Surface molecular relaxation in smectic C* phase as studied by dielectric spectroscopy

A. M. Biradar[ab]; S. Hiller[a]; S. A. Pikin[ac]; W. Haase[a]

[a] Institut für physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt, Germany [b] National Physical Laboratory, New Dehli, India [c] Institute of Crystallographie, Russ. Acad. of Sciences, Moscow, Russia

PLEASE SCROLL DOWN FOR ARTICLE

Surface molecular relaxation in smectic C* phase as studied by dielectric spectroscopy

by A. M. BIRADAR†, S. HILLER*, S. A. PIKIN‡ and W. HAASE

Institut für physikalische Chemie, Technische Hochschule Darmstadt,
Petersenstr. 20, 64287 Darmstadt, Germany

The molecular relaxation process of a ferroelectric liquid crystal with a high tilt angle and a high spontaneous polarization in a homeotropically aligned cell has been studied by the dielectric relaxation method in the frequency range 10 Hz to 10 MHz. The measurements have been done using thin (3·5 μm) cells with gold coated electrodes and samples aligned by a magnetic field. It has been observed that the molecular relaxation around the short axis of the molecule is detected in the chiral nematic and smectic C* phases. The surface molecular process is observed in the S_C^* phase down to nearly 6 to 7 K below the transition temperature of the N* to the S_C^* phase. The experimental results of the surface molecular process are analysed by theoretical calculations. The experimental results agree with the theoretical predictions.
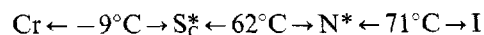
1. Introduction

Dielectric spectroscopy of ferroelectric liquid crystals (FLCs) has become of increasing interest in the past few years. It gives not only the collective modes directly associated with the ferroelectricity (Goldstone mode, soft mode and domain mode), but also the molecular modes. These have been studied very extensively in the past, particularly for second order phase transition FLCs, for which microscopic and statistical theories exist and account for the observed behaviour [1–3]. On the contrary, very little is known [4,5] about first order phase transition FLCs, possessing the S_C^* to N* phase transition, probably due to the difficulty of alignment. However, first order phase transition FLCs are very interesting, because their material constants such as tilt angle are very large and do not depend greatly on temperature and these materials are better suited for preparing electro-optical switches [6] and guest–host displays [7].

In this article, we present dielectric studies of a first order phase transition FLC material using homeotropically aligned cells in the frequency range 10 Hz to 10 MHz. The molecular relaxation around the short axis of the molecule is observed in the chiral nematic (N*) and smectic C* (S_C^*) phases. Deep in the S_C^* phase, the

surface molecular relaxation has been observed experimentally. A theoretical explanation has been given for the surface molecular relaxation process which can exist very close to the surface.

2. Experimental

The dielectric studies were performed mainly using cells with gold coated electrodes, although ITO coated electrodes were used for checking the alignment optically. The dielectric measurements were done in a shielded parallel-plate condenser [8]. The cell thickness was 3·5 μm. The cell was first calibrated using air and toluene as standard references for calculating the absolute values of the electric permittivity. The first order phase transition FLC material (CS-2004, Chisso Corporation, Japan) used in this study has the following phase sequence:

$$\text{Cr} \leftarrow -9°C \rightarrow S_C^* \leftarrow 62°C \rightarrow N^* \leftarrow 71°C \rightarrow I$$

The FLC material was introduced into the cell by means of capillary action in its isotropic phase. To minimize the surface anchoring effect, no surface treatment was given to the electrodes for achieving alignment. Homeotropic alignment was obtained by putting the sample into a magnetic field of 1·2 T and cooling it slowly at the rate 8 K h^{-1} from the chiral nematic to the smectic C* phase. The cooling and heating cycles were done several times to get better homeotropic alignment. The detailed procedure of alignment by a magnetic field is given elsewhere [9].

The dielectric measurements were done using a

* Author for correspondence.
  Permanent addresses:
  † National Physical Laboratory, Dr K. S. Krishnan Road, New Dehli-11012, India.
  ‡ Institute of Crystallographie, Russ. Acad. of Sciences, Leninskii prosp. 59, 117333 Moscow, Russia.

Hewlett–Packard impedance analyser (HP 4192 A), controlled by a modified Atari Mega ST2 computer in the frequency range 10 Hz to 10 MHz using homeotropic alignment. The bias field (generated by the impedance analyser) was used to detect the surface molecular relaxation in the S_C^* phase. The temperature and frequency dependences of the molecular mode in the homeotropic alignment have been analysed experimentally and theoretically in the S_C^* and N* phases.

3. Results and discussion

The measuring electric field in the homeotropically aligned FLC cell is parallel to the liquid crystal molecules and one can measure the $\varepsilon_\parallel$ component of the complex dielectric permittivity, connected with reorientation of the molecules around their short axes. Figure 1 shows the relaxation frequency versus temperature of the molecular rotation around the short axis (squares) i.e. a 180° jump around the short axis over the whole N* phase. This process is seen even in the S_C^* phase, nearly 6 to 7 K into the S_C^* phase. The only difference is that the molecular process is detected when the collective dielectric processes of the planar component are suppressed by applying a high bias field to the cell; this will be discussed in the next paragraph. As seen in the figure the relaxation frequency of the molecular mode is temperature dependent and continuous even at the transition temperature of S_C^* to N* phase.

As mentioned earlier, in the homeotropic alignment, the measuring electric field is parallel to the molecules (i.e. the smectic layers are assumed to be parallel to the sample surface in the S_C^* phase). However, when the FLC material is cooled down to the S_C^* phase, the molecules are tilted, depending upon the tilt angle of the material [10], resulting in tilting of the smectic layers

(instead of parallel orientation) with respect to the sample surface. Particularly, in this FLC material, where the tilt angle of the molecule is quite large (44°), the measuring electric field makes a wide angle relative to the smectic layer plane and hence the dielectric permittivity due to the planar component would be dominant in homeotropic alignment measurements. As is well known [11,12], the dielectric permittivity in the planar component is dominated by collective dielectric processes such as the Goldstone mode, soft mode, domain mode etc. in the S_C^* phase. It should be mentioned here, that the soft mode contribution in the first order materials is usually negligible. To suppress the collective dielectric processes (particularly the Goldstone mode) of the planar component due to the tilting of the smectic layer planes with respect to the sample surface in homeotropic measurements, a strong bias field has been applied to see the pure $\varepsilon_\parallel$ component in the S_C^* phase in the present investigation. It is worth stating here that in a perfectly planar alignment (for the $\varepsilon_\perp$ component), where the measuring electric field is perpendicular to the smectic layer normal, the applied bias field has a pronounced influence on the Goldstone mode (unwinding of the helix) in the S_C^* phase; this has been reported recently [13] for this material. Figure 2 shows the absorption spectra ($\varepsilon_\parallel$ versus frequency) at different temperatures in the S_C^* phase which were obtained at a bias voltage of 30 V. This dielectric process can only be due to the molecular relaxation (vibration) near the surface layers of the substrate, which must be connected with orientational deformations of the molecules near the surface for the following reasons: (i) the Goldstone mode contribution to the dielectric permittivity is suppressed by means of the bias voltage; (ii) soft mode relaxation plays only a negligible role in first order FLC materials (moreover
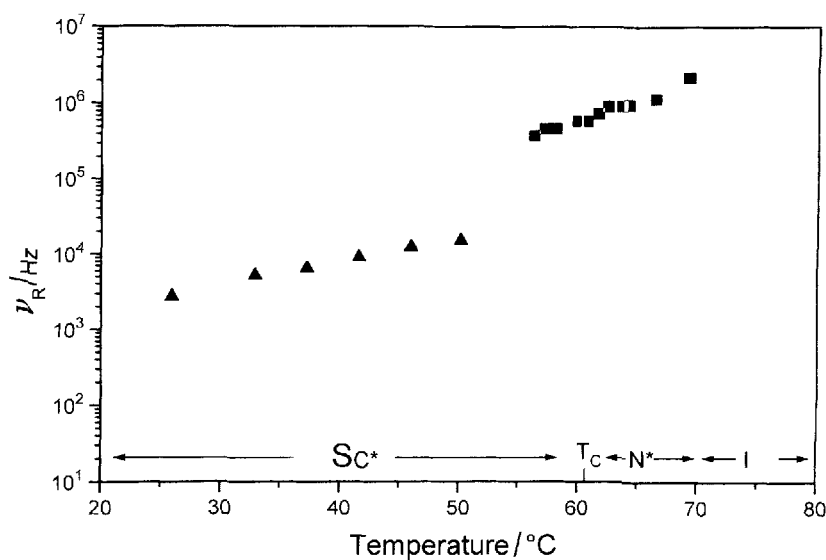

Figure 1. Temperature dependences of the relaxation frequencies of the molecular process in the S_C^* and N* phases with homeotropic alignment ($\varepsilon_\parallel$ component) i.e. molecular relaxation around the short axis of the molecule (■) and surface molecular relaxation (▲).

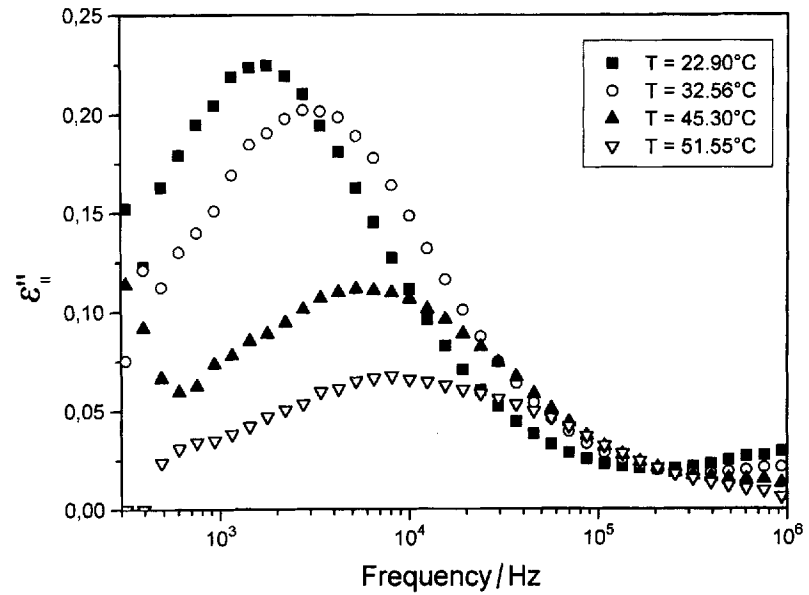Figure 2. Absorption curves ($\varepsilon_{||}''$ versus frequency) for the surface molecular process at different temperatures in the S_C^* phase measured at a bias voltage of 30 V.

the observed process was recorded deep in the S_C^* phase); (iii) in a perfectly planar alignment, which was achieved by applying an electric field, just below the transition temperature of S_C^* to N^* phase [14], we did not observe any dielectric processes (i.e. no domain mode) for high biasing voltages in the S_C^* phase. Therefore, there is no reason why a domain mode process should occur with homeotropic alignment. More experimental evidence of the surface molecular process in the homeotropic alignment of high tilt angle FLC materials, which appears to be due to the tilting of the smectic layers near the sample surface, will be published elsewhere [15]. Similar results have been observed by Pavel and Glogarova [16] in planar aligned FLC cell of S_C^* phase.

As seen in figure 1 (triangles) and figure 2, the surface molecular process is temperature dependent. The molecular process in the N^* and S_C^* phase shows Arrhenius-type behaviour as seen in figure 3. The activation energy calculated for the molecular relaxation around the short axis is about 85 kJ mol^{-1} and for the surface molecular process in the S_C^* phase is about 65 kJ mol^{-1}. The activation energies for the molecular process suggest that the molecular motion in the surface layers is easier in the S_C^* phase than the molecular relaxation around the short axis.

Theoretically, we prove here that surface molecular relaxation should be possible in the S_C^* phase with homeotropic alignment by considering the spontaneous polarization and tilt angle of the FLC material investigated. The theoretical calculations agree well with the experimental results, predicting that the surface molecular process should appear nearly 10 K below the transition temperature of N^* to S_C^* phase. At this temperature, a change in the texture was observed. The homeotropic

alignment disappears and a partial planar alignment becomes visible which was confirmed by the fact that switching in the sample starts to appear at this temperature (approximately 10 K below the transition temperature) when seen in the polarizing microscope. The change of texture in the S_C^* phase with the spontaneous polarization $P_s = \mu\Theta$, where μ is the piezoelectric coefficient, at a certain temperature below the phase transition point T_c, can be related to some orientational deformations in a sufficiently thin sub-surface layer with thickness λ, which appears as a result of the concurrence between a surface influence (the surface tension W) and an internal electric field (E_{in}) effect resulting from the interaction of P_s with E_{in} in such a sub-layer. The surface tension W can be considered as an expansion in terms of the tilt angle Θ,

$$W = \mu\Phi\Theta + w\Theta^2, \tag{1}$$

where Φ and w are the phenomenological parameters; the first term in equation (1) describes, for example, the gain in energy when the spontaneous polarization P_s is parallel to the cell surface (in the homeotropic director orientation), and the second term describes an increase in the surface energy when the director orientation differs from the homeotropic orientation (in the C^* phase, the director takes a position at the cone surface at an angle of Θ to the surface normal). By analogy with consideration of bistability effects [17–20], we shall assume that the field E_{in} tends to change the polarization and director orientations to new orientations if the interaction $P_s E_{in} = \mu\Theta E_{in}$ overcomes the potential barrier $K\Theta^2/\lambda^2$ inside the sub-layer, where sub-layer thickness $\lambda \sim K\Theta^2/W$ is the spatial scale of inhomogeneity arising under the influence of the cell surface. It is useful to note
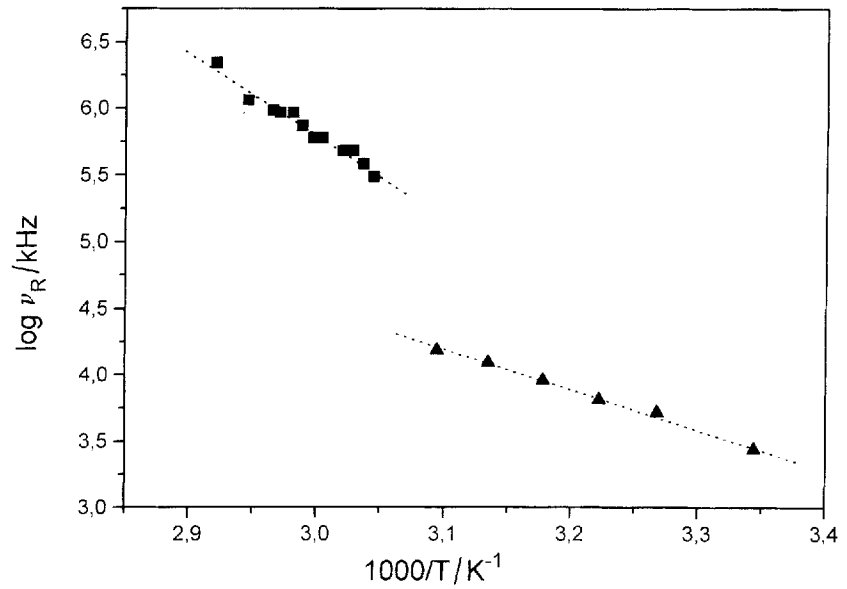
Figure 3. Arrhenius plot for the molecular relaxation around the short axis of the molecule (■) in the S_C^* and N* phases and for the surface molecular process in the S_C^* phase (▲).

that the qualitative condition

$$E_{in} \geqslant E_{th} \propto \frac{K\Theta^2}{\mu\Theta\lambda^2} \propto \frac{W^2}{\mu\Theta^3 K}, \qquad (2)$$

determines the threshold field value E_{th} for the existence of bistability effects [17–19], i.e. the new orientational state could be stored even after switching off the field E_{in}. It was shown analytically [17] and by simulation methods [19] that equation (2) really works for various initial director distributions. Let us consider two limiting cases when (1) $\mu\Phi \gg w\Theta$, i.e. the piezoelectric term in the surface tension is dominant, and (2) $w\Theta \gg \mu\Phi$, i.e. the director anchoring energy in W is predominant. In the first case, it is seen from equation (2) that, at a given field E_{in}, this condition can be fulfilled only if the angle Θ is sufficiently large, i.e. we can estimate the threshold (minimum) value of Θ (Θ_{th}) as a function of E_{in} from equation $E_{th} = E_{in}$:

$$\lambda \propto \frac{K\Theta}{\mu\Phi}, \quad \Theta_{th} \propto \frac{\mu\Phi^2}{KE_{in}}, \quad \lambda_{th} \propto \frac{\Phi}{E_{in}}. \qquad (3)$$

Thus Θ_{th} is finite and, therefore, the effect is only possible at temperatures below the corresponding threshold temperature $T_{th} < T_c$. This effect is more probable for first order phase transitions than for second order ones because the values of the tilt angle Θ can be sufficiently large near to the first order transition point T_c. Though the tilt angle depends weakly on temperature in the case of a first order transition, a certain increase of Θ with decreasing T must exist below T_c, and the value Θ_{th} can occur at an intermediate temperature $T_{th} < T_c$. Since we have no information about all the thermodynamic parameters for the first order phase transition, we shall

use, for rough estimates of the order of the values, typical data for the free energy expansion $F = a(T - T_c)\Theta^2 + b\Theta^4 + \ldots$, describing second order transitions, which is not bad at intermediate temperatures for first order transitions also. Such a rough estimate gives a magnitude $\Theta(T) \sim ((a/b)(T_c - T))^{1/2}$ and the corresponding threshold temperature T_{th}:

$$(T_c - T_{th}) \propto \frac{b}{a}\Theta_{th}^2. \qquad (4)$$

Thus, below the temperature T_{th}, the interaction between the spontaneous polarization and the internal field in the sub-layer with thickness λ is sufficiently strong to create a stable orientational deformation on the scale λ. Therefore, the relaxation frequency

$$\omega \propto \frac{K}{\gamma\lambda^2} \propto \frac{K}{\gamma}\left(\frac{E_{in}}{\Phi}\right)^2 \quad \text{at } T \approx T_{th} \qquad (5)$$

can be observed in the dielectric spectrum.

In the second case, similar calculations taking into account equation (2) result in the estimates

$$\lambda \propto \frac{K}{w}, \quad \Theta_{th} \propto \frac{\mu KE_{in}}{w^2}, \quad \omega \propto \frac{w^2}{\gamma K}. \qquad (6)$$

If one uses some typical data for material parameters,

$$K \approx 10^{-11}\,\text{N}, \quad w(\text{homeotropic}) \approx 10^{-6}\,\text{J m}^{-2},$$

$$\gamma \sim 10^{-1}\,\text{Pa s},$$

then equation (6) results in estimates of $\lambda \sim 10\,\mu\text{m}$ and $\omega \sim 1\,\text{Hz}$, which are obviously incompatible with the

experimental data. If one uses typical data

$$\mu \approx 10^{-4}\,\mathrm{C\,m^{-2}}, \quad a \approx 10^{3}\,\mathrm{J\,m^{-3}\,K^{-1}}, \quad b \approx 10^{6}\,\mathrm{J\,m^{-3}},$$

$$(T_c - T_{th}) \approx 10\,\mathrm{K}, \quad \omega \sim 10^{4}\,\mathrm{Hz},$$

then equations (3)–(5) result in the estimates: $\lambda \approx 0{\cdot}1\,\mu\mathrm{m}$, $\Phi \approx 0{\cdot}1\,\mathrm{V}$, $E_{in} \approx 10^{6}\,\mathrm{V\,m^{-1}}$.

We would like to emphasize here that we determine these unknown parameters from the measured magnitudes ω and T_{th}. Thus, the last estimates are rather more compatible with the experimental data, and, taking into account a possible 'electric' nature of the λ-length appearance, one can conclude that λ represents a typical estimate of $0{\cdot}1\,\mu\mathrm{m}$ of the electric screening radius.

Equations (3) and (5) also show a certain temperature dependence of the relaxation frequency due to the temperature dependence of the viscosity coefficient γ, which must increase gradually with decreasing temperature. Therefore the relaxation frequency must decrease gradually with decreasing temperature below the threshold temperature, this can explain the observed smooth dependence $\omega(T)$.

4. Conclusions

In conclusion, it can be said that there should be a molecular process very close to the surface of the substrate due to deformation of the homeotropic alignment in the S_C^* phase of a high tilt angle FLC material. The experimental results of the surface molecular process agree with the theoretical prediction. The molecular relaxation around the short axis of the molecule (180° jump around the short axis) is also detected in the N* and S_C^* phases in the first order phase transition ferroelectric liquid crystal material investigated.

References

[1] CARLSSON, T., ZEKS, B., FILIPIC, C., and LEVSTIK, A, 1990, *Phys. Rev. A*, **42**, 877.
[2] BATA, L., and BUKA, A., 1981, *Mol. Cryst. liq. Cryst.*, **63**, 307.
[3] BENGUIGUI, L., 1982, *J. Phys. (France)*, **45**, 915.
[4] LEGRAND, C., ISAERT, N., HMINE, J., BUISINE, J. M., PARNEIX, J. P., NGUYEN, H. T., and DESTRADE, C., 1991, *Ferroelectrics*, **121**, 21.
[5] BIRADAR, A. M., BAWA, S. S., SAXENA, K., and CHANDRA, S., 1993, *J. Phys. II (France)*, **3**, 1787.
[6] BIRADAR, A. M., BAWA, S. S., SHARMA, C. P., and CHANDRA, S., 1991, *Ferroelectrics*, **122**, 81.
[7] KONDO, K., KITAMURA, T., ISOGAI, M., and MUKOH, A., 1988, *Ferroelectrics*, **85**, 361.
[8] HAASE, W., PRANOTO, H., and BORMUTH, F. J., 1985, *Ber. Bunsenges. phys. Chem.*, **89**, 1229.
[9] BIRADAR, A. M., WROBEL, S., and HAASE, W., 1989, *Phys. Rev. A*, **39**, 2693.
[10] GOUDA, F., ANDERSON, G., MATUSZCZYK, M., MATUSZCZYK, T., SKARP, K., and LAGERWALL, S. T., 1991, *J. appl. Phys.*, **67**, 180.
[11] GOUDA, F., ANDERSON, G., CARLSSON, T., LAGERWALL, S. T., SKARP, K., STEBLER, B., FILIPIC, C., ZEKS, B., and LEVSTIK, A., 1989, *Mol. Cryst. liq. Cryst. Lett.*, **6**, 151.
[12] WROBEL, S., HILLER, S., PFEIFFER, M., MARZEC, M., HAASE, W., TWIEG, R., and BETTERTON, K, 1995, *Liq. Cryst.*, **18**, 21.
[13] BIRADAR, A. M., HILLER, S., and HAASE, W., *Ferroelectrics* (in the press).
[14] PATEL, J. S., and GOODBY, J. W., 1986, *J. appl. Phys.*, **59**, 2355.
[15] BIRADAR, A. M., HILLER, S., PIKIN, S. A., and HAASE, W., *Ferroelectrics* (Proceedings of the 5th FLC Conference, Cambridge, UK, 1995) (to be published).
[16] PAVEL, J., and GLOGAROVA, M., 1991, *Ferroelectrics*, **121**, 45.
[17] PIKIN, S. A., 1988, *Nuovo Cim.*, **D10**, 1281.
[18] PIKIN, S. A., 1991, *Ferroelectrics*, **117**, 197.
[19] ALLAGULOV, A. S., PIKIN, S. A., and CHIGRINOV, V. G., 1989, *Liq. Cryst.*, **5**, 1099.
[20] BERESNEV, L. A., SCHUMACHER, E., PIKIN, S. A., FAN, Z., OSTROVSKY, B. I., HILLER, S., ONOKHOV, A. P., and HAASE, W., 1995, *Jpn. J. appl. Phys.*, **34**.