CHAPTER III

Dielectric Studies in the Vicinity of the A-C* Transition

3.1 Introduction

Experimental studies on liquid crystals using dielectric\textsuperscript{1,2} measurements as a probe has yielded valuable data which are of great significance from both the fundamental and applied aspects. Through these studies it has been possible to extract information regarding the dipolar ordering in the nematic,\textsuperscript{3} polymorphic forms of smectic A and the smectic C phases\textsuperscript{4,5} and the role played by different material parameters.

The shape anisotropy - length to breadth ratio \( \sim 5 \) - of the molecules manifests itself in the dielectric permittivity of liquid crystals. There are two principal dielectric constants parallel (\( \epsilon_\parallel \)) and perpendicular (\( \epsilon_\perp \)) to the director. \( \epsilon_\parallel \) exhibits a relaxation in the radio frequency region (associated with the flipping of the molecules around their short axis), while \( \epsilon_\perp \) shows a relaxation in the microwave region representing the rotation of the molecules around their long axis. In addition, of course, there will be the very high frequency contribution due to the different parts of the molecules with their own internal degrees of rotation. Thus the measurement of
dielectric constant provides a powerful tool in understanding the static and dynamic behaviour of the system. The importance of these studies in ferroelectric liquid crystalline materials lies in the fact that it relates macroscopic properties like spontaneous polarization to microscopic parameters like the dipole moment of the molecule.

In this chapter we present results of detailed investigations on the influence of various parameters on the dielectric properties in FLCs.

It may be recalled that the $A - C^*$ transition is not driven by the spontaneous polarization $P_s$, but the molecular tilt $\theta$. But as the two are effectively coupled, $P_s$ also goes to zero at the transition to $A$ phase. Hence in analogy with the paraelectric-ferroelectric transition in solid ferroelectrics the transition temperature $T_c$ at which $P_s$ goes to zero is referred to as the Curie point. In fact dielectric measurements near the $A - C^*$ transition reveal some of the features exhibited by the solid ferroelectrics (where $P_s$ is the primary order parameter) near the Curie point.

Earlier dielectric studies on FLCs have established the following:

1. Just like their achiral analogues, there is a low frequency relaxation mode associated with the flipping of the molecules around their short axis. This is observed as a dispersion in the $\epsilon_{||}$ the dielectric constant along the layer normal direction.

2. $\epsilon_{\perp}$ shows two low frequency director relaxation modes, viz., the soft mode (SM) and the Goldstone mode (GM). The former appears both in $C^*$ and the $A$ phases close to $T_c$, but the latter exists only in the $C^*$ phase.

Several studies have been made to characterise these modes by measuring $\epsilon_{\perp}$ as a function of temperature and frequency,$^7$-$^12$ applied field strength,$^{13}$ thickness of
the sample\textsuperscript{15,16} and DC bias field\textsuperscript{18,20} across the A—C* transition. However there are hardly any reports on the effect of the magnitude of $P_e$, alkyl chain length, etc., on the static and dispersion behaviour of $\epsilon_L$. The studies presented in this chapter describes the influence of these parameters. Further the results are discussed in the light of the predictions of the generalized Landau model\textsuperscript{21,22} which has been quite successful in explaining the behaviour of many other ferroelectric properties.

Experiments carried out on a homologues series of compounds help in understanding the role played by the elastic torque and the associated viscosity in determining the relaxation parameters. A novel method of analysing the $SM$ results using which two important Landau coefficients can be calculated, is also presented. We will start with a general introduction to the dielectric studies in FLCs.

### 3.1.1 Dielectric spectra of ferroelectric liquid crystals

As mentioned earlier the behaviour of $\epsilon_\parallel$, the dielectric constant parallel to the director, is very similar in both chiral and achiral systems. On the other hand, the transverse dielectric constant $\epsilon_\perp$ exhibits drastically different behaviour in chiral systems. Figure 3.1 is a schematic representation\textsuperscript{23} of the different types of relaxations seen in $\epsilon_\parallel$ and $\epsilon_\perp$ for a FLC. $\epsilon_\parallel$ has two high frequency relaxations\textsuperscript{21} - one due to the molecular rotation around the short axis (frequency range $10^5$-$10^7$ Hz) and the other due to the molecular reorientation around the short axis (frequency range $10^8$-$10^{10}$ Hz). For $\epsilon_\perp$ there is one dispersion due to molecular rotations around the long axis (frequency range $10^8$-$10^{10}$ Hz) and the other due to the intramolecular rotation at still higher frequency range. At lower frequencies (frequency range of $10^2$-$10^6$ Hz) the spectra contains two more modes identified to the director relaxation modes. These are referred to as soft mode ($SM$) and the Coldstone mode ($GM$).
Fig. 3.1. Frequency dependence of the perpendicular, \( \varepsilon_\perp \), and parallel, \( \varepsilon_\parallel \), components of the complex dielectric permittivity in the A and C* phases, connected to the collective and non-collective molecular mechanisms (From ref. 23).
While both the modes are present in C* phase only SM is observed in the A phase.

The characteristic feature of FLC is the helical distribution of the permanent dipoles of the molecules. When a measuring electric field is applied in a direction parallel to the layers anti perpendicular to the helix, the field will disturb the helix in two ways. First, it induces an additional tilt (due to the electroclinic effect described in Chapter 1) and thus changes the amplitude of the tilt. Secondly, the azimuthal direction of the tilt changes (thus changing the phase) enabling the dipole to orient in the field direction. Hence the disturbance of the equilibrium order parameters due to an applied electric field can be divided into two parts; amplitude and phase parts. As we shall see presently these are denoted as soft mode and Goldstone mode respectively.

Soft mode

Raman and Nedungadi were the first to observe the existence of soft modes in a structural phase transition. Using Raman scattering, they found that the frequency of a totally symmetric optical phonon decreases (softens) as the $\alpha \rightarrow \beta$ transition in quartz is approached. In a similar fashion in FLCs, the elastic forces controlling the tilt fluctuations become soft as the $A \rightarrow C^*$ transition is approached from the A phase, owing to this the amplitude of the tilt fluctuation (see Fig.3.2a) increases drastically and its susceptibility diverges at $T_c$ and its frequency tends to zero. For this reason this tilt amplitude fluctuation mode is called the soft mode ($SM$). The $SM$ exists in non-chiral liquid crystalline system also, however the amplitude would be very small. Since near $T_c$ the molecules are susceptible for tilt fluctuations even a weak electric field applied in a direction perpendicular to the director can easily perturb the equilibrium director orientation. For non-chiral smectic A phase the induced
Fig. 3.2. Schematic diagram illustrating the director fluctuation modes in the C* phase: (a) Soft mode, (b) Goldstone mode.
dipole moment due to the applied field is too small to be detected by dielectric measurements. However, the tilt fluctuations in these systems can be studied by light scattering.\textsuperscript{29} In FLCs the chirality enhances the induced dipole moment due to the electroclinic effect thus permitting the study of $SM$ by dielectric methods.\textsuperscript{23}

Goldstone Mode

One of the characteristic features of $A - C^*$ transition is that $C^*$ phase has lower symmetry than the high temperature $A$ phase, i.e., $A - C^*$ transition involves the breaking of a continuous symmetry group. According to the Goldstone theorem\textsuperscript{30} a symmetry recovering order fluctuation mode - the Goldstone mode - will appear below $T_c$ in addition to the soft mode. In $A$ phase, the molecules are along the layer normal and hence the phase is uniaxial. In the $C^*$ phase the molecules are tilted which breaks the uniaxial symmetry of the molecule and makes it biaxial. However the existence of the helicoidal structure allows the $C^*$ phase to recover the macroscopic uniaxial symmetry. As such the symmetry recovering relaxation mode - referred to as the Goldstone mode (GM) should be related to the helix or equivalently to the phase changes of the tilt order parameter (see Fig. 3.2b). When an AC electric field is applied, the helix gets distorted and the process of the restoring of the distorted helix is described by the relaxation of GM.\textsuperscript{10} Owing to the macroscopic dimension of the helix ($\sim \mu m$), the $GM$ relaxation frequency turns out to be quite low ($10^2 \sim 10^3$ Hz) for the same reason the strength of $GM$ is large.

3.1.2 Thermodynamic model

Attempts have been made to explain various thermodynamic properties of Sm C* phase in terms of phenomenological models\textsuperscript{21,22,31} involving a Landau free energy expansion. These models are based on the idea that the free energy can be expanded in terms of a Taylor series in the order parameter reflecting the symmetry properties
of the medium. It is important to note that the tilt of the molecules drives the $A-C^*$ transition, and, as pointed out in earlier chapters, the appearance of $P_s$, which arises only as an associated effect, is the secondary order parameter.

Just as in the non-chiral $C$ phase the tilt is described by a complex order parameter which can be resolved into a magnitude part and a phase part represented by the polar angle $\theta$ and the azimuthal angle $\phi$ respectively. Geometrically, the tilt vector $\vec{\xi} = (\xi_1, \xi_2)$ is the projection of the director $\vec{n}$ on to the smectic planes. The existence of non-zero tilt breaks the axial symmetry around the long molecular axis. If the substance is chiral this induces an ill-plane polarization $\vec{P} = (I_{\perp}, P_y)$ perpendicular to the tilt direction (see Fig. 3.3). (Here $P_x$ and $P_y$ are the orthogonal components of $\vec{P}$ in the smectic plane.) For a general description of the $C^*$ phase, along with these order parameter terms one has to include terms accounting for the helicoidal structure of the phase. As there are two order parameters one of them being secondary, it is natural to include coupling terms between them. Two simplest types of coupling terms are:

**Piezoelectric.**

The lowest order coupling term of this type is given by $C(P_x \xi_2 - P_y \xi_1)$, $C$ is called the bilinear coupling constant.

**Flexoelectric.**

At the molecular level, flexoelectricity exists due to special shapes of the constituent molecules. But in the $C^*$ phase this is caused by the macroscopic helicoidal structure. The distortion of the director gives rise to contribution of the type $\mu(P_x \frac{\partial \xi_1}{\partial z} + P_y \frac{\partial \xi_2}{\partial z})$, $\mu$ being flexoelectric coefficient. Notice that this term vanishes for an unwound sample.
Fig. 3.3. The components of the order parameter $\bar{\xi}$ and $P_1$. 
Putting together the various terms, the free energy expansion can be written as:

\[
g(z) = \frac{1}{2} a(\xi_1^2 + \xi_2^2) + \frac{1}{4} b(\xi_1^2 + \xi_2^2)^2 - \Lambda(\xi_1 \frac{d \xi_2}{dz} - \xi_2 \frac{d \xi_1}{dz}) + \frac{1}{2} K_3 \left[ \left( \frac{d \xi_1}{dz} \right)^2 + \left( \frac{d \xi_2}{dz} \right)^2 \right] + \frac{1}{2 \epsilon} \left( P_x^2 + P_y^2 \right) - \mu \left( P_x \frac{d \xi_1}{dz} + P_y \frac{d \xi_2}{dz} \right) + C(P_x \xi_2 - P_y \xi_1) \tag{3.1}
\]

where \(a\) and \(b\) are the usual Landau coefficients and it is assumed that '\(a\)' is the only temperature dependent coefficient with \(a = a(T - T_0)\), where \(T_0\) is the transition temperature for the racemic mixtures (without helix and \(A = C = 0\)), \(K_3\) an elastic constant, \(A\) the Lifshitz invariant, \(\epsilon\) is the high temperature dielectric constant.

To simplify eqn. (3.1) the values of \(\xi_1, \xi_2\) and \(P_x, P_y\) have to be found. Figure 3.3 shows the components \(\xi_1, \xi_2\) and \(P_x, P_y\). For small tilt angles,

\[\xi_1 = \theta \cos \phi \quad \text{and} \quad \xi_2 = \theta \sin \phi\]

where \(\phi = \phi(z)\) is the azimuthal angle determining the orientation of the director \(\vec{n}\) with respect to \(z\)-axis, i.e., normal to the smectic layers. If \(q\) is the wavevector of the helix then \(\phi = qz\). Similarly, \(P_x = -P_0 \sin \phi\) and \(P_y = P_0 \cos \phi\) are the components of \(P_s\) along \(x\) and \(y\) axes. Substituting the values of \(\xi_1, \xi_2\) and \(P_x, P_y\) in eqn. (3.1), we get

\[g(z) = g_0 + \frac{1}{2} a \theta^2 + \frac{1}{4} b \theta^4 - \Lambda q \theta^2 + \frac{1}{2} K_3 q^2 \theta^2 + \frac{1}{2 \epsilon} P^2 - \mu P q \theta - C P \theta \tag{3.2}\]

Expressions for the \(A-C^*\) transition temperature \(T_c\), the temperature dependence of the tilt angle \(\theta\), pitch of the helix and polarisation \(P_s\) can be obtained by minimising eqn. (3.2) with respect to \(\theta, I\) and \(q\).

\[T_c = T_0 + \frac{1}{2} \left[ \epsilon C^2 + (K_3 - \epsilon \mu^2) q^2 \right] \tag{3.3}\]

\[\theta = \left[ \frac{\alpha}{b} (T_c - T) \right]^{1/2} \tag{3.4}\]
\[ p = \frac{2\pi}{q} = 2\pi \frac{K_3 - \epsilon \mu^2}{\Lambda + \epsilon \mu C} \]  
(3.5)

\[ P_s = \epsilon (\mu q + C) \theta \]  
(3.6)

Since all the quantities on the RHS of (3.5) are constants pitch \( p \) and hence the ratio \( P_s / \theta \) from (3.6) are independent of temperature. This means that the coupling between \( P_s \) and \( \theta \) is strictly linear. Contrary to this, experiments showed that \( P_s / \theta \) ratio is weakly dependent on temperature away from \( T_c \) but has a precipitous drop near it. The temperature dependence of helical pitch is also seen to have an anomalous variation close to \( T_c \). In order to explain these factors Carlsson et al., 21 have proposed a more generalized mean field (GMF) model which included a 6th order term in tilt and a biquadratic coupling term. Then eqn. (3.2) becomes

\[ g(z) = \frac{1}{2} a \theta^2 + \frac{1}{4} b \theta^4 + \frac{1}{6} c \theta^6 - \Lambda q \theta^2 + \frac{1}{2} K_3 q^2 \theta^2 + \frac{1}{2} \epsilon P^2 - \mu q P \theta \]

\[ -CP \theta - \frac{1}{2} \Omega P^2 \theta^2 + \frac{1}{4} \eta P^4 - dq \theta^4 \]  
(3.7)

Here \( c \) is the Landau coefficient of the 6th order term, \( \Omega \) the biquadratic coupling coefficient, \( d \) the higher order Lifshitz invariant included to account for the anomaly in the temperature variation of pitch. The predictions of the generalised model have found to be in good agreement with the experimentally observed features. Now let us see what this model expects for the thermal variation of SM and GM in the A and C* phases. 32,33,17

\[ \epsilon_0 \Delta \epsilon = \frac{\epsilon_0^2 \epsilon^2 C^2}{[\alpha (T - T_c)] + (K_3 - \epsilon \mu^2)q_o^2} \]  
(3.8)

In smectic A phase,
In smectic C* phase,

For SM

\[ f_s = \frac{a(T - T_c) + (K_3 - \epsilon \mu^2)q^2}{2\pi \eta_{sA}} \]  

(3.9)

\[ \epsilon_0 \Delta \epsilon_s = \frac{2\epsilon^2 \epsilon C^2}{2a(T - T_c) + (K_3 - \epsilon \mu^2)q^2} \]  

(3.10)

For GM

\[ f_s = \frac{a(T - T_c) + (K_3 - \epsilon \mu^2)q^2}{2\pi \eta_{s}} \]  

(3.11)

\[ \epsilon_0 \Delta \epsilon_G = \frac{1}{2K_3} \left( \frac{P}{q\theta} \right)^2 \]  

(3.12)

\[ f_G = \frac{K_3q^2}{2\pi \gamma_G} \]  

(3.13)

In the same paper\(^{32}\) the authors present a few theoretically expected curves in terms of a dimensionless parameter \(\beta\) where \(\beta = \frac{\eta^{1/2} \hat{C}_t}{\Omega}\) the value of \(\beta\) shows the importance of the biquadratic coupling term \(\Omega\). Larger the value of \(\beta\) smaller will be \(\Omega\). And \(\beta=1\) corresponds to the classical case. \(\beta\) is expressed in terms of \(P_s\) and \(\theta\) as

\[ \ddot{P}^3 + (1 - \dot{\theta}^2) \dot{P} - \beta \dot{\theta} = 0 \]  

(3.14)

where \(\dot{P} = P/P^*, \dot{\theta} = \theta/\theta^*\) and \(P^*\) and \(\theta^*\) are the normalising constants. We have
used this equation to evaluate the value of \( \beta \) (see results section). The theoretical plots of \( \Delta \epsilon_G, f_G, \) and \( f_s \) for different values of \( \beta \) are shown in figures 4.4a and 4.4b. At a later stage we compare our data with these theoretical curves.

### 3.2 Experimental

The experimental set up consists of the sample cell, temperature controlled heater and the dielectric measuring set up which includes an impedance analyses and a microcomputer.

#### 3.2.1 Sample cell and alignment of the sample

The method of preparations of the sample cell was exactly similar to the one described in Chapter II. The combined effect of polymer coating and magnetic field (2.4T) applied, along the rubbing direction, while cooling the sample from isotropic to A phase, was utilized to obtain uniform planar alignment of the samples.

A detailed description of the heater assembly and the temperature control and measurement system is given in Chapter II. Since the frequency sweep in the dispersion studies took about 2 minutes, it was necessary to keep the temperature constant over this period. The large thermal capacity of the system enabled to keep the temperature constant at any desired value to within ± 5 mK.

#### 3.2.2 Measurement of dielectric constant

The dielectric constants were determined by measuring the sample capacitance and dielectric loss factor. A versatile variable frequency Impedance Analyser (Hewlett Packard 3192A) with a measuring frequency range of 5 Hz - 13 MHz was employed for this purpose. In fact this instrument can be used to measure as many as eleven
Fig. 3.4a. Theoretical plot of $\Delta \epsilon_G$ versus temperature for different values of $\beta$ (from Ref. 32).

Fig. 3.4b. Theoretical plot of $f_G$ versus temperature for different values of $\beta$ (from Ref. 32).
impedance associated parameters such as capacitance C, conductance G, susceptibility B, dissipation or dielectric loss factor D, etc., with a basic accuracy of 0.1% throughout the range of measurement. In addition, the measuring voltage can be varied over a wide range from 5 mV to 1 V rms. The principle of capacitance measurement function is based on vector-voltage-current ratio measurement method. The capacitance measuring range is 0.1 pF to 100 mF and that of the dielectric loss factor is 0.0001 to 19.999. Experiments were done in the four probe configuration which eliminates errors due to residual impedance of test leads. The analyses has a built-in DC bias supply (providing a maximum ±35 V DC voltage) which can be superimposed on the probing AC measuring field. Interfacing to a computer was established through the IEEE 488 bus. Thus all the functions could be controlled and monitored by the computer which also handled the data acquisition.

### 3.2.3 Static dielectric constant measurement

The block diagram of the experimental set-up used is shown in figure 3.5. Both the impedance analyses and the temperature reading digital multimeter (Keithley 181) were interfaced with a computer. At any desired frequency, the sample temperature was varied uniformly at a slow rate of \( \sim 5^\circ K/\text{hour} \) away from the transition and \( \sim 2^\circ K/\text{hour} \) close to it. The capacitance and temperature readings were continuously collected by the computer. For static measurements with a bias field, the required DC bias voltage was applied and the capacitance was measured at different temperatures.
Fig. 3.5. Block diagram of the dielectric measurement set-up.

H = Heating oven  
M = Microscope

P, A = Polarizer and Analyser
3.2.4 Dispersion measurements

The set-up used is the same as for static measurements. For the frequency dependent dielectric constant measurements, the sample temperature was stabilized at the desired value and the microcomputer handled the frequency sweep by varying the frequency over the range of interest at a desired step value. The capacitance and the dissipation factor were measured as a function of the set frequency. Throughout the frequency sweep, the temperature was continuously monitored. The sweep measurements could also be carried out in the presence of a bias voltage.

The impedance analyser can be used up to a frequency of 13 MHz. But we have limited all our experiments to a maximum frequency of 600 KHz, as beyond this frequency the RC constant of the cell (due to the ITO layer) starts contributing to the measured dielectric values.

3.3 Results and Discussion

3.3.1 Static dielectric constant

Figure 3.6 is a plot of the temperature variation of $\varepsilon_\perp$ measured at different frequencies for the compound $C_{10}$ (see Table 3.1). As seen from the figure, in the A phase, $\varepsilon_\perp$ does not vary much with temperature. But, close to $T_c$, it increases drastically with decreasing temperature. The pretransitional increase in the value of $\varepsilon_\perp$ (in the A phase) shows the existence of SM. In the C* phase the rapid increase in $\varepsilon_\perp$, below $T_c$, confirms presence of GM. In the frequency range studied the behaviour on the C* side, i.e., GM, is strongly dependent on the frequency so much so that at 10 kHz $\varepsilon_\perp$ value would be reduced to SM contribution only. One may observe similar effects with the application of a bias field and this is seen clearly in the figure 3.7. It
Fig. 3.6. Influence of the frequency of measurement on the dielectric constant of compound $C_{10}$. 

Fig. 3.7. Effect of bias field on the static dielectric constant of compound $C_{10}$. 
is evident from these figures that the effects observed as a function of frequency or DC bias voltage is caused by the GM relaxation. Another notable feature in these figures is that, there is a maximum in the dielectric constant at the transition when measured either at high frequency or with a high bias voltage implying that the contribution of SM reaches a maximum at $T_c$. To conclude, the thermal variation of dielectric constant measured at a few selected frequencies show the existence of SM and GM in a FLC. To have better understanding of these two director relaxation modes, we have carried detailed dispersion measurements on three compounds (listed in table 0.1) and the effect on both SM and GM caused by subtle molecular changes which, as seen in results of Chapter II, affects the magnitude of $P_s$. Thus these studies will also reveal, albeit in an indirect fashion, the effect of $P_s$ on the behaviour of SM and GM.

### 3.3.2 Dispersion Studies

Before presenting the results let us recall the equations for the frequency dependence of the complex dielectric constant ($\epsilon^*$). $\epsilon^*$ can be written in terms of its real ($\epsilon'$) and imaginary ($\epsilon''$) components as:

$$\epsilon^*(f) = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\Delta\epsilon}{1 + j\omega\tau}$$  \hspace{1cm} (3.15)

Here $\Delta\epsilon(=\epsilon_0 - \epsilon_\infty)$ is the strength of the mode whose relaxation time is $\tau = \frac{1}{2\pi f_R} f_R$ being the relaxation frequency. $\epsilon_0$ and $\epsilon_\infty$ are the values of the dielectric constant at frequencies far below and far above $f_R$ respectively. $\omega(=2\pi f)$ is the measuring field frequency. A convenient method to determine the two characteristic parameters of the mode, $\Delta\epsilon$ and $f_R$, is to plot an Argand diagram of $\epsilon'$ vs. $\epsilon''$. The plot (Fig. 3.8a) will be a semicircle (corresponding to the positive values of $\epsilon''$). Since eqn. (3.15) represents a Debye type relaxation, this semicircle is called a Debye semicircle, using
Fig. 3.8. Plot of $\varepsilon'$ vs. $\varepsilon''$ showing (a) a pure Debye type of relaxation, (b) a modified Debye, Cole-Cole relaxation.
### Table 3.1

Compounds used and their $P_s$ values at $T_c - T = 10$ °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Structure</th>
<th>$C^*$</th>
<th>$A$</th>
<th>$P_s$</th>
<th>$P_s$ Value [µC/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_7$</td>
<td><img src="image1" alt="D7 Structure" /></td>
<td>61.5</td>
<td>88.0</td>
<td>95.0</td>
<td>$P_s = 1500$ µC/m²</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td><img src="image2" alt="C10 Structure" /></td>
<td>69.0</td>
<td>88.0</td>
<td>92.5</td>
<td>$P_s = 720$ µC/m²</td>
</tr>
<tr>
<td>B$_{11}$</td>
<td><img src="image3" alt="B11 Structure" /></td>
<td>62.5</td>
<td>88.0</td>
<td>85.0</td>
<td>$P_s = 370$ µC/m²</td>
</tr>
</tbody>
</table>
which one can find $\Delta \epsilon = 2 \times \epsilon''_{\text{max}}$ and $f_R = f \times \frac{u}{v}$ with $u$ and $v$ defined as in figure 3.8a. However in the case of materials (like FLCs) which show a broader dispersion curve and lower maximum loss than would be expected from Debye relation, the $\epsilon''$ vs. $\epsilon'$ curve falls within the Debye semicircle (see Fig. 3.8b). For such cases Cole and Cole suggested a modified form of the Debye equation

$$\epsilon'(\omega) = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\Delta \epsilon}{1 + (j\omega\tau)^{1-h}}$$  \hspace{1cm} (3.16)

where $h$ is a constant called the distribution parameter with $0 \leq h < 1$. When $u = 0$ eqn. (3.16) reduces to a pure Debye type of relaxation. When $h$ is non-zero, the centre of the Cole-Cole arc lies in the negative $\epsilon''$ region, as shown in figure 3.8b.

Rationalising eqn. (3.16), one gets,

$$\epsilon' = \epsilon_\infty + \frac{\Delta \epsilon[1 + (\omega\tau)^{1-h} \sin(\frac{\pi h}{2})]}{1 + (\omega\tau)^{2(1-h)} + 2(\omega\tau)^{1-h} \sin(\frac{\pi h}{2})}$$ \hspace{1cm} (3.17)

$$\epsilon'' = \epsilon_\infty + \frac{\Delta \epsilon(\omega\tau)^{1-h} \cos(\frac{\pi h}{2})}{1 + (\omega\tau)^{2(1-h)} + 2(\omega\tau)^{1-h} \sin(\frac{\pi h}{2})}$$ \hspace{1cm} (3.18)

Equation (3.17) or (3.18) can be used to determine the values of $\Delta \epsilon$ and $f_R$. Except near the transition in the C* phase, eqn. (3.17) or (3.18) is sufficient to describe the relaxation behaviour. However, close to the transition, both GM and SM contribute to the dielectric constant. In such cases, it has been shown\textsuperscript{27} that $\epsilon^*$ can be written as a linear combination of the two modes involved.

$$\epsilon^*(f) = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\Delta \epsilon_G}{1 + (j\omega\tau_G)^{1-h_G}} + \frac{\Delta \epsilon_s}{1 + (j\omega\tau_s)^{1-h_s}}$$ \hspace{1cm} (3.19)

where $\Delta \epsilon_i$ ($i = \text{SM and GM}$) represents the strength, $\tau_i$ the relaxation time and $h_i$ the distribution parameters of the modes. Rationalisation of eqn. (3.19) leads to equations similar to equations 3.17 and 3.18.

We have fitted our experimental data of $(\epsilon^*(f), f)$ in the A phase and C* phase (far below $T_c$) to eqn. (3.17), to obtain the dielectric strength, relaxation frequency
of SM and Gh1 relaxations respectively and ($\epsilon_\infty$). The ($\epsilon^*(f)$, $f$) data in the C* phase close to $T_c$ has been fitted to a rationalised expression of eqn. (3.19) to separate out the relaxation parameter of the two modes. The fitting has been carried out using a non-linear "least squares" program based on the Marquardt algorithm by floating all the parameters involved. In all the cases the distribution parameter $h$, was found to be quite small ($\approx 0.1$).

Figures 3.9a-c show representative Cole-Cole diagrams obtained for the compound $C_{10}$; figures 3.9a in the A phase, 3.9b in the C* phase close to $T_c$ and 3.9c in the C* phase away from $T_c$. The solid line in the figures is the fit to eqn. (3.18). Plots in figures 3.9a and 3.9c exhibit single relaxation behaviour due to SM and GM respectively. When the temperature is close to $T_c$ in the C* phase, the Cole-Cole plot (Fig.3.9b) shows the simultaneous existence of both the relaxations (the solid line is fit to eqn. (3.19)). Normally it is difficult to, except very close to the transition, separate out the two modes. This is because, as seen from the figure, the strength of SM is much smaller compared to that of GM. Also the strength of the SM decreases rapidly as $T_c - T$ is increased. However, owing to the large value of $P_3$ in $D_{7}$ we have been able to resolve the two over a temperature range of $0.8^\circ C$ in the C* phase, which is a larger temperature range (in the absence of the bias field) than in any other previous report.\(^{17}\) For the same reason the SM could be studied up to $3^\circ C$ in the A phase. In fact this point is quite clear when we note that for the three compounds these ranges are $0.8^\circ$; $3.0^\circ$ for $D_{7}$, $0.5^\circ$; $1.5^\circ$ for $C_{10}$ and $0.07$; $0.5^\circ C$ for $B_{11}$ respectively.
Fig. 3.9. Representative Cole-Cole diagrams for compound C_{10} in (a) A phase; (b) C* phase near T_c; (c) C* phase away from T_c. Notice the double Cole-Cole behaviour in (b).
3.3.3 Soft mode relaxation

Figures 3.10-3.12 are the plots of inverse soft mode strength $1/\Delta \epsilon_s$ and relaxation frequency $f_s$ for the three compounds. The salient features observed in the figures are (1) In the $A$ phase $f_s$ varies linearly with temperature while $1/\Delta \epsilon_s$ is non-linear. 2) In the $C^*$ phase both $f_s$ and $1/\Delta \epsilon_s$ are linear with temperature. Most of the earlier experiments have also shown the linear behaviour of $f_s$, but only a few observations of non-linear variation of $1/\Delta \epsilon_s$ exist. 3) At $T_c$ both $f_s$ and $1/\Delta \epsilon_s$ reach a non-zero minimum (i.e., the SM strength has a finite maximum). The minima being non-zero is as expected for improper ferroelectrics. $f_o$, the value of $f_s$ at $T_c$ is different for compounds $D_7$, $C_{10}$ and $B_{11} - f_o(D_7) > f_o(C_{10}) > f_o(B_{11})$ and appears to depend on the magnitude of $P_s$. In the following we shall attempt to explain the behaviour of both $f_s$ and $1/\Delta \epsilon_s$ with the help of equations 3.8-3.11 given by the generalised mean field model. According to eqn.(3.9) $f_s$ has a linear temperature dependence if the ratio of $\frac{(K_3 - \epsilon \mu^2)q_o^2}{2\pi \eta_s}$ is independent or weakly dependent on temperature.$^{35}$ The non-linear thermal variation of $1/\Delta \epsilon_s$ may be due to the temperature dependence of the elastic torque $(K_3 - \epsilon \mu^2)q_o^2$ and bilinear coefficient $C$ (see eqn.(3.8)). However it may be recalled that the coefficient $C$ is shown to be independent of temperature for low as well as high $P_s$ materials.$^{36}$ Thus one reason for the 11011-linear behaviour of $1/\Delta \epsilon_s$ could be that the twist to piezo energy ratio $\frac{(K_3 - \epsilon \mu^2)q_o^2}{\epsilon^2 C^2}$ may be changing with temperature (we see later that this is true in the $C^*$ phase). Due to these reasons the product $\Delta \epsilon_s f_s$ should also be non-linear close to $T_c$. This is indeed the case as seen from the plots (figures 3.13-3.15) of $\Delta \epsilon_s f_s$ vs. $T - T_c$ for the three compounds. Following Gouda et al.$^{37}$ we have tried to describe this behaviour of $\Delta \epsilon_s f_s$ in the $A$ phase with a power law of the type $\Delta \epsilon_s f_s \propto (T - T_c)^{\beta}$. The values of $\beta$ for the three compounds are 0.45, 0.37 and 0.2 respectively for $D_7, C_{10}$ and $B_{11}$. 

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Fig. 3.10 Temperature dependence of soft mode relaxation frequency \( f_s \) arid inverse dielectric strength \( 1/\Delta \epsilon_s \) for compound A.
Fig. 3.11. Thermal variation of $f_s$ and $1/\Delta\varepsilon_s$ for compound $C_{10}$. 
Fig. 3.12. Thermal variation of $f_s$ and $1/\Delta \varepsilon_s$ for compound $B_{II}$. 
Fig. 3.13. Plot of the product $\Delta \varepsilon_s f_s$ vs. temperature for compound D7.
Fig. 3.14. Temperature dependence of $\Delta \varepsilon_s / \varepsilon_s$ for compound $C_{10}$. 
Fig. 3.15. Plot of $\Delta \varepsilon_s f_s$ vs. temperature for compound $B_{11}$. 
3.3.4 Goldstone mode relaxation

The thermal variation of $\Delta \epsilon_G$ and $f_G$ for the three compounds are shown in figures 3.16-3.18. Some notable features are -

1. $f_G$ is observed to be weakly dependent on temperature away from the transition, but varies strongly very close to $T_c$.

2. The minimum of $f_G$ is not at $T_c$ but slightly below it.

3. The actual value of $f_G$ seems to be directly related with the magnitude of $P_s$, i.e., $f_G(D_7) > f_G(C_{10}) > f_G(B_{11})$.

4. $\Delta \epsilon_G$ is zero at $T_c$ and increases rapidly in the $C^*$ phase. For $C_{10}$ it appears to stabilise away from $T_c$. Whereas $D_7$ and $B_{11}$ show variation of $\Delta \epsilon_G$ even away from $T_c$.

According to Legrand and Parneix\textsuperscript{38} the relative twist to piezo energy ratio parameter $Q^2$ is defined as $Q^2 = \frac{K q^2}{\chi_\infty e^2}$, where $K$ is the renormalized twist elastic constant and $\chi_\infty = \frac{1}{4\pi}(\epsilon_\infty - 1)$. These authors give a more practical definition for $Q^2$ as $Q^2 = \frac{2\pi \chi_\infty}{\Delta \epsilon_G}$. Using this relation we have calculated $Q^2$ for the compound $C_{10}$ at two different temperatures. The values are 0.004 at $T_c - T = 6^\circ C$ and 0.09 at $T_c - T = 0.02^\circ C$. These numbers may be compared with the value of $Q^2 = 0.2$ for DOBAMBC\textsuperscript{10} ($P_s \approx 30 \mu C/m^2$) and $Q^2 = 0.003$ for a material\textsuperscript{38} with $P_s = 500 \mu C/m^2$ away from $T_c$. This appears to suggest that the value of $Q^2$ is inversely proportional to $P_s$. Also the values of $Q^2$ calculated show that $Q^2$ varies substantially with temperature.
Fig. 3.16. Temperature dependence of Goldstone mode frequency ($f_G$) and dielectric strength ($\Delta \epsilon_G$) for $D_7$. 
Fig. 3.17. Thermal variation of $f_G$ and $\Delta \varepsilon_C$ for compound $C_{10}$. 
Fig. 3.18. Thermal variation of $f_G$ and $\Delta \varepsilon_G$ for compound $B_{11}$. 
3.3.5 Effect of bias field on the soft mode

As mentioned earlier the main problem in studying the SM in the C* phase is that the dielectric strength of the SmI drowns that due to the SmII even slightly away from $T_c$. One well known technique$^{18,19,39}$ to overcome this problem is to apply a DC bias field high enough to unwind the helical structure. We have used this method to study the SM relaxation in one material, viz., $C_{10}$. Figures 3.19 and 3.20 are the plots of $1/\Delta\epsilon_s$ and $f_s$ as a function of temperature obtained using a bias voltage of 20 kV/cm; for the sake of comparison the zero bias values are also plotted. While zero bias data show sharp minima at the transition, the minimum is broad in the presence of a bias voltage. Also, the values of $\Delta\epsilon_s$ and $f_s$ at the transition are different in the two cases: $(\Delta\epsilon_s)_{E=0} = 43.5$ and $(\Delta\epsilon_s)_{E=20} = 5.8$ and $(f_s)_{E=0} = 3.8$ kHz and $(f_s)_{E=20} = 53.7$ kHz. Here E denotes the bias field applied. The higher $f_s$ value in the presence of bias field may be due to the reason that the high bias field rigidly holds the dipoles (molecules) in the direction of the field and this additional rigidity increases the value of $f_s$. For the same reason $A_t$, for the bias case is smaller than that for zero bias.

3.3.6 Effect of chain length on the dielectric properties

The length of the alkyl chain plays a crucial role in liquid crystals. In general this parameter affects the transition temperatures and stability of different mesophases. In FLCs, the alkyl chain length alters, as seen in Chapter II, the magnitude and nature of thermal variation of $P_s$. Results presented in Chapter IV also show that even the rotational viscosity $\gamma_\phi$ is influenced by this. Thus, it would be interesting to study the correlation between this parameter and the behaviour of GM and SM.

For this purpose dielectric measurements were carried out on three homologues $n$
Fig. 3.19. Plot of $1/\Delta \epsilon_s$ vs. temperature with no bias ($\bigcirc$) and 20 kV/cm bias field ($\times$) for compound $C_{10}$. 
Fig. 3.20. Plot of $f_s$ vs. temperature with no bias (O) and 20 kV/cm bias field (x) for compound $C_{10}$. 
= 6 to 8 of the series [5]-4'- (2-chloro-4-methylpentanoyloxy)phenyl trans-4'-n-alkoxy cinnamates (C, series, \( n = 6-8 \)). The transition temperatures and the molecular structure of the compounds is already given in Table 2.3.

Plots of the thermal variation of \( \Delta \epsilon_G \) and \( f_G \) for the three compounds are shown in figures 3.21 and 3.22. The salient features seen are:

1. The value of \( \Delta \epsilon_G \) increases with increasing chain length, but not strictly proportional to it, for e.g., the difference in \( \Delta \epsilon_G \) between \( C_7 \) and \( C_8 \) is larger than that between \( C_6 \) and \( C_7 \).

2. The trend in \( f_G \) (figure 3.22) is different. \( f_G \) for \( C_7 \) is much greater than those for \( C_6 \) and \( C_8 \) so much so that a sort of odd-even effect is observed. The product \( \Delta \epsilon_G f_G \) also shows this type of behaviour. One reason for this could be the odd-even behaviour in the pitch. But that were to be the sole factor it should have been manifested in the \( \Delta \epsilon_G \) behaviour also; but figure 3.21 does not support this idea. In fact, this possibility can be ruled out as the product \( \Delta \epsilon_G f_G \) which is independent of pitch also shows the odd-even effect. We notice from eqn. (3.13) that \( f_G = \frac{K_3 q^2}{2 \pi \gamma_G} \). Thus the odd-even nature in \( f_G \) may be due to the alternation in the value of the ratio \( \frac{K_3 q^2}{\gamma_G} \) with chain length. To verify this we have calculated the value of \( K_3 q^2 \) by using the expression for \( \Delta \epsilon_G \) (details are given in next section) and obtained the value of \( \gamma_G \) from the Diamant method \(^{11} \) (described in the next chapter). The calculated values of the ratio \( \frac{K_3 q^2}{\gamma_G} \) at \( T_c - T = 5^\circ C \) for the three compounds are: 2470 (for \( C_6 \)), 3170 (for \( C_7 \)) and 2850 (for \( C_8 \)), i.e., non-monotonic with chain length. Hence this must be the reason for the alternation in the value of \( f_G \) for the three homologues. The ratio of the quantities \( (P/\theta)^2 \) and \( \gamma_G \) also shows such an alternation and accounts for the odd-even behaviour seen in \( \Delta \epsilon_G f_G \).
Fig. 3.21. Effect of chain length on the temperature dependence of $\Delta \epsilon_G$ for $C_6$ (□), $C_7$ (★) and $C_8$ (■).
Fig. 3.22. Effect of chain length on the thermal variation of $f_G$ for $C_6$ ($\Box$), $C_7$ ($\ast$) and $C_8$ (■).
While looking at the predictions of the generalised mean field theory,\textsuperscript{32} we find a remarkable similarity between the experimental data of figures 3.21 and 3.22 and the theoretical curves obtained for different values of $\beta$ (see figures 3.4a and 3.4b); here $\beta$ is the effective $P - \theta$ coupling constant defined in the earlier section. In particular, as the chain length is varied, drastic changes in the magnitude of $\Delta \epsilon_G$ and $f_G$, presence or absence of a pronounced minimum in $f_G$, etc., are seen. Thus for the compounds $C_6 - C_8$ one should expect the $\beta$ values to change significantly with increase in chain length. We have determined the $\beta$ values by fitting the data of $P_s$ (obtained by Diamant method) and $\theta$ (obtained by X-ray diffraction method) to eqn. (3.14). The parameters $P^*, \theta^*$ and $\beta$ obtained for the three compounds are listed in the Table 3.2. In contrast to the theoretical expectations, the $\beta$ values are the same, within the experimental errors, for all the three homologues. Thus one can conclude that the experimentally observed features are not brought about by any changes in $\beta$ and hence the bilinear to biquadratic coupling effects.

In figures 3.23 and 3.24 we present the results of $\Delta \epsilon_s$ and $f_s$ for the three homologues. Notice that, in contrast to GM frequency $f_G$, both $\Delta \epsilon_s$ and $f_s$ monotonically increase with increasing chain length without any odd-even behaviour.

### 3.3.7 Determination of Landau coefficients by dielectric method

In this section, we present a novel method of determining Landau coefficients by analysing the dielectric data of the soft mode and Goldstone mode for the compound $C_6$ described in the previous sections. The soft mode viscosity ($\gamma_s$) is also calculated and seen to be influencing the thermal variation of $f_s$. 
Values of $P^*, \theta^*$ and $\beta$
for the three homologues of the $C_n$ series

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P^*$ (Cm$^{-2}$)</th>
<th>$\theta^*$ (rad)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>0.66</td>
<td>0.53</td>
</tr>
<tr>
<td>$C_7$</td>
<td>$1.6 \times 10^{-3}$</td>
<td>0.54</td>
<td>0.51</td>
</tr>
<tr>
<td>$C_8$</td>
<td>$1.3 \times 10^{-3}$</td>
<td>0.48</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Fig. 3.23. Temperature dependence of $\Delta\epsilon_s$ for $C_6$ (□), $C_7$ (+) and $C_8$ (▲).
Fig. 3.24. Temperature dependence of $f_s$ for $C_6$ (■), $C_7$ (A) and $C_8$ (□).
Figures 3.25 and 3.26 show the temperature variation of $f_s$ and $\Delta \epsilon_s$ for the compound $C_6$. Since this mode is associated with the order parameter fluctuations (in this case tilt fluctuations), the pretransitional critical behaviour of $f_s$ and $\Delta \epsilon_s$ are governed by the tilt susceptibility exponent $\gamma$ whose value is 1.0 in the mean field (MF) limit and 1.315 if the transition belongs to XY universality class. Tilt angle** and heat capacity43 measurements have shown that this transition is MF like. Early work on the electroclinic effect by Garoff and Meyer26 gave a value of 1.11 for the susceptibility exponent, which is inconsistent with either MF or XY class values. However more recent measurements44,45 are in agreement with the mean field description. With this in mind, we have fitted the $f_s$ and $\Delta \epsilon_s$ versus temperature data to power law equations of the type

$$f_s = \text{constant} \times (T - T_c)^\gamma \quad (3.20)$$

$$\Delta \epsilon_s = \text{constant} \times (T - T_c)^{-\gamma} \quad (3.21)$$

Equations (3.20) and (3.21) appear to describe the data well (solid lines in figures 3.25 and 3.26) but the exponents obtained, 1.19 and 0.88 for $f_s$ and $\Delta \epsilon_s$ respectively, are different from the MF value of 1.0. In order to understand this discrepancy, we consider eqns. (3.5) and (3.9) given by generalized mean field model and instead of assuming the exponents to be equal to 1, introduce two unknown constants $\gamma_1$ and $\gamma_2$ as the exponents and write the equation as

$$f_s = \frac{1}{2\pi \eta_s}[a(T - T_c)^{\gamma_1} + K_3q_0^2] \quad (3.22)$$

$$\epsilon_0 \Delta \epsilon_s = \frac{(\epsilon_0 \epsilon^2 C)^2}{a(T - T_c)^{\gamma_2} + K_3q_0^2} \quad (3.23)$$

In these equations the term $\epsilon^2$, which is known to be very small46 compared to $K_3$ has been neglected. From equation (3.22) we see that for $f_s$ to be linear
Fig. 3.25. Temperature variation of the soft mode relaxation frequency $f_s$ for $C_6$. (□) data, and (---) fit to eqn. 3.20.
Fig.3.26. Thermal variation of the soft mode strength $\Delta \epsilon_s$ for $C_6$. (□) data and (—) fit to eq. 3.21.
with temperature (with $\gamma_1 = 1$), $\eta_s$ should have no or very weak temperature dependence. But experiments indicate that $\eta_s$ is temperature dependent. Hence in the absence of information regarding the temperature dependence of $\eta_s$ the exponent $\gamma_1$ cannot be extracted from eqn. (3.22). However, the $\Delta \epsilon_s$ data will not have such a constraint. Equation (3.23) can be rewritten as

$$\frac{1}{\Delta \epsilon_s} = A(T - T_c)^{\gamma_2} + B$$  \hspace{1cm} (3.24)

where

$$A = \frac{a}{\epsilon_o(\epsilon C)^2} \quad \text{and} \quad B = \frac{K_3 q_0^2}{\epsilon_o(\epsilon C)^2}$$  \hspace{1cm} (3.25)

Figure 3.27 shows the fit to eqn. (3.24). It is seen that this expression describes the data extremely well (solid line in the figure) and the exponent obtained (0.97) is very close to the mean field value. One major advantage of employing eqn. (3.24) is that the constants $A$ and $B$ can be used to calculate the Landau coefficients $a$ and $C$ and the SM viscosity $\eta_s$. For this purpose, we proceed as follows.

The eqn. (3.12) for GM, can be rewritten as

$$K_3 q^2 = \frac{1}{2 \epsilon_o \Delta \epsilon_G} \left( \frac{P}{\theta} \right)^2$$  \hspace{1cm} (3.26)

The value of $K_3 q^2$ has been determined by measuring the thermal variation of $T$ and $\theta$ (see figures 3.28 and 3.29) and using the $\Delta \epsilon_G$ data (figure 3.21). This is plotted as a function of temperature in figure 3.31. In order to have an independent confirmation, we have also used eqn. (3.13) to calculate the value of $K_3 q^2$ as

$$K_3 q^2 = 2 \pi \eta_G \int_G$$  \hspace{1cm} (3.27)

$\eta_G$ has been obtained by the Diamant method\textsuperscript{44} (described in Chapter IV). This method gives $\eta_\phi$, the viscosity associated with the motion of the molecule
Fig. 3.27. Fit of $\frac{1}{\Delta \epsilon_s}$ to eqn. 3.24. (□) data (——) fit.
Fig. 3.28. Temperature dependence of $P_s$ for $C_6$.

Fig. 3.29. Temperature variation of tilt angle for $C_6$. 
around the smectic C' cone. The thermal variation of $\eta_\phi$ is given in figure 3.30.

This semi-log plot shows that away from $T_c$, $\eta_\phi$ has arrenius type of behaviour but deviates significantly from it on approaching $T_c$. However, $\eta_\phi$ is only an effective viscosity and the relevant viscosity of interest in present case is $\eta_G$, given by

$$\eta_G = \frac{\eta_\phi}{\sin^2 \theta} \quad (3.28)$$

A plot of $\eta_G$ as a function of temperature is also shown in figure 3.30. It is observed that $\eta_G$ shows arrhenius behaviour over the entire temperature range of measurements.

Figure 3.31 shows the temperature dependence of $K_3q^2$ calculated from both eqns. (3.28) and (3.29). Note that three different kinds of measurements $P_s$, X-ray tilt angle and dielectric methods are involved in the calculations and the $K_3q^2$ values obtained using the two equations differ by less than 5% throughout the temperature range of measurement. The extrapolated value of $K_3q^2$ at $T_c$ yields $K_3q^2_0$. Substituting this in the expressions for $A$ and $B$, we get,

$$C = \left( \frac{K_3q^2_0}{\varepsilon_0 \varepsilon^2 B} \right)^{1/2}$$

and

$$a = \frac{A}{B} K_3q^2_0.$$
Fig. 3.30. Variation of $\eta_0$ (×) and $\eta_0$ (□) as a function of temperature. Note that $\eta_0$ remains Arhenius right up to the transition.
Fig. 3.31. Variation of $K_3 q^2$ as a function of temperature, $\triangle$ symbols obtained from eqn. (3.26) and $\square$ obtained from eqn. (3.27).
Exponents and Landau coefficients obtained for $C_6$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponent $y$ (from $f_s$ fit)</td>
<td>1.19</td>
</tr>
<tr>
<td>$\gamma_2$ (from $1/\Delta \epsilon_s$ fit)</td>
<td>0.97</td>
</tr>
<tr>
<td>$\gamma - \gamma_2$</td>
<td>0.22</td>
</tr>
<tr>
<td>Exponent $x$ (from $\eta_s$ fit)</td>
<td>0.27</td>
</tr>
<tr>
<td>$K_3 q_0^2$</td>
<td>4300 Nm$^{-2}$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>3.03</td>
</tr>
<tr>
<td>$a$</td>
<td>$1.24 \times 10^5$ Jm$^{-3}$K$^{-1}$ rad$^{-2}$</td>
</tr>
<tr>
<td>$C$</td>
<td>$1.07 \times 10^8$ JC$^{-1}$ m$^{-1}$ rad$^{-1}$</td>
</tr>
</tbody>
</table>
\( \eta_s \) can be extracted rising the relation

\[ \eta_s = \frac{c_0 (cC)^2}{2 \pi \Delta \epsilon_s f_s} \]

in the limit of \( \gamma_1 = \gamma_2 = \gamma = 1 \).

The temperature variation of \( \eta_s \) is shown in figure 3.32. We have tried to express \( \eta_s \) data by a power law type of equation considering the usual arhenienius background contribution by an equation of the form

\[ \eta_s = A(T - T_c)^x + \eta_0 \exp\left(\frac{B}{T}\right) \]

Here \( A \) and \( B \) are constants and the second term on the R.H.S represent the arhenienius background contribution. This expression fits the data well with \( x = -0.27 \), which is in fair agreement with the value of \(-0.25\) obtained\(^{37}\) for another compound. Earlier, by considering \( \eta_s \) to be independent of temperature, the exponent for the thermal variation of \( f_s \), \( \gamma \) was found to be 1.19 which is much higher than the mean field value of 1. However, from eqn. (3.23), where the GMF relation for \( \Delta \epsilon_s \) was considered, we got \( \gamma_2 = 0.97 \). Significantly, the difference between \( \gamma \) and \( \gamma_2 \) \((= 0.22)\) is approximately the same as the value \( x \) obtained. Thus the divergence in \( \eta_s \) on approaching the transition appears to be largely responsible for the difference between the exponents \( \gamma \) and \( \gamma_2 \).
Fig. 3.32. Soft mode viscosity $\eta_s$ variation as a function of temperature. (□) data and (—) fit to a simple power law.
References


[46] See for e.g., T.Carlsson, B.Zeks, C.Filipic, A.Levstik and R.Blinc, Mol. Cryst. Liquid Cryst., 163, 11 (1988). In this paper it was shown that for DOBAMBC, the $\epsilon \mu^2$ value is at least two orders of magnitude smaller than $K_3$.
