Constraining the value of the dielectric constant of the ferroelectric nematic phase

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Ferroelectric nematic liquid crystals are currently being subject to a plethora of investigations since they are of great fundamental interest and could potentially foster promising applications. However, many basic aspects are still poorly understood, among which the problem of the dielectric constant stands out. Ferroelectric nematics have previously been reported to exhibit giant dielectric constants whose value depends on the thickness of the measurement cell, claims that have recently been shown to be the result of an incorrect interpretation of the experimental data. The intrinsic permittivity of these materials has not been determined yet. In this work, we tackle this problem by modeling the dielectric response of the liquid crystal filled cell through an equivalent circuit proposed by Clark *et al.* [Phys. Rev. Res. **6**, 013195 (2024)] accounting for polarization reorientation and the effect of insulating interfacial layers. We arrive at the conclusion that the perpendicular component of the permittivity $\varepsilon_\perp$ is of the order of 10 in the prototypical ferroelectric nematogen DIO, while the parallel component $\varepsilon_\parallel$ is of the order of 150. In this way, the dielectric tensor of DIO has been fully determined.

Materials with high permittivity have always garnered substantial interest due to their potential applications as capacitive elements in electronics, energy storage, sensors, actuators, etc. A high dielectric response is expected near the paraelectric-ferroelectric transition temperature in traditional ferroelectric materials [1]. However, since a few decades ago, materials with permittivity values exceeding 10^3 started to be reported to maintain this so-called "colossal" response over a wide temperature range showing a seemingly relaxational (and Arrhenius-like) behavior. The intrinsic nature of those colossal permittivity (CP) values was soon questioned and finally attributed to extrinsic effects stemming from electrode/sample interfaces or domain boundary effects (see, e.g., [2]). It is interesting to note that this does not hinder their usability in applications and it is still a very active field [3].

The recent discovery of the ferroelectric nematic phase (N_F) has sparked a new research area at the intersection of many disciplines such as soft matter, ferroelectrics, and liquid crystal chemistry and physics. The interest is fueled by its unique fundamental properties and, again, potential impact in applications. Materials in the N_F phase exhibit polar properties comparable to those of solid ferroelectrics, i.e., spontaneous polarization values ranging from 1–6 μC/cm^2 [4–6], large nonlinear optical coefficients [7,8], and also, very interestingly, CP effects [9–12], all with the added advantage of fluidity. The field is now at the stage of studying the origin of these properties, first, to understand the fundamental physics behind them and, second, to be able to design materials with tailored and improved characteristics for applications.

The origin of the CP in N_F materials is a subject of debate. Initially, it was attributed to the high polar ordering of the molecules in the N_F phase [5], and later more specifically

described as collective relaxation phenomena [13]. However, large discrepancies among reported measurements are found in the literature typically spanning two orders of magnitude (10^3–10^5, see, e.g., [5,6,9,11]). This clearly hints at the existence of some nonintrinsic conditions related to the measurements themselves such as the method, sample preparation, confinement conditions, or even sample purity. This motivated a systematic study of the dielectric properties of the two prototypical N_F materials RM734 and DIO by our group as reported in Refs. [14] and [15], respectively. In these works, a dependence of the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ ($\omega = 2\pi f$ is the angular frequency) with the sample thickness in the N_F phase was clearly quantified. Furthermore, we proposed an interpretation of the observed relaxation processes in the entire phase sequence. In the N_F phase, the overwhelmingly dominant relaxation observed in both materials was a low-frequency ($\sim 10^3$ Hz) mode attributed to the collective director orientation fluctuations, known as Goldstone mode.

Clark *et al.* proposed that, if the permittivity is measured in the typical parallel-plate configuration with the material planar aligned so that the polarization **P** lies parallel to the electrode surface (which is the configuration of minimum energy and observed experimentally), the reorientation of the large **P** results in a near perfect cancellation of the applied field in the bulk leading to a very low effective resistance of the LC sample [16]. All the voltage drop occurs at the two electrode interfacial layers acting as capacitors whose thickness is in the range of tens to hundreds of nanometers. What is measured in this picture is a very large capacitance independent of the sample thickness that results in a very large and thickness-dependent permittivity.

Recently, we noticed that suppressing the Goldstone mode through the application of a DC bias field in the N_F phase resulted in strikingly similar dielectric spectra in RM734 [14], DIO [15], and UUQU-4-N [17], regardless of the sample

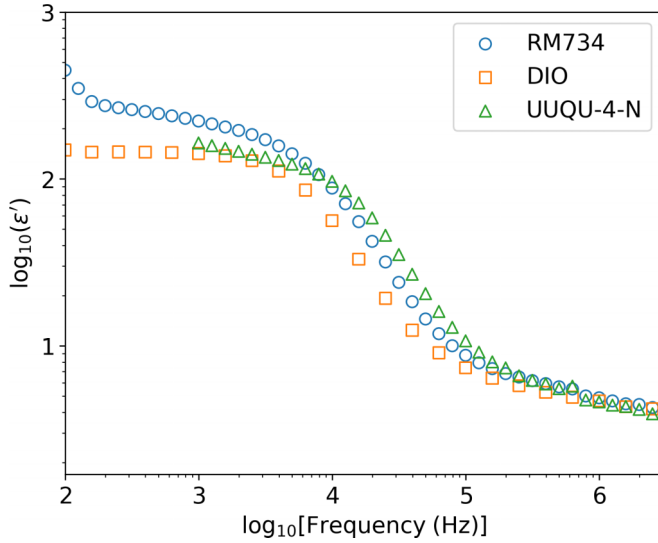*Contact author: aitor.erkorekap@ehu.eus

FIG. 1. Spectrum of the real component of the complex dielectric permittivity of RM734, DIO, and UUQU-4-N in the N_F phase upon suppression of the Goldstone mode. These measurements correspond to 25, 5.1, and 30 μm thick cells with bias fields of 0.32, 1.10, and 0.27 V_{DC}/μm, respectively. Original data from Refs. [14,15,17].
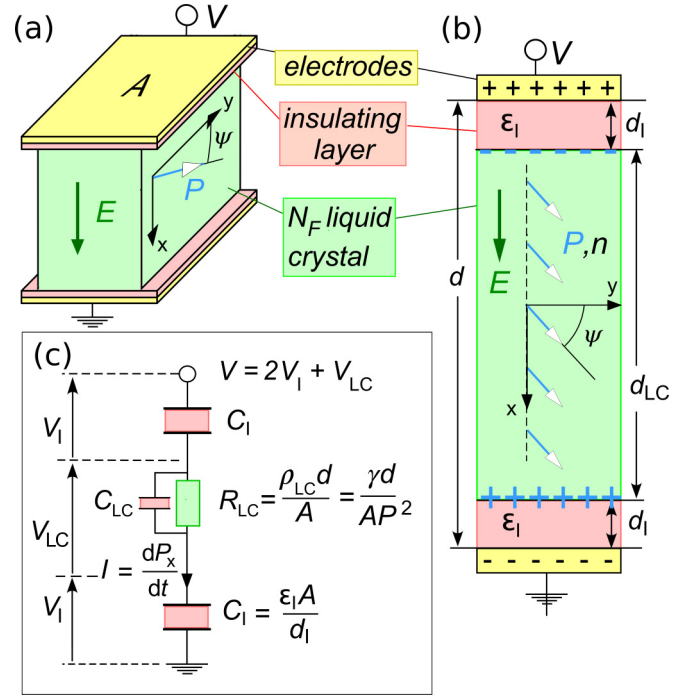

FIG. 2. (a), (b) Sketch of the typical measurement cell used in dielectric spectroscopy experiments. It is a parallel-plate capacitor of area A filled with the N_F material of thickness d_{LC} and bounded by two insulating interfacial layers of thickness d_I at the electrodes. When an electric field **E** is applied across the cell, the polarization vector **P**, which is initially spatially uniform and parallel to the plates, rotates through an angle ψ. This leads to the accumulation of bound charge at the insulating layers. Its low-frequency dielectric response can be modeled by the equivalent circuit shown in (c). Adapted from Ref. [16].

thickness. This can be seen in Fig. 1, where the permittivity of the three materials coalesces to a common value at low frequencies. This is to be expected, since the dipole moments of these molecules are very similar (DFT-calculated values are 11.4 D for RM734 and UUQU-4N, and 10.3 D for DIO). Thus, it follows that measurements under a DC bias field strong enough to suppress polarization reorientation processes provide their actual dielectric spectra. In this case, the parallel component of the permittivity is probed, and a common value of $\varepsilon_\parallel \approx 150$ can be estimated. As it can be seen in Fig. 1, it could be somewhat larger ($\approx$200) for RM734, but one should note that in this material there is an increase in the real part of the permittivity at low frequencies due to electrode polarization effects. These values are compatible with those reported by Vaupoti *et al.* [13] for a RM734 homologue.

However, for a complete characterization of the uniaxial N_F phase, the perpendicular component of the permittivity $\varepsilon_\perp$ is yet to be determined. As explained by Clark *et al.* (see Fig. 2), an externally applied electric field reorients the polarization vector, which is, as explained above, initially spatially homogeneous and parallel to the electrode plates, by an angle ψ (the Goldstone variable) [16]. In their words, this process charges the interfacial insulating layers of thickness d_I that bound the sample in typical measurement cells. These layers can be polyimide layers typically used to align liquid crystal molecules but, in cells with no alignment layers, they can also be liquid crystal molecules which cannot reorient due to surface pinning. The latter is the case in our experiments in which surface agents were not employed. The low-frequency dielectric response of such a cell can then be modeled as two series capacitors C_I associated with the insulating layers at each electrode in series with the LC sample modeled as a resistance R_{LC} in parallel with the capacitance of the liquid crystal C_{LC}. In mathematical form, the complex impedance of

the circuit and its relation with $\varepsilon^*(\omega)$ are

$$Z^*(\omega) = \frac{2}{i\omega C_I} + \frac{1}{i\omega C_{LC} + \frac{1}{R_{LC}}} = \frac{d}{i\omega A \varepsilon_0 \varepsilon^*(\omega)}. \quad (1)$$

The capacitor C_{LC} contains its actual dielectric constant, while the resistance R_{LC} mainly accounts for the transport of bound charge due to the polarization reorientation, the resistivity being $\rho_{LC} = \gamma/P^2$ (γ is the rotational viscosity). Since the N_F phase is highly fluid and exhibits a large spontaneous polarization, both R_{LC} and ρ_{LC} are very low, effectively shorting the LC part of the circuit. In this case, the high-capacitance insulating layers would be measured, giving an apparently large and thickness-dependent dielectric constant. It is important to note that, according to the PCG model, the effective conductivity (and, thus, resistivity) of the LC depends on the angle ψ. Therefore, the model described above is a simplified version of Ref. [16] around $\psi \to 0$. As mentioned earlier, after our comprehensive dielectric study of three ferroelectric nematogens, the PCG mechanism is, in our view, the most feasible explanation for the reported large permittivity values. In fact, Adaka *et al.* have recently verified the PCG model by constructing cells with variable thickness of the insulating layers [18]. We now postulate that, if this is indeed the case, it would be possible to estimate $\varepsilon_\perp$ by fitting the dielectric spectroscopy data for cells with no alignment layers to the

equivalent circuit of Fig. 2, and considering a reasonable value range for d_I. This is because $\varepsilon_I = \varepsilon_{LC} = \varepsilon_\perp$ due to the molecules being pinned parallel to the bounding electrodes.

In order to test this idea, we have used the results of previously reported dielectric spectroscopy experiments performed on DIO [15] in which cells of various thicknesses were employed. In this material, the conductivity and electrode polarization are less prominent than in RM734 [14] for which a more complicated equivalent circuit would be necessary to fit the data, thereby complicating the analysis and obscuring the conclusions to be drawn. We have considered the data for the 14.7, 36, and 57 μm thick cells, excluding the 5.1 μm thick one because it is slightly affected by the cell relaxation at high frequencies. These measurements were done with an oscillator voltage $V_{osc} = 30$ mV$_{rms}$ and no DC bias. We set out to fit the data for all thicknesses simultaneously, and require that the intrinsic material parameters ε_{LC} and ρ_{LC} be the same for all cells. The capacitance of the insulating layers is modeled as $C_I = C_0 df$ [12], where C_0 is the capacitance of the empty cell and d is the sample thickness, allowing $f = \varepsilon_I/d_I$ to change because, although we expect d_I to be similar for all cells, this quantity is determined by complex surface interactions and may slightly vary from cell to cell. First of all, we focused on the imaginary component of the permittivity. Solving for ε'' in Eq. (1), we arrive at the following formula:

$$\varepsilon''(\omega) = \frac{\omega \rho_{LC} \varepsilon_0 d^2 f^2/4}{1 + \omega^2 \rho_{LC}^2 \varepsilon_0^2 (2\varepsilon_{LC} + d\,f)^2/4}, \qquad (2)$$

which we can readily identify with the imaginary permittivity component of a Debye relaxation. Fitting our experimental data to Eq. (2), we obtained $\rho_{LC} = 360\ \Omega$ m, while the fitting process forced $\varepsilon_{LC} \to 0$ independent of its starting value. This does not mean that $\varepsilon_{LC} = 0$ but that R_{LC} is so low (and $1/R_{LC}$ so large) that the $i\omega C_{LC}$ contribution is negligible, in accordance with the PCG model [16]. The fitted values for f are, as expected, similar: 2.2, 2.9, and 2.7 nm^{-1} in order of increasing thickness. To complete the analysis, the real component of the permittivity should also be considered. In this case, neglecting C_{LC} in light of the previous results and connecting a capacitance $C_\infty = C_0 \varepsilon_\infty$ in parallel to the circuit to account for the high-frequency dielectric constant, the complex impedance of the equivalent circuit would be

$$\frac{1}{Z^*(\omega)} = \frac{1}{R_{LC} + \frac{2}{i\omega C_I}} + i\omega C_\infty = i\omega C_0 \varepsilon^*(\omega). \qquad (3)$$

Solving for ε', we get

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{d\,f/2}{1 + \omega^2 \rho_{LC}^2 \varepsilon_0^2 d^2 f^2/4}, \qquad (4)$$

which is the real permittivity component of a Debye relaxation. In this case, $\rho_{LC} = 340\ \Omega$ m and $\varepsilon_\infty = 6$ is obtained, while $f = 2.1, 2.6$, and 2.5 nm^{-1}. These results prove the equivalence of both fits, which can be seen in Fig. 3. One further confirmation of the PCG mechanism can be obtained by comparing the fitted ρ_{LC} to the theoretical estimate. Taking $\gamma \approx 0.25$ Pa s and $P \approx 5$ μC/cm^2 [19], we obtain $\rho_{LC} \approx 10^2\ \Omega$ m, which is of the same order of magnitude as the fitted value. Furthermore, with our experimental conditions, we can check whether assuming that $\psi \to 0$ is reasonable.
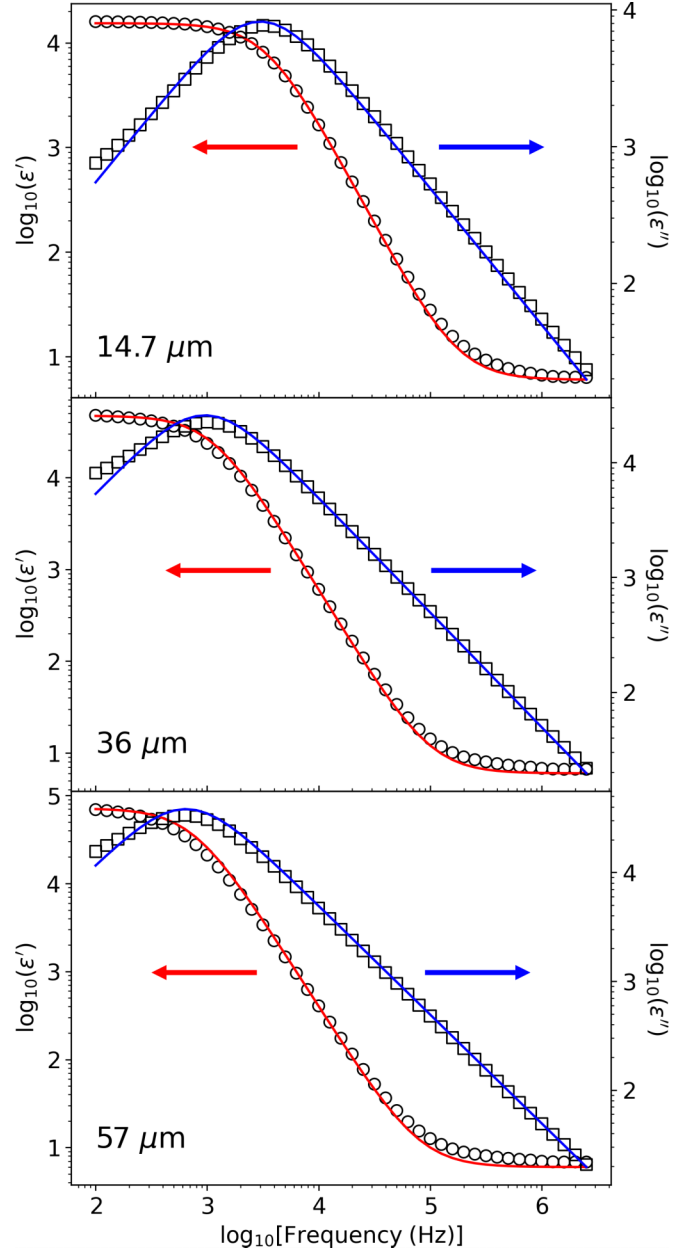

FIG. 3. Spectra of the real and imaginary components of the complex dielectric permittivity of DIO in the N_F phase (60 °C) measured in 14.7, 36, and 57 μm thick cells with their respective fits performed as explained in the text. Original data from Ref. [15].

According to the PCG model, the dependence of ψ on the applied voltage V below V_{sat} is given by the following equation: $\sin \psi(V) = V/V_{sat}$, where $V_{sat} = 2P/\varepsilon_0 f$ is a saturation voltage at which **P** becomes normal to the electrode plates [16]. Taking $P \approx 5$ μC/cm^2, the average fitted value $f = 2.5$ nm^{-1}, and $V = 30$ mV, we obtain $V_{sat} \approx 4.5$ V and, thus, $\psi < 1°$, thereby confirming our assumption.

With this information we can already estimate $\varepsilon_\perp$. The average of f with the obtained values is ~ 2.5 nm^{-1}. Considering a generous range for the insulating layer thickness d_I from 2–3 nm up to 10 nm, the possible values of $\varepsilon_\perp$ would be in the range 6–25. The lower bound would mean that, aside from the Goldstone mode, there is no other underlying relaxation

in the low-frequency range, while a higher value would imply a hidden relaxation process below 10^5–10^6 Hz. The estimated dielectric anisotropy is then $\delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp = 125$–$144$. Thus, the dielectric anisotropy is positive, as expected from the molecular structure of DIO and ferroelectric nematogens in general, and large, due to its large dipole moment.

In this paper, we have once again ruled out the CP values of the N_F phase. In doing so, we have followed the classical definition of permittivity, which does not include the spontaneous polarization, as in solid ferroelectrics. Mathematically, the total polarization in the ith direction is the sum of the spontaneous and induced polarizations, namely $P_{total,i} = P_i + \varepsilon_0(\varepsilon_{ij} - \delta_{ij})E_j$, where δ_{ij} is the Kronecker delta and summation over repeated indices is assumed. However, it could be argued that, since the spontaneous polarization in the N_F phase is reoriented under an applied electric field (torque density $\tau = |\mathbf{P} \times \mathbf{E}|$), a feature unique to fluid ferroelectrics, such a contribution should be allowed to enter into ε. This was indeed the case in ferroelectric SmC* LCs [20]. Following this way of thinking, the permittivity would in fact be very large, but rigorously quantifying it would then be tricky. Leaving out the spontaneous polarization and following our interpretation, on the other hand, allows us to obtain thickness-independent dielectric constants $\varepsilon_\perp$ and $\varepsilon_\parallel$, with $\varepsilon_\parallel > \varepsilon_\perp$, which are in accordance with the typical dipole moments of ferroelectric nematogens. In any case, for practical applications involving polarization switching, the important term is the coupling between the spontaneous polarization and the electric field. Since these materials have a large spontaneous polarization and are also highly fluid, this effect can be greatly exploited. Now that the two independent components of the dielectric tensor in the N_F phase have been estimated, it would be of utmost interest to seek a theoretical model, analogous to Maier-Meier theory [21], that can predict these values from molecular/structural parameters in order to obtain a complete microscopic understanding of the phase. To this end, it is also crucial to maintain ongoing experimental research so as to discriminate between the particular properties of the different compounds and the universal properties of the phase itself. In terms of the method used in this work, it would also be helpful to somehow improve the estimate d_I in order to reduce the lower and upper bounds of $\varepsilon_\perp$.

[1] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (John Wiley & Sons, Nashville, TN, 2004).

[2] P. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus, and A. Loidl, Nonintrinsic origin of the colossal dielectric constants in CaCu$_3$Ti$_4$O$_{12}$, Phys. Rev. B **70**, 172102 (2004).

[3] Y. Wang, W. Jie, C. Yang, X. Wei, and J. Hao, Colossal permittivity materials as superior dielectrics for diverse applications, Adv. Funct. Mater. **29**, 1808118 (2019).

[4] X. Chen, E. Korblova, D. Dong, X. Wei, R. Shao, L. Radzihovsky, M. A. Glaser, J. E. Maclennan, D. Bedrov, D. M. Walba, and N. A. Clark, First-principles experimental demonstration of ferroelectricity in a thermotropic nematic liquid crystal: Polar domains and striking electro-optics, Proc. Natl. Acad. Sci. USA **117**, 14021 (2020).

[5] H. Nishikawa, K. Shiroshita, H. Higuchi, Y. Okumura, Y. Haseba, S.-i. Yamamoto, K. Sago, and H. Kikuchi, A fluid liquid-crystal material with highly polar order, Adv. Mater. **29**, 1702354 (2017).

[6] S. Brown, E. Cruickshank, J. M. D. Storey, C. T. Imrie, D. Pociecha, M. Majewska, A. Makal, and E. Gorecka, Multiple polar and non-polar nematic phases, ChemPhysChem **22**, 2506 (2021).

[7] C. L. Folcia, J. Ortega, R. Vidal, T. Sierra, and J. Etxebarria, The ferroelectric nematic phase: An optimum liquid crystal candidate for nonlinear optics, Liq. Cryst. **49**, 899 (2022).

[8] R. Xia, X. Zhao, J. Li, H. Lei, Y. Song, W. Peng, X. Zhang, S. Aya, and M. Huang, Achieving enhanced second-harmonic generation in ferroelectric nematics by doping dπa chromophores, J. Mater. Chem. C **11**, 10905 (2023).

[9] A. Manabe, M. Bremer, and M. Kraska, Ferroelectric nematic phase at and below room temperature, Liq. Cryst. **48**, 1079 (2021).

[10] R. J. Mandle, N. Sebastián, J. Martinez-Perdiguero, and A. Mertelj, On the molecular origins of the ferroelectric splay nematic phase, Nat. Commun. **12**, 4962 (2021).

[11] J. Li, H. Nishikawa, J. Kougo, J. Zhou, S. Dai, W. Tang, X. Zhao, Y. Hisai, M. Huang, and S. Aya, Development of ferroelectric nematic fluids with giant-ε dielectricity and nonlinear optical properties, Sci. Adv. **7**, eabf5047 (2021).

[12] V. Matko, E. Gorecka, D. Pociecha, J. Matraszek, and N. Vaupoti, Do ferroelectric nematic liquid crystals really have a huge dielectric permittivity? arXiv:2401.16084 [cond-mat.soft].

[13] N. Vaupotič, D. Pociecha, P. Rybak, J. Matraszek, M. epi, J. M. Wolska, and E. Gorecka, Dielectric response of a ferroelectric nematic liquid crystalline phase in thin cells, Liq. Cryst. **50**, 584 (2023).

[14] A. Erkoreka, J. Martinez-Perdiguero, R. J. Mandle, A. Mertelj, and N. Sebastián, Dielectric spectroscopy of a ferroelectric nematic liquid crystal and the effect of the sample thickness, J. Mol. Liq. **387**, 122566 (2023).

[15] A. Erkoreka, A. Mertelj, M. Huang, S. Aya, N. Sebastián, and J. Martinez-Perdiguero, Collective and non-collective molecular dynamics in a ferroelectric nematic liquid crystal studied by broadband dielectric spectroscopy, J. Chem. Phys. **159**, 184502 (2023).

[16] N. A. Clark, X. Chen, J. E. MacLennan, and M. A. Glaser, Dielectric spectroscopy of ferroelectric nematic liquid crystals:

Measuring the capacitance of insulating interfacial layers, Phys. Rev. Res. **6**, 013195 (2024).

[17] A. Erkoreka, N. Sebastián, A. Mertelj, and J. Martinez-Perdiguero, A molecular perspective on the emergence of long-range polar order from an isotropic fluid, J. Mol. Liq. **407**, 125188 (2024).

[18] A. Adaka, M. Rajabi, N. Haputhantrige, S. Sprunt, O. D. Lavrentovich, and A. Jákli, Dielectric properties of a ferroelectric nematic material: Quantitative test of the polarization-capacitance goldstone mode, Phys. Rev. Lett. **133**, 038101 (2024).

[19] X. Chen, Z. Zhu, M. J. Magrini, E. Korblova, C. S. Park, M. A. Glaser, J. E. Maclennan, D. M. Walba, and N. A. Clark, Ideal mixing of paraelectric and ferroelectric nematic phases in liquid crystals of distinct molecular species, Liq. Cryst. **49**, 1531 (2022).

[20] *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhals (Springer, Berlin, Heidelberg, 2003).

[21] W. Maier and G. Meier, Eine einfache theorie der dielektrischen eigenschaften homogen orientierter kristallinflüssiger phasen des nematischen typs, Z. Naturforsch. A **16**, 262 (1961).