

Introduction to Dielectric Measurements of Nematic Liquid Crystals

Andrii B. Golovin

Liquid Crystal Institute, Kent State University, Kent, OH, 44242

Outline:

1. Introduction.
2. The Complex Dielectric Permittivity.
3. Dielectric Permittivity of Liquid Crystal:
 - 3.0. Liquid Crystal Cell Preparation;
 - 3.1. Two cell methods;
 - 3.3. Method of Cole-Cole Plot.

References.

- Appendix #1: Hints for Dielectric Measurements;
- Appendix #2: Screenshots of Available Software;
- Appendix #3: Gallery of Dielectric Permittivity.

Abstract:

We describe a technique of dielectric measurements available for the material characterization of the liquid crystals at Liquid Crystal Institute, Kent State University, Kent, OH. We provide the dielectric permittivity plots of popular nematic mixtures for liquid crystal applications.

1. Introduction

The permanent electric field may cause a **static** polarization of **dielectric**¹. Applied electric field pushes electron clouds in one direction and the nucleus in opposite direction. The molecules of the dielectric are distorted, as a result, the center of the atom's negative charge does not coincide with the positive nucleus². For ordinary applied electric fields, the induced electric dipole moment of each atom is proportional to the field³ [1]:

¹ A dielectric material is a substance that is a poor conductor of electricity, but an efficient supporter of static electric field. Most dielectric materials are solid, e.g. porcelain, mica, glass, plastics, and the oxides of various metals. Some liquids and gases also are dielectric materials as well. Dry air and oils are excellent dielectrics, and are used in variable capacitors. Distilled water is a fair dielectric. Vacuum is an exceptionally efficient dielectric.

² In some molecules, such as water, the displacement of charges is always present, such molecules are often called **polar molecules**. Molecules that do not possess a permanent polarization are called **nonpolar molecules**. The applied field causes redistribution of charges within the molecules, such dipoles often are called **induced dipoles**. With either polar or nonpolar molecules, redistribution of charges caused by external applied field leads to the formation of layer of charge on each surface of the dielectric.

³ All expressions are written by using the International System of Units (**SI**).

$$\mathbf{p} = \alpha \varepsilon_0 \mathbf{E}, \quad (1a)$$

where α is the electronic polarizability of the atom and ε_0 is the free space permittivity. The distorted atoms have electric dipole moments of

$$\mathbf{p}_i = q_i l_i, \quad (1b)$$

where q is total charge of i 's nuclei and l_i is a distance between the center of negative charge and nucleus. If there are n dipoles per square unit volume of the dielectric, its polarization is

$$\mathbf{P} = \lim_{V \rightarrow 0} \left(\frac{1}{V} \sum_{i=1}^N \mathbf{p}_i \right) \approx n\mathbf{p} = n\alpha \varepsilon_0 \mathbf{E} = \chi \varepsilon_0 \mathbf{E}, \quad (2a)$$

where N is the number of dipoles in dielectric's volume V and $\chi = n\alpha$ is the **dielectric susceptibility** that depends on the temperature, pressure, and composition of the material. The polarization \mathbf{P} of the dielectric caused by the time independent field is balanced by the strength of the field \mathbf{E} . In Maxwell's theory the matter is pictured as a continuum. The electric field inside of dielectric is decreased by the electric field of the surface charges caused by the polarization. The external applied field \mathbf{E}_o and electric field of surface charges \mathbf{E}' are anti-parallel, thus the internal field \mathbf{E} is governed by sum:

$$\mathbf{E} = \mathbf{E}_o + \mathbf{E}' = \frac{\mathbf{D}}{\varepsilon_0} - \frac{\mathbf{P}}{\varepsilon_0}, \quad (3a)$$

where $\mathbf{D} = \varepsilon \mathbf{E}$ is so-called **vector of the dielectric displacement**. The vector field \mathbf{D} is useful to describe the electric field inside matter:

$$\mathbf{D} = \varepsilon_a \mathbf{E} = \varepsilon \varepsilon_0 \mathbf{E} = \mathbf{P} + \varepsilon_0 \mathbf{E}, \quad (3b)$$

where $\varepsilon = 1 + \chi$ is **dielectric permittivity** and $\varepsilon_a = \varepsilon_0 \varepsilon$ is **absolute dielectric permittivity**⁴ of the material.

The time dependent $\mathbf{E}(t)$ causes **dynamic** effects in the media, for example the media not necessarily follows the changes of the applied field. The motions of molecules, ions, atoms, and electrons needed to get a polarized state have characteristic times, e.g. at room temperature generally of the order 10^{-9} s or lees. If time of the electric field variation is

⁴ Value of the absolute dielectric permittivity is important material parameter of the electrical capacitors, e.g. the capacitance of plane capacitor is governed by $C = \varepsilon_a S / d$, where S is the aria of electrodes and d is size of the gap between electrodes. Consequently, the stored energy of the charged capacitor also

depends on ε_a :

$$W = \frac{CU^2}{2} = \varepsilon_a \frac{SU^2}{2d}$$

shorter than characteristic time of the microscopic particles, the media cannot have a polarization balanced with electric field. Usually, the caused value of the polarization falls behind the varying electric field.

Contrary, if the speed of electric field changes is slower than motion of the microscopic particles, the media maintains the equilibrium polarization with electric field in any time. This case is called as **quasi-static** [2]. For the quasi-static case of linear and isotropic dielectrics one can write that

$$\mathbf{P}(t) = \chi \varepsilon_0 \mathbf{E}(t) \quad (2b)$$

where $\mathbf{P}(t)$ is the time-dependent electric polarization, χ is the susceptibility depended on the temperature, pressure, and composition of the dielectric, but not on time.

The time-dependent dielectric displacement $\mathbf{D}(t)$ caused by relatively small amplitude of $\mathbf{E}(t)$ can be derived for the quasi-static case:

$$\mathbf{D}(t) = \varepsilon \varepsilon_0 \mathbf{E}(t). \quad (3c)$$

As one may see the theory developed for the static case works for the quasi-static case as well.

In the dynamic case with very high frequency of field $\mathbf{E}(t)$, the motion of microscopic particles cannot follow the changes of the fast field, thus $\mathbf{P}(t)$ and $\mathbf{D}(t)$ cannot be described by using relations (2b) and (3c). For a harmonic wave $\mathbf{E}(t) = \mathbf{E}_o \cos(\omega t)$ with amplitude \mathbf{E}_o and angular frequency ω applied to a linear and isotropic dielectric media, one may describe the dielectric displacement as harmonic function of the same frequency, but with certain phase retardation $\delta(\omega)$ [2]:

$$\mathbf{D}(t) = \mathbf{D}_o \cos(\omega t - \delta(\omega)), \quad (4)$$

where \mathbf{D}_o is amplitude of the dielectric displacement and for the low frequency wave $\delta(0) = 0$.

The harmonic $\mathbf{D}(t)$ can be divided into two harmonic parts:

$$\mathbf{D}(t) = \mathbf{D}_o \cos(\delta(\omega)) \cos(\omega t) + \mathbf{D}_o \sin(\delta(\omega)) \sin(\omega t), \quad (5)$$

where the first part is in phase with the wave $\mathbf{E}(t)$ and another is phase shifted by $\pi/2$.

We can re-write (5) by using a new notation:

$$\mathbf{D}(t) = \varepsilon'(\omega) \mathbf{E}_o \cos(\omega t) + \varepsilon''(\omega) \mathbf{E}_o \sin(\omega t), \quad (6)$$

where $\varepsilon'(\omega) = D_o \cos(\delta(\omega))/E_o$ and $\varepsilon''(\omega) = D_o \sin(\delta(\omega))/E_o$.
 For the low frequency case, the equations (3b) and (6) are similar:

$$D(t) = \varepsilon'(0)E_o \quad (6b)$$

or $\varepsilon'(0) = \varepsilon_a$. Thus, $\varepsilon'(\omega)$ is the **frequency-dependent dielectric permittivity** of the dielectric media for the harmonic wave $E(t)$.

The phase shift of $\varepsilon''(\omega)$ is $\pi/2$ with respect to the harmonic wave $E(t)$, thus this component of the dielectric permittivity describes the loss of energy in the dielectric media. Because of this reason, $\varepsilon''(\omega)$ is so-called **loss factor** in the dielectric media, obviously at low frequency $\varepsilon''(0)$ is zero because $\delta(0) = 0$.

The dispersion of the dielectric polarization with the polar molecules contains two parts, Fig. 1. First part is so-called the **orientational polarization** of molecules and ions. Second part is so-called the **induced polarization** of the atoms and electrons. Both parts are caused by difference in the characteristic times of molecular, ionic, atomic, and electronic motions. As a result, in the spectrum of the loss factor $\varepsilon''(\omega)$ has peaks at frequencies where $\varepsilon'(\omega)$ changes. Non-equilibrium effects appear successively for the different polarizations. At very low frequency, when the applied electric field is zero, the polar molecules of the dielectric relax to disoriented state because of the molecular motion and interaction with surrounding media. Relaxation time is temperature dependent, it may vary in the range $\eta = 10^{-10} - 10^{-12}$ s. The dipoles cannot follow the changes of the electric field at frequencies close to $1/\eta$, thus the phase shift between field E and polarization P has maxima, as result dielectric heating caused by the energy dissipation appears in the experiment.

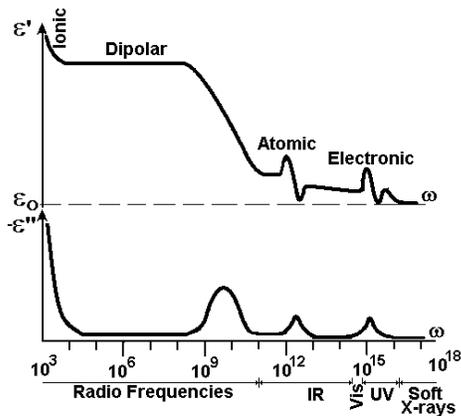


Fig. 1. Simplified plot of the complex dielectric permittivity parts ε' and ε'' versus frequency.

At high frequencies (optical part of spectrum) the dielectric properties are determined by the induced polarization of atoms and electrons. At the frequency range from infrared to

ultraviolet (UV) the dielectric permittivity is defined as $\sqrt{\varepsilon} = n$, where n is the refractive index of the material. Due the discrete energy levels of atoms and electrons, the peaks of $\varepsilon''(\omega)$ are sharper than dissipation peaks of the orientational polarization. In condensed matter, no such discrete energy levels exist for the rotational motions of the molecules and ions, thus the orientational polarization leads to a broader absorption. The orientational polarization has the dynamic behavior of **relaxation** process⁵. In contrast dynamics of the induced polarizations is issue of a number of **resonance** processes. At the very higher frequencies even electrons can not follow changes of the electric field, it means that there the dielectric permittivity of any material including dielectrics is equal to free space permittivity [3]: $\varepsilon_a(\infty) = \varepsilon_o$.

2. The Complex Dielectric Permittivity

In complex notation the harmonic wave is described in more compact way:

$$\hat{E}(t) = E_o \cos(\omega t) + iE_o \sin(\omega t) = E_o e^{i\omega t} \quad (7)$$

The description using the complex electric field needs a complex dielectric displacement:

$$\hat{D}(t) = D_o e^{i(\omega t - \delta)}. \quad (8)$$

Similar to eq.(3b) in the static case, one may describe relation between $\hat{D}(t)$ and $\hat{E}(t)$ by using a **complex dielectric permittivity**:

$$\hat{\varepsilon}(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \quad (9)$$

and as a result the eq.(6) may be re-written as:

$$\hat{D}(t) = \hat{\varepsilon}(\omega) \hat{E}(t). \quad (10)$$

In the range of radio frequencies, the **real** $\varepsilon'(\omega)$ and **imaginary** $\varepsilon''(\omega)$ parts of complex dielectric permittivity can be measured in an experiment. For example, a layer of dielectric material is sandwiched between two plane electrodes of known area S and gap thickness d , Fig. 2. The electrodes of the assembled electric capacitor should be connected to an impedance meter. One may measure the electrical impedance $Z(f)$ of

⁵ The relaxation of orientational polarization is described by Debye equations [5]:

$$\varepsilon'(\omega) = \varepsilon'(\infty) + \frac{\varepsilon'(0) - \varepsilon'(\infty)}{1 + \omega^2 \eta^2}, \quad \text{and} \quad \varepsilon''(\omega) = (\varepsilon'(0) - \varepsilon'(\infty)) \frac{\omega \eta}{1 + \omega^2 \eta^2}.$$

the assembled capacitance by applying a permanent voltage $U(f)$ and scanning frequency f , where $\omega = 2\pi f$. In experiments the measured parameters are magnitude $|Z(\omega)|$ and phase retardation $\theta(\omega)$ of the impedance⁶:

$$\hat{Z}(\omega) = |Z(\omega)|e^{i\theta(\omega)} = |Z(\omega)|(\cos(\theta(\omega)) + i \cdot \sin(\theta(\omega))). \quad (11)$$

The impedance of the electrical capacitor is expressed as:

$$\hat{Z}(\omega) = \frac{1}{i\omega C}. \quad (12)$$

By using the eq. (11), (12) and formula for capacitance ($C = \frac{\epsilon\epsilon_0 S}{d}$) we find the expressions for the real and imaginary parts of the complex dielectric permittivity:

$$\hat{\epsilon}(\omega) = \frac{Cd}{\epsilon_0 S} = \frac{C}{C_0} = \frac{1}{i\omega C_0 Z(\omega)} = -\frac{\sin(\theta(\omega))}{\omega C_0 |Z(\omega)|} - i \frac{\cos(\theta(\omega))}{\omega C_0 |Z(\omega)|} \quad (13)$$

$$\epsilon'(f) = -\frac{d \sin(\theta(f))}{2\pi f \epsilon_0 S |Z(f)|}, \quad (14a)$$

$$\epsilon''(f) = -\frac{d \cos(\theta(f))}{2\pi f \epsilon_0 S |Z(f)|}. \quad (14b)$$

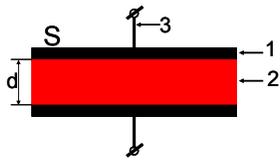


Fig. 2. Capacitor as a sample for dielectric measurements: 1 is plane electrode, 2 is layer of a dielectric, and 3 is a short wire.

Note that eq. (10) is correct for isotropic dielectrics, e.g. gases and liquids. For anisotropic dielectrics, as crystals, the correct way to express the linear dependence of \mathbf{D} from \mathbf{E} is by writing dielectric permittivity as tensor of second order:

⁶ Complex value of the impedance is defined as $\hat{Z}(\omega) = \hat{U}(\omega) / \hat{I}(\omega)$, where $\hat{I} = |I|e^{i\omega t}$ is circuit current, $\hat{U}(\omega) = |U|e^{i\omega t + \theta}$ is voltage, and θ is phase retardation between current and voltage.

$$\begin{aligned}
D_x &= \varepsilon_{xx}\varepsilon_o E_x + \varepsilon_{xy}\varepsilon_o E_y + \varepsilon_{xz}\varepsilon_o E_z \\
D_y &= \varepsilon_{yx}\varepsilon_o E_x + \varepsilon_{yy}\varepsilon_o E_y + \varepsilon_{yz}\varepsilon_o E_z \\
D_z &= \varepsilon_{zx}\varepsilon_o E_x + \varepsilon_{zy}\varepsilon_o E_y + \varepsilon_{zz}\varepsilon_o E_z
\end{aligned} \tag{15a}$$

or in short form:

$$D_n = \sum_m \varepsilon_{nm} \varepsilon_o E_m \tag{15b}$$

where $n, m = x, y, z$. The dielectric permittivity tensor is symmetric ($\varepsilon_{nm} = \varepsilon_{mn}$), thus it has only six independent components. By selecting laboratory system of coordinate one may reduce the number of the tensor components to **three fundamental components**: $\varepsilon_{xx} = \varepsilon_1$, $\varepsilon_{yy} = \varepsilon_2$, and $\varepsilon_{zz} = \varepsilon_3$.

Note that vectors \mathbf{D} and \mathbf{E} coincided if for some reason $\varepsilon_1 = \varepsilon_2 = \varepsilon_3$, in this case such crystal acts as a isotropic media. Also one should keep in mind that the value of dielectric permittivity can not be infinitely high because of many reasons, e.g. molecular motion and interactions, crystallographic defects. Just at very low temperature ($T \approx 0$ °K) or with very high electric field ($E \rightarrow \infty$) all dipoles are oriented in one direction and ε is significantly high.

Note that the current value of the vector \mathbf{D} is caused by the current and past values of vector \mathbf{E} [3], thus more general form of eq.(3b) is

$$\hat{\mathbf{D}}(t) = \int_{-\infty}^t dt' \hat{\varepsilon}_a(\omega, t, t') \hat{\mathbf{E}}(t'). \tag{16a}$$

If the properties of dielectric do not change with time, the dielectric permittivity depended only on $t - t'$:

$$\hat{\mathbf{D}}(t) = \int_{-\infty}^t dt' \hat{\varepsilon}_a(\omega, t - t') \hat{\mathbf{E}}(t'). \tag{16b}$$

By using Fourier transform, one may simplify (16b) to obtain equation for dispersion of dielectric permittivity:

$$\hat{\mathbf{E}}(t) = \int_{-\infty}^{\infty} \mathbf{E}(\omega) e^{-i\omega t} d\omega; \quad \hat{\mathbf{D}}(t) = \int_{-\infty}^{\infty} \mathbf{D}(\omega) e^{-i\omega t} d\omega \tag{17}$$

$$\int_{-\infty}^{\infty} \mathbf{D}(\omega) d\omega \int_{-\infty}^{\infty} e^{i(\omega' - \omega)t} dt = \int_{-\infty}^{\infty} e^{i\omega' t} dt \int_{-\infty}^t \varepsilon_a(t - t') dt' \int_{-\infty}^{\infty} \mathbf{E}(\omega) e^{-i\omega t'} d\omega$$

$$\hat{D}(\omega) = \hat{\varepsilon}_a(\omega) \hat{E}(\omega) \quad (18)$$

where

$$\hat{\varepsilon}_a(\omega) = \int_0^{\infty} \varepsilon_a(\tau) e^{i\omega\tau} d\tau = \int_0^{\infty} \varepsilon_a(\tau) \cos(\omega\tau) d\tau + i \int_0^{\infty} \varepsilon_a(\tau) \sin(\omega\tau) d\tau = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

and $\tau = t - t'$.

Note that at the high frequency range, even electrons can not follow changes of the electric field, which means that the dielectric permittivity of any material including dielectrics is limited by the free space permittivity ε_o :

$$\varepsilon_a(\omega) = \varepsilon_o + \varepsilon_o \int_0^{\infty} \chi(\tau) e^{i\omega\tau} d\tau, \quad (19)$$

$\varepsilon_a(\infty) = \varepsilon_o$. After the applied electric field is removed the media relaxes and loses polarization because of the molecular motion, this means that the dielectric susceptibility $\chi(\tau)$ is decreasing ($\chi(\infty) = 0$).

3. Dielectric Permittivity of Liquid Crystal

Liquid crystals (LCs) are unusual soft matter with properties of liquids and solid state crystals. LCs have restricted or even absent long-range positional order, but there is nevertheless a long-range orientational correlation between the molecules. There are two broad groups of LCs: **thermotropic** and **lyotropic**. Thermotropic LCs exhibit a phase transition into the LC phase as temperature is changed, whereas lyotropic LCs exhibit phase transitions as a function of mesogen concentration in a solvent (typically water) as well as temperature. Depending on compound, LC materials have rod-like elongated, banana-shaped, or disk-like molecules [4].

There are different types of liquid crystals. In a **nematic**, molecules have long-range correlation of the orientations of their long axes but not of their positions. Molecules of nematic material rest within cylindrical symmetry of their long axes along a direction often called as the **director**. In a **smectic** material, molecules stay within certain equidistant planes, as a result smectic molecules show a long-range positional order additionally to the long-range orientational order. If molecules planes are normal to the director, the crystalline structure is uniaxial (smectic-A), otherwise it is biaxial (smectic-C). Other type of LCs is **chiral**, in such material molecules show a twist of the long axis and director is normal to the twist axis. If molecules have no long-range positional order, LC material is called chiral nematic or **cholesteric**. Chiral LC with the long-range positional order is called chiral smectic. In the examples of our measurements we describe our experiments with thermotropic nematics.

Due to cylindrical symmetry of crystalline structure the number of fundamental components of LCs is reduced to two: ε_{\parallel} and ε_{\perp} are dielectric permittivity components along and perpendicular to the director, respectively, while the dielectric anisotropy is $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$. The description of procedures to measure ε_{\parallel} , ε_{\perp} , and $\Delta\varepsilon$ are the prime objective of this presentation.

3.0. Liquid Crystal Cell Preparation.

The first step of the cell preparation deals with the cell substrates with plane electrodes. For this purpose, one may use parallel glass plates covered with a thin metal layer from one side of the plate. In LC display production, thin layer (~25 nm) of Indium Tin Oxide (ITO) is traditionally used as optically transparent electrode. Unfortunately, ITO electrodes show relatively high resistance for electric current, because of that this material is not the best choice for the dielectric measurements especially at the high frequencies. Gold, silver, and aluminum are more suitable materials for the dielectric studies. Electrodes should be etched by using standard photolithography technique to get well defined form and size of the capacitor. Note that very thin metals layers with thickness around or less than 100 \AA usually show an island structure and poor conductivity.

The second step involves a preparation of alignment layer. To get a uniform structure of LC inside cell, one should use alignment layers on the top of the plane electrodes, e.g. rubbed polyimide PI2555⁷.

The third step is necessary to assemble the LC cell by using spacers and chemically non-reactive glue. Spacers should be mixed with glue and placed outside of the plane electrodes. Two substrates should be joined together to get a small gap between the layers of alignment. Assembled cell should be partially sealed from sides, and then short wires (10-20 mm) should be attached to the cell.

The LCs dielectric measurements require characterization of the empty cell. The cell gap d may be measured by using a spectrometer.⁸ The impedance of empty cell should be measured for the desirable frequency range and temperature.

The fourth step is necessary to fill the cell with LC material and completely seal the cell from the sides.

⁷ Rubbed layer of polyimide PI2555 gives low pre-tilt angle between the director and substrate. To get a high pre-tilt angle one may use polyimide SE7511.

⁸ The cell gap can be evaluated by using a formalism developed to describe an optical interferometer of Fabry-Perot: $d = \lambda_{\max} \cdot \lambda_{\min} / (4 \cdot |\lambda_{\min} - \lambda_{\max}|)$, where λ_{\max} and λ_{\min} are the wavelengths of neighboring maximum and minimum intensities in the spectrogram. Alternative way to find the cell gap for non-transparent windows is by measuring capacitance C_o of the empty cell: $d = \varepsilon_o \cdot \varepsilon_{air} \cdot S / C_o$.

The final cell design should look as is shown in Fig. 3 (not to scale). The LC cell with director aligned parallel to the plane of electrodes is often called as a **planar** cell, Fig. 3a. The LC cell with director aligned normally to the plane of electrodes is often called as a **homeotropic** cell.

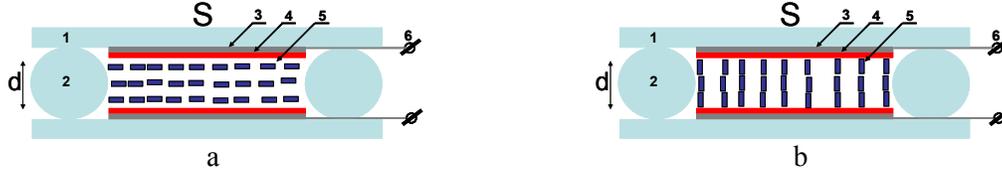


Fig. 3. Planar (a) and homeotropically (b) aligned liquid crystal (LC) cells: 1 is substrate, 2 is spacer, 3 is plane electrode, 4 is alignment layer, 5 is elongated rod-like molecule, and 6 is conductive wire.

Note that in some cases the empty cell with rubbed aligned layers can contain dust which is necessary to wash out by using volatile solvent, e.g. chloroform, and vacuum pump. This procedure should be made right before 4th step of the LC cell preparation. The chloroform flow should be directed parallel to the rubbing direction and dried out at the elevated temperature (~ 70 °C).

3.1 Two cell methods

Method I. The presence of alignment layers in the LC cell complicates the dielectric measurements of LC material. Indeed, in the case of LC cell, dielectric permittivity calculated by using simple capacitor model shown in Fig. 2 and eq. (11 - 14) contains a dielectric contribution of the aligned layers.

To overcome this problem, dielectric measurements should be contained in two sets of measurements [6].

First of all, the impedance of the empty LC cell should be measured for the desirable frequency range and temperature. The *rms* amplitude of applied AC⁹ voltage for these measurements should be quite low because the same voltage will be applied to the filled LC cell. For many LC nematics the *rms* voltage about 1 V is critical to start Frederiks transition [4, 7], thus the *rms* amplitude of applied voltage around 0.2 V is appropriate for this experiment.

Before second set of measurements, the LC material in an isotropic phase should be filled into the cell, then the cell should be sealed and left to relax at least for 24 hours.

The second set of measurements, the impedance of the filled LC cell should be found for the same frequencies, temperatures, and applied voltage ($\square 0.2 V_{rms}$) as for the empty cell.

Further calculations of dielectric permittivity require analysis of the equivalent circuits. Let us start from the empty cell. Figure 4 shows the equivalent circuit of the empty cell's

⁹ Root mean square (RMS) amplitude for sinusoidal alternating current (AC) is defined as the ratio of the peak amplitude over square root of two: $I_{rms} = I_p / \sqrt{2} \approx 0.7 I_p$.

contained capacitance and resistance of the electrodes (C_o and R_o , respectively), and capacitance and resistance of the polyimide layers (C_p and R_p , respectively).

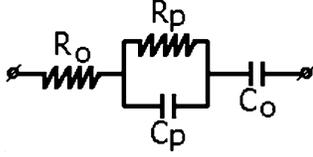


Fig. 4. Equivalent circuit of the empty cell: C_o and R_o are capacitance and resistance of the electrodes, C_p and R_p capacitance and resistance of the polyimide layers, respectively.

The impedance of empty cell is calculated as a sum of impedances:

$$\hat{Z}_e = \hat{Z}_{R_o} + \hat{Z}_{C_o} + \hat{Z}_{R_p C_p} = R_o + \frac{1}{i\omega C_o} + \frac{R_p}{1 + (\omega C_p R_p)^2}, \quad (20)$$

or as $\hat{Z}_e = \text{Re}[\hat{Z}_e] + i \cdot \text{Im}[\hat{Z}_e]$, where $\text{Re}[\hat{Z}_e] = R_o + \frac{R_p}{1 + (\omega C_p R_p)^2}$ and

$$\text{Im}[\hat{Z}_e] = -\left(\frac{1}{\omega C_o} + \frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} \right). \quad (21)$$

The effective circuit of the filled LC cell contains resistance of the electrodes (R_o), capacitance and resistance of the polyimide layer (C_p and R_p), and capacitance and resistance of the LC layer (C_{lc} and R_{lc}), respectively.

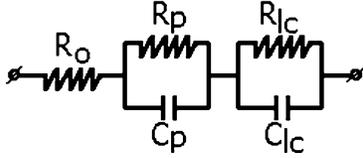


Fig. 5. Effective circuit of the filled cell: R_o is resistance of the electrodes, C_p and R_p are capacitance and resistance of the polyimide layer, and C_{lc} and R_{lc} are capacitance and resistance of the LC layer, respectively.

The impedance of the effective circuit shown in Fig.5 is calculated as a sum of impedances:

$$\hat{Z}_f = \hat{Z}_{R_o} + \hat{Z}_{R_p C_p} + \hat{Z}_{R_{lc} C_{lc}} = R_o + \frac{R_p}{1 + i\omega R_p C_p} + \frac{R_{lc}}{1 + i\omega R_{lc} C_{lc}} = \dots = \text{Re}[\hat{Z}_f] + i \cdot \text{Im}[\hat{Z}_f], \quad (22)$$

where

$$\text{Re}[\hat{Z}_f] = R_o + \frac{R_p}{1 + (\omega R_p C_p)^2} + \frac{R_{lc}}{1 + (\omega R_{lc} C_{lc})^2} \quad \text{and} \quad \text{Im}[\hat{Z}_f] = -\left(\frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \frac{\omega C_{lc} R_{lc}^2}{1 + (\omega C_{lc} R_{lc})^2} \right). \quad (23)$$

Equations (23) can be re-written by using eq.(21):

$$\text{Re}[\hat{Z}_f] = \text{Re}[\hat{Z}_o] + \frac{R_{lc}}{1 + (\omega R_{lc} C_{lc})^2} \quad \text{and} \quad \text{Im}[\hat{Z}_f] = -\left(\text{Im}[\hat{Z}_o] + \frac{1}{\omega C_o} + \frac{\omega C_{lc} R_{lc}^2}{1 + (\omega C_{lc} R_{lc})^2} \right). \quad (24)$$

By introducing new variations α and β , we may express eq.(24) in shorter form:

$$\operatorname{Re}\left[\hat{Z}_f\right]-\operatorname{Re}\left[\hat{Z}_e\right]=\alpha \quad \text{and} \quad \operatorname{Im}\left[\hat{Z}_f\right]-\operatorname{Im}\left[\hat{Z}_e\right]-\frac{1}{\omega C_o}=\beta, \quad (25)$$

$$\text{where } \alpha=\frac{R_{lc}}{1+\left(\omega R_{lc} C_{lc}\right)^2} \quad \text{and} \quad \beta=-\frac{\omega C_{lc} R_{lc}^2}{1+\left(\omega R_{lc} C_{lc}\right)^2}. \quad (26)$$

New variations α and β depend only on ω , C_{lc} and R_{lc} , thus α and β can be easily calculated by using the experimental data collected for the empty and filled LC cells. Finally, one may use $\alpha(\omega)$ and $\beta(\omega)$ to find the complex permittivity of the LC material:

$$\hat{\varepsilon}_{lc}(\omega)=\varepsilon_{lc}'(\omega)+\varepsilon_{lc}''(\omega). \quad (27)$$

To find $\hat{\varepsilon}_{lc}$ we recall the equation for the impedance of the parallel circuit formed by C_{lc} and R_{lc} in Fig. 5:

$$\frac{1}{\hat{Z}_{RlcClc}}=\frac{1}{R_{lc}}+i\omega C_{lc} \quad (28)$$

We re-write eq.(28) by using $\alpha(\omega)$ and $\beta(\omega)$:

$$\frac{1}{\hat{Z}_{RlcClc}}=\frac{\alpha}{\alpha^2+\beta^2}-i\frac{\beta}{\alpha^2+\beta^2}, \quad (29)$$

$$\text{where } \frac{\alpha}{\alpha^2+\beta^2}=\frac{1}{R_{lc}} \quad \text{and} \quad \frac{\beta}{\alpha^2+\beta^2}=-\omega C_{lc}. \quad (30)^{10}$$

We also use eq.(27) to express capacitance value C_{lc} :

$$C_{lc}=\varepsilon_o\hat{\varepsilon}_{lc}S/d=\hat{\varepsilon}_{lc}C_o, \quad (31)$$

where $C_o=\varepsilon_oS/d$ is capacitance of the electrodes. We use eq.(31) in eq.(28 and 29):

$$\frac{1}{R_{lc}}+iC_o\omega\varepsilon_{lc}'-C_o\omega\varepsilon_{lc}''=\frac{\alpha}{\alpha^2+\beta^2}-i\frac{\beta}{\alpha^2+\beta^2}. \quad (32)$$

¹⁰ One can check that eq.(30) are correct by using eq.(26).

From eq.(32) it is easy to compare real and imaginary parts of complex values:

$$\varepsilon_{lc}'(\omega)\omega C_o = -\frac{\beta}{\alpha^2 - \beta^2} \quad \text{and} \quad \frac{1}{R_{lc}} - \varepsilon_{lc}''(\omega)\omega C_o = \frac{\alpha}{\alpha^2 + \beta^2}. \quad (33)$$

Assuming that the resistance of LC is high, we finally find expressions to calculate $\varepsilon_{lc}'(\omega)$ and $\varepsilon_{lc}''(\omega)$:

$$\varepsilon_{lc}'(\omega) = -\frac{\beta}{\omega C_o(\alpha^2 - \beta^2)} \quad \text{and} \quad \varepsilon_{lc}''(\omega) \approx -\frac{\alpha}{\omega C_o(\alpha^2 + \beta^2)}. \quad (34)$$

Note that in experiments the measured parameters of the impedance are magnitude $|\hat{Z}_*|$ and angle θ_* , thus one should use equations $\text{Re}[\hat{Z}_*] = |\hat{Z}_*| \cos \theta_*$ and $\text{Im}[\hat{Z}_*] = |\hat{Z}_*| \sin \theta_*$ in eq.(25) to calculate parameters $\alpha(\omega)$ and $\beta(\omega)$.

Note that in the calculations according to eq.(34) we assumed that the polarization of polyimide layers in the empty and filled cells are approximately the same.

Method II. There is another, more stride forward, way to evaluate the complex dielectric permittivity of nematic liquid crystal from data of impedance magnitude collected from empty and filled cells. On one hand, by using the expressions for complex capacitances of empty and filled cells: $\hat{C}_o = \frac{\varepsilon_o S}{d}$ and $\hat{C}_* = \frac{\hat{\varepsilon} \varepsilon_o S}{d}$ with corresponding complex impedances $\hat{Z}_o(\omega) = \frac{1}{i\omega\hat{C}_o}$ and $\hat{Z}_*(\omega) = \frac{1}{i\omega\hat{C}_*}$ one may deduce the expression for complex permittivity:

$$\frac{\hat{Z}_o}{\hat{Z}_*} = \frac{1}{i\omega\hat{C}_o(\omega)} \cdot \frac{i\omega\hat{C}_*(\omega)}{1} = \frac{C_*(\omega)}{C_o(\omega)} = \hat{\varepsilon}(\omega) \quad (35)$$

On other hand, the ratio of complex impedances is

$$\frac{\hat{Z}_o}{\hat{Z}_*} = \frac{|\hat{Z}_o|}{|\hat{Z}_*|} (\cos(\theta_o - \theta_*) + i \sin(\theta_o - \theta_*)) \quad (36)$$

Now the real and imaginary part of dielectric permittivity can be easily deduced from expressions (35) and (36) as

$$\varepsilon'(\omega) = \frac{|\hat{Z}_o|}{|\hat{Z}_*|} (\cos(\theta_o - \theta_*)) \quad \varepsilon''(\omega) = \frac{|\hat{Z}_o|}{|\hat{Z}_*|} (\sin(\theta_o - \theta_*)) \quad (37).$$

Method of Cole-Cole Plot

So-called Cole-Cole plot [8] method helps to easily find the relaxation frequency f_r of orientational polarization, value of $\varepsilon'(f)$ corresponded to minimum dielectric losses ($\varepsilon''(f) \rightarrow 0$), and value of $\varepsilon'(\infty)$ at high frequencies. Cole-Cole plot is a graph of $-\varepsilon''(f)$ versus $\varepsilon'(f)$. As an example, the Cole-Cole plot of nematic mixture E7¹¹ is depicted in Fig. 6.

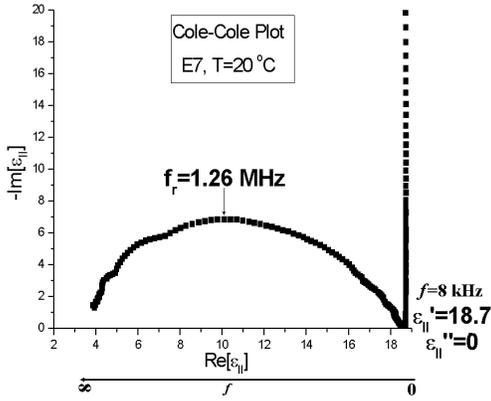


Fig. 6. Cole-Cole plot of the nematic mixture E7 at temperature $T=20^{\circ}C$.

We can easily find at what frequency $\varepsilon''(f)$ corresponds to the top point of semi-circle curve of the Cole-Cole plot. Frequency of this top point is relaxation frequency f_r of the orientational polarization ($f_r=1.26$ MHz in Fig. 6), at this frequency dielectric hitting is maximum. The frequency, where the semi-circle crossed with ordinate axis, corresponds to the minimum dielectric losses of applied field ($f=8$ kHz in Fig. 6).

Pure Debye relaxation¹² corresponds to semi-circle curve (no negative values of $-\varepsilon''$) with a center on axis of ordinate and radius $\frac{\chi}{2}$.

Note that the relaxation frequency $f_{r||}$ of $\varepsilon_{||}$ is much lower than $f_{r\perp}$ of ε_{\perp} . The relaxation of $\varepsilon_{||}$ is exclusively a liquid crystal property determined by the interaction between the molecules. Long-range ordered nematic structure increases the time of the rotation around short molecular axis, as a result $f_{r||}$ belongs to radio

¹¹ Nematic E7 is the mixture containing 47% of 5CB, 25% of 7CB, 18% of 8OCB, and 10% T15 [9].

¹² Debye's model concedes molecules (dipoles of sphere form) that move inside of a viscose isotropic media, with no interactions between molecules. The relaxation of the dipoles depends only on the viscosity and size of the molecules.

frequency range. The relaxation frequency $f_{r\perp}$ of ε_{\perp} coincides with Debay's relaxation of isotropic media at much higher frequency [7].

References:

1. C. J. F. Bottcher, "Theory of Electric Polarization" vol. 1, Elsevier, New York, 1973.
2. C. J. F. Bottcher and P. Bordewijk, "Theory of Electric Polarization" vol. 2, Elsevier, New York, 1978.
3. V. I. Sugakov, "Theoretic Physics: Electrodynamics", Visha Skola, Kiev, 1974.
4. P. G. de Gennes and J. Prost, "The Physics of Liquid Crystals", 2nd edition, Clarendon Press, Oxford, 1993.
5. P. Debye, "Polar Molecules", Chemical Catalogue Co., New York, 1927.
6. A. Jakli and A. Saupe, "One and Two Dimensional Fluids: Properties of Smectic, Lamellar and Columnar Liquid Crystals", CRC Press, 2006.
7. L. M. Blinov and V. G. Chigrinov, "Electrooptics Effects in Liquid Crystal Materials", Springer, New York, 1996.
8. K. S. Cole and R. H. Cole, J. Chem. Phys., **9**, p. 341 (1941).
9. P. Yeh and C. Gu, "Optics of Liquid Crystal Displays", Wiley, New York, 1999.

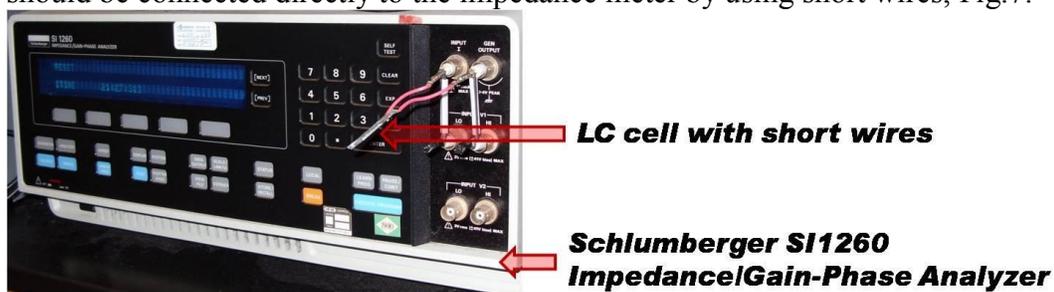
Appendix #1: Hints for Dielectric Measurements.

Hint #1:

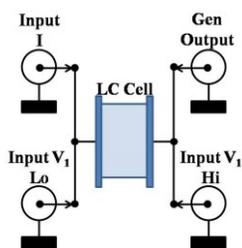
To remove a dust from LC cells with rubbed polyimide, one may wash the LC cell gap by using a vacuum pump and chloroform. The procedure can not be applied to cells with the homeotropic alignment.

Hint #2:

Long wires of the cell and leads of the impedance meter attachment add a parasitic capacitance, induction, and resistance to the experimental circuit. Signals from the parasitic capacitance and induction quit pronounced at frequencies higher than 100 kHz. For high frequencies measurements, the LC cell should be connected directly to the impedance meter by using short wires, Fig.7.



a



b

Fig. 7. LC cell connected directly to Schlumberger SI1260 Impedance/Gain-Phase Analyzer by using short wires: photographic picture (a) and diagram of the connection (b).

Hint #3:

Exposition of LC material to epoxy glue (even to polymerized one) gives additional ions to the LC material. Suggested glue to assemble the LC cell is non-reactive UVS 91 from Norland Inc. (Cranbury, NJ).

Hint #4:

Exposition of the filled LC cell to UV light causes ionization of the LC material. To protect the LC material during polymerization of glue, the windows of the LC cell should be covered with a not transparent material, e.g. aluminum foil.

Appendix #2: Screen Shots of Available Software.

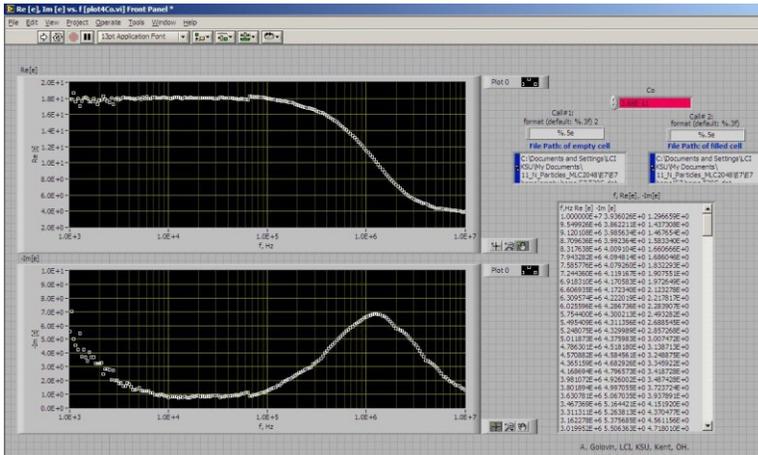


Fig. 8. Screenshot of the software to calculate dielectric permittivity by using “ α & β ” method.

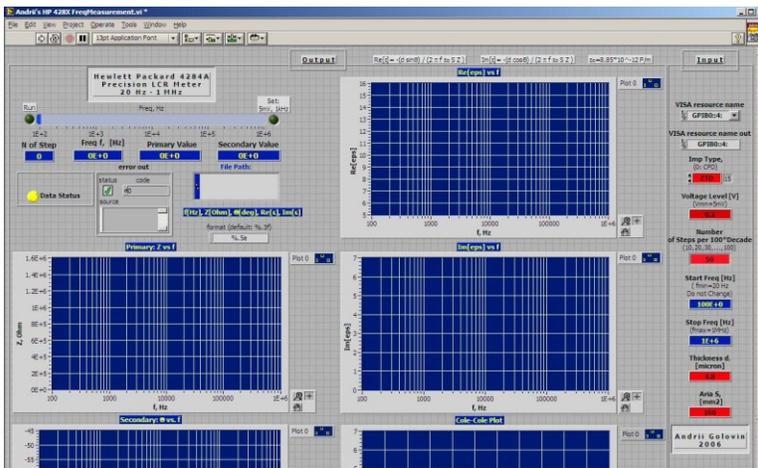


Fig. 9. Screenshot of the software to control impedance meter within measurement of the dielectric permittivity by applying AC voltage of the permanent amplitude and scanning frequency in the range 20Hz – 1MHz.

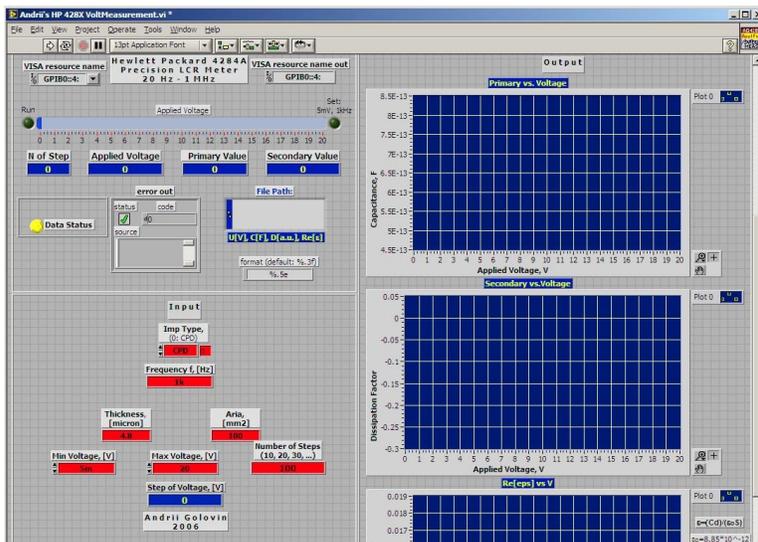


Fig. 10. Screenshot of the software to control the impedance meter within measurement of the dielectric permittivity by using a fixed frequency and varied the amplitudes of AC voltages in the range 0 to 20 V_{rms} .

Appendix #3: Gallery of Dielectric Permittivity

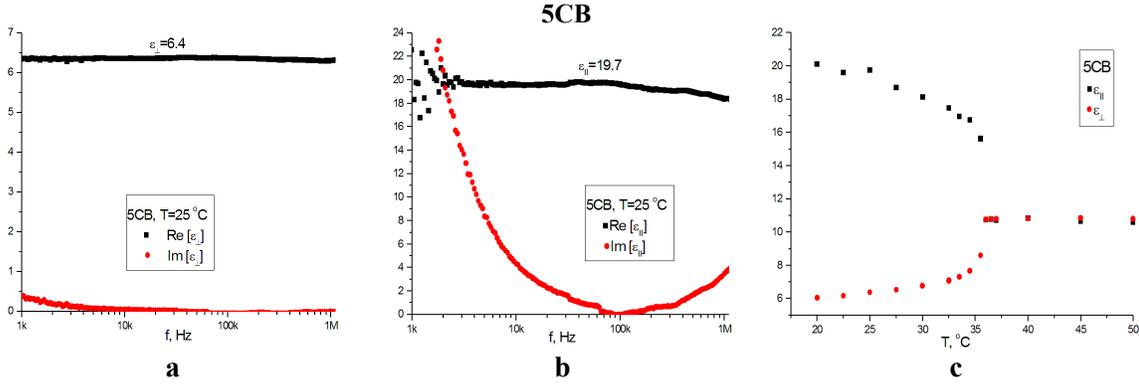


Fig. 11. Dielectric permittivity of nematic liquid crystal 5CB: a) $\text{Re}[\varepsilon_{\perp}]$ and $\text{Im}[\varepsilon_{\perp}]$ vs. f at temperature $T=25^{\circ}\text{C}$; b) $\text{Re}[\varepsilon_{\parallel}]$ and $\text{Im}[\varepsilon_{\parallel}]$ vs. f at $T=25^{\circ}\text{C}$; c) $\text{Re}[\varepsilon_{\perp}]$ and $\text{Re}[\varepsilon_{\parallel}]$ vs. T .

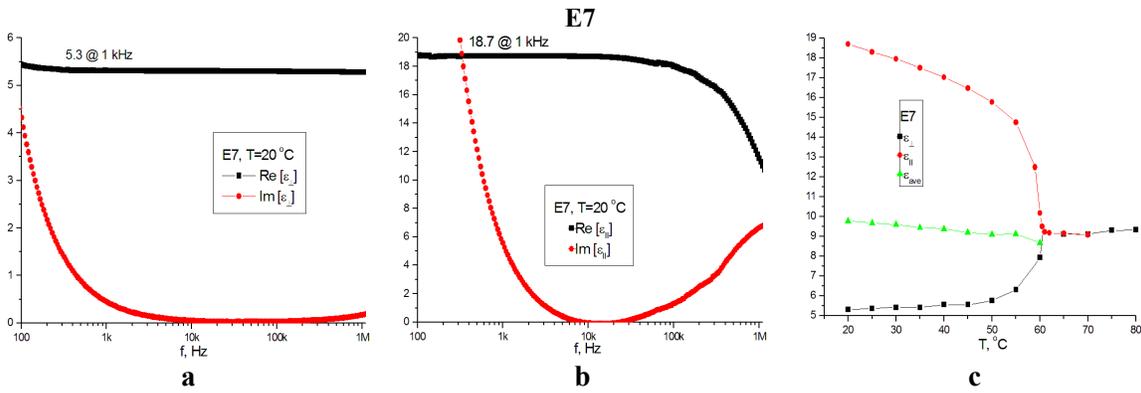


Fig. 12. Dielectric permittivity of nematic mixture E7: a) ε_{\perp}' and ε_{\perp}'' vs. f at $T=20^{\circ}\text{C}$; b) $\text{Re}[\varepsilon_{\parallel}]$ and $\text{Im}[\varepsilon_{\parallel}]$ vs. f at $T=20^{\circ}\text{C}$; c) $\text{Re}[\varepsilon_{\perp}]$, $\text{Re}[\varepsilon_{\parallel}]$, and ε_{ave} vs. T , where $\varepsilon_{ave} = (2\text{Re}[\varepsilon_{\perp}] + \text{Re}[\varepsilon_{\parallel}])/3$ is average dielectric permittivity.

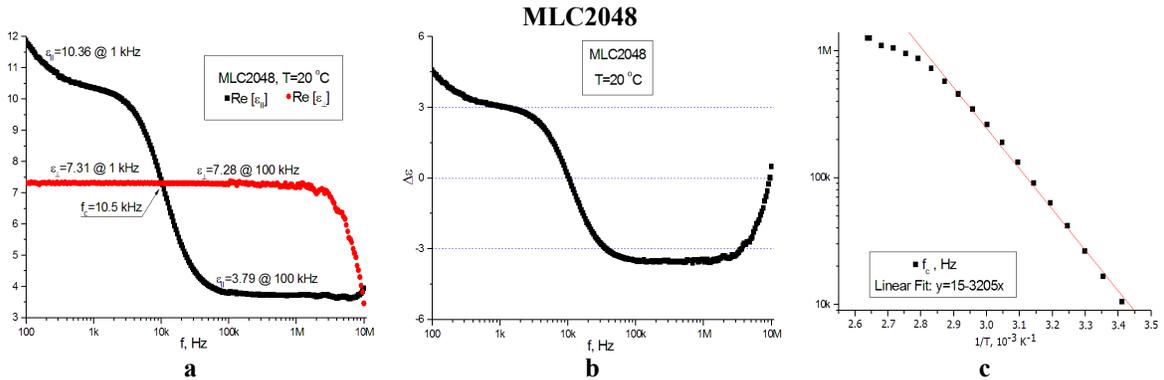


Fig. 13. Dual-frequency nematic mixture MLC2048: a) $\text{Re}[\varepsilon_{\perp}]$ and $\text{Re}[\varepsilon_{\parallel}]$ vs. f at $T=20^{\circ}\text{C}$; b) $\Delta\varepsilon$ vs. f at $T=20^{\circ}\text{C}$; c) f_c vs. $1/T$, where f_c is so-called crossover frequency of the dual-frequency nematic ($\Delta\varepsilon(f_c) = 0$).