Dielectric properties of ferroelectric and antiferroelectric liquid crystals

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It is well known that ferroelectric and antiferroelectric liquid crystals and liquid crystalline polymers are interesting candidates for their exclusive physical properties and industrial applications. For this reason, a wide variety of ferroelectric and antiferroelectric liquid crystals and liquid crystalline and polymers have been examined already and many are on the growing stage of investigation. The study of complex dielectric constant provides important evidences for understanding the interesting static and dynamic properties of these materials. In this review, we attempt to describe in detail about the collective and molecular dynamics of ferroelectric and antiferroelectric liquid crystals using broadband dielectric spectroscopy. Here, we have shown the dielectric properties of ferroelectric and antiferroelectric liquid crystals and polymers by varying the physical parameters, such as, temperature, frequency, bias field and the thickness of the liquid crystal films.

Key words: Ferroelectric liquid crystal; Antiferroelectric liquid crystals; Dielectric relaxation; Phase transition; Molecular dynamics

1. INTRODUCTION

Liquid crystals have been recognized for more than 100 years. Subsequently, in early 1960's liquid crystals have become a subject of particular interest equally to the Physicists and Chemists due to their exclusive physical properties and numerous practical applications, for example, electronics, display units, etc. Liquid crystals and solar cells have paved the way in the development of modern electronic equipments also. For the development of microelectronics, liquid crystals play a major role. Liquid crystal ordering in polymers is also known for last three to four decades [1-3] which has also been the major subject in fundamental applied researches. Depending on the detailed molecular geometries, the system may pass through one or more liquid crystal phases, before it is transformed into the isotropic liquid. The phase transitions to these intermolecular states are induced by completely thermal processes, named, Thermotropic Liquid crystal or by the influence of the solvents, named, Lyotropic Liquid Crystal. Based on the molecular ordering, there exhibits a wide variety of mesophases, such as, Nematic, SmA, SmA*, SmC, SmC*, SmC_A, SmC_A*, SmC_α, SmC_γ, etc. By considering the kind of mesophases observed, the liquid crystals are named as Nematic liquid crystal, Ferroelectric liquid crystal, Antiferroelectric liquid crystals, etc.

The objective of this review article is to describe the dielectric property of mainly the ferroelectric and antiferroelectric liquid crystals and polymers. To achieve this goal, we have illustrated the topics in several headings such as ferroelectric liquid crystals with and without application of bias electric field,

thickness dependent phase transition, antiferroelectric liquid crystals and finally concluding remarks.

2. FERROELECTRIC LIQUID CRYSTALS

Ferroelectricity was mainly the subject of solid state material research because of its symmetry requirement. Ferroelectric materials with non-centrosymmetric space group must show reversible spontaneous polarization which was not expected in liquids and glassy materials. The appearance of ferroelectricity is prevented by the presence of symmetry in liquid crystals [4]. However, in 1975, Meyer et al. [5] obtained the spontaneous electric polarization in the plane of the smectic layers for the chiral compounds in chiral smectic C (SmC*) phase. At higher temperature, in the smectic A (SmA) phase of a chiral compound, a center of inversion was found, where the molecules were normal to the smectic layers but ferroelectricity was absent. The molecular tilt in the SmC* phase always supports the appearance of the spontaneous polarization, which is the important (order) parameter for the ferroelectric (FE) transition. Because of the molecular chirality, a helix texture is found in the SmC* phase where the pitch of the helix is of the order of few microns. However, the introduction of parallel bounding surfaces normal to the layers that interacts with the director as well as with the spontaneous polarization, prevents the helix formation and leads to bookshelf or chevron geometry. It was found that in many aspects, clear understanding of the phenomenon of ferroelectricity [5] in liquid crystals, necessary for its potential applications had not been possible. For instance, the order parameter and free energy play a general role of flexoelectricity, electroclinic effect etc. in the ferroelectric (FE) and antiferroelectric (AFE) phase

boundary. Also both the pyroelectric [6] and electroclinic effects [7,8] are promising fields of research besides the basic intrinsic ferroelectricity, which is a common characteristics for all the chiral tilted smectics. From the practical point of view, the ferroelectric liquid crystal (FLC) may be appeared in two fashions i) giving a possibility of 45° switching angle (22.5° tilt, corresponding to a 2nd order transition into a tilted state) and ii) giving 90° switching angle (45° tilt in substances having a 1st order transition).

Ferroelectric liquid crystals have drawn a major attention for last four decades, which are known as promising materials for potential applications in low power, paper-like portable display devices etc. as well as rare examples of two-dimensional (2D) ferroelectrics [9]. Beside the Langmuir–Blodgett ultra-thin polymeric films, which have been designed for intrinsic 2D ferroelectrics [10], FLCs are another class of improper 2D ferroelectrics [11]. In these materials, the role of dimensionality in structural phase transitions and the ferroelectricity has been one of the central topics of basic research in both the theory [12–14] and experiments [13, 15–19] for last few decades. In these circumstances, the study of complex dielectric constant provides important evidences for understanding the interesting static and dynamic properties of FLCs [20]. Because, from the same experiment, one can study the static (low frequency dielectric constant) as well as the dynamic (frequency dependent dielectric constant) properties of such scheme. The dielectric measurement is very significant since they contribute to characterize the materials that provide various technical parameters. The results obtained using the dielectric spectroscopic method are valuable for understanding the dynamics of the respective systems. Some dielectric investigations on single component and mixtures were published elsewhere [21–25]. However, in order to describe the ferroelectric (FE) SmC* phase, one can introduce two order parameters i) primary order parameter i.e., two-component order parameter $\xi = (\xi_1, \xi_2)$ and ii) secondary order parameter i.e., the in-plane polarization $P = (P_x, P_y)$. Consequently, the dielectric response of the system consists (apart from the usual electronic contribution) of four modes [26–28]. Two of these are contributed to fluctuations of the polarization order parameter and have [29] relaxation frequencies of the order of 500MHz [27]. The other two are connected with the relaxation of the director fluctuations [12,26] appears in lower frequencies which are commonly denoted by the Goldstone (G–mode) mode and Soft mode (S–mode). These two modes are usually observed in, the Hz and kHz regions, respectively [12,23,29–45]. In the case of G–mode [26,27,46], the equilibrium can be described if at least one of the characteristic structure parameters is changed. For the helical structure, this parameter should be the azimuthal angle ϕ that describes the position of the tilt angle. Its equilibrium behavior is given by $\phi = (2\pi/p_0)z$, where p_0 is the pitch of the helix and z is the coordinate normal to the smectic plane. A weak electric field [5,47,48] or a shear flow [49] applied perpendicular to the helix axis can change the azimuthal angle, ϕ . The typical relaxation frequency for the G–mode is in the range of 10Hz to 2kHz with relatively weak temperature dependence [29–45,50]. The corresponding dielectric strength increases rapidly as the temperature of the

system is lowered from SmA*-SmC* or SmA-SmC* phase transition temperature $T_{C^*A^*}$ or T_{C^*A} , and adopts a plateau-like maximum from a few degrees below $T_{C^*A^*}$ or T_{C^*A} . As the dielectric constant and relaxation time of the G–mode are usually large, this mode is predominant over the other dielectric response in the SmC* phase except at the vicinity of SmA-SmC* or SmA*-SmC* phase transition.

In the case of uniform structures, the structure parameter can be the molecular tilt θ_0 , which is the angle between the director $\vec{n}$ and the layer normal z . Its equilibrium position can be described by means of a strong electric field (electroclinic effect [7]) or a short thermal pulse (e.g. pyroelectric effect [51]). The S–mode appears practically in the neighborhood of the SmA*-SmC* or SmA-SmC* phase transition point. In addition to these modes, a new mode called the ‘domain mode’ is also detected [52]. In soft materials, such as, liquid crystals and polymers, their response to external field is expected to become nonlinear even under the small applied field. The dielectric relaxation spectroscopy has been extended to the nonlinear regime and applied to the research on polymers [53–55] and liquid crystals [56–58]. The S–mode relaxation frequency is usually obtained in the range of 1kHz–1MHz that varies almost linearly with temperature. The corresponding dielectric strength shows a pronounced decrease when approaches to $T_{C^*A^*}$ or T_{C^*A} in the SmC* phase or increases when away from $T_{A^*C^*}$ or T_{AC^*} in the SmA or SmA* phase. The difference between the low- and high-frequency contributions of the mode to the total dielectric constant is called the dielectric strength $[\Delta\epsilon(T)]$. In the SmA* or SmA phase, the G–mode is absent and the system exhibits a doubly degenerate S–mode.

The relaxation frequency of the G–mode is weakly dependent on temperature and is usually lower than 2 kHz [59]. The S–mode in the SmC* phase could be resolved from the G–mode within a few degree below the SmC*-SmA or SmC*-SmA* transition temperature [59]. The S–mode relaxation frequency observed in the SmC* phase decreases critically with increasing temperature. The S–mode relaxation frequency is suppressed by the G–mode well below the transition temperature because the dielectric strength of the S–mode is too low to be extracted from that of the G–mode. In the SmA or SmA* phase, only the S–mode is present. In this phase, the S–mode dielectric strength decreases and the relaxation frequency increases with temperature and reaches a minimum at the phase transition point. A similar but opposite behavior is found in the SmC* phase [59].

2.1. Theoretical description of the dielectric constant at zero bias field

The complex dielectric constant can be written as

$$\epsilon^*(\omega, T) = \epsilon'(\omega, T) - i\epsilon''(\omega, T) \quad (1)$$

where $\omega = 2\pi f$ is the angular frequency of the applied electric field and T is the temperature of the system. In general, several relaxation mechanisms, each of which is connected to the characteristic eigen-frequency f_i , are contributing to $\epsilon^*(\omega, T)$. The SmC* phase in FLCs is characterized by two two-component order parameters.

In this phase, two relaxation modes connected to the reorientation of the director, two polarization modes, and (at least) one mode connected to the electronic properties of the medium are expected. For each mode, at a given temperature, the contribution to the dielectric constant decreases with increasing frequency of the field, from the low frequency value ($f \ll f_i$) to zero, which is the value adopted when the frequency of the applied electric field is so high ($f \gg f_i$) that the mode cannot follow the electric field. This quantity is related to the average induced polarization $\langle P_i \rangle$ of the corresponding mode by the relation

$$\Delta\epsilon_i(T) = \lim_{E \rightarrow 0} \frac{\langle P_i \rangle}{E} \quad (2)$$

where, E is the magnitude of the applied field. Here it has considered that the applied electric field is only applied parallel to the smectic liquid crystal layers.

Landau theory has been used extensively for the second order phase transitions to describe the Sm C*–SmA phase transition [26,60-65]. Indenbom and co-workers [60] introduced $\vec{\xi}(\vec{r})$, the quadratic components of the molecular director $\vec{n}(\vec{r})$ as the primary order parameter for the SmC*–SmA phase transition:

$$\vec{\xi} = (\xi_1, \xi_2) = (n_x n_z, n_y n_z) \\ = [\sin \theta \cos \theta \cos \phi(z), \sin \theta \cos \theta \sin \phi(z)]$$

The in-plane components of the instantaneous polarization $\vec{P}(\vec{r})$ is the secondary order parameter of the phase transition and is given by

$$\vec{P}(\vec{r}) = (P_x, P_y) = [P_0 \sin \phi(z), P_0 \cos \phi(z)]$$

where θ is the tilt angle, ϕ is the azimuthal angle and P_0 is the polarization of the system.

It has been considered that, in the limit of small tilt angle, the primary order parameter is the projection of

the director to the smectic layers. The tilt of the long molecular axis possesses helicoidal structure as one goes from one smectic layer to another. The projection of the molecules into the smectic planes (which are taken to be parallel to the xy plane) is described by the order parameter $\vec{\xi} = \xi_1 \hat{x} + \xi_2 \hat{y}$. Due to the chirality of the molecules, the tilt of the molecules locally breaks the axial symmetry around the long molecular axis and induces a transverse in-plane polarization $\vec{P} = P_x \hat{x} + P_y \hat{y}$ perpendicular [5] to the director to the tilt. Representing the wave vector of the helix by $q = 2\pi/p$ (where p is the pitch of the helix), it can be written for small tilt angles as (Fig. 1)

Fig. 1 Schematic representation of the order parameter $\vec{\xi}$ and polarization $\vec{P}$ to the system

$$\xi_1 = \theta_0 \cos(qz), \quad \xi_2 = \theta_0 \sin(qz) \quad (3a)$$

$$P_x = -P_0 \sin(qz), \quad P_y = P_0 \cos(qz) \quad (3b)$$

where z is the coordinate of the smectic plane normal, θ_0 and P_0 are the tilt angle and the polarization of the system, respectively. Consequently, it is found that even if the system exhibits a net local polarization, then the macroscopic average will be zero.

In order to describe the thermodynamic properties of the FE SmC* – PE SmA phase transition, the free energy density is given by [12,27]

$$g_0(z) = \frac{1}{2}a(\xi_1^2 + \xi_2^2) + \frac{1}{4}b(\xi_1^2 + \xi_2^2)^2 + \frac{1}{6}c(\xi_1^2 + \xi_2^2)^3 - \Lambda \left[\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz} \right] + \frac{1}{2}K_3 \left[\left(\frac{d\xi_1}{dz} \right)^2 + \left(\frac{d\xi_2}{dz} \right)^2 \right] \\ + \frac{1}{2\epsilon} (P_x^2 + P_y^2) - \mu \left[P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz} \right] + C(P_x \xi_2 - P_y \xi_1) - \frac{1}{2}\Omega (P_x \xi_2 - P_y \xi_1)^2 + \frac{1}{4}\eta (P_x^2 + P_y^2)^2 \\ - d'(\xi_1^2 + \xi_2^2) \left[\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz} \right] \quad (4)$$

where z axis is normal to the smectic layers, a , b and c are the mean-field or Landau coefficients. Here, a varies linearly with temperature, $a = \alpha(T - T_0)$, T_0 is the Curie temperature and α is the phenomenological constant of the Landau free energy density expansion. ϵ is the generalized susceptibility. K_3 is the elastic modulus, Λ the coefficient of the Lifshitz term responsible for the modulation μ and C are the coefficients of the flexo- and piezoelectric bilinear coupling. Ω is the coefficient of the biquadratic coupling term inducing transverse quadrupole ordering and the η term has been added to stabilized the system. The d' term describes the monotonous increase of the pitch with temperature at low temperature. The sixth order term (the c term) has

been added to account for the temperature dependence of specific heat of the system [66,67].

Using Eq. 4, Carlsson et al. [27] calculated theoretically the dielectric strength and the relaxation frequency and their products for different relaxation modes present mainly in the SmC* and SmA phases of ferroelectric liquid crystals which are as below:

For the polarization modes-high frequency dielectric constant, contributions of the dielectric strength and the relaxation frequency are given by:

$$\epsilon_0 \Delta\epsilon_{PS} = \frac{1}{2 \left[\frac{1}{\epsilon} - \Omega \theta_0^2 + 3\eta P_0^2 \right]} \quad (5a)$$

$$\varepsilon_0 \Delta \varepsilon_{PG} = \frac{1}{2 \left[\frac{1}{\varepsilon} + \eta P_0^2 \right]} \quad (5b)$$

$$f_{PS} = \frac{1}{\pi \gamma_{PS}} \left[\frac{1}{\varepsilon} - \Omega \theta_0^2 + 3 \eta P_0^2 \right] \quad (6a)$$

$$f_{PG} = \frac{1}{\pi \gamma_{PG}} \left[\frac{1}{\varepsilon} + \eta P_0^2 \right] \quad (6b)$$

The suffix PG and PS indicate the polarization modes that are related to the rotation of the molecules around their long axis. ε_0 is the dielectric permittivity in free space. Here, θ_0 and P_0 are the amplitudes of the order parameters and γ_{PG} and γ_{PS} connected to the polarization modes which are related to the molecular rotation around their long axis.

Equations (5) and (6) imply very simple results concerning the product of the dielectric strength and the relaxation frequency of the polarization modes which are

$$\varepsilon_0 f_{PS} \Delta \varepsilon_{PS} = \frac{1}{2 \pi \gamma_{PS}} \quad (7a)$$

$$\varepsilon_0 f_{PG} \Delta \varepsilon_{PG} = \frac{1}{2 \pi \gamma_{PG}} \quad (7b)$$

Thus one can determine both γ_{PS} and γ_{PG} directly from the measurement of the high frequency complex dielectric constant of the FLC system.

For director modes-low frequency dielectric constant, the G-mode and S-mode contributions of the dielectric strength and the relaxation frequency are given by

$$\varepsilon_0 \Delta \varepsilon_S = \frac{b_3^2}{2 X b_7^2} \quad (8a)$$

$$\varepsilon_0 \Delta \varepsilon_G = \frac{1}{2 \tilde{K}_3} \left[\frac{P_0}{q \theta_0} \right]^2 \quad (8b)$$

$$f_S = \frac{X}{2 \pi \gamma_S} \quad (8c)$$

$$f_G = \frac{q^2 \tilde{K}_3}{2 \pi \gamma_G} \quad (8d)$$

Where, b_3 and b_7 are constants [27] $\tilde{K}_3$ is the renormalization constant, $X = 2\alpha (T_c - T)$, T_c is the ferroelectric-paraelectric phase transition temperature, γ_G and γ_S are the ordinary rotational viscosities [69,70] for the G-mode and S-mode, respectively. At very close to T_c , $\gamma_G \cong \gamma_S$.

Equations (8) imply very simple results concerning the product of the dielectric strength and the relaxation frequency of the G-mode and the S-mode which are

$$\varepsilon_0 \Delta \varepsilon_S f_S = \frac{1}{2 \pi \gamma_S} \left[\frac{b_3}{b_7} \right]^2 \quad (9a)$$

$$\varepsilon_0 \Delta \varepsilon_G f_G = \frac{1}{2 \pi \gamma_G} \left[\frac{P_0}{\theta_0} \right]^2 \quad (9b)$$

Equations (9) show that it is possible to experimentally determine the G-mode rotational viscosity by measuring four parameters viz. $\Delta \varepsilon_G$, f_G , P_0 and θ_0 without making

assumption about the materials parameters which enter into the model.

In the SmA phase, only amplitude fluctuations are present that exhibits a doubly degenerated S-mode and a doubly degenerate high frequency polarization mode. In this phase, ξ and P are zero in equilibrium. The dielectric response is taken in the limit of zero electric field, and thus one can only recall the second order term of ξ and P from Eq. (4). Moreover, the system being in the SmA phase, a homogeneous electric field are coupled to specially uniform changes of the order parameters. Carlsson et al. [27] calculated the relaxation frequency and the dielectric strength for the polarization which are given by mode (PA) and the S-mode (SA) in the SmA phase,

$$f_{PA} = \frac{1}{2 \pi \varepsilon \gamma_{PA}} \quad (10a)$$

$$\varepsilon_0 \Delta \varepsilon_{PA} = \varepsilon \quad (10b)$$

$$f_{SA} = \frac{1}{2 \pi \gamma_{SA}} \left[\alpha (T - T_c) + (K_3 - \varepsilon \mu^2) q_0^2 \right] \quad (10c)$$

$$\varepsilon_0 \Delta \varepsilon_{SA} = \frac{\varepsilon^2 C^2}{\alpha (T - T_c) + (K_3 - \varepsilon \mu^2) q_0^2} \quad (10d)$$

Finally the expressions for the products of relaxation frequency with the corresponding dielectric strength of the two modes are given as

$$\varepsilon_0 f_{SA} \Delta \varepsilon_{SA} = \frac{\varepsilon^2 C^2}{2 \pi \gamma_{SA}} \quad (11a)$$

$$f_{PA} \Delta \varepsilon_{PA} = \frac{1}{2 \pi \gamma_{PA}} \quad (11b)$$

On the other hand, Gouda et al. [35] calculated the G-mode relaxation frequency, dielectric strength, etc. very simply from the viscoelastic property.

2.2 Experimental results and discussion on some typical ferroelectric liquid crystals

Xu et al. [71] studied the frequency dependence of the dielectric absorption in the frequency range from 5 Hz to 13 MHz measured for the FLC material W314 and obtained the values of the dielectric strength $\Delta \varepsilon$ and relaxation frequency f_m by varying temperature for the collective modes. They found that the G-mode as well as S-mode relaxation frequency was temperature dependent. In the SmA phase, $\Delta \varepsilon$ referred to the dielectric strength of the S-mode. In the SmC* phase in close to the transition, it referred to the combined strengths of G-mode and S-mode and away from the transition it referred to the G-mode alone as the strength of S-mode was significantly reduced. The plot of f_m similarly referred to the S-mode in the SmA phase and G-mode in the SmC* phase. No S-mode was found near the SmA-SmC* transition temperature in the SmC* phase when the bias field is zero. These data were obtained from typical bulk FLCs [72]. For some materials, the G-mode and the S-mode were well observed [73] when the bias field was set to zero. For such materials, the G-mode relaxation frequency was almost temperature independent. This is a non-activated process. The S-mode relaxation frequency was also

decreased in the SmC* phase and increased in the SmA phase with temperature. However, a different trend of variation of $\Delta\epsilon$ as well as f_m with temperature was noticed for these liquid crystalline materials. This difference seems to be associated with the different nature of the intermolecular dipolar ordering, which changes with temperature.

Kocot et al. [73] obtained the relaxation time τ_s for G-mode and S-mode with varying temperature for the material siloxane copolymer. They found that τ_s decreased and hence f_s ($= 1/2\pi\tau_s$, frequency of the S-mode) increased rapidly with decreasing temperature in contrast to the observed behavior of the G-mode except for temperatures close to T_c . Nevertheless the variation of τ_G seemed to be much stronger for the polymer than for low molar mass FLCs. This is because the viscosity of the polymer strongly influences this behavior. They also obtained temperature dependence of the dielectric strength for the G-mode and S-mode. In the SmC* phase, the dielectric strength of the G-mode was found to be almost constant with temperature in contrast to the behavior observed for the soft mode. For the ferroelectric liquid crystalline polymer (FLCP), these detailed results, which showed a splitting up of a single mode into two modes at $T = T_c$ in both frequencies and dielectric strengths, are the first of its type being reported in the literature. Note that these observations are connected with the requirement of having an almost perfect homogeneous alignment of the sample which has been made possible for this case by the dilution of the polysiloxane as effected here and a reduction in its ionic conductivity. For the low molar mass FLCs however, these observations have been made before by Cava et al. [31], Gouda et al. [35] and Kremer et al. [74].

In some materials [45,75], the molecular mode, domain mode and the mode x are present in the SmC and SmC* phases. The high frequency process is mainly related to the rotation around the molecular long axis called the molecular mode due to the transverse dipole moment. The low frequency process is mainly related to the rotation around the molecular short axis called the domain mode due to the longitudinal dipole moment. However, in the high frequency side another relaxation with very small amplitude was needed for describing the data. This mode is called the mode x . It was also found that the G-mode and S-mode were strongly temperature dependent [75]. This temperature dependence of the G-mode clearly indicates that this process is an activated process.

The domain mode related to the reorientation of the molecular long axis around the short axis showed a typical behavior in frequency and amplitude [76-82]. In the isotropic phase, its amplitude was lower than that of the molecular mode indicating that μ_l is smaller than μ_t , as one might expect from the molecular structure, where μ_l is the longitudinal dipole moment and μ_t is the transverse dipole moment. μ_l is usually smaller than μ_t as is expected from the molecular structure. It suffers a decrease at isotropic to chiral nematic (Iso. – N*) (or nematic, N) phase transition, which must be due to the onset of some planer order. In the smectic mesophases, it showed a continuous but very small decrease with decrease of temperature. If the planar alignment is

perfect, no contribution from this mode could be observed in the permittivity. It is observed in the orthogonal SmA phase, although with a very small amplitude ($\Delta\epsilon_l \cong 0.5$), indicated that the alignment was not perfect. The relaxation frequency showed a jump at the isotropic (Iso.)– chiral nematic (N*) (or nematic, N) phase transition due to the onset of the nematic order. No jump was observed at the SmA – SmC* (or SmC) transition. The observed frequency was fitted with the Arrhenius law in the Isotropic and SmA phases:

$$f_1 = f_{\infty 1} \exp\left(-\frac{E_a}{k_b T}\right) \quad (12)$$

where, $f_{\infty 1}$ is the pre exponential factor and k_b is the Boltzmann constant. The activation energy E_a , is 80 kJ mol⁻¹ in the Isotropic phase and 98 kJ mol⁻¹ in the SmA phase. This increase of E_a is also expected and is due to the hindrance of this rotation by the smectic (or nematic) potential. However, in the SmC phase the relaxation frequency followed the Vogel–Fulcher–Tammann (VFT) law:

$$f_1 = f_{\infty 1} \exp\left(-\frac{A'}{T - T_0}\right) \quad (13)$$

In this expression T_0 is the so called Vogel or ideal glass transition temperature (30–50 K below the calorimetric glass transition T_g), and A' is a constant. For this mode Palacios et al. [82] obtained $f_{\infty 1} = 7.6 \times 10^7$ Hz, $A' = 480$ K and $T_0 = 207$ K.

The observed high frequency relaxation is mainly due to the molecular mode, which relates to the overall rotation around the long axis and this relaxation process is very broad. On analyzing the dielectric data at different temperatures, another relaxation process called the mode x with different (smaller) thermal activation was present [45,82]. In this mode, the dielectric amplitude, which dependent on the transverse dipole moment, μ_t , exhibited an increase on cooling down from the Iso. phase ($\Delta\epsilon_t \cong 1.8$) through the N* (or N) phase into the SmA phase ($\Delta\epsilon_t \cong 1.9$). In the SmA and high temperature side of the SmC* (SmC) phase it was almost constant with a very small but very small continuous decrease. Near the glass transition the dielectric amplitude decreased. The relaxation frequency did not show any jump at the phase transitions, but only continuous non-Arrhenius temperature dependence was observed. It was described by the VFT law (eq.13). For this mode, the parameters $f_{\infty 1} = 5.9 \times 10^{10}$ Hz, $A = 414$ K and $T_0 = 207$ K were obtained. The spectral shape depended on the temperature. The spectral shape is easily explained by the well know Havriliak-Negami equation [83] and the shape parameters α' and β' can be obtained. In the Iso and the N* (or N) phases, the parameter α' increased smoothly from 0.78 to 0.81, then jumped in the SmA phase up to 0.85. This value was maintained in the SmC* (SmC) phase and then decreased when the temperature was close to the glass transition. The behavior of the parameter β' was different. The value of this parameter decreased continuously from the value 0.77 in the Iso. phase, 0.66 in the N* phase and from 0.63 to 0.41 in the SmA phase. The same tendency was observed in the SmC* phase

where this parameter reached around 0.31 at temperatures close to the glass transition. The parameter β' showed clearly the tendency of this relaxation to become broader upon cooling towards T_g .

The relaxation mode x is perhaps not very well characterized because it has very small dielectric strength, around 0.1, at high frequency (near the broader of our experimental window), and is very near to the molecular mode, above all on the high temperature side. Its behavior is Arrhenius-like with E_a around 24 kJmol⁻¹. This mode is not affected by the glass transition and it might be related to the internal degree of freedom of the molecule associated with a polar group or also to a vibrational motion [71]. In 1989, Gouda et al. [35] obtained the dielectric strength and relaxation frequency for the S-mode below and above the SmC*-SmA phase transition for the material 4-[(S)-2-chloro-3-methylbutanoyloxy]-4'-decyloxy-biphenyl. It was found from their observation that the plot of the inverse of dielectric strength ($1/\Delta\epsilon$) and the relaxation frequency showed 'V' shape with temperature. Therefore, the ferroelectric phase transition is of the second order in nature [71]. $1/\Delta\epsilon_S$ for the SmA phase and f_S in the SmC* phase intersect near $T = T_c$. The discontinuity in $1/\Delta\epsilon_S$ at the phase transition is due to the reason that the S-mode in the SmA phase is doubly degenerate, hence the amplitude of $1/\Delta\epsilon_S$ is two times $\Delta\epsilon_S$ at $T = T_c$. These results are explained by the molecular-field approximation [26]. According to this approximation, the critical frequency of the S-mode should follow the following relation: $\nu_c = m(T - T_c) + m'$, where m and m'

are constants. According to this approximation, the slope ratio is predicted to be two. In the case of the siloxane copolymer, the slope of the straight line $\Delta(1/\epsilon_S)/\Delta T$ in the SmA phase was slightly higher than in the SmC* phase. The result was found to be the reverse to that determined for the low molecular mass liquid crystals by Cava et al. [31] and Glogarova and Pavel [84] where $\Delta(1/\epsilon_S)/\Delta T$ is higher in the SmC* phase than in the SmA phase. The observation was explained by the generalized Landau model [84,85] in terms of having a large biquadratic coupling relative to the bilinear coupling between P_s and θ , i.e., by relatively low value of β [73] (is the dimensionless parameter). Similar observations are obtained from the plot of relaxation frequency vs. temperature data.

For the G-mode it is possible to derive [14,26] expression where the dielectric strength and the relaxation frequency are expressed in terms of the spontaneous polarization P_0 , tilt angle θ_0 and the wave vector of the pitch q (Equations 8(b) and d)). The physics behind these expressions is easy to understand. The coupling of the spontaneous polarization to the external field increases with P_0 . This suggested $\Delta\epsilon_G \sim P_0^2$ as the response cannot depend on the sign of P_0 . Furthermore, the elastic energy associated with the pitch is given by $g_k = K_3 q^2 \theta_0^2 / 2$. This suggested $\Delta\epsilon_G \sim 1/K_3 q^2 \theta_0^2$. Therefore, it is expected the G-mode dielectric strength can obey the relation $\Delta\epsilon_G \sim P_0^2 / K_3 q^2 \theta_0^2$, which is simply the result of Eq. 8(b). The restoring torque of the G-mode is determined by the twist elasticity of the

system. Applying a uniform electric field, it is observed that wave vector q is distorted and thus the restoring torque is proportional to $K_3 q^2$ since it is not dependent on the sign of q . This torque is counteracted by a rotational torque (Γ) which is proportional to the rotational viscosity $\gamma_1 = 1/\Gamma$. It is thus expected that the G-mode relaxation frequency $f_G \sim K_3 q^2$, in accordance with Eq. 8(d). The product of dielectric strength and the relaxation frequency of the G-mode is given by Eq. 9(b). It is expected that this product is proportional to $(P_0/\theta_0)^2$ [86]. Filipic et al. [13] obtained this product experimentally for the material {16. wt.% 4 [(S)-2-chloro-3-methylbutanoyloxy]-4'-(4-cyloxybenzoyloxy)-biphenyl, 48.2 wt.% {4-[(S)-2-chloro-3-methylbutanoyloxy]-phenyl}-4-decyloxybenzoate, and 35.1 wt. % {4-[(S)-2-methylbutanoyloxy]-phenyl}-4-octyloxybenzoate}. One finds that this quantity increased with decreasing temperature. However, it was not saturated as P_0/θ_0 but started to decrease with decreasing $T_c - T$ at lower temperatures. One reason behind this might be due to the temperature dependence of $\Gamma = 1/\gamma_1$. Being a viscosity, γ_1 should be expected to decrease with increasing temperatures. This could be the probable reason for the reduction of the product $\Delta\epsilon_G f_G$ varies with $T_c - T$ at lower temperature. Similarly, one finds that the product of the $\Delta\epsilon_S$ and ν_S of the S-mode in the SmC* phase (Eq. 9a) should also be proportional to $(b_3/b_7)^2$. The ratio of the quantity b_3/b_7 plays an analogous role for the S-mode, as does P_0/θ_0 for the G-mode. Similar result was also obtained on other FLCs viz. Falix-SCE9, ZLI-4851 [42,87].

In the SmA phase the theoretical model predicted [14] that the inverse dielectric strength and the relaxation frequency of the S-mode decrease linearly with temperature when approaching T_c (Eqs. 10(c) and d)). The product of dielectric strength and the relaxation frequency ($\Delta\epsilon_{SA} f_{SA}$) of the soft mode given by Eq. 11(a) is simply dependent on the term viscosity. Any Landau model, however complicated, would give the result that this product is constant in the SmA phase if the dynamics are assumed to be described by a single kinetic coefficient Γ . Experimentally, it was observed that for the material {4-[(S)-2-chloro-3-methylbutanoyloxy]-4'-decyloxy-biphenyl}, in most of the temperature interval this product is constant, however, it showed a pronounced drop close to T_c [13]. Thus the expressions 10 (c) and 10(d) describe that the experimental situation is fairly well. Only very close to T_c does the theory predict too large a value of f_{SA} or $\Delta\epsilon_{SA}$ or both. This type of discrepancy between the theory and the experiments was also well known from the study of the other ferroelectric systems [88].

2.3 Bias field dependence of the dielectric behavior

To characterize the properties of FLCs [5] near the SmC*-SmA phase transition, the determination of the complex dielectric constant is of great interest, because in the same experiment the low frequency dielectric constant (static) as well as the frequency dependence of the dielectric constant (dynamic) of the system can be studied. The ferroelectric properties can be appeared in the different tilted chiral smectic mesophases also (C*,

I*, F*, G*, J*, H*, K*). From all of these possible phase transitions yielding a ferroelectric phase, only the SmC*-SmA* and SmC*-SmA transitions have been described theoretically so far [12,26,27]. It is generally considered that these transitions, when approaching from the SmA* and SmA phases, are due to softening of the spatially inhomogeneous fluctuations of the molecular tilt with respect to the smectic layer normal. Below the transition, in the ferroelectric phase, a spontaneous tilt of the molecules appeared at an angle θ with the smectic-layer normal is formed a helicoidal structure. In the vicinity of the transition, the S-mode gives a contribution ε_s to the permittivity. In the SmA or SmA* phase ε_s is the contribution of the permittivity due to the occurrence of the phase transition [89]. But in the SmC* phase ε_s is overwhelmed by the contribution ε_G from the G-mode. This is a vibration of the helical structure that appears below the transition [89]. In general ε_s and ε_G can be distinguished by their different relaxation frequencies f_s and f_G , but near the transition, f_s and f_G can be differed by only one order of magnitude [90], i.e. ε_s is overwhelmed by ε_G even at f_s . Therefore, for the determination of ε_s near the transition, it is necessary to unwind the helicoidal structure. The unwinding is achieved by decreasing the sample thickness d to the value comparable to the helicoidal pitch p [91]. In such a case, owing to the polar anchoring at the sample boundaries, a twist along the sample thickness takes place [92]. Deformations of the twist in the electric field contribute to the permittivity with a similar strength and can exhibit a similar relaxation frequency to the G-mode [93]. For still thinner samples ($d \approx 1\mu\text{m}$), which provide a specially homogeneous structure [94], the smectic layers are usually tilted [95,96] from the sample plane normal that results in a complicated defect structure. Moreover the properties of extremely thin samples are determined mostly by the boundary conditions.

Unwinding the helicoidal structure by electric or magnetic field in thick samples is the best way to obtain a homogeneous structure with which ε_s is determined in the vicinity of the transition in the SmC* phase. On the other hand, the field considerably influences the phase transition as well as the ε_s contribution. A static electric field applied perpendicular to the helix axis in the SmC* phase loosens the stability of the spiral structure. In the limiting strong field, the dipole moments align themselves along the field and the twisted SmC* phase becomes unwound [97,98]. The critical field for unwinding the helix depends on the dielectric anisotropy, the tilt angle and the pitch as well as the elastic and piezo- and flexo-coefficients of the material [34]. The static electric field is also an important experimental variable for the dielectricity of ferroelectric materials.

Tilted FLCs in surface stabilized geometry offer high speed, high contrast and bistable electro-optic switching characteristics [99,100]. Surface stabilized geometry allows the superposition of the intrinsic helix of FLC's and produces two stable states with opposite P_s , which can be switched from one state to another with a time constant of a few microseconds by applying a relatively small amount of external voltage. P_s exists only in the

chiral tilted smectic phases. However, in non-tilted chiral smectic liquid crystals such as SmA phase, there exist a different and a faster switching mechanism, typically 100 times faster. This is due to the electroclinic effect [8,101]. Such effect arises when an electric field is applied parallel to the smectic layers that induces a molecular tilt relative to the smectic layer normal [7]. The practical applications require an understanding of the electroclinic response by an applied electric field.

2.3.1 Experimental results and discussion on the bias field dependent relaxation behavior

One can see below the intensity of the S-mode is rapidly suppressed from the G-mode as the temperature of the system is lowered from the SmA*-SmC* or SmA-SmC* transition temperature. It makes it possible to separate [12,13,29] the contribution from the two modes only in a temperature interval which is far below the SmC*-SmA* or SmC*-SmA phase transition temperature. One way is to study the S-mode in a broader temperature interval into the SmC* phase by applying a bias electric field parallel to the smectic layers. The G-mode can be completely suppressed if the bias field is strong enough so that the helix of the system is unwound. Different types of studies of the dielectric properties under the bias electric field near the SmA*-SmC* or SmA-SmC* transition have been performed [36,94,103]. It is well known that close to the SmC*-SmA* or SmA-SmC* transition temperature, the tilt is strongly affected [7,67,103,104] by the bias field in both the SmC* and SmA phases. This change of tilt angle should, of course, be estimated to the influence of the dielectric properties of the system.

The strong process of the SmC* phase shows typical G-mode relaxation behavior [12,23,29-45]. It can be suppressed by the DC bias field. In the year 1991, Pfeiffer et al. [105,106] studied the bias field dependence of ε'' of the G-mode at 303.3 K with increasing bias field for the material alkoxyphenylthiobenzoate FLC [73] in the SmC* phase. They found that at this temperature, field strength of about 10 kV/cm completely suppressed the G-mode [105]. In this case two weak relaxation peaks were seen. The only the mode close to the SmC*-SmA phase transition, the S-mode is detected in the SmC* phase. The other processes seemed to be a domain mode were seen. Kocot et al. [73] successfully separated the G-mode and S-mode by the application of bias electric field of 1V/3 μm . The G-mode is observed relatively lower frequency side and appears distinct and well separated S-mode. They also studied the variation of the dielectric strength as well as relaxation frequency with the bias field for the material ferroelectric copolysiloxane [73] in the SmC* phase. The S-mode was detected when the bias field of 1V/3 μm was applied. But when the bias field is higher than 2 V/3 μm , the G-mode was significantly reduced. It was found that the dielectric strength (from 40 to 0.08) as well as relaxation frequency (from 200 Hz to 20 MHz) shifted towards lower values when the bias field is increased from zero. Note that this material is very sensitive to biasing. Though the dielectric strength followed the

same behavior as above, the relaxation frequency followed the opposite behavior [87,106,107].

The most interesting result was the drastic decrease or increase of the relaxation frequency (f_G) of the G-mode with an increase of bias field. The values of f_G were obtained by fitting the Cole–Cole equation of the experimental points. Pfeiffer et al [105,107] analyzed the behavior of the G-mode on the basis of the assumption that the f_G measured by dielectric spectroscopy has the same physical nature viz. a characteristic frequency of an electrooptical response of helical FLC under a weak a.c. field (deformed helix ferroelectric (DHF)-effect) [48]. Then the following equation was used:

$$f_G \sim \frac{K \Theta_0^2}{\gamma_\phi P_0^2} \quad (14)$$

where K is the effective elastic modulus, γ_ϕ is the rotational viscosity and Θ_0 is the molecular tilt angle. On the other hand, the increase of f_G with the bias electric field is connected to the increase of effective value of the elastic modulus K in Eq. (14). Detailed discussion has been made by Pfeiffer et al. [105,106]. They described it in a way that without any bias field, the “classical” helicoidal structure takes place. Moving along the z axis (normal to smectic layers), the molecular tilt plane rotates uniformly, and the dependence of the azimuthal angle $\phi(z)$ can be described as

$$\phi(z) = \sin(2\pi z/p_0) \quad (15)$$

A weak bias field induces a helix deformation, which could be described as a deviation of the curve $\phi(z)$ from the sine wave form [47]. It is clear that, the larger the value of the bias voltage, larger is the area of the sample (or a part of the helix along the z -axis), uniform states take place (here uniform states are the states of the molecular director $\vec{n}$ being parallel to the samples of the electrode [88]). These uniformly oriented states do not give any contribution of the G-mode [108]. Therefore, the absolute value of the dielectric permittivity (both ε' and ε'') should decrease due to the fact that the remaining non-uniformly oriented parts of the sample area are decreasing. At the same time in these non-uniformly ordered areas the helix deformation increased (due to twist and bend deformations), and because of this an increase of the elastic modulus should take place. This is similar to a string, which increases its elasticity under increasing deformation. In both cases (FLC and string) an increase of the characteristic frequency should be observed.

2.4 Thickness dependent dielectric relaxation behavior

Liquid crystals, like water, conform the shape of its vessel. The vessel contains not only shape but also the molecular alignment at least near the cell surface. Molecular alignment plays an important role in homogeneous cells of FLCs. The FE ordering in the SmC* phase is usually denoted by two-order parameters [64]: one is the molecular tilt angle (θ) and the other is spontaneous polarization (P_s). The tilt angle of the long molecular axis with the smectic layer normal, processes a helicoidal structure from one smectic layer to the other

with helical axis coincident with the layer normal. Spontaneous polarization developed in the plane of the smectic layers, perpendicular to the tilt plane and also processes from layer to layer that forms a helix. Due to existence of the helix, there is no net polarization on a macroscopic level. However, the introduction of parallel bounding surfaces normal to the layers, which interact with the director as well as P_s , prevents the helix formation and leads to bookshelf or chevron geometry. This is the basis of the surface stabilized ferroelectric liquid crystals [15].

Sample thickness is another important parameter that specifies the dielectric properties of the FLC cells. Because, it affects the helical structure of the cell, the transition temperature [109,110] and the magnitude of P_s [111,112]. Moreover the switching mechanism in electro-optical devices depends on the sample thickness, surface condition, temperature and even on material parameters such as tilt angle and spontaneous polarization. The dielectric response of FLCs depends on the sample thickness especially in the SmC* phase. It has been reported that in the specimens whose sample thickness is less than the helical pitch, the helical structure is completely unwound [15]. The dielectric behavior of the surface stabilized FLC could be to some extent different from that of the specimens with helical structures. The dielectric behavior due to the G-mode cannot be estimated to have the same sense as of thick cells since there is no helical structure observed in the surface stabilized FLCs. Although measurements of the dielectric properties have been performed on various FLCs, less attention has been paid to their sample thickness dependence. Systematic investigation of the sample thickness dependence of the dielectric properties will be expected to clarify the effect of inter-surface interaction between the cell surfaces and the molecules on the dielectric properties.

2.4.1 Theoretical analysis of the thickness dependent dielectric behavior

It is well known that ferroelectric crystals are divided into domain at a temperature below the Curie point. This is due to the fact that when the crystal is divided into the domains, the energy of the depolarizing field diminishes and correspondingly polarizability of the developed P_s into the crystal emerges. Chenskii [113] considered the layer like domain structure of a ferroelectric crystal with a phase transformation of 2nd kind in a free plate of thickness ' L ' having a 180° domain of width ' d '. Let the ferroelectric be an ideal dielectric, uniaxial with ferroelectric axis directed along the z axis, perpendicular to the direction of the plate. The total free energy of the ferroelectric takes the form

$$I = \int \left[\frac{A}{2} P_z^2 + \frac{B}{4} P_z^4 + \frac{E_z^2}{8\pi} + \frac{\varepsilon_y}{8\pi} E_y^2 + \frac{\chi}{2} (\nabla P_z)^2 \right] dV \quad (16)$$

where $A = \alpha(T - T_C)$, B is a constants, $A > 0$ and $B > 0$, P_z is the ferroelectric polarization and E_y , E_z are the electric field along the y and z directions respectively, ε_y is the background permittivity and χ is the dielectric susceptibility.

The energy density of the plate now may be expressed in the form

$$F = \frac{A}{2} P_{0z}^2 + \frac{B}{4} + P_{0z}^4 + \frac{1}{L} f_{el} + \frac{\sigma}{d'} \quad (17)$$

f_{el} is the energy of the depolarizing field per unit surface of the plate and σ is the energy of the unit surface of the domain wall.

Chenskii considered the limiting cases: i) a plate is so thick that in the center of the domain, polarization is close to the spontaneous value $P_{0z} \approx P_s(-A/B)^{1/2}$ and ii) the plate is so thin that the polarization in the center of the domain is close to zero ($P_{0z} \ll P_s$). The equilibrium values of the P_{0z}^2 and F (Eq. 17) are given by

$$P_{0z}^2 = -\frac{A}{B} \left(1 - \sqrt{\frac{L_{\min}}{L}} \right) \quad (18)$$

$$F = -\frac{A^2}{4B} + \left(1 - \sqrt{\frac{L_{\min}}{L}} \right) \quad (19)$$

where $L_{\min} = \frac{8\pi l}{|A|}$ is the minimum plate thickness in

which the ferroelectricity is possible at the specified temperature and this plate thickness ($L = L_{\min}$) corresponds to the width of the equilibrium domains $d'_{\min} = 2\pi l$, where l is the thickness of the domain wall.

It is seen from Eq. (18) that the spontaneous polarization in the free plate appears not at Curie point T_c but at a temperature lower than this. The temperature of the phase transformation T_x can be obtained from the equation at $L = L_{\min}$ which is

$$T_x = T_c - \frac{10^{-4}}{L} \quad (20)$$

where T_x is the maximum critical temperature, when the thickness $L \rightarrow \infty$

Magnetic phase transitions among conduction electrons can lead to instability of an electron gas in normal metals under condition of the de Hass-Vann Alphen effect [dHVA]. This instability is known as diamagnetic phase transition [114]. A series of phase transitions takes place at discrete values of the external magnetic field. The reason for this collective effect is that the electrons are subjected to the magnetic induction instead of the magnetic field [115]. When the magnetization shows dHVA oscillations, the domain state reoccurs periodically in each cycle of oscillation. This instability is known as diamagnetic phase transition. Several workers [113,115-123] have studied domain formation at diamagnetic phase transitions theoretically. The 2nd order phase transitions are accompanied by critical phenomena by causing large temperature anomalies. Diamagnetic phase transitions have only been observed by using local microscopic experimental methods such as the nuclear magnetic resonance and muon spectroscopy. But they have not been observed by non-local experimental methods such as susceptibility, specific heat and sound-velocity measurements near the phase transitions. According to mean field theory, the derivatives of the thermodynamic potential, susceptibility and the specific heat exhibits the discontinuities at the transition points [124]. This theory describes the specific heat temperature jump and the susceptibility-temperature anomaly at a 2nd order

diamagnetic phase transition that deals with the transition into a single domain state.

From the mean field theory, Gordon and Wyder considered the finite size effect at diamagnetic phase transition and according to multi domain structure influence on the specific heat is more at the diamagnetic phase transition. The finite size effect on the magnetic ordering of the orbital magnetic moments of the conduction electrons in 3D normal metals under conditions of the dHVA effect was taken care of it. It has to be considered as the slab of the infinite planar extent ($L_x, L_y \rightarrow \infty$) and of finite thickness L_z . Gordon and Wyder examine this sample geometry because all the direct measurements of Condon domains [126-131] were made for plane like samples, when two dimensions of the specimen were much larger than its thickness. Additional reason for this consideration was the stripe nature of Condon domains following from the available measurements [122,126-131]. It was shown that a rectangular, ideally uniaxial slab with the magnetization direction perpendicular to the thickness L breaks up into domains of alternating slices of up and down-magnetization with a domain width D . The demagnetization energy per unit volume is reduced to $14/\pi^2 \xi(3) M^2 D/L$, [132,1133] where ξ is the ξ function, M is the oscillatory part of the magnetization.

Gordon and Wyder derived equilibrium value of the magnetization M_0 in the domain center by minimizing the thermodynamic potential with reverence to magnetization, for a given slab of thickness L and a domain width D

$$M_0 = \left[\frac{3(\zeta-1)}{8\pi^2 k^2 \zeta} \left(1 - \left(\frac{L_{\min}}{L} \right)^{1/2} \right) \right]^{1/2} \quad (21)$$

$$D = \frac{5}{3} (L)^{1/2} K^{1/4} (\zeta-1)^{1/4} \quad (22)$$

where ζ is the reduced amplitude of oscillation, k and K are the typical parameters [134], $L_{\min}$ is the minimum slab thickness for which the magnetized state is possible (here, the order parameter is non zero)

$$L_{\min} = \frac{9K^{1/2}}{2[\pi(\zeta-1)]^{3/2}} \quad (23)$$

Equation (22) is the well-known Kittel relation: $D \sim L^{1/2}$ [132,133] for stripe domains. Using equation (21) and (23), the obtained phase transition temperature is of the form:

$$T_x = T_c - \left(\frac{3^{4/3}}{\lambda} \right)^{2/3} \left(\frac{2}{L} \right)^{2/3} K^{1/3} \quad (24)$$

where T_c is the Curie temperature for the sample, T_x is the temperature of the magnetic order onset of the slab and λ is the screening length. It follows from Eq.(24) that the magnetized state appears in the slab not at the Curie temperature T_c of the finite sample but at a temperature T_x lower than this. As the film becomes thinner, demagnetization fields become important, lowering both the Curie temperature and spontaneous magnetization. This equation is strongly different from that derived for ferroelectric domains [113,135] by the same method of minimization because Gordon and Wyder took properly into account the surface tension of domain walls and the temperature dependence of the

domain wall width in this case. Thus, diamagnetic phase transition temperature is shifted to a lower temperature with decreasing slab or film size. In the limiting case of a very thick specimen, the two temperatures of the phase transition for infinite and finite size samples coincides at $L \rightarrow \infty$, $T \rightarrow T_c$. This phase transition temperature shift is expected from the character of the phase transition.

In the frame work of phenomenological Landau theory the Gibb's free energy density F [136] for a non-chiral SmC phase at temperature T is given by an even power series expansion of the tilt angle θ which is the primary order parameter of the SmC*-SmA transition

$$F = a\theta^2 + b\theta^4 + \frac{1}{2}g\left(\frac{\partial\theta}{\partial x}\right)^2 \quad (25)$$

where $a = \alpha(T - T_c)$, $a > 0$, $b > 0$ and g is the elastic modulus and the phase transition point T_{cmax} corresponding to $d \rightarrow \infty$.

The polarization components P_x and P_y along X and Y direction are given by

$$P_x = \chi\left(\mu - \frac{2\pi f}{h}\right)\theta(x)\sin\phi(z) \quad (26)$$

$$P_y = -\chi\left(\mu - \frac{2\pi f}{h}\right)\theta(x)\cos\phi(z) \quad (27)$$

where $\phi(z) = 2\pi z/h$, μ and f are the piezoelectric and flexoelectric moduli respectively and χ is the dielectric susceptibility.

For the theoretical calculation of thickness dependence of T_c , Pikin and Yoshino [110] considered typical planar orientation of the molecules on two boundaries with crystalline axis Z being parallel to the flat solid surfaces. For strong anchoring conditions, the director orientation is parallel to the Z-axis at $x = 0$ and $x = d$, where d is the sample thickness. The tilt angle $\theta = 0$ on the boundaries i.e. the boundary condition is $\theta(0) = \theta(d) = 0$. In this case, the azimuthal angle $\phi(z)$ in the SmC* phase has the same value for $0 \leq x \leq d$, i.e., the helix has the unperturbed pitch h for any layer thickness. Under these conditions, Pikin and Yoshino obtained the thickness dependent phase transition temperature

$$T_x = T_c - \left(\frac{\pi^2 g}{2a}\right) \frac{1}{d^2} \quad (28)$$

where T_x is the observed transition temperature for a particular thickness of the cell, T_c is the Curie temperature observed by polarizing microscopic technique, ' g ' is the elastic modulus and $\bar{a}$ is a parameter. By considering anchoring energy W , they also obtained the phase transition temperature

$$T_x = T_c - \left(\frac{\pi^2 g}{2a}\right) \frac{1}{\left(d + \frac{2g}{|W|}\right)^2} \quad (29)$$

where T_c = normal transition temperature, T_{cmax} is the maximum value of transition temperature and W is the anchoring energy.

When $|W|d \gg g$, then $|T_c - T_{cmax}| \sim d^2$ and at $|W|d \ll g$, the shift of $T_c(d)$ is very small and at $|W|d \sim g$, the dependence of $T_c(d)$ is smooth.

Thus it is possible to estimate the material parameters of the chiral smectics and the anchoring energy from the

experimental data of $T_c(d)$ in the case of the geometry shown in Fig. (2).

Fig.2 Geometry of a chiral smectic layer for strong planar anchoring conditions.

2.4.2 Experimental results and discussion on the thickness dependent relaxation behavior

Miyata et al. [137] obtained the frequency dependence of the real part (ϵ') of dielectric absorption for the different fixed sample thickness for the FLC material CS-1022. The dielectric constants of the specimens with sample thickness of 2, 3 and 8 μm , which are less than the helical drawpitch in the SmC* phase are much smaller than those of the specimen with a thicker cells.

The frequency dependence of the imaginary part (ϵ'') of the dielectric constant at room temperature was measured with varying the frequency from 1 Hz to 1 MHz for the specimens with sample thicknesses from 2 μm to 50 μm . These results showed that there exists a typical Debye type relaxation around several hundred Hz. The relaxation frequency shifted to the higher frequency side with diminishing the sample thickness. It indicates that the characteristic molecular motion is responsible for the fluctuation of the azimuthal angle in the thick cell is slower than that of the thin specimen. The molecular motion in the thick cell was somewhat restricted due to the surface anchoring. Note that at room temperature, the dielectric strength increased with increasing sample thickness whereas the relaxation frequency increased remarkably with diminishing sample thickness because, the response in the thick cell is more freer than that of the thin cell specimens in the region below 20 μm .

Miyata et al. [137] also studied the sample thickness dependence of the SmC*-SmA transition and obtained the thickness dependent phase transition temperature for the material CS-1022. The nature of this type of transition was also detected in some other FLCs [109,137]. The transition temperatures for those of the bulk specimens were almost independent of the sample thickness but for the surface stabilized FLC, the transition temperature was rapidly decreased with further decrease of the sample thickness. The SmC*-SmA transition dependent on the sample thickness for the materials viz. CS-1022, p-decyloxybenzylidene-p'-amino-2methylbutyl cinnamate (DOBAMBC), etc. agrees qualitatively with the theoretical result obtained by Pikin and Yoshino [110]. The result indicated that the effect of surface anchoring

cannot be neglected for the thin cell [109]. The "Pikin and Yoshino" [110] has also reported their results on the material p-decyloxybenzylidene-p'-amino-2methylbutyl cinnamate. Kondo et al [109] has reported their result in the material (S)2-methylbutyl p-[(p-n-decyloxybenzylidene) amino] cinnamate. As evident from the nature of the thickness dependent phase transition on the material p-decyloxybenzylidene-p'-amino-2methylbutyl cinnamate, the transition temperature T_c decreased remarkably with decreasing cell thickness, indicating good agreement with the theoretical predictions (Eq. 29). The value of the surface energy ($|W| \sim 10^{-2}$ cgs esu) was estimated for sufficiently strong anchoring conditions. The material (S)2-methylbutyl p-[(p-n-decyloxybenzylidene)amino] cinnamate (DOBAMBC) exhibited the same tendency with p-decyloxybenzylidene-p'-amino-2methylbutyl cinnamate but there was a great difference between them. That difference originated from surface conditions because it forces the molecules not only to become parallel to the surfaces but also to orient along a particular direction, namely, the layer normal. Hence the decrease in the phase transition temperature for the material p-decyloxybenzylidene-p'-amino-2methylbutyl cinnamate was larger than (S)2-methylbutyl p-[(p-n-decyloxybenzylidene)amino] cinnamate when the compound at the same thickness. But the theoretical prediction made by Pikin and Yoshino was not fitted well for the materials (S)2-methylbutyl p-[(p-n-decyloxybenzylidene)amino] cinnamate. Note that the transition temperature calculated from dielectric measurements and from spontaneous polarization measurements exhibited the same tendency. Kundu et al. [41] obtained the thickness dependent SmC*-SmA phase transition temperature by varying the sample thickness in the range of 6 to 80 μm . They found that dielectric constant as well as SmC*-SmA phase transition temperature increased with increasing sample thickness. The phase transition temperature T_c increased non-linearly with cell thickness. For describing this non-linear dependence of the SmC*-SmA phase transition, they proposed an empirical formula which is below:

$$T_x = T_c - \zeta d^{-n} \quad (30)$$

Since the sample thickness d causes a change of domain width, both these parameters are domain width dependent and hence they are associated with the molecular ordering or dipolar interaction. It indicates that the magnitudes of the values of ζ and n give a measure of the degree of molecular ordering and hence dipolar interactions which are different for different FLCs. Different values of molecular interaction strengths are actually responsible for different magnitudes of thickness dependent T_x values.

3. ANTIFERROELECTRIC LIQUID CRYSTALS

In chiral smectic phases, the average direction of elongated molecules is tilted at an angle with respect to the layer normal. Smectic layers are spontaneously polarized in the plain of the layer and perpendicular to the direction of the tilt. Among these polar smectics, the most widely experimentally and theoretically studied materials are FLCs. In 1989, synthetic FLCs with large

spontaneous polarization, antiferroelectric liquid crystals (AFLCs) were discovered [138]. One of the most interesting phenomena of the antiferroelectric (AF) phase of AFLCs is its ability to exhibit tristable switching, which makes it interesting for the use in display devices. The structure of SmC_A* phase is found to possess AF ordering [138,139]. In the SmC_A* phase, the molecules in adjacent layer are tilted in opposite directions and consequently the dipoles are cancelled out and so no net spontaneous polarization appears. The SmC_A* phase has been confirmed to exist in many substances [140]. Most of these substances show a number of sub-phases designated by SmC _{α} *, SmC _{γ} * and some others in addition to the ferroelectric (FE) SmC* phase and AF SmC_A* phase [141-145]. The appearance of these sub-phases can be understood due to the result of the competition between AF and FE interactions in adjacent smectic layers that stabilize the SmC_A* and SmC* phases. This competition produces various ferroelectric subphases with a different sequence of AF and FE ordering among the smectic layers. Several different theoretical approaches have been advanced for explaining a variety of sub-phases and these postulates are based mostly on the expanded Landau model [146-148] or on the Ising model [149-151]. The transitions from the SmC* to SmC _{γ} * phase and from the SmC _{γ} * to SmC_A* phase are of first order [151-154]. In the antiferroelectric-paraelectric transitions, the first order phase transition has also been observed [155]. This fact, together with narrow temperature range of the SmC _{γ} * phase, has important implications for the observed properties and their interpretations [156]. Dielectric relaxation spectroscopy is a powerful tool for studying the molecular dynamics in these systems because it covers wide frequency range (10^{-3} Hz – 10^{12} Hz). Thus the dielectric relaxation spectroscopic technique has the ability to describe the collective and non-collective molecular processes. As an example of a collective process, in the ferroelectric phase, the dielectric permittivity ϵ has a contribution from the director tilt fluctuation (S-mode), or phase fluctuations (G-mode). The G-mode is characterized by a relaxation frequency, which, for most of the compounds investigated so far, does not exceed a few kHz. On approaching the paraelectric SmA – FE SmC* transition, the S-mode dielectric strength and its relaxation frequency softens i.e. it exhibits a critical slowing down. While the dynamics of the S-mode and G-mode in the FE and paraelectric chiral smectics have been extensively investigated by the variety of groups [13,157-160], the excitations observed in the ferroelectric and AF phases are poorly characterized and understood. Their molecular aspects are further a subject of controversy [13,153,161-170].

The relaxation behavior in the AF phase is still more or less unknown although some contributions developed to detailed dielectric measurements of AFLCs have been published [154,163,171]. The results obtained so far show that the relaxation behavior in the SmC_A* phase is rather complex. Three different AF absorption processes were attributed in the literature. One of them is related to the distribution of the AF ordering [163]. The second process is attributed to the rotation of the molecules around their short axis [163]. The third process is

claimed to be a 'non-collective Goldstone-like mode, due to the fact that the G-mode in the AF phase is not polar and can only be observed under special experimental conditions. In the dielectric spectrum of the ferroelectric phase, there is a low frequency absorption ascribed [15,161,164,167,168,172,173] to the G-mode. A high frequency peak has also been observed in the SmC_γ^* phase [145,161,167,168] attributed [161] to the S-mode.

3.1 Experimental results and discussion on some typical antiferroelectric liquid crystals

In 1995, Buivydas et al. [161] obtained the frequency dependence of the dielectric absorption in the frequency range of 100 Hz to 10 MHz for the AFLC material CS-4000. In the SmA^* phase, the dielectric spectrum contained only one peak. In the SmC_A^* phase, dielectric spectrum exhibited two absorption peaks (P_L , P_H) [164,173] observed in the kHz and MHz range respectively. The dielectric strength of P_L and P_H is much smaller than in the SmA^* phase. In the SmA^* phase, the relaxation frequency exhibited slowing down behavior with decreasing temperature and the dielectric strength showed a diverging-like behavior when approaching the A^* to SmC_A^* transition temperature T_c [161]. This temperature dependence is typical for the S-mode. Note that at T_c , the cut-off frequency is about 10 kHz, a value which is much higher than that usually obtained in compounds which do not possess an AF phase [13,174]. Buivydas et al. [161] also reported that in the temperature range between 79 to 80 °C, the dielectric spectrum exhibited, besides the S-mode, an additional low frequency absorption peak appeared around 15 Hz with a large value of the dielectric strength. That phase might be either FE SmC^* phase or the ferroelectric SmC_γ^* phase, both possessing G-mode [174]. However, since the observation of the dielectric strength of the G-mode, in this case, is not as large as that one usually observed in the FE SmC^* phase, one can designate the phase as the ferroelectric SmC_γ^* phase.

For the material AS-573, the three relaxation modes (1,2 and 3) were found in the AF phase in the absence of a bias field and an additional relaxation process also observed under the bias field. The low frequency process '0', with a relaxation frequency of about 2.5 kHz was reported [154] and the relaxation frequency shifted upto 10MHz under the bias electric field [164,172]. Panarin et al. [175] reported that this process was found to exist even without the bias voltage. However, due to its reduced dielectric strength and lower relaxation frequency, it is considerably superimposed by the dielectric loss arising from the ionic conductivity. The relaxation frequency of process 1 lies in between 10 and 70 kHz and is higher than that of process '0'. The mechanism could be either the S-mode or the antiphase motion. Hiraoka et al. [164] suggested an 'anti-ferroelectric-like' G-mode for this type of motion. But Panarin et al. [175] suggested that the process 1 is due to the S-mode.

The mechanism of the relaxation process 2 was not so obviously clear. The magnitude of the relaxation strength and the frequency of the molecular relaxation

process around the molecular short axis are relatively low and the process is also screened by the dominant G-mode in the SmC^* and SmC_γ^* phases. However, the temperature dependence of the frequency of process 2 in the AF phase can be extrapolated to that around the molecular short axis in the isotropic phase. In order to confirm the assignment for this mode, one can perform the dielectric measurements on the homogeneously aligned cells. For such aligned cells, the collective relaxation processes are superposed and the temperature dependence of the dielectric parameters for the molecular relaxation processes is found over the entire temperature range [164-173]. The relaxation frequency continuously decreased with decreasing temperature according to the Arrhenius law and was found to have the same value as the frequency for process 2 in the AF phase. Comparing the relaxation frequencies for homogeneously and homeotropically aligned cells, it was concluded that the process 2 in the AF phase is caused by molecular rotation around the short axis.

The molecular relaxation process around the long axis can easily be observed over a wide range of temperature because of its high relaxation frequency. The dependence of the relaxation frequency of this process on temperature was governed by the Arrhenius law over the intermediate liquid crystalline phase. Process 3 in the AF phase was therefore be unambiguously assigned to the molecular rotation around the long axis.

Hou et al. [176] observed a mode called the low mode in the ferroelectric phase for the material (R)-MHPOBC which is strongly affected under the application of bias electric field. The dielectric strength of this mode initially increased at the application of low bias field and then suppressed gradually by further increasing the bias field. The relaxation frequency of this mode was almost unchanged at low bias fields and then started increasing at a field of about 0.2 MVm^{-1} . The bias field is also affected on the SmC_A^* phase. The field induced dielectric behavior in the SmC_A^* phase of the material (R)-MHPOBC is different as compared with the other compounds. The absorption peak appeared near 1 MHz at zero bias field. By applying bias field, another absorption peak was appeared at several kHz due to the director fluctuation around the molecular short axis.

Continuous evaluation of the polar properties from ferro- to antiferro- has been observed in the binary mixtures of compounds having AF and FE phases [177]. The dielectric constant in the antiferroelectric-like smectic phase increased continuously upon increasing the ferroelectric component concentration. The variations of the AF phase properties could be attributed to changes of the azimuthal tilt angle correlations, which resulted in frustration between AF and FE interactions and formation of clusters of both the phases.

4. CONCLUSION

A wide variety of ferroelectric and antiferroelectric liquid crystals have been examined already and many are on the growing stage of investigation. Here we have described in detail about the collective and molecular dynamics of ferroelectric and antiferroelectric liquid

crystals using broadband dielectric spectroscopy by varying the physical parameters, such as, temperature, frequency, bias field and the thickness of the liquid crystal films. The explicit study of the above mentioned properties of liquid crystal compounds is needed to throw more light on the proper mechanism responsible for the critical behavior near the ferro-para, antiferro-para, ferro-antiferro and antiferro-ferrielectric phase transitions in Ferro/Antiferroelectric liquid crystals and polymers. Not only these materials, it needs to investigate the dielectric relaxation behavior of similar kind of other liquid crystalline materials with variations of temperature, frequency, thickness and bias field. Electro-optic, Pyroelectric, Polarization, tilt angle, and other related properties should be measured to get more information on ferroelectric and antiferroelectric liquid crystals and other systems. It is well known that ferroelectric and antiferroelectric liquid crystals and liquid crystalline polymers are interesting candidates for device applications (in opto-electronics, sensing devices etc.). The behavior of ferro- and antiferroelectric liquid crystals in very thin planar cells can be used for the applications in fast switching devices. In addition to direct structural analysis, the investigation of physical properties of ferroelectric and antiferroelectric systems may also provide useful information about the structural features.

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