Relaxation modes in ferroelectric smectic C liquid crystals: Effects of bias field

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Dielectric properties of a large spontaneous polarisation ferroelectric liquid crystalline mixture FLC-6430 (Hoffman-La-Roche) have been studied in the SmC* and SmA phase in the frequency range 100Hz to 1MHz in planar oriented cells under the influence of varying external dc bias. Several relaxation modes were observed. The effect of bias field and temperature on these relaxation modes has been investigated. The observation of a relaxation mode namely new relaxation modes (NRM) in the high frequency range above 100 kHz has been reported. The dielectric increment of NRM was very small ($\Delta \varepsilon_{NRM} = 5.84$) as compared to the Goldstone mode ($\Delta \varepsilon_{GM} = 390$).

1 Introduction

The existence of ferroelectric properties in chiral smectic C (SmC*) liquid crystals was first demonstrated by Meyer et al., and is now firmly established on the basis of experimental and theoretical investigations. The ferroelectric smectic C phase is low symmetric with $C_2$ symmetry element. It has a layer structure and is formed due to the modulation of an incommensurate structure. The azimuthal angle of long molecular axis processes helicoidally around layer normal while going from one smectic layer to another. During this process a helical stripe texture appears in the sample.

Dielectric spectroscopy studies of ferroelectric smectic C liquid crystals (FLC) has been carried out in large number of liquid crystalline compounds and their mixture. It gives information about various collective and molecular processes associated with the helix dynamics. Dielectric response of FLCs mainly consists of four relaxation modes. Two modes are due to the fluctuations of polarization order parameter having relaxation frequencies of the order of ~ 500 MHz. The other two important relaxation modes connected to the director fluctuations are usually referred as the Goldstone mode (GM) and the Soft mode (SM). These modes occur due to the phase fluctuations of the azimuthal angle ($\phi$) and the amplitude of the tilt angle ($\Theta$) in the SmC* phase. At the ferro-to-para electric transition temperature ($T_{cA}$), only SM is observable as both $\phi$ and $\Theta$ fluctuations become indistinguishable. In some of the multi-component FLC mixtures, it was found that the intensities of relaxation processes coming from the chiral molecules are distinctly reduced. Moreover some single component systems show a deficient SM due to the weak coupling between the chiral centres and the permanent dipole moments. Detailed investigations in a series of FLC mixtures showed that in addition to the GM and SM other relaxation modes also do appear depending upon certain molecular properties.

The complex dielectric permittivity as a function of frequency and temperature for a FLC material is given by:

$$\varepsilon^{*}(\omega , T) = \varepsilon' (\omega , T) - i \varepsilon'' (\omega , T)$$

where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of complex permittivity respectively, $\omega = 2\pi f$ is the angular frequency of the applied field and $T$ is the temperature of the system.

Generally, several relaxation mechanisms each of which is connected to a characteristic frequency $f$ contributes to $\varepsilon^{*}(\omega , T)$, to characterize the temperature dependence of the observed dielectric relaxation, $\varepsilon^{*}(\omega , T)$ can be expressed in terms of the Debye relation:

$$\varepsilon^{*}(\omega , T) = \varepsilon_{\infty} + \frac{\Delta \varepsilon (T)}{1 + i \omega \tau_{g}}$$

where $\tau_{g}$ and $\alpha$ are the characteristic relaxation time and distribution parameter respectively, $\Delta \varepsilon (T)$ is the dielectric strength of the mode.

In this paper, we present dielectric relaxation studies in a large spontaneous polarisation multi-component
FLC mixture in SmC* and SmA phases and report the observation of new relaxation mode in it. Effects of bias field on various relaxation modes have been investigated in different frequency regions.

2 Experimental Details

The frequency and temperature dependence of the complex dielectric permittivity has been studied in a novel ferroelectric liquid crystal mixture FLC-6430 (obtained from Hoffmann-La Roche, Switzerland). At 22°C, this mixture has short helical pitch (−0.43 μm), large spontaneous polarisation (−90 nC/cm²) and large tilt angle 27°. It has a wide SmC* phase from −11°C to 55°C followed by SmA phase.

We carried out dielectric measurements on the FLC mixture in 7.5 μm thick LUCID cell. This cell thickness was large in comparison to the helix pitch (−0.43 μm) of the mixture. The sample was sandwiched between two conducting indium tin oxide (ITO) coated glass substrates. The substrates have been pretreated with polyimide (parallel rubbing direction). The liquid crystal mixture was filled in the cell by the capillary action at 65°C (above isotropic temperature of the sample) and then cooled to SmA phase at 1°C/min. in presence of an ac electric field of (−10Hz and 10Vpp) in a LINKAM temperature programmer (model TP90) cum hot stage (THS 600). The effect of the electric field on a randomly aligned sample was to force the molecules in a layer to lie parallel to the rubbing direction so that a mono-domain well aligned sample cell could be obtained. This texture was observed through GETNER polarising microscope. The complex permittivity was measured using Hewlett-Packard Impedance Analyser (model HP-4192A) in the frequency range 100 Hz—1 MHz at different temperatures. The effect of bias fields and temperature on various relaxation modes was then investigated. The sample cell was calibrated using air and benzene as standard reference media.

3 Theoretical Background

It is known that due to the presence of chirality in SmC* phase, the in-plane polarisation perpendicular to the direction of the tilt is given by \( P - P_x X + P_y Y \), therefore the order parameter \( \xi \) and the polarisation \( P \) can be written as:

\[
\xi_1 = \theta_0 \cos (q Z), \quad \xi_2 = \theta_0 \sin (q Z) \quad \text{...(3)}
\]

\[
P_y = P_q \sin (q Z), \quad P_y = P_q \cos (q Z) \quad \text{...(4)}
\]

where \( Z \) is the coordinate axis normal to smectic layer plane, \( q = 2\pi n/L \) is the wave-vector of helical pitch (L) \( \theta_0 \) and \( P_q \) are the tilt angle and spontaneous polarisation respectively.

In the absence of an external dc bias GM appears at low frequencies whereas in the high frequency region (>50 kHz), SM is observable near \( T_{cA} \). The dielectric response in terms of dielectric susceptibility of these two modes is related to the dielectric strength as \( \chi = \epsilon_0 \Delta \epsilon \); where \( \epsilon_0 \) is the absolute permittivity of free space and \( \Delta \epsilon = \epsilon_{sm} - \epsilon_{in} \), \( \epsilon_{sm} \) and \( \epsilon_{in} \) are the static and infinite frequency dielectric constants respectively.

The external dc bias applied to the sample disturbs the helix in two ways: firstly in weak fields, the helix is disturbed due to the linear coupling between polarisation \( P \) and the electric field \( E \). The net induced polarisation thus increases. The dielectric response in that case will be \( \chi = \chi_{GM} + \chi_{SM} \), where \( \chi_{GM} \) and \( \chi_{SM} \) are the dielectric susceptibility of GM and SM respectively. Here GM appears with suppressed dielectric response. The dielectric response is thus defined as:

\[
\chi = \chi_{GM} \frac{P_i}{E} \quad \text{...(5)}
\]

where \( P_i \) is the average induced polarisation and \( E \) is the magnitude of the applied static electric permittivity.

Secondly in presence of both strong dc and ac field, the coupling between \( P \) and \( E \) becomes so strong that the helical texture breaks up into the modulated domain structures as shown in Fig. 1. It reduces the electrostatic energy. The dielectric response to the susceptibility

![Fig. 1 — Influence of dc and alternating field on the structure of ferroelectric Smectic C phase. The dc field strength is increasing from (b) to (c). \( E_0 \) is the zero bias and \( E_c \) is the critical field. Nails represent the molecules and arrows the SmC director](image-url)
would then be $\varepsilon_{\text{DM}} + \varepsilon_{\text{SM}}$, $\varepsilon_{\text{DM}}$ and $\varepsilon_{\text{SM}}$ are the domain
mode DM and SM susceptibilities respectively.

4 Results and Discussion

Fig. 2(a) shows a typical relaxation process in the
form of Cole-Cole plot in FLC mixture at 35°C. It is seen
that in addition to GM, one more relaxation mode ap-
pears above 1200 kHz. This mode could not be
completely suppressed by an external dc field of magnitude
$0.67\text{V/\mu m}$. In the absence of external bias, it was found
that its dielectric increment ($\Delta\varepsilon \approx 5.84$) was small as
compared to that of GM ($\Delta\varepsilon_{\text{GM}} = 390$). We call it a new
relaxation mode NRM. The origin of this mode can be
attributed to the surface effects and thus could have
resulted from the surface pinning and tiny domains,
which contribute to helix unwinding at the surfaces\(^{27,28}\).
It is also clear from Fig. 2(b) [inset] that NRM strongly
depends on cell thickness. This dependence may be due
to the increase in surface anchoring energy. Fig. 2(a)
[inset] shows contribution of GM to dielectric permittiv-
ity in the form of absorption [$\varepsilon'(\omega)$] and dispersion
[$\varepsilon''(\omega)$] curves at 35°C.

In the SmC\(^*\) phase the dielectric permittivity consists
of contributions due to the GM and NRM. In alternating
field, contributions to the complex permittivity due to
to these modes\(^{18}\) shall be:

$$
\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_{\text{GM}} + \frac{\Delta\varepsilon_{\text{GM}}}{1 + (i\omega\tau_{\text{GM}})^{-1}} + \frac{\Delta\varepsilon_{\text{NRM}}}{1 + (i\omega\tau_{\text{NRM}})^{-1}} \varepsilon_{\text{NRM}} \tag{6}
$$

$\Delta\varepsilon_{\text{GM}}$ and $\Delta\varepsilon_{\text{NRM}}$ are the dielectric strengths, whereas $\pi$
and $\alpha$ represents the relaxation times and the distribution
parameters of GM and NRM respectively. The NRM
relaxation frequency ($f_{\text{NRM}}$) in 5\,$\mu m$ cell at 35°C without
bias was calculated to be 427.8 kHz. The $f_{\text{NRM}}$ has not
been measured in 7.5\,$\mu m$ cell due to its partial reflection
as shown in Fig. 2(b) [inset]. The empty cell did not show
any relaxation up to 1 MHz (measurable range of fre-
quency in our case). As we approach near $T_{\text{NI}}$, the SM
dominates over both GM and NRM as in shown in Fig.
3(a,b). We found that the bias $0.67\text{V/\mu m}$ was not
sufficient to suppress the GM. In order to study the
presence of other relaxation processes, we applied a dc
field up to $2.0\text{V/\mu m}$ to the sample cell to suppress the
GM mode. The typical frequency dependence of the
imaginary part of the complex permittivity at different
bias fields is shown in Fig. 4. We notice that at $1.3\text{V/\mu m}$,$\varepsilon''$ decreases rapidly due to the suppression of helix.
Here NRM is clearly reflected due to the surface pinning
at higher bias as can be seen in Fig. 4 [inset].

Fig. 5 shows the effect of bias on the relaxation
frequency of GM. It is seen that with the increase of
external dc field, $f_{\text{GM}}$ increase from $0.6\text{kHz}$ at $1.3\text{V/\mu m}$
to $2.86\text{kHz}$ at $2.0\text{V/\mu m}$. Corresponding distribution
parameter also changes from $0.18$ at $0.67\text{V/\mu m}$ to $0.27$

![Fig. 2](image-url) — (a) Cole-Cole plots of GM and NRM in the SmC\(^*\) phase. [Inset] shows the dispersion [$\varepsilon'(\omega)$] curves at different
external dc bias fields in the SmC\(^*\) phase.

(b) Cell thickness dependence of the GM and NRM in the ab-
sence of external dc bias.
at 1.3 V/μm and then increases further. At bias greater than 1.3 V/μm, we believe that the changes in α and f are due to the appearance of DM (considered to be a residual part of GM). In our opinion, the DM has appeared due to the formation of modulated domain structures in bulk interface in the presence of strong electric field\textsuperscript{19}. We call it Bulk domain mode BDM. An observation to this effect has been made in one of our experiments discussed elsewhere\textsuperscript{19}. The \( f_{\text{BDM}} \approx 198 \text{ kHz} \) was found to be almost independent of bias from 1.3 V/μm to 2.0 V/μm. We assume that due to the bulk properties of sample (large cell thickness to pitch ratio), the contributions to DM may be due to the bulk domain mode BDM and the NRM. Wrobel et al.\textsuperscript{13,15} have also hinted at the appearance of such modes in large \( P_0 \) materials. In bulk region, the helix is completely unwound above the threshold field, whereas it is suppressed at the surfaces.

Under these conditions the complex permittivity shall become:

\[
\varepsilon^{\ast} = \varepsilon^\prime - i \varepsilon^\prime \prime = \varepsilon_\infty + \frac{\Delta \varepsilon_{\text{BDM}}}{1 + (i \omega \tau_{\text{BDM}})^{-\alpha_{\text{BDM}}}} + \frac{\Delta \varepsilon_{\text{NRM}}}{1 + (i \omega \tau_{\text{NRM}})^{-\alpha_{\text{NRM}}}}
\]

By splitting Eq. (7) into real and imaginary parts we get:

\[
\varepsilon^\prime (\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon_{\text{NRM}}}{\pi \alpha_{\text{NRM}}/2} \left[ 1 - \frac{\sinh A}{A} \right]
\]

Fig. 3 — (a) Cole-Cole representation of GM and SM in the vicinity of transition temperature \( T_{\text{c-A}} \) at 54 °C
(b) Cole-Cole plot of FLC-643) in the absence of dc bias and at 0.67 V/μm at 57 °C (SmA phase) reflecting SM

![Fig. 3](image)

Fig. 4 — Frequency dependence of \( \varepsilon^\prime (\omega) \) at 35 °C

![Fig. 4](image)
where $A = (1 - \alpha_{\text{NRM}}) \ln(\omega \tau_{\text{NRM}})$, $B = (1 - \alpha_{\text{BDM}}) \ln(\omega \tau_{\text{BDM}})$ and other terms have their usual meanings. The relaxations corresponding to NRM and BDM at 2.0 V/µm in the form of Cole-Cole plot are shown in Fig. 6. Solid line represents the BDM and NRM evaluated by fitting experimental data in Eq. (8a,b). A good agreement between theory and our experimental results has been found.

A typical dependence of relaxation frequency ($f_\tau$) and dielectric strength ($\Delta \varepsilon$) of above relaxation modes as a function of temperature is shown in Fig. 7(a,b). As seen, $f_{\text{GM}}$ and $f_{\text{NRM}}$ are almost independent of temperature in the SmC* phase. As we approach $T_{\text{CP}}$, SM appears with a sudden rise in the relaxation frequency. Measurements very close to $T_{\text{CP}}$ have not been taken due to large fluctuations in the experimental values, it could be due to the segregation and pre-transitional effects at this temperature because of the multi-component nature of the FLC mixtures. It is seen that SM obeys Curie-Weiss law governed by $f_{\text{GM}} = a (T - T_{\text{CP}}) + b$, where $a$ and $b$ are constants.

The dependence of $f_{\text{BDM}}$ and $\Delta \varepsilon_{\text{BDM}}$ as a function of temperature at 2V/µm is shown in Fig. 8(a,b). We notice...
that $f_{NRM}$ is much higher in magnitude than $f_{BDM}$ ($f_{NRM} > f_{BDM}$). Similarly, the dielectric strength of NRM ($\Delta \epsilon_{NRM}$) is found to be 2 times more than that of $\Delta \epsilon_{BDM}$ ($\Delta \epsilon_{NRM} = 2\Delta \epsilon_{BDM}$). These results suggest that the surface anchorage energy dominate over the bulk property of the sample.

5 Conclusions

Dielectric relaxation modes have been investigated in a novel FLC-6430 mixture under the influence of external bias in the low and high frequency regions. It is found that:

A new relaxation mode namely NRM appears both with and without external bias. NRM is a consequence of the strong surface interactions and contributions from the tiny domains formed at the surfaces, which in turn contribute to the helix unwinding at the surfaces. A complete reflection of NRM is observed at higher bias (1.3 V/µm) due to the coupling of surface domains with electric field. The $f_{NRM}$ is almost independent of temperature but strongly depends on sample thickness. The $f_{NRM}$ is 19.8 kHz and its $\Delta \epsilon_{NRM} = 11.07$ at 35 °C.

Goldstone mode GM and Bulk domain mode BDM appear in low frequency region. BDM is basically a residual part of the GM and appears due to the formation of modulated domain structures in the bulk interface. The $f_{GM}$ and $f_{BDM}$ are 0.83 kHz at 0.0V/µm and 2.86 kHz at 2.0V/µm respectively at 35 °C. Their corresponding dielectric strength is $\Delta \epsilon_{GM} = 390$ and $\Delta \epsilon_{BDM} = 5.25$.

Soft mode SM parameters satisfy the Curie-Weiss law as we approach near $T_{C}$. 

![Fig. 7 - Temperature dependence of (a) relaxation frequency $f_i$ and (b) dielectric strength $\Delta \epsilon$ of GM, SM, and NRM in the SmC* and SmA phase](image-url)
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