# From Very Low to High Fields: The Dielectric Behavior of the Liquid Crystal 5CB

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**Abstract:** The liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) is investigated regarding its nonlinear dielectric behavior as reflected in the dependence of the static dielectric constant $\varepsilon_s$ on the magnitude of the electric field. The initial flow-induced homogeneous orientation of nematic domains can be erased by moderate electric fields, yielding states with little to no preferred orientation. Such samples are then subjected to ac and dc electric fields of various amplitudes, covering more than four orders of magnitude, between < 10 V cm$^{-1}$ to 220 kV cm$^{-1}$. Their regime of linear dielectric response, i.e., field invariant static permittivity, is limited to fields less than 10 V cm$^{-1}$, equivalent to a voltage less than 50 mV$_{rms}$ across a 50 μm thick sample. The Piekara factor, which gauges the sensitivity of $\varepsilon_s$ to $E^2$, is a factor of $10^8$ times larger at low fields than its counterpart at elevated fields, where the nematic domains are highly aligned in homeotropic orientation. After removing the electric field, the nematic system returns to a state with little residual alignment, as judged by the dielectric constant settling near the value of the orientational average, $\langle\varepsilon\rangle = (\varepsilon_{||} + 2\varepsilon_{\perp})/3$, and not far from that of the isotropic phase, $\varepsilon_{iso}$. The structural recovery associated with a field induced change in alignment is slow compared with dipole reorientation. For a different nematogen, itraconazole, no such extreme sensitivity to electric fields is found.

**Keywords:** liquid crystal, 4-cyano-4'-pentylbiphenyl, nonlinear dielectric effect

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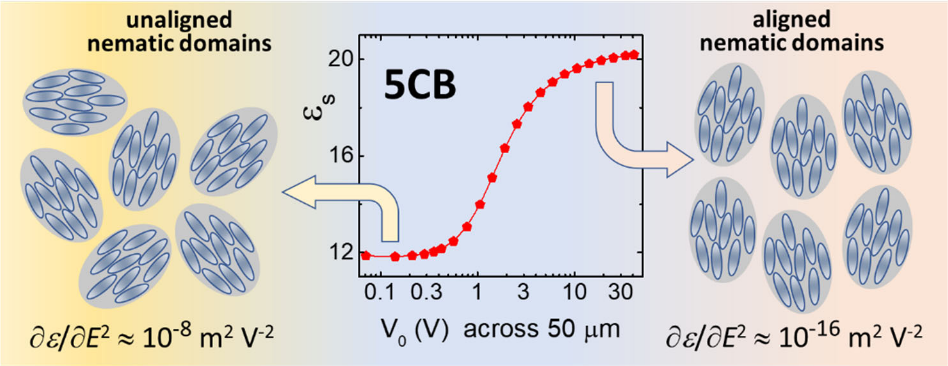
**TOC Graph**


unaligned
nematic domains
aligned
nematic domains
5CB
$\varepsilon_s$
20
16
12
0.1
0.3
1
3
10
30
$V_0$ (V) across 50 μm
$\partial\varepsilon/\partial E^2 \approx 10^{-8}$ m$^2$ V$^{-2}$
$\partial\varepsilon/\partial E^2 \approx 10^{-16}$ m$^2$ V$^{-2}$

## I. INTRODUCTION

Liquid crystalline (LC) materials have received considerable attention regarding their various structures, dynamics, and phase transitions. LC systems are not only technologically useful, e.g., as LCD type displays, but also interesting and challenging in terms of fundamental aspects of the physics involved [1,2,3]. A classical example that has been the subject of numerous studies is 4-cyano-4'-pentylbiphenyl (5CB) [4,5,6,7,8,9,10,11,12,13,14]. The family of cyano-biphenyl LCs is characterized by a large dipole moment of around 3.7 to 4.8 D [4,15,16] which originates from the cyano group and is thus oriented mostly parallel to the long molecular axis [5]. This leads to considerable dielectric anisotropy [6], i.e., a difference between the dielectric constants $\varepsilon$ measured with the long molecular axis oriented parallel ($\varepsilon_{\|}$) and perpendicular ($\varepsilon_{\perp}$) to the direction of the electric field [8]. In their nematic phases, these LCs are easily oriented, e.g., via flow alignment, patterning of interfaces, or external electric or magnetic fields. In fact, most literature results on 5CB are reported for deliberately aligned materials, either homogeneously or homeotropically [4,5,6,7,8,10,11,14].

Due to the high dipole moment and dielectric anisotropy of 5CB and similar nematogens, dielectric relaxation spectroscopy is an effective tool for characterizing the alignment and dynamics of the LC in its isotropic and nematic phase. Above the nematic/isotropic transition temperature at $T_{\mathrm{N/I}} = 308$ K, the static dielectric constant of 5CB is about $\varepsilon_{\mathrm{s}} = 11$ [8,11], and the peak relaxation frequency is near 10 MHz or above [5]. In the nematic state with $T < T_{\mathrm{N/I}}$, the dielectric anisotropy increases with decreasing temperature, reaching $\varepsilon_{\perp} \approx 6$ and $\varepsilon_{\|} \approx 20$ at $T = T_{\mathrm{N/I}} - 15$ K [8]. It has also been stated that the orientationally averaged permittivity, $\langle\varepsilon\rangle$, determined via

$$\langle\varepsilon\rangle = \frac{\varepsilon_{\|} + 2\varepsilon_{\perp}}{3}, \tag{1}$$

is very close to the value of $\varepsilon_{\mathrm{iso}}$, the static permittivity in the isotropic state near $T_{\mathrm{N/I}}$ [4]. Note, however, that $\langle\varepsilon\rangle$ is calculated based on mean-field assumptions, not an observation. For more detailed experimental evidence and discussions on this matter, particularly in view of critical phenomena, see the work of Drozd-Rzoska *et al.* [9]. The liquid crystal 5CB has also been subject to a number of studies that focus on the effect of pre-transitional fluctuations on the dielectric constant, the nonlinear dielectric effect (NDE), and the dielectric relaxation dynamics. For these features related to critical phenomena, the reader is referred to the extensive work of Drozd-Rzoska *et al.* [9,12,13,17] and Rzoska *et al.* [18].

In this study, we examine how small an electric field needs to be in order not to impose an alignment by virtue of a dielectric relaxation experiment alone. This is equivalent to asking: beyond which field amplitude is the dielectric response of unaligned nematic 5CB no longer in the linear regime? For the case of 5CB, we find that electric fields as small as 50 mV/50 μm = 10 V cm$^{-1}$ already have a noticeable effect on the permittivity via promoting a preferred alignment of the long molecular axis parallel to the electric field. This implies that an ordinary dielectric relaxation experiment will already reside outside the limit of the linear response regime, i.e., the observed permittivity will already be dependent on the field magnitude [19]. The results obtained for 5CB will be compared with a different LC system: itraconazole.

## II. EXPERIMENTAL SETUP

The compounds 4-cyano-4'-pentylbiphenyl (5CB, > 98.0 %) and itraconazole (ITZ, > 98.0 %) were used as received from TCI. For experiments on 5CB, the sample material was placed in a spring loaded titanium plate capacitor cell with electrode diameters 17 mm and 20 mm, *cf.* supplementary material of a previous publication [20]. Teflon spacers with 50 μm or 100 μm thickness (Goodfellow Corp.) were employed to define the electrode separation, leaving an inner diameter of 14 mm for the sample. Thinner samples were prepared by mixing a very small amount of silica spheres with 9.2 μm diameter (Cospheric LLC) into the liquid sample. In order to control and measure the sample temperature, we used a Leybold RDK 6–320 closed cycle He-refrigerator cryostat with a Lakeshore Model 340 temperature controller with Si-diode (DT-470-CU, $\Delta T = 0.3$ K) sensors. One experiment has been performed with the sample situated within a 5 mm outer diameter NMR tube, which is hugged by two electrodes covering an angle of 90° each [21]. In this case, the temperature is controlled using a Novocontrol Quatro nitrogen gas cryostat system. In all cases, 5CB has been filled into the sample container at room temperature, where the material is in the nematic state, but heated above the clearing point $T_{\mathrm{N/I}}$ prior to any measurement.

Samples of ITZ were prepared by mixing the powder with a small amount of silica spheres (2.65 wt%). The mixture was then melted on a brass plate (diameter 20 mm) under dry nitrogen atmosphere and topped with a smaller plate (diameter 8.1 mm) to form a capacitor, which is then quickly cooled to ambient conditions via contact to a cold metal surface. Using the Novocontrol Quatro cryostat, the sample is heated to reach the isotropic state prior to the measurements.

Values of the static permittivity $\varepsilon_s$ were determined using a Solartron SI-1260 gain/phase analyzer, set to a frequency of $\nu = 8$ kHz, where $\varepsilon'(\nu)$ is located at the static plateau value. For experiments that do not apply voltages in excess of 1 V, the current is measured via a DM-1360 transimpedance amplifier. For higher voltages, the generator output of the SI-1260 is supplemented with a Trek PZD-350 voltage amplifier and the current is measured by the voltage drop across a 100 Ω shunt resistor.

In order to observe the time-resolved response to elevated ac-fields, dc-bias free voltage patterns, $V(t) = V_0 \sin(\omega t)$, were generated by a Stanford Research Systems DS-345 arbitrary waveform generator and increased in amplitude by a factor of 100 via a Trek PZD-350 amplifier. A Nicolet Sigma 100 digital oscilloscope then acquired the current and voltage traces as a function of time, with the low potential side of the sample capacitor being connected to the ground via a 300 Ω shunt. The applied field patterns consist of five zones with distinct amplitudes at a fixed frequency, as described earlier [22]. With a low repetition rate that corresponds to a duty cycle of < 10 %, the field pattern of only several milliseconds duration is applied 5000 times to improve the signal-to-noise ratio by averaging. Each zone spans multiple wave periods, and dielectric properties are calculated for each period separately, thus leading to time-resolved permittivity data.

## III. RESULTS

Based on the discontinuity of the dielectric constant at the isotropic to nematic transition, the present date place $T_{N/I}$ close to 308 K, consistent with the more accurate value of 35.1°C reported previously [9]. The dc-conductivity of the 5CB samples ranged from $2\times10^{-10}$ S cm$^{-1}$ at 280 K to $2\times10^{-9}$ S cm$^{-1}$ at 315 K, indicating that the dielectric results of interest are not affected by impurity ions. Dielectric constant data for 5CB above and below $T_{N/I}$ are shown in Fig. 1, with the literature data representing homeotropically and homogeneously aligned samples, leading to the dielectric constants $\varepsilon_{||}$ and $\varepsilon_{\perp}$, respectively. The $\varepsilon_s(T)$ data clearly reveal both the nematic to isotropic transition at $T_{N/I}$ and the dielectric anisotropy for temperatures below $T_{N/I}$. The results in Fig. 1 obtained from the present experiments have been recorded at peak electric fields below about $E_0 = 10$ V cm$^{-1}$, in order to suppress field induced homeotropic alignment. Even though we have avoided deliberate alignment, the permittivity does not match the level of $\langle\varepsilon\rangle$ expected for the LC with no preferred orientation of its nematic domains on the basis of mean-field approaches. As is well documented in the literature [9], the critical behavior of 5CB near $T_{N/I}$ modifies this expectation. Instead of $\langle\varepsilon\rangle$ determined via Eq. (1), we find permittivity values near $\varepsilon_\perp$, indicative of a prevalence of homogeneous alignment for both cases: the sample between parallel titanium disks with 100 μm separation and within an NMR tube with 5 mm outer diameter. The agreement found for these two different sample dimensions suggests that geometric confinement or the effect of thin layers is not a relevant factor regarding these results, which is not a trivial finding for liquid crystals.

For the other extreme of field amplitudes, we have applied peak voltages up to 200 V to a sample that is 9.2 μm thin, which leads to electric fields as high as $E_{\max} = 220$ kV cm$^{-1}$ (= 22 MV m$^{-1}$). At a fixed frequency of $\nu = 8$ kHz, the voltage is applied using five distinct zones, each one with a constant peak voltage $V_0$, as indicated in Fig. 2(a). As shown in Fig. 2(b), the response of nematic 5CB at $T = 295$ K to the first field step from $E_0 = 0$ to 22 kV cm$^{-1}$ is a change from $\varepsilon' \leq 11.9$ to $\varepsilon' = 14.95$. Note that even for the average over 5000 field cycles indicated in Fig. 2(a), this initial low field value of $\varepsilon'$ is close to the orientational average $\langle\varepsilon\rangle$. The subsequent larger field steps lead to much smaller increases in $\varepsilon'$. A common metric for the sensitivity of the dielectric constant to the electric field is the value of the nonlinear dieletric effect (NDE), more recently also referred to as Piekara factor $a$ [23,24], which is defined as

$$a = \frac{\varepsilon_E - \varepsilon}{E^2} = \frac{\Delta\varepsilon_E}{E^2}, \tag{2}$$

where $\varepsilon_E$ is the static dielectric constant observed at a high field $E$, and $\varepsilon = \varepsilon_{E\to 0}$ is its low field limit counterpart. From a sequence of high field data, the Piekara factor can also be determined via $a = \partial\varepsilon_E/\partial E^2$ [22]. Regarding nematic 5CB, from the change $\Delta\varepsilon_E \geq 3.05$ for the first field step from 0 to 20 V (first zone in Fig. 2) we obtain a Piekara factor $a = +6.5\times10^{-13}$ m$^2$ V$^{-2}$. This compares to the much smaller value of $a = +7.4\times10^{-17}$ m$^2$ V$^{-2}$ derived from subsequent zones in Fig. 2, where nematic 5CB is subject to fields in excess of 22 kV cm$^{-1}$.

Interestingly, the Piekara factor derived from the data in Fig. 2 changes by a factor of about $10^4$ as a matter of the field magnitude. One consequence of this drastic change in $a$ is that $\varepsilon_E$ of nematic 5CB does not follow the expected quadratic field dependence. Thus, a sample for which an alignment of nematic domains has been erased is extremely field sensitive, until the field reaches a level that leads to considerable homeotropic alignment. In that field-induced homeotropic state, its field sensitivity is reduced to a value similar to that of the isotropic state at $T = 310$ K, where $a = +4.0\times10^{-17}$ m$^2$ V$^{-2}$. Another feature of the data of Fig. 2 is that the response of the nematic 5CB to the first field step is slow compared with that to the subsequent field changes, while the isotropic state does not display a similar behavior. According to the data of Fig. 1, the high fields applied to 5CB at $T = 295$ K are expected to give rise to $\varepsilon'$ values as high as $\varepsilon_{\|} = 18$. That this level is not quite reached could also be a matter of the slow development of complete alignment, which may not reach steady state within the 8 ms of applying a field in the experiment of Fig. 2.

The following addresses the question of how strong a field is required for a sample with permittivity near the orientational average $\langle\varepsilon\rangle$ to reach the value of $\varepsilon_{\|}$, and to what extent that resulting alignment is reversible when the field is removed. These experiments are performed at $T = 280$ K, i.e., below the melting temperature of the crystal and thus in the slightly supercooled nematic state of 5CB [5]. Fig. 3 shows the effect of applying ac voltages with a stepwise increasing peak voltage in the range 70 mV $\leq V_0 \leq$ 41 V, *cf.* Fig. 3(a). Each high voltage segment lasts about 500 s, with the duration of the intermittent low-voltage being three times longer. The $\varepsilon'$ values in Fig. 3(b) reveal that the permittivity saturates near $\varepsilon' = 20$ for voltages around $V_0 = 20$ V applied across a 50 μm thick sample, equivalent to $E_0 = 4$ kV cm$^{-1}$. As the values of $\varepsilon'$ approach saturation levels, the low field value of $\varepsilon' \approx 12$ is not entirely recovered when the field amplitude is reduced back to $V_0 = 70$ mV. Also note that the low-field steady states have lost the memory of the initial homogeneously aligned state featuring $\varepsilon_{\perp} \approx 6$. The analogous measurement with high dc bias fields in the 10 mV $\leq V_{DC} \leq$ 10 V range is shown in Fig. 4, again with 500 s long applications of the dc bias field, but in this case nine times longer segments with only a small $V_0 = 100$ mV ac field applied. In the dc bias field case, a lower field saturates $\varepsilon'$, and the reduction of $\varepsilon'$ after removing the dc field is rather slow.

Similar to the results of Fig. 3, the data in Fig. 5 shows $\varepsilon'$ versus ac voltage on a logarithmic scale for the nematic 5CB at $T = 280$ K. In this case, it can be observed that the change in $\varepsilon'$ for voltages up to $V_0 = 4.1$ V, i.e., just below the onset of saturation, is completely reversible on lowering the voltage back to below 100 mV, *cf.* Fig. 5(a). By contrast, increasing the ac voltage to $V_0 = 41$ V results in $\varepsilon'$ not fully recovering the level of $\varepsilon' = 12$ observed for the low fields at the start of this experiment, see Fig. 5(b). From the open symbols in Fig. 5(b), it can also be seen that only for intermediate levels of $\varepsilon'$, the final permittivity value is not yet established in the first of 100 data points recorded at each voltage. The effect of temperature on such $\varepsilon'$ versus $V_0$ curves is shown in Fig. 6, suggesting that the main impact of temperature is to modify the saturation level of $\varepsilon'$ at high fields. The lines included in Fig. 6 are empirical fits using the relation

$$\varepsilon_{\mathrm{E}}(V_0) = \varepsilon_{\mathrm{lo}} + \frac{\varepsilon_{\mathrm{hi}} - \varepsilon_{\mathrm{lo}}}{1 + \gamma V_0^{-1.74}}, \tag{3}$$

where $\varepsilon_{\mathrm{lo}}$ and $\varepsilon_{\mathrm{hi}}$ represent the level of $\varepsilon_{\mathrm{E}}(V_0)$ in the limits of low and high fields, respectively. The value of $\varepsilon_{\mathrm{lo}}$ shows no systematic dependence on temperature, whereas $\varepsilon_{\mathrm{hi}}$ decreases significantly as the temperature is increased, approximately following $\varepsilon_{\|}$ of Fig. 1. The fit parameter $\gamma$ also changes with $T$ in a systematic fashion, from 3.1 at $T = 280$ K to 1.3 at $T = 306$ K. For the higher temperatures, this implies that a somewhat smaller field is required to obtain a certain ratio $\varepsilon_{\mathrm{E}}/\varepsilon_{\mathrm{hi}}$. For all temperatures $T < T_{\mathrm{N/I}}$, the level $\varepsilon_{\mathrm{E}}(V_0)$ reaches its high field plateau value ($\approx \varepsilon_{\|}$) at $V_0 = 41$ V, equivalent to a field of $E_0 = 8.2$ kV cm$^{-1}$, indicative of a sample that is completely aligned.

In order to observe the field effect with high time-resolution, the sample is exposed to 64 periods of a high field after a long zero-field duration, repeated 5000 times for signal averaging. The initial part (0 - 8 ms) of this field induced rise of $\varepsilon'$ is depicted in Fig. 7 for peak voltages in the range 15 V $\leq V_0 \leq$ 100 V (3 kV cm$^{-1}$ $\leq E_0 \leq$ 20 kV cm$^{-1}$). These results reveal that the ac field magnitude has a considerable influence on the rate at which $\varepsilon'$ increases with time. The lines in Fig. 7(a) are exponential fits to the data, $\left(\varepsilon'(t) - \varepsilon'(0)\right) \propto \exp(-t/\tau)$, with the time constants $\tau$ versus peak voltage $V_0$ shown in Fig. 7(b). The limiting values $\varepsilon'(0) = 10.72 \pm 0.13$ and $\varepsilon'(\infty) = 12.57 \pm 0.06$ are practically field invariant at these field strengths, consistent with the data of Fig. 6. The high sensitivity of $\tau$ to the magnitude of the field emphasizes the pronounced nonlinear dielectric behavior of unaligned 5CB. By comparison to this field effect, the dependence of this time constant on temperature for nematic 5CB is weaker, as shown in Fig. 7(c).

Finally, we demonstrate that the behavior observed for 5CB is not common to all liquid crystals. To this end, itraconazole is subjected to a sequence of ac fields with amplitudes reaching

$E_0 = 50$ V / 9.2 μm = 54 kV cm$^{-1}$, analogous to the experiment of Fig. 2. The data in Fig. 8 show a very small nonlinear effect with a Piekara factor of $a \approx +1\times10^{-16}$ V$^2$ m$^{-2}$, which is about the same for the nematic and isotropic state. In particular, there is no enhanced field sensitivity for nematic itraconazole at low fields, which contrasts the behavior of 5CB qualitatively, *cf.* Fig. 2.

## IV. DISCUSSION

According to the literature on 5CB, the dielectric properties of the homogeneously and the homeotropically aligned nematic phase as well as those of the isotropic material are well documented [4,5,6,8,10,11]. Here, we focus on the effect of electric fields on nematic 5CB that has been prepared into an initial state with little or no macroscopic alignment of the nematic domains. In particular, we address the question of how small a field needs to be in order to leave the sample in a state of no or little preferred orientation of the nematic domains. This is akin to the question of the regimes of linear response in the various states of 5CB, i.e., the field ranges within which the permittivity is field invariant.

Based on the results of this work presented in Fig. 1, avoiding exposure to peak electric fields in excess of $E_0 = 10$ V cm$^{-1}$ leaves the sample homogeneously aligned with $\varepsilon_s \approx \varepsilon_\perp$. A typical dielectric experiment applies 1 $V_{\mathrm{rms}}$ across a 50 μm thick sample, equivalent to a peak field of $E_0 \approx 300$ V cm$^{-1}$. We observe that after nematic 5CB has been subjected to a field of such magnitude, its low field permittivity settles near values in the range $11 \le \varepsilon_s \le 12$, i.e., just above the $\langle\varepsilon\rangle \approx 10.5$ level and still considerably below $\varepsilon_\parallel$, *cf.* Fig. 1. These states with $\varepsilon_s \approx \langle\varepsilon\rangle$ and thus very little alignment preference can be observed as initial ($t \to 0$) or low field ($E_0 \to 0$) cases in Fig. 2 through Fig. 7. The solid interfaces at the sample boundary (titanium or silica glass surface) appear not to be responsible for the homogeneous alignment seen in Fig. 1 (solid symbols), because temporarily applying a moderate field leaves the system with $\varepsilon \approx \langle\varepsilon\rangle$ instead of the orientation reverting back to yield $\varepsilon \approx \varepsilon_\perp$. A likely cause for these $\varepsilon \approx \varepsilon_\perp$ situations of as-prepared samples is alignment induced by the flow process during sample loading [25]. Consistent with this interpretation, the original alignment by capillary flow is erased by the subsequent field-induced domain reorientation, and the new steady state at zero field has no memory of the previous homogeneous alignment.

In this context it is interesting to note that such a field induced change from $\varepsilon_\perp$ to $\langle\varepsilon\rangle$ takes the system from a macroscopically well aligned to a less ordered state, thus increasing the entropy $S$ with electric field $E$. According to thermodynamics, the field induced entropy change $\Delta S_\mathrm{E}$ is given by [26]

$$\Delta S_\mathrm{E} = \upsilon \frac{\varepsilon_0}{2}\left(\frac{\partial \varepsilon_\mathrm{s}}{\partial T}\right) E^2 \,, \tag{4}$$

where $\upsilon$ is the molar volume, $\varepsilon_0$ the permittivity of vacuum, and the derivative $(\partial\varepsilon_\mathrm{s}/\partial T)$ is taken at constant volume. Therefore, an increase of $S$ with $E$ requires the unusual situation of a positive slope, $\partial\varepsilon_\mathrm{s}/\partial T > 0$. For $\varepsilon_\perp(T)$ just below $T_\mathrm{N/I}$, this requirement is indeed fulfilled, *cf.* Fig. 1. For non-LC type materials such as simple molecular liquids, $\partial\varepsilon_\mathrm{s}/\partial T$ is usually negative, consistent with high fields leading to a reduction in entropy in most cases [27].

As mentioned above, the temporary application of a moderate field can produce nematic 5CB samples with little to no preferential alignment, as observed repeatedly via $\varepsilon \approx \langle\varepsilon\rangle$. The data of Fig. 2 indicate that this mostly unaligned state is much more susceptible to field induced changes of permittivity ($a = +6.5\times10^{-13}$ m$^2$ V$^{-2}$) relative to the more aligned state with a Piekara factor ($a = +7.4\times10^{-17}$ m$^2$ V$^{-2}$) that is smaller by a factor of $10^4$. However, the field associated with the initial 20 V step in Fig. 2 is about twice as high as the highest field applied in the experiment leading to Fig. 3, and thus not representative of the nonlinear behavior in the limit of small fields. According to Fig. 6, temperature has little impact on the level of the electric field required to induce a certain degree of alignment. Naturally, however, $\varepsilon_\mathrm{s}$ of the completely aligned sample will follow the temperature dependent $\varepsilon_\parallel(T)$, *cf.* Fig. 1.

A more detailed scrutiny of the field effect of Fig. 3 (and similarly of Fig. 4) reveals that the quadratic field dependence expected for defining a Piekara factor is limited to fields corresponding to $V_0 < 0.5$ V across 50 μm. Analyzing the data within this range yields a low-field ($E_0 < 0.1$ kV cm$^{-1}$) Piekara factor of $a = +5\times10^{-9}$ m$^2$ V$^{-2}$, about $10^8$ times higher than the high-field (22 kV cm$^{-1}$ $\leq E_0 \leq$ 220 kV cm$^{-1}$) limit of $a$ observed in Fig. 2. On the basis of this high value of $a = \Delta\varepsilon_\mathrm{E}/E^2$ and assuming that a relative deviation of permittivity of $\Delta\varepsilon_\mathrm{E}/\varepsilon \geq 0.1\%$ may be considered a sign of nonlinearity, the linear regime of unaligned nematic 5CB is limited to voltages of about 50 mV$_\mathrm{rms}$ across a 50 μm sample, i.e., to fields of 10 V cm$^{-1}$. Accordingly, a 10% rise in permittivity is expected already for voltages of 500 $\text{mV}_{\text{rms}}$ for a 50 μm sample. Therefore, contrary to expectation [28], a typical dielectric relaxation experiment does not necessarily observe the behavior associated with the low field limit. For aligned samples, the regime of linear response extends to significantly higher fields.

In the absence of considerable structural changes, i.e., for simple molecular liquids, dielectric saturation is the most common nonlinear dielectric effect (NDE) [29,30]. The signature of saturation is a reduction of the dielectric constant at high electric fields, often associated with Piekara factors of order $a \approx -10^{-16}$ m$^2$ V$^{-2}$ [31]. The opposite NDE with $a > 0$ is associated with a field induced rise of the dielectric constant and is referred to as 'chemical effect' [32]. This latter NDE is found for 5CB in both the isotropic state and in the highly aligned nematic state, both with positive values near $a = +6\times10^{-17}$ m$^2$ V$^{-2}$. A likely source of this chemical effect is the preference of 5CB molecules as well as domains to arrange in mutually antiparallel configurations, as revealed by the low (macroscopically averaged) Kirkwood correlation factor [26], reported for 5CB as $g_{\text{K}} = 0.53$ at $T = T_{\text{N/I}}$ [16]. The high Piekara factor $a$ in the nematic state with little alignment of the domains implies that $\varepsilon_{\text{s}}$ and thus $g_{\text{K}}$ are very sensitive to an electric field, since the dipole density is approximately field invariant. High electric fields are known to shift the equilibrium constant of coexisting species of different polarities towards higher $g_{\text{K}}$ values, thus increasing the dielectric constant [33,34]. In the present case, species with different polarities are the nematic domains with distinct alignments relative to the field, perpendicular or parallel. Furthermore, the fact that the value of $a$ is very large only in the unaligned nematic state suggest that the nematic domains have large dipole moments, i.e., $g_{\text{K}}$ is high within each domain, but neighboring domains prefer antiparallel configurations in the absence of a significant external field [35]. As a crude approximation for a given temperature, the value of the static dielectric constant in the range $\varepsilon_{\perp} \le \varepsilon_{\text{s}} \le \varepsilon_{||}$ reflects the volume fraction of parallel and perpendicular domain orientations. Note, however, that the state with $\varepsilon_{\text{s}} = \varepsilon_{||}$ is not the equivalent of saturated orientation with $\langle\cos\theta\rangle \approx 1$, as we observe $a > 0$ and $\varepsilon_{||} >> \varepsilon_{\infty}$ where $\varepsilon_{\text{s}}$ has reached its high field values.

As can be seen from Fig. 3, Fig. 4, and Fig. 5, the field induced alignment is completely reversible upon removing the field only for moderate fields. From all three figures one can conclude consistently that $\varepsilon_{\text{s}}$ recovers the low field value near 11.8 after fields corresponding to $V_0 < 5$ V across 50 μm, i.e., $E_0 < 1.0$ kV cm$^{-1}$, have been applied. For higher fields, $\varepsilon_{\text{s}}$ settles closer to 13 after the field has been reduced/removed, and for dc-fields this relaxation takes longer relative to the ac field cases. The higher fields may lead to larger oriented domains which can stabilize themselves, thus giving rise to residual homeotropic orientation even after the field has been removed. As can be seen from the strong field dependence of the $\varepsilon_s(t)$ curves in Fig. 7, the change of $\varepsilon_s$ with field is not instantaneous, and thus the duration of applying a certain field amplitude will be a factor in the alignment and the persistence time of nematic domains. Within this 3 to 20 kV cm$^{-1}$ field range of Fig. 7, the observed time constants associated with the system responding to a change in field magnitude range from 0.1 to 10 ms at $T = 295$ K. Therefore, this process is slow compared with the (linear regime) polarization response time, which is characterized by a dielectric loss peak positioned at $\nu_{\max} > 2$ MHz for temperatures above 285 K [5], equivalent to time constants less than 80 ns. It is well established that ac and dc electric fields induce pattern formation on 10 to 100 μm length scales [14,36], and time scales of milliseconds have been reported for domain pattern appearance and disappearance [35]. Therefore, changes in size and/or structure of nematic domains are likely a factor in the time required for the system to establish a steady state value of $\varepsilon_s$, which is analogous to physical aging and structural recovery [37,38].

Finally, we compare the case of 5CB with a different LC, itraconazole (ITZ), which shows a nematic to isotropic transition at $T_{N/I} = 363$ K [39]. Whether the ITZ mesophase at $T < T_{N/I}$ is a genuine nematic structure or nematic-like is a matter of debate [40,41]. ITZ and other LCs of the conazole family have a reduced propensity to ordering relative to 5CB, likely due to the more complex molecular structure of the conazoles. As a result, fast cooling can reduce or eliminate the nematic to smectic ordering [42,43]. Moreover, the dielectric relaxation time at a temperature just below $T_{N/I}$ of ITZ is 20 μs [39], i.e., a factor of 1000 longer than the corresponding value of 20 ns [5,13] for 5CB. This suggests that any restructuring of nematic domains in ITZ is expected to be a slow process compared with the 5CB case. An additional factor is the dipole moment of ITZ (1.24 D [39]), which is much smaller than that of 5CB (3.7 - 4.8 D [15,16]) and has considerable contributions perpendicular to the molecule's long axis. A small molecular dipole moment and the lack of significant dipole correlations via large ordered domains strongly reduce the interaction of ITZ with an external electric field. As a result, field induced ordering in the nematic state similar to the 5CB case could not be observed, and the only nonlinear effect is the slight enhancement of

$\varepsilon_s$ with field, *cf.* Fig. 8, and its magnitude is characterized by $a = +1\times10^{-16}$ m$^2$ V$^{-2}$. For ITZ, the nonlinear behavior in the nematic phase ($T = 360$ K) is practically identical to that in the isotropic state ($T = 364$ K), and both values of $a$ compare with the high-field 'chemical effect' of 5CB.

## V. SUMMARY AND CONCLUSIONS

We have managed to prepare samples of 5CB with minimal anisotropy regarding the orientation of nematic domains, as judged by the dielectric constant being close to the value, $\langle\varepsilon\rangle = (\varepsilon_{\|} + 2\varepsilon_{\perp})/3$, expected in the absence of a preferred orientation. It is found that the static permittivity, $\varepsilon_s$, remains field invariant only for electric fields as small as 10 V cm$^{-1}$, implying that a voltage of 50 mV across as 50 μm thick sample is already at the threshold of nonlinear dielectric behavior. Higher fields impose a net alignment on the nematic domains, increasing the permittivity from $\langle\varepsilon\rangle \approx 11$ towards $\varepsilon_{\|} \approx 18$ (at $T = 295$ K). This alignment and concomitant change in the dielectric constant is reversible upon removing the field, as long as the sample has not been exposed to fields in excess of 1 kV cm$^{-1}$ or not longer than several milliseconds.

The sensitivity of the dielectric constant to the electric field can be quantified by the Piekara factor $a = \Delta\varepsilon_E/E^2$. For homeotropically aligned as well as for isotropic 5CB, positive values around $a = +7\times10^{-17}$ m$^2$ V$^{-2}$ were observed. For unaligned 5CB at $T < T_{N/I}$, however, the Piekara factor is about $10^8$ times higher, $a = +5\times10^{-9}$ m$^2$ V$^{-2}$, if determined in the limit of low fields where alignment effects remain negligible. For such situations, the Piekara slope, $\partial\varepsilon_E/\partial E^2$, appears to be a superior metric over the standard Piekara factor $\varepsilon_E/E^2$, as the quadratic field dependence is not obeyed across the entire experimental range of electric fields.

The Kirkwood correlation factor of 5CB near $T_{N/I}$ has been reported to be $g_K = 0.53$ [16], and because $\langle\varepsilon\rangle$ ($T < T_{N/I}$) is close to the value of $\varepsilon_{iso}$ ($T > T_{N/I}$), the macroscopically averaged value of $g_K$ is practically the same in the isotropic and in the unaligned nematic state. In the isotropic state, $g_K = 0.53$ implies that neighboring molecules prefer an antiparallel alignment. For $T < T_{N/I}$, however, the orientational correlation within a nematic domain must be high to explain the strong interaction with external electric fields via a large effective dipole moment of each domain with ferroelectric order. Still, the macroscopically averaged $g_K$ remains small due to the antiparallel alignment preference of nematic domains, unless the system is macroscopically aligned. The high Piekara factor of unaligned nematic 5CB is an indication of a Kirkwood correlation factor that is very sensitive to the magnitude of the electric field. Such a situation requires a large molecular dipole moment parallel to the long molecular axis and large nematic domains with near ferroelectric order, explaining the absence of similarly strong field effects in LCs such as itraconazole.

## DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## ACKNOWLEDGMENTS

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## FIGURES

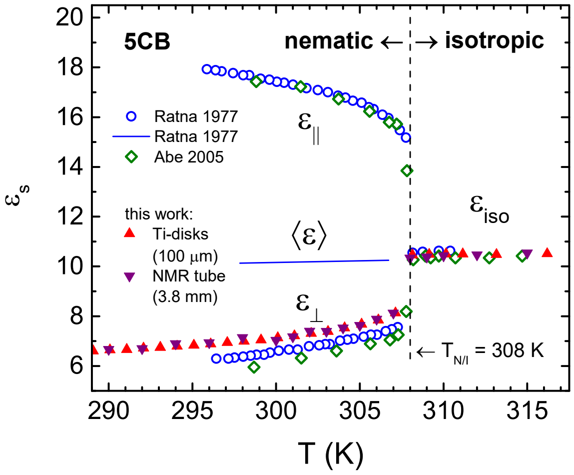

**FIG. 1.** Static dielectric constant, $\varepsilon_S$, versus temperature for 5CB in the nematic ($T < 308$ K) and the isotropic ($T > 308$ K) phase. Open symbols are data taken from Ratna *et al.* [4] and Abe *et al.* [11], both for pre-oriented samples. The line represents the orientational average, $(\varepsilon_{||} + 2\varepsilon_{\perp})/3$, based on the data from Ratna *et al*. [4]. Solid symbols are results from this work using peak fields below $E_0 = 20$ V cm$^{-1}$, with no deliberate orientation imposed on the sample. Triangles up are for measurements using titanium disk electrodes with 100 μm PTFE spacer, and triangles down are for data taken with the sample in a 5 mm ∅ NMR tube which is hugged by outer electrodes.

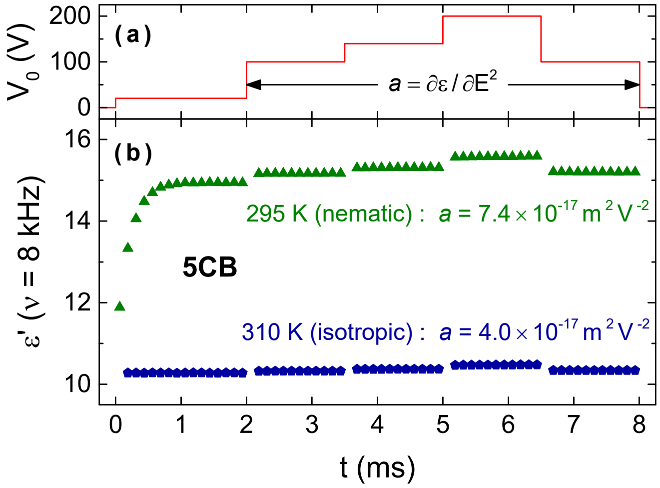

**FIG. 2.** (a) Peak voltage of the ac electric field applied to 5CB in order to obtain the field dependent permittivity, with the field being constant within each of the five zones. (b) Permittivity $\varepsilon'$ of a $d = 9.2$ μm sample of 5CB measured at $\nu = 8$ kHz for the sequence of field amplitudes shown in (a) for two temperatures. Each symbol corresponds to a single period. The Piekara factors, $a$, are determined from the final four zones, see arrows in (a).

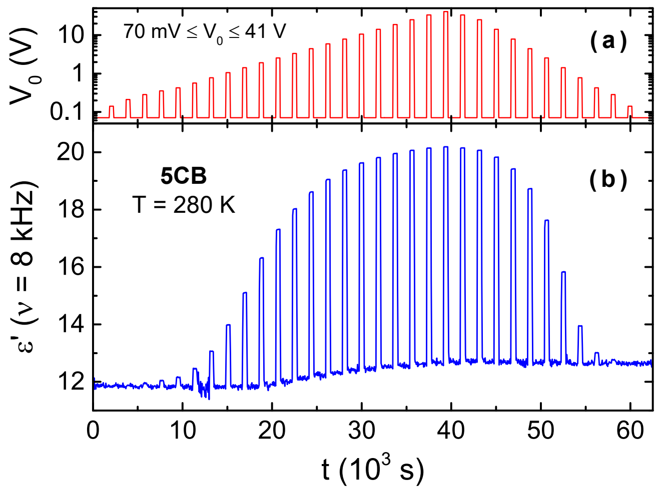

**FIG. 3.** (a) Time sequence of the ac field with the peak voltage $V_0$ rising exponentially from 70 mV to 41 V and then decreasing again. The low voltage (70 mV) segments have three times the duration of the high voltage ones. (b) Permittivity $\varepsilon'$ of a $d$ = 50 μm sample of 5CB measured at $\nu$ = 8 kHz for the sequence of field amplitudes shown in (a) for $T$ = 280 K.

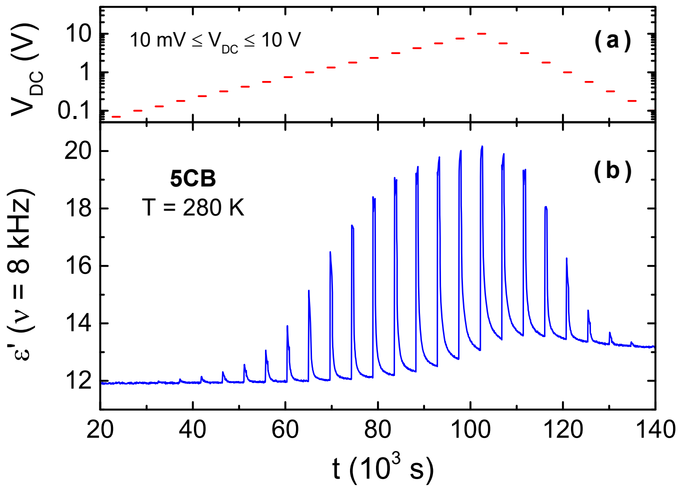

**FIG. 4.** (a) Time sequence of the dc field with voltage $V_{DC}$ rising exponentially from 10 mV to 10 V and then decreasing again. The low voltage segments have nine times the duration of the high voltage ones. Thus, the lengths of the bars do no reflect the time duration of the high voltage segments. (b) Permittivity $\varepsilon'$ of a $d$ = 50 μm sample of 5CB measured at $\nu$ = 8 kHz and $V_0$ = 100 mV for the sequence of field amplitudes shown in (a) for $T$ = 280 K.

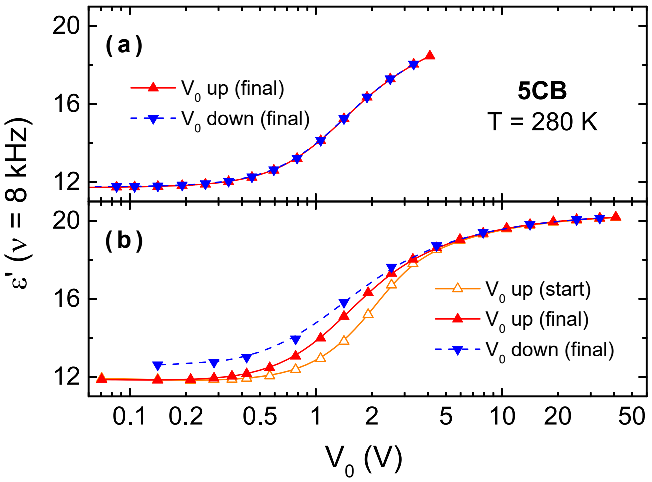

**FIG. 5.** Permittivity $\varepsilon'$ of a $d$ = 50 μm sample of 5CB measured at $\nu$ = 8 kHz versus the peak value $V_0$ of the ac voltage. All data are taken at a temperature $T$ = 280 K. In each case, the voltage is increased in exponential steps and then decreased, and 100 measurements are taken at each voltage. The first of the 100 points is indicated as 'start', the average over the last 10 points is labeled as 'final'. (a) Voltage sequence ranging from 7 mV to 4.1 V, but showing only the $V_0$ > 60 mV results. (b) Same sample subject to a voltages between 70 mV and 41 V.

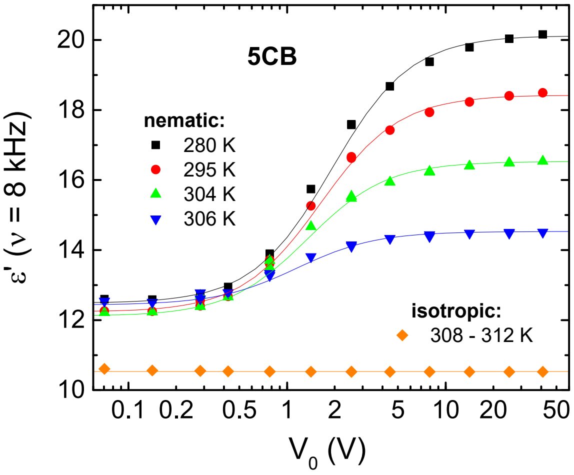

**FIG. 6.** Permittivity $\varepsilon'$ of a $d$ = 50 μm sample of 5CB measured at $\nu$ = 8 kHz versus the peak value $V_0$ of the ac voltage. Different curves are for different temperatures as indicated. The lowest curve with no discernable voltage dependence reflects all data taken for the isotropic state between 308 and 312 K.

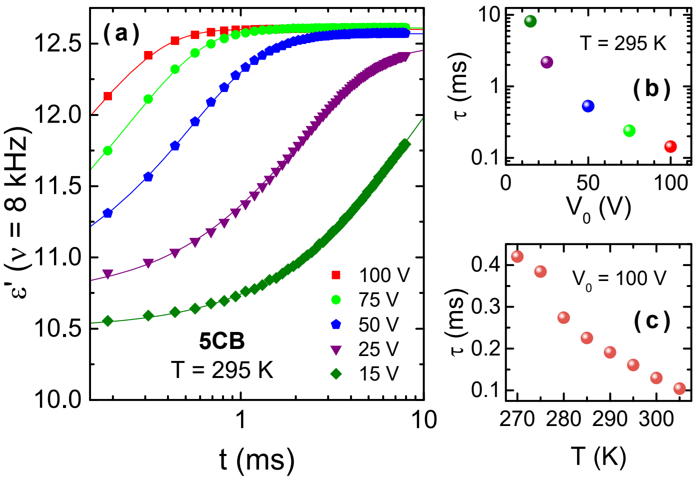

**FIG. 7.** (a) Time dependence of the rise in permittivity ($\varepsilon'$ at $\nu = 8$ kHz) for a $d = 50$ μm sample of 5CB at 295 K. Peak voltages $V_0$ of five different amplitudes have been applied for $t > 0$, and the values of $\varepsilon'$ have been determined for each of the 64 periods spanning a total of 8 ms. Lines are exponential fits. (b) Time constants of the exponential fits of (a) versus peak voltage $V_0$ at a fixed temperature $T = 295$ K. (c) Time constant of exponential fits to the rise of $\varepsilon'(t)$ versus temperature $T$ at a fixed peak voltage $V_0 = 100$ V.

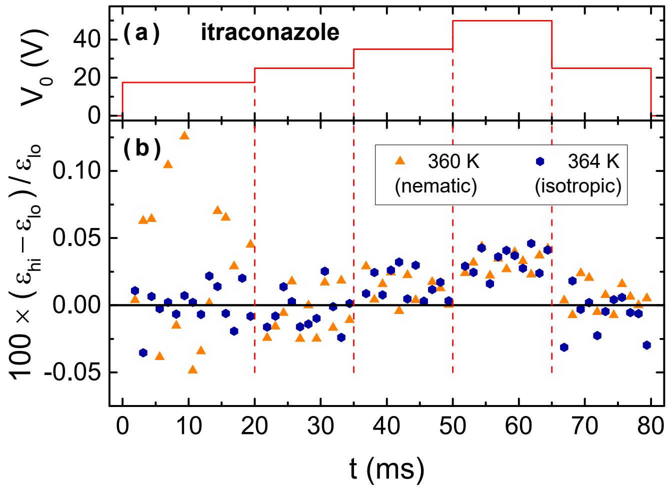

**FIG. 8.** (a) Peak voltage of the ac electric field applied to itraconazole (ITRC) in order to obtain the field dependent permittivity, with the field being constant within each of the five zones. (b) Field induced relative change of permittivity, $(\varepsilon_{\mathrm{hi}} - \varepsilon_{\mathrm{lo}})/\varepsilon_{\mathrm{lo}}$, of a $d = 9.2$ μm sample of ITRC measured at $\nu = 800$ Hz for the sequence of field amplitudes shown in (a) for two temperatures. Each symbol corresponds to a single period. The Piekara factors, $a$, determined from the final four zones are approximately $1\times10^{-16}$ $\mathrm{m}^2$ $\mathrm{V}^{-2}$ for both temperatures.

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