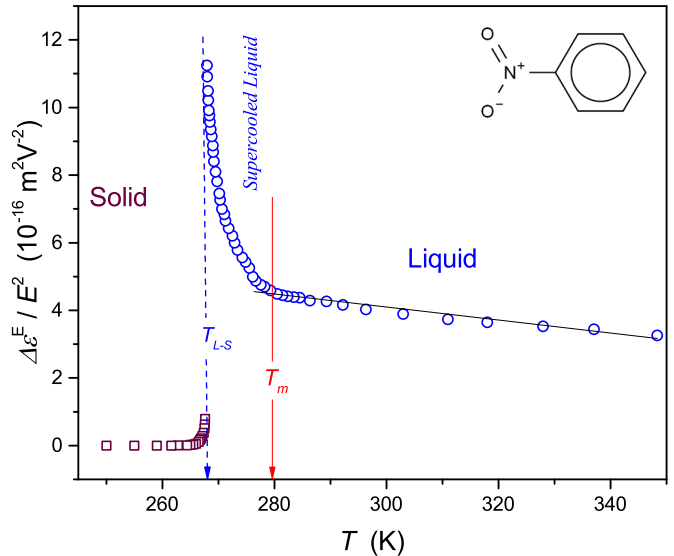


FIG. 1. Temperature behavior of the nonlinear dielectric effect in the liquid, supercooled, and solid states of nitrobenzene. The form of nitrobenzene molecule is shown. The crystallization took place at $T_{L-S} \approx 267.1$ K. The straight line shows the possibility of portrayal via the linear dependence above the melting temperature.

To describe this phenomenon Piekara and Piekara developed the Herweg-Debye local field approach [12,25]:

$$\frac{\Delta \varepsilon^E}{E^2} = -F(\varepsilon, T) \frac{N \mu^4}{45 k_B^3 T^3} R_S, \quad (4)$$

where k_B denotes the Boltzmann factor, $f(\varepsilon, T)$ is the term describing the impact of the local field, R_S is the term describing the dipole-dipole correlation, and N is for the number of permanent dipole moments in a unit volume.

This formula enables the analysis of the isothermal concentration-related ($\sim N$) behavior of the NDE in nitrobenzene plus nonpolar solvent mixtures, in fair agreement with experimental data [12]. However, the parametrization of the temperature evolution was puzzling due to the complex and model-dependent forms of $F(\varepsilon, T)$, $R_S(T)$, and $N(T)$. Nevertheless, the experimental evidence showed that in the limited range of temperatures the NDE behavior in nitrobenzene can be well approximated by a linear dependence [12]. Piekara presented also evidence for a strong increase of the NDE on approaching the critical consolute temperature T_C in a binary critical mixture of limited miscibility [12,26,27]. This phenomenon was explained a half of century later, as the result of the appearance of critical fluctuations and their elongation under the strong electric field [11,13]:

$$\begin{aligned} \left(\frac{\Delta \varepsilon^E}{E^2} \right)_{\text{critical}} &= \left[\frac{\Delta \varepsilon^E}{E^2} \right]_{\text{measured}} - \left(\frac{\Delta \varepsilon^E}{E^2} \right)_{\text{bckg}} \\ &\propto \chi_0 \Delta \varepsilon_0^2 \Delta \varepsilon_f^2 (T - T_C)^{-\phi}, \end{aligned} \quad (5)$$

where bckg denotes the noncritical molecular background term, $\Delta \varepsilon \approx \varepsilon_1 - \varepsilon_2$, and ε_i ($i = 1, 2$) denotes the dielectric permittivities of components of the given mixture.

The model developed in Refs. [9,11,13] gave $\phi \approx 0.4$ (for $1/f > \tau_{\text{fluct}}$) for the critical exponent close to T_C and $\phi \approx 0.6$ (for $1/f < \tau_{\text{fluct}}$) remote from the critical temperature. Results for NDE studies below the melting temperature in nitrobenzene ($T_m \approx 6^\circ\text{C}$) were presented in [19]. The anomalous increase up to approximately $T \approx 268$ K was observed and the possible parametrization via Eq. (1) was indicated. Nevertheless, this result suffered from a notable uncertainty associated with the preliminary character of studies and the multiparameter fitting associated with the notable molecular background effect. It is worth recalling that for NDE studies in the homogeneous phase of critical binary mixtures, values of the critical exponent ranging between $\phi \approx 0.2$ and $\phi \approx 0.8$ to describe the pretransitional anomaly were initially reported (see [10,12] and references therein). This scatter, which is unusual for strong pretransitional anomalies [6], was caused by problems with estimating the molecular noncritical background effect.

The universal value of the critical exponent was finally estimated from the NDE measurement in a reference mixture of unlimited miscibility [10]. Unfortunately, such a procedure cannot be applied in pure nitrobenzene.

This paper presents results of a NDE measurement carried out in a way minimizing the undesired impact of parasitic heating and in the extended temperature range. This way of data analysis avoids problems associated with the molecular background effect. To generalize the discussion let us consider

the pretransitional behavior in the form

$$L(T) = [L_0 | T - T_C |^\phi]_{\text{critical}} + [a + bT]_{\text{bckg}}, \quad (6)$$

where $L(T)$ denotes the given physical magnitude, for instance, the NDE, and L_0 is the critical amplitude.

The possibility of approximating the molecular background term via a linear function of temperature, in its limited range, has been proved and was applied earlier to solve the mentioned puzzle associated with the scatter of the exponent ϕ for the NDE in critical mixtures [10]. Taking the first and second derivatives of Eq. (6), one obtains

$$\frac{dL(T)}{dT} = -\phi L_0 (T - T_C)^{-\phi-1} + b \quad (7)$$

and subsequently

$$\begin{aligned} \frac{d^2 L(T)}{dT^2} &= -\phi(-\phi-1)L_0 (T - T_C)^{-\phi-2} \\ &= \phi(\phi+1)L_0 (T - T_C)^{-\phi} (T - T_C)^{-2}. \end{aligned} \quad (8)$$

The rearrangement yields

$$[d^2 L(T)/dT^2](T - T_C)^2 = \phi(\phi+1)L_0 (T - T_C)^{-\phi}. \quad (9)$$

Using the linearization via the log-log plot one obtains

$$\begin{aligned} \log_{10}\{[d^2 L(T)/dT^2](T - T_C)^2\} \\ &= \log_{10}[\phi(\phi+1)L_0 (T - T_C)^{-\phi}] \\ &= \log_{10}[\phi(\phi+1)L_0] - \phi \log_{10}(T - T_C) \\ &= f(x) = a + bx \rightarrow D_{\text{lin}}. \end{aligned} \quad (10)$$

Hence, the simple plot of transformed $L(T)$ experimental data via $f(x) = (T - T^*)^2 \log_{10}[d^2 L(x)/dT^2]$ vs $x = \log_{10}(T - T_C)$ should yield a linear dependence with the slope $b = -\phi$ and the interception $a = \log_{10}[\phi(\phi+1)L_0]$ and then $\phi(\phi+1)L_0 = 10^a$. The results of such an analysis, supported by the numerical filtering based on the Savitzky-Golay principle [28], are presented in Fig. 2. They are based on experimental data from Fig. 1. The presented distortion-sensitive analysis reveals a clear critical-like pretransitional behavior both in the solid ($\phi \approx 1.5$) and in the liquid phase (the exponent $\phi \approx 0.5$). The latter value differs from the one reported in Ref. [18]. Notable is the very large temperature range of the critical-like behavior.

The analysis is based on the distortion-sensitive method minimizing the biasing impact of the poorly known noncritical background effect. Regarding the transition from the liquid to the solid (crystal), earlier dielectric constant and electric conductivity measurements revealed only very subtle anomalous changes in the immediate vicinity of the transition [6,29–31].

The question arises whether unique strong pretransitional effects for the NDE in nitrobenzene [19] and the optical Kerr effect in *p*-terphenyl [18] are not the consequence of the strong electric field associated with these methods. The present paper may indicate the affirmative answer to this question. Hanus [32] considered the phenomenon of self-focusing of laser beams in liquids and indicated the appearance of multimolecular filaments that can lead to the anomalous increase of the Kerr effect on cooling. The generalized Hanus

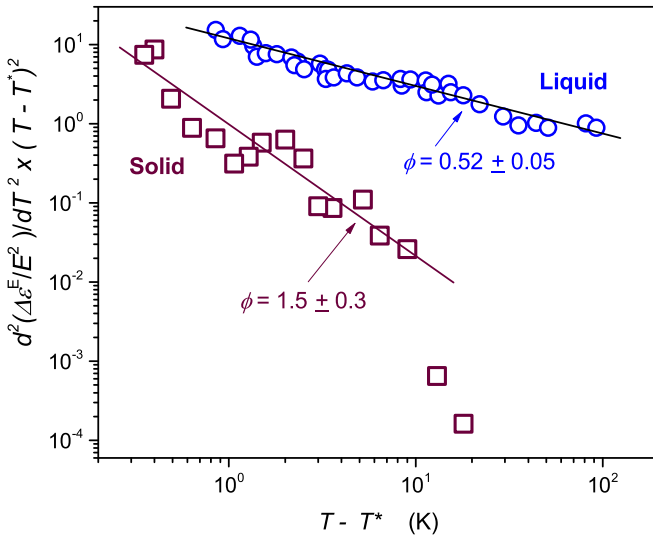


FIG. 2. The NDE experimental data from Fig. 1 transformed via the derivative analysis defined in Eq. (8). The plot enables the characterization of the critical effect (the range and parameters) without the knowledge of the noncritical background effect. The plot is associated with following singular temperatures: $T^* = 266.25$ K ($L \rightarrow S$) and $T^* = 267.45$ K ($S \rightarrow L$).

formula [32] can be written as

$$\frac{\Delta \varepsilon^E}{E^2}, \quad \frac{\Delta n^E}{E^2} \propto C f'(\varepsilon) \frac{\Delta \alpha \Delta \alpha'}{T - T_i}, \quad (11)$$

where $f'(\varepsilon)$ is the local field factor and C is a constant: In the case of the NDE, $C = 16\pi/45k_B$. In addition, T_i is the lowest temperature to which the liquid can be supercooled, which coincides with the meaning of T^* .

Hanus suggested that the anomalous behavior should extend for a relatively broad temperature range up to at least $T \sim 1.05T_m$ [32]. He indicated the appearance of such behavior for CS_2 for intensities in the electric field $E > 10^8$ V/m and for nitrobenzene for $E \sim 10^6$ V/m, which are much lower due to the presence of the phenyl ring [32]. The latter value is in the range applied in NDE studies [9–17]. Hanus suggested the emergence of behavior leading to Eq. (11) also for rodlike liquid-crystal materials with two phenyl rings [32], which indeed was subsequently discovered [see Eq. (1)].

It is notable that although *p*-terphenyl does not exhibit the liquid-crystal mesomorphism, its structure is associated with three phenyl rings and the molecule has the elongated form and the relatively large anisotropy of polarizability [17]. All these can facilitate the formation of nematiclike filaments under a strong electric field. When discussing the pretransitional behavior of the KE and NDE the difference between the critical exponent in the isotropic phase of nematogels [Eq. (1)] and in the homogeneous phase of critical mixtures is notable. For the isotropic phase the rodlike structure induces the crossover to the mean-field domain [1,6] and consequently in Eq. (2) the term $\langle \Delta M^2 \rangle_V = \text{const}$, which leads to the LdG model (1) with the power exponent $\phi = \gamma = 1$. For critical mixtures there is no such mechanism and the interaction between neighboring fluctuations takes place. Consequently, $\langle \Delta M^2 \rangle_V$ changes on approaching the critical point, which introduces an extra contribution to the temperature dependence, yielding $\phi \approx 0.85$ for the Kerr effect and $\phi \approx 0.5$ for the NDE [7–11,13]. The latter value coincides with the one obtained for nitrobenzene. One may speculate that the virtual rodlike structure of nitrobenzene is not able to create the prenematic structure and interactions between fluctuations take place. Nevertheless, the phenomena discussed in this paper require the final modeling.

IV. CONCLUSION

This paper has shown quantitative evidence for the pretransitional behavior of the nonlinear dielectric effect for the liquid to solid and solid to liquid transitions in nitrobenzene. The discussion indicates that there is a possibility that in some organic liquids with the clear discontinuous liquid-solid transition the strong electric field may induce the critical-like behavior. In fact, such phenomenon may have also some practical importance due to the transformation of a normal liquid into the supercritical one, with its unique properties [33].

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