

Interpretation of dielectric spectroscopy measurements of ferroelectric nematic liquid crystals

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The magnitude of the relative permittivity of the ferroelectric nematic phase (N_F) has been the subject of lively scientific discussion since the phase was recently discovered. Dielectric spectroscopy measurements (DSMs) give a huge value of relative permittivity, which depends on the cell thickness, but this is argued to result from a misinterpretation of the DSM results. We have conducted DSM using a set of cells differing in thickness of the N_F layer, type of electrodes, and presence/absence of nanoscale-thick surface polymer layers. To model the DSM results, cells are presented by an equivalent electric circuit that includes a capacitor due to the N_F layer with frequency dependent complex relative permittivity, capacitors due to surface layers, and a resistor describing the limited conductivity of electrodes. DSM results for different cells with the same liquid crystal in the N_F phase are semiquantitatively reproduced by the same set of physical parameters if a huge relative permittivity of the N_F , which is even orders of magnitude larger than the measured apparent values, is assumed. We show that the capacitance of surface layers should also be considered in cells with no polymer alignment layer on the electrodes.

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Ferroelectric nematic (N_F) liquid crystalline (LC) phase is a polar phase with the highest possible symmetry ($C_{\infty v}$). Its recent discovery [1,2] immediately attracted wide research interest [3–8]. N_F materials, although fluidic, are characterized by a strong order of dipoles resulting in a large spontaneous electric polarization of the order of 10^{-2} Cm^{-2} [2,9,10], high values of the second-order susceptibility and electro-optic coefficients [11–13], giant flexoelectric effect [14], and potentially phototunable permittivity [15]. These physical properties position ferroelectric nematics as promising candidates for diverse applications and are opening alternative roads to designing photonic structures [13]. Applications became even more promising with the experimental realization of chiral N_F materials [16–19] and synthesis of materials having a N_F phase at room temperature [9,20–22]. Another distinguishing feature of ferroelectric nematics is their remarkably high relative permittivity ($\sim 10^4$), within a frequency range up to the kHz regime [2,10,12,23–27]. This huge relative permittivity is attributed to the ease of thermally activated fluctuations of polarization direction. However, the relative permittivity in the N_F phase appears to be strongly influenced by the thickness of cells and their surface treatment [23–27]. A similar effect is well documented in ferroelectric

smectic-C [28] and orthogonal ferroelectric smectic-A phases [29] and is explained by constraints of polar fluctuations by cell surfaces. However, because in the N_F phase the effect is observed also in very thick cells, where surface interactions are negligible, this raised doubts about the interpretation of dielectric spectroscopy measurements (DSMs) and posed a question on whether these materials are indeed characterized by large relative permittivity. Clark *et al.* suggested [30] that in liquid crystalline materials with very high spontaneous polarization, the large measured values of the relative permittivity are only apparent values, which result from the measured capacitance being misinterpreted as a capacitance of the whole cell, while the capacitance of very thin surface layers of surfactant is measured instead. Namely, the block reorientation of polarization in ac fields renders the N_F layer effectively electrically conductive, which enables charging of very thin surface layers. The N_F layer acts as a resistor with low ohmic resistance, its resistivity ρ_{LC} being dependent on the material rotational viscosity γ and polarization P as $\rho_{LC} = \gamma/P^2$. The relaxation time measured by DSM is that of a series connection of surface capacitors (very thin surface layers) and a low-value resistor (N_F layer); the relaxation mode observed by DSM is called the polarization-external capacitance Goldstone reorientation mode (PCG).

Proposition of the PCG mode inspired several research groups to do further study of a proper interpretation of the DSM results of the ferroelectric nematics. Vaupotič *et al.* [23] pointed out that in the case of the relative permittivity of the studied material being very large, the capacitance of the LC layer becomes comparable to the capacitance of surface polymer layers; thus all capacitors are charged. In this case

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the interpretation of the DSM results becomes very complex (as noticed also by Yadav *et al.* [27]), so they focused on DSM in cells with bare gold electrodes (no surface layers of surfactant). They performed DSM for cells in a bias dc electric field and the behavior of the observed low-frequency mode was explained by a continuous phenomenological model (CPM), which couples fluctuations of the nematic director and polarization. Erkoreka *et al.* [24] performed a systematic DSM as a function of cell thickness and discussed the results within both the PCG and CPM models. Clark *et al.* [30] interpreted results from Ref. [24] as evidence of the PCG model, because it was observed that the low-frequency impedance of the studied cells does not depend on cell thickness. However, even though the dependence on the cell thickness is weak, it is there. By further investigations, Erkoreka *et al.* [25] observed also high-frequency relaxation processes predicted by CPM, thus confirming that relaxation processes within the N_F phase are essentially detected by DSM.

During the refereeing process of the present Letter, Adaka *et al.* [31] reported on a DSM performed in a set of cells, varying the thickness of the N_F layer and the thickness of the surface layer of the surfactant. They found the apparent relative permittivity as well as the relaxation frequency being linearly dependent on the ratio between the thickness of the surface layer and the N_F layer, as predicted by the PCG model. While the simplest (linear) dependence is an obvious first choice, a closer inspection of Fig. 2 in Ref. [31] shows that the experimental data, especially the dependence of the relaxation frequency, could also be fitted by a nonlinear dependence.

In this Letter, we present DSM on a set of cells, differing in thickness, type of electrodes, and the presence/absence of a thin surface layer of surfactant. As mentioned above, the DSM results reported in Ref. [24] show that the low-frequency impedance of the studied cells exhibits dependence on the cell thickness. We also observed that cells with different thickness, but the same type of electrodes and thin surface layer, have different low-frequency capacitance, contrary to the prediction of the PCG model. Moreover, analysis of our DSM results within the PCG model framework gives rather large resistance of the N_F layer (leading to very large rotational viscosity); thus we decided to focus on the possibility of N_F having a large relative permittivity, as, in fact, expected for a nonconductive ferroelectric material. This large value is due to the ease of polarization reorientation in the N_F layer, while the layer is treated as an insulator. This approach is further supported by the observation of two low-frequency dielectric modes in bias electric fields [23,29], suggesting that by DSM the frequency response of the N_F is measured as well, not only charging and discharging of the thin surface layers.

Measurements were performed by using a standard material (analog of RM734 [1]; see compound I-5 in Ref. [18]) exhibiting a monotropic nematic and N_F phases (melting point 130.4°C, phase sequence on cooling: I 60.0°C N 52.7°C N_F). Material was filled in cells (planar capacitors) with gold or indium tin oxide (ITO) electrodes. Cells with gold electrodes were without polymer surface layers, while cells with ITO electrodes were either without or with a surface layer of surfactant enforcing homeotropic anchoring. Information on the used cells is collected in Table I. To make sure that systematic tendencies are observed, measurements were also performed

TABLE I. Used cells, thickness [d (μm)], capacitance of empty cells [C_0 (pF)], and electrode surface area [S (mm^2)]. Low-frequency (at 10 Hz) capacitances [C (μF)] of cells and capacitances per unit surface area [C/S (nFmm^{-2})] for material in the N_F phase at 49.0°C. Electrodes: gold with no surfactant layer (G) and ITO, with no surfactant layer (NA), and with surface layer of surfactant enforcing homeotropic anchoring (HT).

Cell	d	C_0	S	C	C/S
G5	5.0	44	25	0.32	13
G10	10.0	22	25	0.25	10
NA3	3.0	485	164	2.5	15
NA5	4.9	95	53	0.52	9.8
NA10	9.7	150	164	1.9	12
HT10	10.0	77	87	0.29	3.3
HT20	20.0	41.5	94	0.18	1.9

for another ferroelectric nematic material (see Supplemental Material (SM) [32]).

To obtain the frequency (ν) dependence of the real and imaginary part of the impedance of the cell filled with material in the N_F phase, we measured voltage on the cell and the phase shift between the voltage across the cell and the voltage applied by a generator [Bode plot method (BPM)] in a frequency (ν) range from 10 Hz to 1 MHz. Details on the method are given in the SM [32], where we also give a procedure for calculating the cell impedance (Z) and phase angle (α) between the voltage across and current through the cell. For signal generation, a Siglent SDG6022X 200 MHz Function/arbitrary waveform generator (16 bit) was used and measurements were recorded by a Siglent SDS6054A 4CH 500 MHz 5 GSa/s oscilloscope (16 bit). The generator output voltage was set to 100 mVpp for all the cells, much below the Fréedericksz transition voltage. Generator voltages from 10 to 200 mVpp were tested, as well, and BPM results differed only in the amount of noise at frequencies below 100 Hz (larger noise at lower amplitudes). Cells were heated by using a PCB heating platform HPB100 from iTECH; temperature was measured by a PT100 temperature sensor and was stabilized with an accuracy of 0.1 K. The Siglent oscilloscope has four channels; one was used to measure the voltage output of the function generator and the rest to simultaneously measure three cells, for which experimental conditions were thus identical.

The impedance Z and phase angle α calculated from the BPM measurements in the N_F phase are given in Figs. 1(a) and 1(b), raw data are given in the SM (Fig. S2) [32]. While Z and α are obtained from the measured data without making any assumptions on the equivalent electric circuit of the cell, assumptions are needed to obtain the real and imaginary part of the complex relative permittivity of the N_F phase. To get some information on a proper equivalent electric circuit, we first interpret the measured Z and α as if resulting from a capacitor with capacitance C_S and resistor with resistance R_S in a series connection [Figs. 1(c) and 1(g)]. These results can be analyzed within the scope of the PCG model, because the simplest equivalent circuit for the PCG model is a series connection of a capacitor due to thin surface layers (C_S) and a resistor due to the N_F layer (R_S). We observe that the values of C_S and R_S are frequency dependent; moreover, R_S values

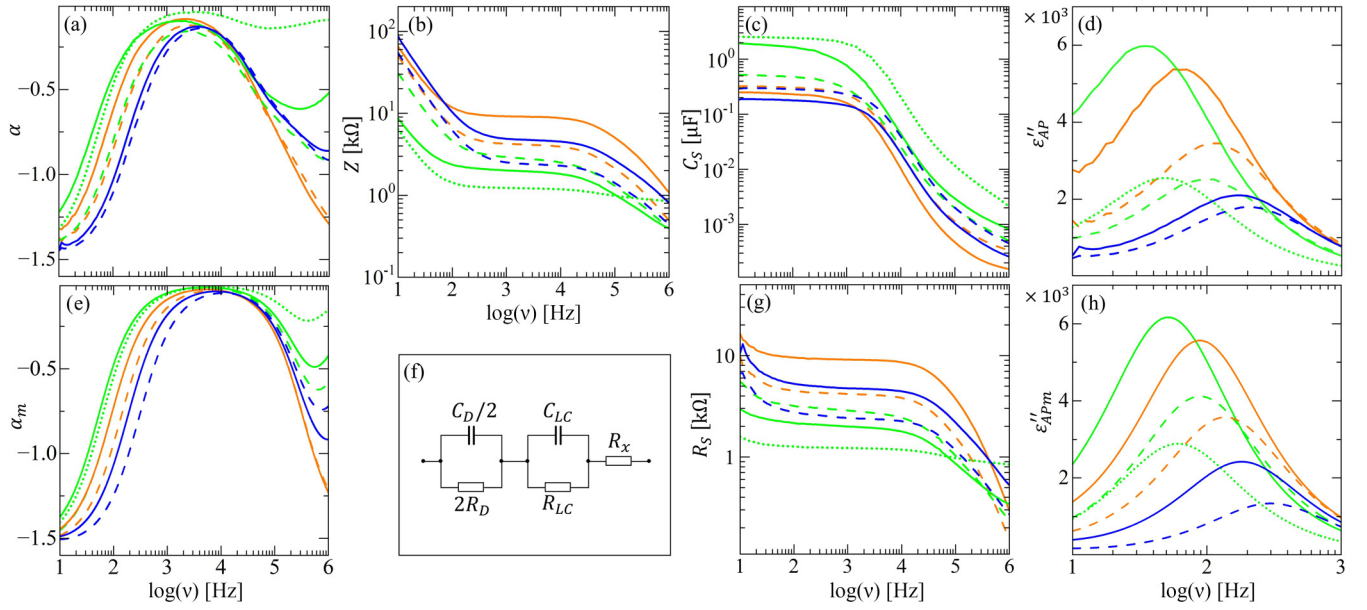


FIG. 1. Frequency (ν) dependence of (a) phase angle (α) between the current through and voltage across the cell and (b) impedance (Z) calculated from the BPM measurements for the studied material in the N_F phase at 49.0°C . Apparent (c) capacitance (C_S) and (g) resistance (R_S) of the cell obtained by simulating the measured Z and α as resulting from a series connection of an ideal resistor and capacitor. (d) Apparent imaginary part of complex permittivity (ε''_{AP}) calculated from the measured data by using Eq. (3). (f) Equivalent electric circuit of the cell filled with N_F ; C_D is capacitance of one surface layer and R_D its resistance; C_{LC} is capacitance and R_{LC} resistance of the N_F layer; R_x is parasitic resistance. Simulated values of (e) α_m and (h) ε''_{APm} , calculated for the equivalent circuit given in (f); material parameter values $\varepsilon_s = 2.5 \times 10^4$, $\tau = 4$ ms, $\varepsilon_\infty = 3$, and $\rho_{LC} = 10^7 \Omega\text{m}$ are the same for all cells; $R_D = 1$ M Ω . Values of C_D and R_x depend on the type of cells and are given in the main text. Green: NA10 (solid), NA5 (dashed), NA3 (dotted). Orange: G10 (solid), G5 (dashed). Blue: HT20 (solid), HT10 (dashed).

determined from the experimental data are very high, up to $R_S \sim 10$ k Ω for the G10 cell. With typical values (by orders of magnitude) of polarization and rotational viscosities, $P \sim 5 \times 10^{-2} \text{ Cm}^{-2}$ and $\gamma \sim 1$ Pas, and the surface area (S) and thickness (d) of the G10 cell (see Table I), we estimate that within the PCG model the resistance of the N_F layer should be $\gamma d / (SP^2) \sim 160 \Omega$. However, the experimental value for the G10 cell ($R_S \sim 10$ k Ω) could be modeled only by an extremely high value of rotational viscosity (of the order of 10^2 Pas). In addition, the PCG model predicts that one should measure the same capacitance per unit surface of the capacitor for all cells with the same type of electrodes and surface alignment layer, because the capacitance should depend only on the thickness of the surface layers. As seen in Table I, the measured low-frequency capacitances per unit surface area differ, but not in the ratio of cell thicknesses.

Based on the above observations we searched for an alternative model to explain the results of DSM. Because the ratio of the low-frequency capacitances does not equal the ratio of the cell thicknesses (see Table I), we conclude that the influence of the thin surface layers cannot be neglected, not even in cells with bare electrodes, which is in line with the argument by Clark *et al.* [30] that a thin layer of liquid crystal molecules close to an electrode acts in the same way as a thin layer of surfactant. This stimulated us to revisit and modify the model equivalent circuit which considers both the capacitance of surface layers and the capacitance of the N_F layer (see Appendix in Ref. [23]). The proposed equivalent electric circuit is given in Fig. 1(f). The capacitance of one

thin layer of surfactant (or a thin layer of LC molecules) is C_D and its resistance R_D ; the net capacitance of two surface layers is $C_D/2$ and their net resistance $2R_D$. This resistance is important only at very low frequencies (lower than 10 Hz) and is in the model only for the sake of completeness. In general, R_D can be assumed to be very large and as such can be omitted from the model equivalent circuit. We set R_D to a constant value of 1 M Ω .

The capacitance of the N_F layer (C_{LC}) is expressed as $C_{LC} = C_0 \varepsilon(\omega)$. C_0 is the capacitance of an empty cell and $\varepsilon(\omega)$, where $\omega = 2\pi\nu$, is a complex relative permittivity, which we approximate by the Debye relaxation model:

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}, \quad (1)$$

where ε' and ε'' are the real and imaginary parts of the complex relative permittivity, respectively; ε_∞ is a high-frequency and ε_s low-frequency permittivity and τ is the Debye relaxation time. The more general Havriliak-Negami equation [33] could be used instead, but to show the principle and have a lower number of fitting parameters we decided on the simplest relaxation model. The resistance of the liquid crystalline material is $R_{LC} = \rho_{LC}d/S$. The resistor with resistance R_x takes account of parasitic resistances of electrodes and wiring. We point out that, except for the R_x and R_D , the latter being irrelevant at $\nu > 10$ Hz, the equivalent circuit in Fig. 1(f) is the same as the one used in the PCG model (see Fig. 1 in Ref. [30]). The difference is in the value of N_F resistivity, ρ_{LC} , and the treatment of C_{LC} . In our model, ρ_{LC} is large

(characteristics of insulators), and is mainly due to ionic impurities. In the PCG model, ρ_{LC} is low, and is due to the block reorientation of polarization. In the here-proposed model the reorientation of polarization in the bulk N_F layer is accounted for in the complex relative permittivity of N_F .

The complex impedance (Z_c) of the equivalent electric circuit [Fig. 1(f)] is

$$Z_c = R_x + \left(\frac{1}{2R_D} + \frac{i\omega C_D}{2} \right)^{-1} + \left(\frac{1}{2R_{LC}} + i\omega C_{LC} \right)^{-1}, \quad (2)$$

which can be expressed as a sum of the real (Z_r) and imaginary (Z_i) parts of complex impedance as $Z_c = Z_r + iZ_i$, the expressions for Z_r and Z_i being functions of ε' and ε'' . When the circuit (cell) is connected to an ac voltage generator [$U(\omega) = U_{\text{cell}}e^{i\omega t}$, U_{cell} being the amplitude of the voltage on the cell], the current $I(\omega) = U(\omega)Z_c^{-1} = I_0(\omega) + iI_{\pi/2}(\omega)$ through the circuit can be divided into current in phase with the voltage ($I_0 = U_{\text{cell}}Z_r|Z_c|^{-2}$) and current that is phase shifted by $\pi/2$ ($I_{\pi/2} = U_{\text{cell}}Z_i|Z_c|^{-2}$). The phase angle between the current and voltage is given by $\tan \alpha_m = Z_iZ_r^{-1}$, where the subscript m next to α is used to differentiate the model phase angle from the one obtained from DSM. For $C_D \gg C_{LC}$, R_D and R_{LC} being large and R_x small, the complex impedance simplifies to $Z_c \approx i\omega C_{LC}$; thus only the LC capacitor is charged when the cell is connected to an ac voltage generator. In this case it is straightforward to see that the imaginary part of the complex permittivity is related to the current in phase with the voltage across the cell as $\varepsilon'' = I_0/(\omega C_0 U_{\text{cell}})$ and the current that is phase shifted by $\pi/2$ is related to the real part of the complex permittivity as $\varepsilon' = I_{\pi/2}/(\omega C_0 U_{\text{cell}})$. However, when C_D and C_{LC} are comparable, $I_0/(\omega C_0 U_{\text{cell}})$ becomes a complex function of C_0 , ε' , ε'' , R_D , R_{LC} , C_D , and R_x , so we call this ratio an apparent value of the imaginary part of the complex relative permittivity ($\varepsilon''_{\text{AP},m}$):

$$\varepsilon''_{\text{AP},m} = \frac{I_0}{\omega C_0 U_{\text{cell}}}. \quad (3)$$

In DSM, ε'' of the studied material is usually calculated by using the expression on the right-hand side of Eq. (3), which means that only an apparent value of the imaginary part of the complex relative permittivity is obtained. The same argument goes for the real part of the complex permittivity.

Our goal was to find such values of model parameters that would give at least a semiquantitative fit with the DSM results. The major objective was to find a set of material parameters (ε_s , τ , ε_∞) that are common for all the cells, regardless of their thickness and the presence/type of a thin layer of surfactant. In the search for this set of parameters we noticed that the physical quantities that are most sensitive to changes in parameter values are $\alpha(\omega)$ and $\varepsilon''_{\text{AP}}$.

The $\varepsilon''_{\text{AP}}$ calculated from the measured data by using Eq. (3) is given in Fig. 1(d). The maximum value of $\varepsilon''_{\text{AP}}$ strongly depends on the cell thickness and type of the cell (NA, G, or HT). Within the proposed model, this dependence is a consequence of a huge value of the low-frequency relative permittivity (ε_s) of N_F , due to which the condition $C_D \gg C_{LC}$ is not satisfied. In this case, the maximum of $\varepsilon''_{\text{AP}}$ as given by Eq. (3) is not half the value of $\varepsilon_s - \varepsilon_\infty$; neither is the position of the peak at frequency $1/(2\pi\tau)$.

Figure 1(h) gives $\varepsilon''_{\text{AP}}$ as predicted from the model equivalent circuit of the LC cell. The plots are obtained for $\varepsilon_s = 2.5 \times 10^4$, $\tau = 4$ ms, $\varepsilon_\infty = 3$, and $\rho_{LC} = 10^7 \Omega\text{m}$ for all cells, while the thickness (d_D) of the surface layer (and thus capacitance C_D) and parasitic resistance R_x depend on the type of cell. All the cells of the same type (G, NA, or HT) were fitted with the same R_x and the same thickness of surface layers. The capacitance of surface layers was modeled as $C_D = C_0 d f_D$, where $f_D = \varepsilon_D/d_D$ and ε_D is a relative permittivity of the surface layer, for which we assume that it is frequency independent within the measured frequency range. The plots are given for f_D being 5 and 4 nm^{-1} in the NA and G cells, respectively, while for HT cells $f_D = 0.6 \text{ nm}^{-1}$. These values are physically sensible as one would expect the surface layer to have approximately the same thickness in cells with no thin layer of surfactant as in this case the thin layer is made of LC molecules (NA and G cells), while in HT cells a surface polymer layer is expected to be thicker. By taking $\varepsilon_D \sim 10$, we find $d_D \sim 2\text{--}3$ nm in NA and G cells, while in HT cells $d_D \approx 17$ nm.

The position and magnitude of the peak value of $\varepsilon''_{\text{AP}}$ are strongly sensitive to ε_s , τ , ρ_{LC} , and f_D , while the major effect of ε_∞ and R_x is on the higher frequency dependence of α . A reduction in R_x increases the magnitude of α at high frequencies, while the increase in ε_∞ shifts the peak (the lowest magnitude of α) to lower frequencies. The best fit was obtained for $R_x = 600 \Omega$ for NA cells, $R_x = 500 \Omega$ for HT cells, i.e., by similar values for the cells with ITO electrodes, as expected, and much lower, $R_x = 50 \Omega$ for G cells. When we used the PCG model to explain the DSM results, we found that R_x is crucial in fitting the position of the peak value of $\varepsilon''_{\text{AP}}$ because R_x can be comparable to R_{LC} (see the SM [32]); thus it essentially affects the time constant of charging/discharging the thin layer surface capacitors.

By considering that inaccuracy in the cell thickness and electrodes' surface area can lead to the capacitances of cells to differ by up to 10% from ideal values, we conclude that the proposed equivalent circuit gives not only good qualitative but also semiquantitative agreement with the experiment. The agreement between model predictions and measurements is obtained only if very high low-frequency relative permittivity of the N_F phase is assumed, which is approximately four times higher than the maximum of $\varepsilon''_{\text{AP}}$ measured in the NA10 cell. The presented model explains why the apparent relative permittivity increases with increasing cell thickness: by increasing the cell thickness, C_{LC} decreases and we are moving towards the limit $C_{LC} \ll C_D$ in which the apparent relative permittivity values would coincide with the actual material parameters (Fig. S3 [32]). We used the obtained parameters to estimate C_{LC} and C_D for different cells and obtain $C_{LC} \approx 0.6C_D \approx 0.5 \mu\text{F}$ for the G10 cell, $C_{LC} \approx 4C_D \approx 2 \mu\text{F}$ for the HT10 cell, and $C_{LC} \approx 0.5C_D \sim 3.8 \mu\text{F}$ for the NA10 cell; thus the capacitances are indeed comparable. To fulfill the condition $C_{LC} \ll C_D$ the cell thickness should be of the order of millimeters, while in standard experiments cells not thicker than approximately $100 \mu\text{m}$ are used.

To conclude, we have shown that the low-frequency (up to 1 MHz) response obtained by DSM of a ferroelectric nematic material filled in thin planar capacitors can be interpreted in

terms of the same complex relative permittivity, independent of cell thickness, type of electrodes, and surface treatment of electrodes. The standard procedure, in which the complex impedance is calculated from the current through the cell, gives only an apparent complex relative permittivity which is related to material properties in a rather comprehensive way. The reason lies in a huge relative permittivity of the LC in the N_F phase, so the capacitance of the N_F layer becomes comparable to the capacitance of a thin surface layer of surfactant, or, in the case of bare electrodes, a thin layer of LC molecules anchored to the electrodes. DSM results are explained by modeling the LC cell with an equivalent circuit presented in Fig. 1(f). By using the same complex relative permittivity for all the studied cells, it is shown that the apparent relative permittivity will increase with increasing cell thickness, while the apparent relaxation frequency does not necessarily behave in a monotonic way, as observed experimentally and

predicted by the model (see Figs. 1(d) and 1(h), graphs for NA cells, and Fig. S3 [32]). We conclude that the low-frequency relative permittivity (ϵ_s) of the ferroelectric nematics is indeed huge, and it is even higher than the apparent measured values. Therefore, the interpretation of DSM for strongly polar LC phases (for example, interpretation of the apparent complex relative permittivity as a function of temperature or bias field) should be revisited also within the scope of the here-proposed model. The model might also explain the unusual temperature dependence of the amplitude mode close to the $N_F - N$ transition, reported in Ref. [23].

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