Overview
The dielectric spectroscopy of a dielectric material gives useful information about the basic thermodynamic properties of the material. This chapter mainly deals with different polarization mechanisms possible in liquid crystals and their Nano-composites. A review of non-collective re-orientation mechanisms, which are common to all liquid crystals and the collective polarization mechanisms, in the smectic phase of liquid crystal, has been discussed. Theory of electro-optic phenomenon in these materials is also given.

A. Dielectric Relaxations

2.1 Theoretical Background

2.1.1 Polarization of Dielectrics
Liquid crystals are dielectric materials. Dielectrics possess low electrical conductivity but polarize in the presence of field (Jan P.F. Lagerwall 2000, Vera V. Daniel, Dielectrics, E Fattuzzo, Ferroelectricity, H. Frohlich, Theory of Dielectrics, Von Hipple, Dielectric Polarization). The electric field ‘E’ induces a polarization ‘P’ in these materials. The magnitude and direction of polarization is a characteristic of the material and it is related to the dielectric susceptibility ‘χ’ by

\[ P = \chi \varepsilon_0 E \]  

(2.1)

where \( \varepsilon_0 \) is permittivity of free space. The susceptibility is related to the relative permittivity (\( \varepsilon_r \)) as

\[ \chi = \varepsilon_r - 1 \]  

(2.2)

So, equation 2.1 reduces to

\[ P = \varepsilon_0(\varepsilon_r - 1)E \]  

(2.3)

So the permittivity relates electric field with the macroscopic polarization. This macroscopic polarization is of course a result of microscopic polarizations, which are divided in to two main categories: charge displacement polarization and orientation polarization. In the first case, a dipole moment is induced due to the displacement of the charges. This process is very fast and contributes to \( \varepsilon_r \) at very high frequencies. In the second case, on application of electric field, the aligning
force opposes the thermal disorder of the permanent dipole leading to a bias in the molecular vibration and rotation corresponding to partial orientation of the dipoles, which gives a contribution to the permittivity.

Certain crystals and liquid crystals (in special geometry) have symmetry allowing ferroelectric and anti-ferroelectric polarization. If a sufficiently strong electric field is applied over a ferroelectric material, the spontaneous polarization will line up with the field and as a result such materials have large dielectric permittivity. In contrast to the above mentioned non-collective molecular re-orientation process, this dipole movement is collective i.e. a large no. of molecules move in phase with each other.

When a DC field is applied, all mechanisms will be present, but for AC field, contribution from each mechanism will eventually disappear when the frequency is raised. Each mechanism is counteracted by the viscous forces and hence it can’t be driven at infinite speed. If it is driven back and forth at too high frequency, it will not have time to be activated before the driving field changes sign. So at very high frequency there will be no contribution to the permittivity. On approaching a certain characteristic frequency the driven motion seriously begin to lag behind the force. At this frequency, the polarization is $90^\circ$ out of phase with $E$. The fluctuation amplitude has then decreased to half of its maximum value and at this point maximum energy is absorbed from the electric field and transform into the heat of the material.

**Table 2.1: The polarization mechanisms possible in liquid crystals**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Type</th>
<th>Method of Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic polarization</td>
<td>Induced dipole</td>
<td>UV/VIS-absorption spectroscopy</td>
</tr>
<tr>
<td>Non-collective orientational</td>
<td>Permanent dipoles align</td>
<td>Dielectric spectroscopy, IR absorption spectroscopy</td>
</tr>
<tr>
<td>polarization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collective orientational (Ferro-electric) polarization</td>
<td>Permanently aligned dipole</td>
<td>Dielectric spectroscopy</td>
</tr>
<tr>
<td></td>
<td>reoriented</td>
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</table>
In nematics, we have two modes of orientational polarization and in SmA* we have a collective mode known as an electroclinic or Soft mode (SM). In the SmC* phase we have a strong mode giving contribution to $\varepsilon$, from the important polarization of each layer which tries to align in the direction of field by the easy azimuthal motion around the smectic cones. This mode is often called Goldstone mode (GM). The polarization mechanisms possible in liquid crystals are described in table 2.1 (Jan P.F. Lagerwall 2000).

The charge displacement and polarization modes due to their high frequencies could not be studied due to experimental limitations.

### 2.1.2 Debye Type Relaxation

On application of an electric field, the polarization of the medium approaches its equilibrium value exponentially with a characteristic time constant $\tau$.

$$P = P_f (1 - e^{-t/\tau})$$  \hfill (2.4)

where $P_f$ is the saturation value of polarization. If the field is switched off, the polarization will decay according to the relation

$$P = P_f e^{-t/\tau}$$  \hfill (2.5)

The Decay function $\alpha(t)$ is defined by

$$\alpha(t) \propto \exp(-t / \tau)$$  \hfill (2.6)

where, $\tau$ is the relaxation time, which is independent of time but depends on temperature.

In the presence of an AC field, the response of the material changes as a function of frequency and temperature. Thus, with the assumption that relaxation behaviour of each mode is characterized by single relaxation frequency, the complex dielectric constant (permittivity) can be written as

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T)$$  \hfill (2.7)

Where $\omega = 2\pi f$ is the angular frequency of applied field and $T$ is the temperature of the system. $\varepsilon'(\omega, T)$ is the real part and $\varepsilon''(\omega, T)$ is the imaginary part of the dielectric constant respectively. It can also be written as

$$\varepsilon^*(\omega, T) = \frac{\Delta \varepsilon_r(T)}{1 + i\omega\tau_r} + \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau_r} + \varepsilon_\infty$$  \hfill (2.8)

where

$$\Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty$$  \hfill (2.9)
is the dielectric strength of the material and $\varepsilon_0$ and $\varepsilon_\infty$ are the static and infinite frequency dielectric constants respectively. $\tau_r$ is the relaxation time of the corresponding mode. Separating it in to real and imaginary parts, we obtain

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$

(2.10)

$$\varepsilon''(\omega) = \omega \tau \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$

(2.11)

$\varepsilon''$ is also known as the dielectric loss factor. $D$ the dissipation factor i.e. the dielectric loss is given by

$$D = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}$$

(2.12)

Eqn. (2.10) and Eqn. (2.11) are Debye equations. This type of relaxation is known as Debye type relaxation. The generalization of the Debye formulation describes a dielectric process with a discrete distribution of relaxation times associated with a single dielectric process. The plots of these equations are shown in Fig. 2.1. If we sweep the frequency from zero to infinity it is seen from the equation that the $\varepsilon'$ has practically constant value till frequency approaches to relaxation frequency. It then decreases having an inflexion point at $\omega \tau = 1$ and becomes zero for $\omega \tau >> 1$. $\varepsilon''$ is vanishingly small except in the neighborhood of $\omega \tau = 1$, where it has maximum value. This is where the absorption occurs.

Fig. 2.1:- The Simple Debye type relaxation behavior of real and imaginary part of permittivity.
By successively increasing the frequency of measuring field, the real part of permittivity decreases stepwise; (Fig 2.2), each time the frequency passes the relaxation frequency. The difference between the low and high frequency contributions of the mode to the total dielectric constant is called the dielectric strength of the mode.

If several modes influence the experiment, one gets several ‘\(\varepsilon\)’ and ‘\(f_r\)’ values, each corresponding to one contributing mechanism. Each mode will then also get its specific set of ‘\(\varepsilon_0\)’ and ‘\(\varepsilon_\infty\)’ and dielectric strength i.e. the maximum contribution of the mode to the real part of the dielectric permittivity.

\[
\varepsilon''(\omega) = \frac{f}{f_r} \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \left(\frac{f}{f_r}\right)^2}
\]  

(2.14)

Fig. 2.2: Different relaxations present in the materials with a range of frequencies represented in the form of variation of real and imaginary part of permittivity

2.1.3 Non-Debye Type Behavior

When applying the Debye results to actual experimental data, one soon realizes that the Debye equation seldom works. For polymer systems and in many cases of low molar mass liquid crystals, a mode turns out to be characterized by the distribution
of relaxation time, and therefore it is impossible to obtain a good fit of equation (2.13) and (2.14) to experimental data. In order to cope with this problem, the above results will have to be modified. Such a modification was first introduced by K S Coles and R H Coles, in 1941, and their starting expression bears the name Cole-Cole equation.

\[
\varepsilon^*(\omega, T) = \frac{\Delta \varepsilon_i(T)}{1 + (i \omega \tau_i)^{1-\alpha}} + \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \left(i \frac{f}{f_r}\right)^{1-\alpha}} + \varepsilon_\infty \tag{2.15}
\]

where \(\alpha\) is the distribution parameter i.e. spreading factor for a particular re-orientation process. For \(\alpha=0\) the above expression is equivalent to equation 2.8, considering that \(\omega \tau = 1\) or \(f/f_r = 1\). Separating in to real and imaginary components we get the following expressions.

\[
\varepsilon'(\omega, T) = \varepsilon_\infty + \Delta \varepsilon_i(T) \frac{1 + \left(\frac{f}{f_r}\right)^{1-\alpha} \sin \left(\frac{\alpha \pi}{2}\right)}{1 + 2 \left(\frac{f}{f_r}\right)^{1-\alpha} \sin \left(\frac{\alpha \pi}{2}\right) + \left(\frac{f}{f_r}\right)^{2(1-\alpha)}} \tag{2.16}
\]

\[
\varepsilon''(\omega, T) = \Delta \varepsilon_i(T) \frac{\left(\frac{f}{f_r}\right)^{1-\alpha} \cos \left(\frac{\alpha \pi}{2}\right)}{1 + 2 \left(\frac{f}{f_r}\right)^{1-\alpha} \sin \left(\frac{\alpha \pi}{2}\right) + \left(\frac{f}{f_r}\right)^{2(1-\alpha)}} \tag{2.17}
\]

The above equations can also be written as

\[
\varepsilon' - \varepsilon_\infty = \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \left[1 - \frac{\sinh(1-\alpha) \ln \omega \tau_0}{\cosh(1-\alpha) \ln \omega \tau_0 + \sin \frac{1}{2} \pi \alpha}\right] \tag{2.18}
\]

\[
\varepsilon'' = \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \left[\frac{\cosh \frac{1}{2} \pi \alpha_0}{\cosh[(1-\alpha) \ln \omega \tau_0] + \sin \frac{1}{2} \pi \alpha}\right] \tag{2.19}
\]

When \(\alpha=0\), the Cole-Cole equation reduces to the previous Debye expression, but for non-zero values of \(\alpha\) we get distribution of relaxation time, which in the dispersion plot gives less distinct peak and in the absorption plot results in the broader and flatter peak as shown in the Fig 2.3. The value of \(\alpha\) can vary from zero to one.
By eliminating the frequency in the Debye equation one gets the equation of the circle. This is the basis for a very illustrative way of presenting the experimental permittivity data. The parameter $\alpha$ is purely empirical and there is no microscopic theory for it. Imagining certain dipole being in a liquid crystal containing only single molecular species, it will exhibit a pure Debye type behaviour. Very often, however we are investigating the multi-component behaviour, in which each particular dipole would not have a unique environment. This would lead to smear out of the relaxation process and $\alpha$ is not equal to zero. In polymers the environment is even much more complex and varying, resulting in very large value of $\alpha$ (up to 0.9).

### 2.1.4 Cole-Cole Plots

By eliminating the frequency from the equation (2.13) and (2.14) we get

![Cole-Cole Plot](image)
\[(\varepsilon' - \left(\varepsilon_\infty + \frac{\Delta \varepsilon}{2}\right))^2 + \left(\varepsilon''\right)^2 = \left(\frac{\Delta \varepsilon}{2}\right)^2\]  \hspace{1cm} (2.20)

This is an equation of the circle centered around the point \(\varepsilon' = \varepsilon_\infty + \Delta \varepsilon/2, \varepsilon'' = 0\), and a Debye type process should therefore produce a semicircle if \(\varepsilon''\) is plotted against \(\varepsilon'\), Fig. 2.4(a). This type of plot is known as Cole-Cole plot. Much qualitative information can be gathered from this type of representation of data. Since maximum absorption occurs at relaxation frequency, the top of the semicircle corresponds to this frequency.

However, as discussed earlier, real polarization mechanisms are often characterized by a distribution of relaxation time, and in order to cope this behaviour, Cole and Cole proposed equation (2.13). If we eliminate frequency from equations (2.14) and (2.15), again the equation of circle is obtained, but with some important difference in relation to Debye case.

\[
\left[\varepsilon - \left(\varepsilon_\infty + \frac{\Delta \varepsilon}{2}\right)\right]^2 + \left(\varepsilon'' + \frac{\Delta \varepsilon}{2} \tan\left(\frac{\alpha \pi}{2}\right)\right)^2 = \left(\frac{\Delta \varepsilon}{2 \cos\left(\frac{\alpha \pi}{2}\right)}\right)^2
\]  \hspace{1cm} (2.21)

The radius of the circle has now grown by a factor \(1/\cos(\alpha \pi/2)\), and the center has moved to \(\Delta \varepsilon \tan(\alpha \pi/2)\) below the \(\varepsilon'\) axis. So the permittivity data from a distributed mode will produce an arch with an opening angle less than \(180^0\), as shown in the Fig 2.4(b). If we can locate the center of the circle, or measure the radius of it, we can determine the value of\(\alpha\). Debye type and Non Debye relaxations are best visualized by Cole-Cole plot as shown in Fig 2.4(a, b) respectively.

When plotting the real experimental data one often encounter the problem of partially overlapping modes. The shape of Cole-Cole plot changes as shown in the Fig. 2.5 for the cases where relaxation frequencies of the modes can’t be determined easily (Jan P.F. Lagerwall 2000).
2.2 Dielectric Relaxations in Low Molar Mass Liquid Crystals

As discussed earlier in section 2.1, any fluid with polar molecules will show orientational polarization. So, liquid crystals are also expected to show orientational polarization. Both collective and non-collective relaxations are expected in these materials. The first kind involves the coherent motion of a large number of molecules, while the second is related to non-correlated motion. An easily observable change in the two fluctuation types is that, the collective processes being related to a macroscopic configurational change will lead to change in the optical properties of the sample while non-collective will not.
2.2.1 Collective Polarization Mechanism in Chiral Smectic Phases


In SmC* phase, the chirality of molecules break the mirror symmetry with respect to the plane of tilt and normal to the smectic layers. Therefore, a transverse spontaneous polarization is induced locally, which is perpendicular to tilt direction and is normal to the layers. The molecules within one layer are tilted uniformly but the direction of tilt precesses helicoidally as one goes from one smectic layer to another. Together with the tilt, the transverse electric polarization forms a helicoidal structure (SmC* phase). The macroscopic polarization of such a helicoidal structure is equal to zero, but the systems are nevertheless called ferroelectrics because of the existence of a local spontaneous polarization and because of their characteristic behaviour in electric fields (O. Hudak 1983, Brigita Urbanc et al. 1989, A. Levstik et al. 1987, C. Fillipic et al. 1988, T. Carlsson et al. 1990).

Blinc and Zeks studied the dielectric mechanisms in SmA* and SmC* phase theoretically, with the focus on the fluctuation to be expected in these systems. They studied XY model of polarization and tilt without a fixed relation between them. They concluded that in equilibrium configuration polarization ($P_S$) is perpendicular to tilt ($\xi$).

Application of electric field of magnitude $E$, parallel to the smectic layers, disturbs the helix in such a way that an average macroscopic polarization $<P_T>$ is induced. It also influences the molecular tilt. So, the dielectric relaxation in these systems is due
to the disturbance of order parameters by the electric field. This disturbance can be divided into two parts.

- Amplitude changes (change in the magnitude of tilt $\theta_0$ and polarization $P_0$)
- Phase changes (changes in the direction of tilt and the polarization)

Hence, dielectric response of the system will consist of four different active type of fluctuations (apart from the high frequency electronic response): one amplitude (amplitudon mode) and one orientational (phason mode) connected to each order parameter, $\xi$ and $P$. The two connected to the fluctuation of polarization order parameter have relaxation frequency of the order of 500Hz. The other two are connected to relaxation of the director fluctuation and are of low frequency (Y. Kimura et al. 1993, Y. P. Panarin et al. 1994, J. Zubia et al. 1991, S. Markscheffel et al. 1996, A.M. Biradar et al. 1996).

In the SmA* phase, the phason are degenerate with amplitudon (instead of amplitude fluctuation along $\hat{r}=\sqrt{\hat{x}^2+\hat{y}^2}$, and orientational fluctuations along $\hat{\phi}$, we have amplitude fluctuation along x-axis and y-axis). It is due to the homogeneous arrangement of the molecules in the layers. So here we should only be able to observe two modes. As all modes are related to the polarization, they should be observed with measuring field applied along the smectic layers i.e. in planar geometry.

Denoting the amplitude changes by $\delta \theta_1$ and $\delta P_1$ and the phase changes by $\delta \theta_2$ and $\delta P_2$ [Fig. 2.6(a,b,c)], we can express order parameter as (Brigita Urbanc et al. 1989, A. Levstik et al. 1987, C. Fillipic et al. 1988, T. Carlsson et al. 1990).

$$\begin{align*}
\xi_1(t) &= \theta_0 \cos(qZ) + \delta \theta_1(t) \cos(qZ) - \delta \theta_2(t) \sin(qZ) \\
\xi_2(t) &= \theta_0 \cos(qZ) + \delta \theta_1(t) \sin(qZ) - \delta \theta_2(t) \cos(qZ) \\
P_X(t) &= -P_0 \sin(qZ) + \delta P_1(t) \sin(qZ) - \delta P_2(t) \cos(qZ) \\
P_Y(t) &= -P_0 \cos(qZ) + \delta P_1(t) \cos(qZ) - \delta P_2(t) \sin(qZ)
\end{align*}$$

Linear combinations of the amplitude change of the order parameter are denoted as the soft mode (SM) and linear combination of the phase change of the order parameter are denoted as the Goldstone mode (GM). The modes due to director...
reorientation are commonly denoted by the SM and the GM whereas the modes connected with polarization reorientation are known as the polarization soft mode “PSM”, and the polarization Goldstone mode “PGM”. So in general, we can say that the soft mode can be identified as the response connected to the amplitude changes and Goldstone mode connected with the phase change of order parameter.

The nature of polarization modes is rather puzzling, and was first described by Carlsson et. al. They described that these two modes appear due to the molecular rotation around long axis of the molecule. They also stated that the total dielectric permittivity is equal to the sum of permittivities due to the director fluctuations, polarization fluctuations and electronic contribution. They did not consider the non-collective excitations. This, together with high absorption frequencies predicted for the polarization modes, give impression that these are actually equivalent to the non-collective mechanism.

For each mode at a given temperature, contribution to the dielectric constant decreases with increasing frequency of the field from the low frequency value ($f<\langle f_{r}\rangle$) to zero. This value is adopted when the value of the applied electric field frequency is so high ($f>>\langle f_{r}\rangle$) that the molecular motion cannot follow the electric field, where $f_{r}$ is the characteristic relaxation frequency of that mode. The difference between the low and high frequency contributions of the mode to the total dielectric constant gives the dielectric strength of the mode. The dielectric strength is related to the average induced polarization as (B. Zeks et al. Preprint)

$$\varepsilon_{0}\Delta\varepsilon(T) = \lim_{E \to 0} \frac{P}{E}$$

where E is the magnitude of a static applied electric field. Here it has been assumed that the field acts in the X-direction. On the other hand, there exists a quadratic field effect, which originates in the dielectric anisotropy of molecules. The dielectric anisotropy is defined as

$$\delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$$

This describes the tendency of electric field to align the molecules with their axis of the largest dielectric susceptibility in the direction of field. Several relaxation mechanisms, each of which is connected to a characteristic relaxation frequency contributes to complex dielectric constant $\varepsilon^*(\omega,T)$, as given by (Jan P.F. Lagerwall...
Where $\omega = 2\pi f$ is the angular frequency of applied field and $T$ is the temperature of the system. $\varepsilon'(\omega,T)$ is the real part and $\varepsilon''(\omega,T)$ is the imaginary part of the dielectric constant respectively.

Fig. 2.6: Variation of amplitude and phase of the polarization and tilt order parameters.

**Fig. 2.6:** Variation of amplitude and phase of the polarization and tilt order parameters.
i) Distribution of Relaxation Times in Chiral Smectic phase


\[
\varepsilon^*_{\perp}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_{GM}}{1 + (i\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\Delta\varepsilon_{SM}}{1 + (i\omega\tau_{SM})^{1-\alpha_{SM}}} + \frac{\Delta\varepsilon_{PGM}}{1 + (i\omega\tau_{PGM})^{1-\alpha_{PGM}}} + \frac{\Delta\varepsilon_{PSM}}{1 + (i\omega\tau_{PSM})^{1-\alpha_{PSM}}}
\]  

(2.26)

Here the second term is connected with \( GM \), third with the \( SM \), fourth and fifth term is connected with the molecular reorientation around their long and short molecular axes defined as the polarization modes due to the \( PGM \) and the \( PSM \).

In the SmA phase, \( \theta_0 = P_0 = 0 \), so that only amplitude changes occur. The system thus exhibits a double degenerated soft director mode and a double degenerated high-frequency polarization mode. The complex dielectric constant in this case is written as

\[
\varepsilon^*_{\perp}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_{SM}(T)}{1 + (i\omega\tau_{SM})^{1-\alpha_{SM}}} + \frac{\Delta\varepsilon_{PSA}(T)}{1 + (i\omega\tau_{PSA})^{1-\alpha_{PSA}}}
\]  

(2.27)

However, the valid expression for frequencies up to approximately 50 MHz is

\[
\varepsilon^*_{\perp}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_{GM}(T)}{1 + (i\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\Delta\varepsilon_{SM}(T)}{1 + (i\omega\tau_{SM})^{1-\alpha_{SM}}}
\]  

(2.28)

The \( SM \) contribution shows up practically in the vicinity of SmC*-SmA transition \( (T_{C*A}) \). On approaching the transition, the elastic constant that constitutes the restoring force against the tilt fluctuations weakens or softens. These tilt fluctuations constitutes a soft mode which grows in strength as the transition is approached. Not only this softening of the elastic constant results in the increasing strength of the mode but also in the rapidly diminishing value of relaxation frequency.

Accordingly, we can say that soft mode on approaching \( T_{C*A} \) is characterized by (Tomoko Sekine et al. Preprint).
The softening of this elastic constant means that the phase will lose its stability gradually until it becomes unstable and the molecules fluctuate collectively [Fig. 2.7].

1. When a weak electric field is applied in a direction perpendicular to the director, in the SmC* phase, it can easily perturb the tilt fluctuation depending on how close the system is to $T_{C^*A}$. The mechanism is usually observed in the kHz range with strong temperature dependence. In other words, the molecules collectively oscillate around the smectic cone. This mode is called $GM$ [Fig. 2.7]. This process has a characteristic frequency, which varies in the range of a few kHz with weak temperature dependence. These modes are thermally activated and can be measured in the planar orientation (Y. Kimura et al. 1993).

\[ \varepsilon = \varepsilon_0 \rightarrow \infty \text{ and } \omega \rightarrow 0 \] (2.29)

By splitting Eq. (2.27) into its real and imaginary parts we obtain

\[ \varepsilon^\prime_1 (\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{0SM} - \varepsilon_{\infty}}{2} \left[ 1 - \frac{\sinh A}{\cosh A + \sin(\pi \alpha_{SM} / 2)} \right] + \frac{\varepsilon_{0GM} - \varepsilon_{0SM}}{2} \left[ 1 - \frac{\sinh B}{\cosh B + \sin(\pi \alpha_{GM} / 2)} \right] \] (2.30)

\[ \varepsilon^* (\omega) = \frac{\varepsilon_{0SM} - \varepsilon_{\infty}}{2} \left[ \frac{\cos(\pi \alpha_{SM} / 2)}{\cosh A + \sin(\pi \alpha_{SM} / 2)} \right] + \frac{\varepsilon_{0GM} - \varepsilon_{0SM}}{2} \left[ \frac{\cos(\pi \alpha_{GM} / 2)}{\cosh B + \sin(\pi \alpha_{GM} / 2)} \right] \] (2.31)

Fig. 2.7:- Geometry for the maximum a) Goldstone mode contribution b) Maximum Soft mode contribution
It was assumed that the molecular term (i.e. the polarization modes and electronic mode) is included in $\varepsilon_{\infty}$, when our measurements are limited to $1\text{MHz}$ range only.

**ii) Temperature and Frequency Dependence of Dielectric Permittivity**

**a) Generalized Landau Model**

In order to obtain the proper temperature and wave vector dependence of the order parameter excitation modes, the generalized Landau model is used. The free energy density $g_0(z)$ is given by (Y. P. Panarin et al. 1994, J. Zubia et al. 1991)

\[
g_0(z) = \frac{1}{2} a(\xi_1^2 + \xi_2^2) + \frac{1}{4} b(\xi_1^2 + \xi_2^2) + \frac{1}{6} c(\xi_1^2 + \xi_2^2)^3 - \Lambda \left( \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz} \right) + \frac{1}{2} K \left[ \xi_1 \left( \frac{d\xi_1}{dz} \right)^2 + \xi_2 \left( \frac{d\xi_2}{dz} \right)^2 \right] + \frac{1}{2} \varepsilon (P_x^2 + P_y^2) - \mu \left( P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz} \right)
\]

\[+ C(P_x \xi_2 - P_y \xi_1) - \frac{1}{2} \Omega (P_x \xi_2 - P_y \xi_1)^2 + \frac{1}{4} \eta (P_x^2 + P_y^2)^2 - d(\xi_1^2 + \xi_2^2) \left( \xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz} \right) \]

(2.33)

Where the only coefficient ‘a’ is assumed to be temperature dependent: $a = \alpha(T - T_{C_A})$, $\alpha > 0$. Thus ‘a’ is positive for $T > T_{C_A}$. $K$ is the elastic modulus. $\Lambda$ is the coefficient of Lifshitz term responsible for the modulation, and $\mu$ and $c$ are the coefficient of the flexo- and piezoelectric bilinear coupling term inducing transverse quadrupole ordering and the $\eta$ term has been added to stabilize the system. The ‘d’ term describes the monotonous increase of the pitch with temperature at low temperature. The sixth order term in tilt (the C term) has been added to account for the specific heat temperature dependence of the system (R.B. Meyer et al. 1975).

From Eq. (2.21) and Eq. (2.33) one can derive equations governing the tilt, polarization, and pitch of the system:

\[
\tilde{a} \theta_0 + \tilde{b} \theta_0^3 + \tilde{c} \theta_0^5 - \Omega \theta_0 P_0^2 - \left( C + \frac{3 \varepsilon d}{K} \theta_0^2 \right) P_0 = 0, \quad (2.34)
\]
\[ \eta p_0^3 + \left( \frac{1}{\epsilon} - \Omega \theta_0^2 \right) p_0 - \left( \frac{\tilde{C} + \frac{\mu d}{K} \theta_0^2}{\theta_0} \right) \theta_0 = 0 \quad (2.35) \]

\[ q = \frac{1}{K} \left( \Lambda + \mu \frac{p_0}{\theta_0} + d \theta_0^2 \right) \quad (2.36) \]

Where \( \tilde{a}, \tilde{b}, \tilde{c}, \tilde{e} \) and \( \tilde{C} \) are renormalized constants:

\[ \tilde{a} = a - \frac{\Lambda^2}{K}, \quad \tilde{b} = b - \frac{4 \Lambda d}{K}, \quad \tilde{c} = c - \frac{3 d^2}{K} \]

\[ \frac{1}{\epsilon} = \frac{1}{\epsilon} - \frac{\mu^2}{K}, \quad \tilde{C} = C + \frac{\Lambda \mu}{K} \quad (2.37) \]

The dynamic equations of the system in the presence of a homogeneous time-dependent field \( E = E_0 e^{i \omega t} \) applied in the X-direction can be formulated as a set of torque equations:

\[ \Gamma^{\text{elastic}} + \Gamma^{\text{viscous}} = 0 \quad (2.38) \]

Here, \( \Gamma^{\text{elastic}} \) is given by the Euler-Lagrange terms using Eq.(2.24), whereas

\[ \Gamma^{\text{viscous}} = -\gamma r \delta \theta_1 = -i \omega \gamma_r \delta \theta_{10} \sin(qZ) e^{i \omega t}, \] with \( \gamma \) being a viscosity coefficient.

The dynamic equations are

\[
\begin{align*}
(b_1 - i \omega \gamma_{SM}) \delta \theta_{10} + b_2 \delta \theta_{20} + b_3 \delta \varphi_{10} + b_4 \delta \varphi_{20} &= 0 \\
b_2 \delta \theta_{10} + (b_3 - i \omega \gamma_{GM}) \delta \theta_{20} + b_4 \delta \varphi_{10} + b_6 \delta \varphi_{20} &= 0 \\
b_3 \delta \theta_{10} + b_4 \delta \theta_{20} - (b_5 + i \omega \gamma_{PSM}) \delta \varphi_{10} &= E_0 \\
b_4 \delta \theta_{10} + b_6 \delta \theta_{20} - (b_7 + i \omega \gamma_{PGM}) \delta \varphi_{20} &= E_0
\end{align*}
\] (2.39)

The constants \( b_i \) are here defined as
Four different viscosities in the dynamic equations have been introduced. Two of these, $\gamma_{GM}$ and $\gamma_{SM}$, are the ordinary rotational viscosities connected to director reorientations. The way $\gamma_{GM}$ and $\gamma_{SM}$ have been introduced in these equations, $\gamma_{GM} \approx \gamma_{SM}$ can be expected while approaching $T_{C^*A}$. The two viscosities $\gamma_{PGM}$ and $\gamma_{PSM}$ connected to the polarization modes are related to the rotation of the molecules around their long axis. The relaxation frequencies of the four eigen modes fall into two groups ($f_{SM}$, $f_{GM} \ll f_{PSM}$, $f_{PGM}$) allowing to simplify Eq. (2.39).

**Relaxation Modes in SmC* Phase**

**The Polarization Modes**

When solving the dynamic equations, the fact is used that the eigen frequencies of director modes are well separated from those of the polarization modes. Thus when studying the polarization modes, we deal with frequencies which are so high that the director can no longer follow the electric field and $\delta\theta_{10}$ and $\delta\theta_{20}$ can go to zero. The high frequency response of $\delta P_{10}$ and $\delta P_{20}$ is then given by the two last dynamic Eqs. (2.39). The dielectric strengths and the eigen frequencies of the polarization modes are now obtained as (C. Fillipic et al. 1988, T. Carlsson et al. 1990)

$$
\varepsilon_a \Delta \varepsilon_{PSM} = \frac{1}{2(1/\varepsilon - \Omega \theta_0^2 + 3\eta P_o^2)} , \quad \varepsilon_a \Delta \varepsilon_{PGM} = \frac{1}{2(1/\varepsilon + \eta P_o^2)} ,
$$

$$
f_{PSM} = \frac{1}{\gamma_{PGM}} \left( \frac{1}{\varepsilon} - \Omega \theta_0^2 + 3\eta P_o^2 \right) , \quad f_{PGM} = \frac{1}{\gamma_{PGM}} \left( \frac{1}{\varepsilon} + \eta P_o^2 \right) ,
$$

Eq.(2.41) and Eq.(2.42) imply a result concerning the product of the dielectric strengths and the eigen frequencies of the polarization modes:
\[ \varepsilon_a f_{rPSM} \Delta \varepsilon_{PSM} = \frac{1}{2\pi \gamma_{PSM}}, \quad \varepsilon_a f_{rPGM} \Delta \varepsilon_{PGM} = \frac{1}{2\pi \gamma_{PGM}} \]  

(2.43)

Thus, it is possible to determine \( \gamma_{PSM} \) and \( \gamma_{PGM} \) directly from a measurement of the high frequency dielectric constant of the system.

**The Director Modes**

The director modes are of much lower frequency than the polarization modes. The calculations are performed in the limit when the eigen frequencies of the polarization modes are assumed to be infinite. This means that the molecular rotation around the long axis is so fast that for each director configuration the polarization takes its corresponding equilibrium value infinitely fast. Mathematically, this can be expressed by setting \( \gamma_{PS} \) and \( \gamma_{PG} \) equal to zero in the dynamic equations. Thus, the last two dynamic equations can be written as:

\[
\delta \theta_{10} = \frac{1}{b_7} \left( -E_0 + b_3 \delta \theta_{10} + b_4 \delta \theta_{20} \right),
\]

(2.44)

\[
\delta \theta_{20} = \frac{1}{b_8} \left( -E_0 + b_4 \delta \theta_{10} + b_6 \delta \theta_{20} \right),
\]

(2.45)

Substituting these two expressions into the first two dynamic equations [Eq 2.39], we obtain

\[
(X + i \omega \gamma_{SM}) \delta \theta_{10} + qZ \delta \theta_{20} = -E_0 \left( \frac{b_1}{b_7} + \frac{b_4}{b_8} \right),
\]

(2.46)

\[
qZ \delta \theta_{10} + (Y + i \omega \gamma_{GM}) \delta \theta_{20} = -E_0 \left( \frac{b_4}{b_7} + \frac{b_6}{b_8} \right),
\]

(2.47)

Where the quantities \( X, Y \) and \( Z \) have been introduced:

\[
X = -b_1 - \frac{b_1^2}{b_8} - \frac{b_1^2}{b_7},
\]

(2.48)

\[
Y = -b_5 - \frac{b_4^2}{b_7} - \frac{b_5^2}{b_8} = q^2 \left( K - \frac{\mu^2}{1/\varepsilon - \Omega \theta_0^2 + 3\eta P_0^2} \right) \equiv q^2 K,
\]

(2.49)

\[
qZ = -b_1 \left( \frac{b_2}{b_4} + \frac{b_3}{b_7} + \frac{b_5}{b_8} \right)
\]

(2.50)
Taking \( K \approx 5 \times 10^{12} \text{N}, 2\pi/q \sim 2\mu\text{m}, \) and \( \alpha = 5 \times 10^4 \text{N/m}^2 \text{K}, \) it is seen that \( X \) is much larger than both \( Y \) and \( qZ, \) except in a narrow interval \( \Delta T = 0.01 \text{K} \) just below \( T_{C^A}. \)

When diagonalizing the above two dynamic equations [Eq.(2.46) and Eq.(2.47)] to obtain the eigen modes of the system, we get

\[
(X + i\omega \gamma_{SM})(Y + i\omega \gamma_{GM}) - q^2Z^2 = 0. \tag{2.51}
\]

Excluding the small temperature interval \( \Delta T \) estimated above, the term \( q^2Z^2 \) in this equation \( (T_{C^A} - T \gg \Delta T \Rightarrow q^2Z^2 \ll XY) \) can be neglected. The solution is then given by setting each of the two parentheses equal to zero. The eigen frequencies of the \( SM \) and the \( GM \) are then obtained by identifying \( X + i\omega \gamma_{SM} = X(1 + i\omega \gamma_{SM} / X) = X(1 + i\omega \gamma_{SM}), \) and so on.

Corresponding eigen frequencies \( f_i = 1/2\pi\tau_i, \) are

\[
\gamma_{GM} = \frac{1}{4\pi e_a} \frac{P^2}{\theta^2(\Delta\varepsilon_{GM} f_{GM})} \tag{2.52}
\]

\[K = \frac{1}{2\varepsilon_a \Delta\varepsilon_{GM}} \left( \frac{P}{\varepsilon \theta} \right)^2 \tag{2.53}
\]


\textbf{Relaxation Modes in SmA Phase}

In this phase, only amplitude fluctuations are present. Using a parallel procedure as in the SmC* phase, we get

\[
f_{PA} = \frac{1}{2\pi e \gamma_{PA}}, \tag{2.54}
\]

\[\varepsilon_a \Delta\varepsilon_{PA} = \varepsilon, \tag{2.55}
\]
It has been reported that the $SM$ dielectric spectrum in the SmA phase is almost a single Debye-type process. However, the distribution parameter is not zero in the SmA phase. This might be due to some anisotropy of the tilt fluctuations in the pretransitional region or overlapping of the $SM$ spectrum with some molecular relaxation processes.

The SmA phase $SM$ dielectric strength and relaxation frequency are given by the relation

$$f_{rSA} = \frac{1}{2\pi\gamma_{SA}} \left[ \alpha(T - T_{C^{*A}}) + \left(K_3 - \varepsilon\mu^2\right)q_0^2 \right]$$

and

$$\varepsilon_a \Delta \varepsilon_{SA} = \frac{\varepsilon^2 C^2}{\alpha(T - T_{C^{*A}}) + \left(K_3 - \varepsilon\mu^2\right)q_0^2}.$$  

From the above equations the expressions for the products of the relaxation frequencies with the corresponding dielectric strengths of the two modes are:

$$\varepsilon_a f_{rSA} \Delta \varepsilon_{SA} = \frac{\varepsilon^2 C^2}{2\pi\gamma_{SA}},$$

$$f_{rPA} \Delta \varepsilon_{PA} = \frac{1}{2\pi\gamma_{PA}}.$$  

The theory worked out by Blinc and Zeks [9] predicts Curie-Weiss behaviour of the $SM$ dielectric parameters in the pretransitional region. The inverse of $SM$ dielectric increment $[\Delta \varepsilon_{SM}]^{-1}$ i.e. $\Delta \varepsilon_{SM}^{-1}$ and relaxation frequency $f_{rSA}$ should decrease linearly with temperature upon approaching the $T_{C^{*A}}$ on both sides. Accordingly, slope of $\Delta \varepsilon_{SM}^{-1}$ below $T_{C^{*A}}$ is greater by a factor of about $-2$ than the slope above $T_{C^{*A}}$. This relation is also valid for the relaxation frequency as a function of temperature. However, both $\Delta \varepsilon_{GM}^{-1}$ and $f_{GM}$ are temperature independent in the SmC* phase (C. Fillipic et al. 1988, T. Carlsson et al. 1990).

The dielectric strength of the sample using Curie-Weiss law is given by

$$\Delta \varepsilon_{SM}^{-1} = a' (T - T_{C^{*A}}) + b'$$

Where $a'$ and $b'$ are the constants.

**Domain Mode in SmC* Phase**
The new periodical structure (ferroelectric domains) in the planarly oriented FLCs with high spontaneous polarization \( P_s \geq 50 \text{nC/cm}^2 \) has been found (Leonid Beresnev et al. 1992, S. Hiller et al. Preprint). This mode, introduced by the Darmstadt group, corresponds to cross layer phase angle fluctuations in the absence of a helix, which may be observed in the SmC* phase with a higher value of spontaneous polarization. Detailed electro-optical and dielectric investigations of these systems were made and the model of novel organization of smectic layers in FLCs with high \( P_s \) was proposed. The conditions under which it appears are not very clear, but it seems to exist in the presence of the bias field where the helix remains unwind but the phase angle is not completely uniform throughout the sample, as shown in Fig. 2.8 (S. Markscheffel et al. 1996). Researchers have explained that the new periodical structure appears when dc bias is applied on the GM. It suppresses the GM and at a certain bias (higher than the critical field), a new modulated structure gives rise to a domain mode “DM”.

The field dependence of the inverse SM dielectric strength (\( \Delta \varepsilon_{\text{SM}} \)) close to the phase transition temperature (SmC*-SmA) is given by

\[
\frac{1}{\Delta \varepsilon_{\text{SM}}} = \frac{q}{4\varepsilon_a^2 \varepsilon_\infty^2 C^2} \left\{ \frac{1}{b^3} \left[ \varepsilon_a \varepsilon_\infty \right]^{2/3} \right\} E^{2/3}
\]  

(2.61)

![Diagram](image)

**Fig. 2.8:** The formation of domains in the Liquid crystals sample

Relaxation frequency varies with the same extent and is given by

\[
f_{\text{rSM}} = 3b^{1/2} \left[ \frac{\varepsilon_a \varepsilon_\infty C}{2\pi \gamma_{\text{SM}}} \right]^{2/3} E^{2/3}
\]

(2.62)
It has been explained that after the suppression of \( GM \), the \( DM \) can be observed. It is also explained that the weaker bulk domain mode is covered in the low frequency part of the absorbed peak of the surface domain mode.

### 2.2.2 Non-Collective Polarization Mechanism

The existence of collective dynamics is a consequence of ordering and hence collective fluctuations are unique to crystalline and liquid crystalline phases. In spite of long range nematic order no collective mechanism of this phase can be excited by dielectric spectroscopy due to the quadrupolar character of the nematic order. The same is valid for the materials possessing non-chiral smectic phases, which show only non-collective relaxations.

The direction of molecular dipole moment depends upon the chemical structure of the compound, and in general it may have component both parallel and perpendicular to the long axis of the molecules as shown in the Fig. 2.9 (Jan P.F. Lagerwall 2000).

In dielectric spectroscopy experiment, we apply a measuring field perpendicular to the plane of the cell i.e. perpendicular or parallel to the director depending upon whether the cell is homogenously or homeotropically aligned. So, only the dipole in the direction of the field will interact with it and give a contribution to the dielectric permittivity. Since the re-orientational order is never perfect, both longitudinal and transverse dipole moment will in principle have a projection both along and perpendicular to the director but one component usually dominates heavily. In homeotropic alignment, the field couples mainly to the longitudinal dipole moment and field induced fluctuation bias is therefore equivalent to the reorientation around the short molecular axis as shown in Fig. 2.10.
If in the relaxed state half of the molecules are oriented up and half are oriented down, an orientational polarization must effectively mean that the field flip the molecules. Such flips are much hindered and we expect the absorption frequency for this process to be substantially lower than in the isotropic phase. In planar on other hand the similar reasoning leads to the conclusion that the relative non-collective mechanism will be the re-orientation around the long axis.
i) Dielectric Relaxation in the Materials Possessing Glass Transition Temperature

Polymers are generally characterized by the presence of various dipolar units in different environments. This leads to a broad distribution of relaxation times. The corresponding loss peaks are usually extended over several frequency decades.

Starting isothermally at low frequencies generally the $\alpha$ relaxation is found which accompanies the glass transition in the amorphous part of the material, that marks the onset of segmental movements of the polymer chains (O. Ahumada et al. 1996, Aranzazu del Campo et al. 2002, A. Hohmuth et al. 1986, I. Alig et al. 1995). The loss peak of the $\alpha$ relaxation has an asymmetric shape. Its temperature dependence obeys the Vogel-Fulcher-Tammann law (VFT law), which can be derived from the theory of the glass transition:

$$
\tau(T) = \tau_o \exp \frac{T_a}{T - T_V}
$$

(2.63)

where $\tau_o$ and the activation temperature $T_a$ are fit parameters and $T_V$ is the Vogel temperature that is related to the dynamic glass-transition temperature. The asymmetric shape and the VFT behaviour are typical features of a co-operative process. Generally, the $\alpha$ relaxation has the highest strength, therefore it is often called the primary or main relaxation. At higher frequencies, the $\beta$-relaxation is present which involves local intra-molecular movements. It is sometimes followed by the $\gamma$-relaxation of even smaller molecular units. Consequently, they are called secondary relaxations. Finally, $\delta$ relaxation due to isolated molecules of impurities can be present at the high-frequency end of the spectrum. The loss peaks of these processes are symmetric and they show Arrhenius temperature dependence. These are typical features of a non-cooperative process.

Dielectric spectroscopy can only determine the relaxation parameters of these processes. A relation to movements of certain molecular species has to be found with the help of detailed knowledge about the chemical synthesis and by additional non-dielectric investigations. As an example, for partially crystalline polymers separate $\alpha$ and so-called $\alpha_c$ relaxations have to be distinguished, the later originating from polymer chains in amorphous regions, which are partly immobilized by pinning on crystals. On the low-frequency end of the spectrum, frequently a charge carrier relaxation appears particularly in the presence of ionic impurities. It has been
already pointed out that the movement of charged particles between boundaries (electrodes or phase boundaries) is very efficient because it generates a large effective dipole moment due to larger charge displacements than in case of rotating dipoles and huge losses due to strong internal friction. It can obscure the dipolar processes and it is not typical for a special polymer. Therefore, it should be avoided by carefully purifying the substance and carefully preparing the electrical contacts. The charge carrier relaxations exhibit an Arrhenius temperature dependence because they are closely related to the exponential temperature dependence of the conductivity. All glass forming materials show the $\alpha$–$\beta$ bifurcation; above a crossover temperature $T^*$, the glass $\alpha$ transition and the $\beta$ transition merge together. Below this temperature, the relaxation times $\tau$ and $\tau_\beta$ of the cooperative ($\alpha$) and non-cooperative ($\beta$) movements confirm Vogel-Fulcher-Tammann and Arrhenius laws respectively.

### ii) Distribution of Relaxation Time in Glass Forming Materials

Amorphous polymers and supercooled liquids near the glass transition temperature exhibit strongly non-exponential response and relaxation functions in various experiments. Dielectric spectroscopy experiments show an asymmetrically broadened relaxation peak, often called the $\alpha$-relaxation peak that flattens into an excess wing at high frequencies. Most theoretical and experimental works use a small number of empirical expressions such as the Cole–Davidson, Havriliak–Negami or Kohlrausch–Williams–Watts formulae for fitting of the asymmetric $\alpha$-relaxation peak. All of these phenomenological fitting formulae are obtained by the method of introducing a fractional ‘stretching’ exponent into the standard Debye relaxation in the time or frequency domain. In the frequency domain the relaxation is described in terms of a normalized complex susceptibility

$$
\chi(u) = \frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty}
$$

(2.64)

where $u = -i\omega$, $\omega$ is the angular frequency, $\chi(\omega)$ is a dynamic susceptibility normalized by the corresponding isothermal susceptibility, $\chi_0 = \lim\omega\to0 \text{Re } \chi(u)$ is the static susceptibility, and $\chi_\infty = \lim\omega\to\infty \text{Re } \chi(u)$ gives the ‘instantaneous’ response. For dielectric relaxation experiments $\chi$ is just the complex frequency-dependent dielectric susceptibility (often denoted by $\varepsilon$), and the more general notation $\chi$ is used
as a reminder that the same expressions apply for other relaxation experiments, such as for mechanical relaxation.

Dielectric loss spectra very often show a marked excess contribution at frequencies few decades above the peak frequency of the \( \alpha \)-relaxation. The three-parameter formula for a two-step Debye relaxations:

\[
\hat{X}(u) = \frac{1 + u \tau_1 (1 - C)}{(1 + u \tau_1)(1 + u \tau_2)}
\]

where \( 0 < \tau_1 < \tau_2 < \infty \) are the two relaxation times and \( C \) is a parameter that fixes the relative dielectric strength of the two relaxation processes. Of course, this formula is equivalent to the popular relaxation time distribution model

\[
\hat{X}(u) = \int_0^\infty \rho(\tau) \frac{d\tau}{(1 + u \tau)}
\]

with a sum of two \( \delta \)-distributions for the probability density function of relaxation times \( 0 < \tau_1 < \tau_2 < \infty \)

\[
\rho(\tau) = \left(1 - \frac{C}{\tau_1/\tau_2} - 1 - \left(\frac{\tau_1}{\tau_2}\right)\right)\delta(\tau - \tau_2) + \left(\frac{C}{1 - \left(\frac{\tau_1}{\tau_2}\right)}\right)\delta(\tau - \tau_2)
\]

Relaxation time distributions with more parameters will give better fits at the expense of introducing more parameters, but here consideration will be restricted to fit functions with two or three parameters. Davidson and Cole discussed the two-parameter expression

\[
\hat{X}(u) = \frac{1}{(1 + u \tau_\gamma)^\gamma} \quad 0 < \gamma \leq 1
\]

for the normalized susceptibility containing a single stretching exponent \( 0 < \gamma \leq 1 \) and single relaxation time constant \( 0 < \tau_\gamma < \infty \)

Another popular three-parameter fitting formula for the frequency-dependent susceptibility was discussed by Havriliak and Negami:

\[
\hat{X}(u) = \frac{1}{(1 + (u \tau_\mu)^\alpha)^\gamma}
\]

with two stretching exponents \( 0 < \alpha : \gamma \leq 1 \) and one relaxation time \( 0 < \tau_\mu < \infty \).

Much of the work on dielectric relaxation utilize also the earlier Cole–Cole formula (obtained by setting \( \gamma = 1 \) in equation (8)). Consequently this yields a symmetrically broadened peak in contrast with most experimental observations on \( \alpha \)-peaks. All of
the fitting formulae above were defined in the frequency domain. They can be transformed into the time domain using equation (3). A widely used fitting formula in the time domain, on the other hand, is the stretched-exponential relaxation function

\[ f(t) = \exp\left[-\left(t/\tau_\beta\right)^\beta\right] \quad 0 < \beta \leq 1 \]  

(2.70)

with exponent \(0 < \beta \leq 1\) and time constant \(\tau_\beta\). The stretched-exponential relaxation function can be transposed to the frequency domain using (3). One obtains for the susceptibility the little known result

\[ \hat{X}(u) = 1 - H_\beta\left(-(u\tau_\beta)^\beta\right) \]  

(2.71)

where \(H_\beta\) is defined by the series

\[ H_\beta(x) = \sum_{k=0}^{\infty} \frac{\Gamma(\beta k + 1)}{\Gamma(k + 1)} x^{-k} \]  

(2.72)

convergent for all \(0 < x < \infty\). This Kohlrausch susceptibility function was recently discussed in together with the time domain relaxation functions corresponding to the HN susceptibility and its special cases in terms of \(H\)-functions.

A simple three-parameter fit function that seems to work well not only for fitting to the asymmetric \(\alpha\)-peak, but also for the excess wing at high frequency has functional form (R Hilfer 2002)

\[ \hat{X}(u) = \frac{1 + (u\tau_\alpha)^\gamma}{1 + (u\tau_\alpha)^\gamma + u\tau_\alpha} \]  

(2.73)

containing a single stretching exponent \(0 < \gamma \leq 1\) and relaxation times \(0 < \tau_\alpha, \tau_\alpha < \infty\). This functional form was obtained from the theory of fractional dynamics (FD). Similarly to the CD or the Kohlrausch susceptibilities but in contrast to the Havriliak–Negami function as well as a combination of Cole–Davidson and Cole–Cole fits, the new function requires only a single stretching exponent and is a good fit to the relaxation behaviour of glass forming materials.

**B. Theory of Electro-Optic**

Electro-topic is the light modulation effect i.e. scattering and rotation of the plane of polarization. Liquid crystals are ideally suited for electro-optic devices. Ferroelectric liquid crystals possess microsecond switching response and bi-stability. These states can be readily switched with a time constant of few \(\mu\)s on application of external...
field which depends upon the polarization and viscosity of the materials. The switching time can also be described in terms of dielectric strength and relaxation frequency of the goldstone mode (GM).


\[
\gamma \phi \frac{d\phi}{dt} = K \phi^2 \phi_0^2 - P_s E(t) \sin(\phi)
\]

(2.74)

Where \( \phi \) is the azimuthal angle and \( \gamma \) is the rotational viscosity w. r. t. the rotations about smectic layer normal which defines z-direction. K is mean elastic constant, \( P_s \) is the magnitude of spontaneous polarization of smC* phase and E is the amplitude of applied electric field.

It has been confirmed by experiments that normal vector and tilt angle (\( \theta \)) between director and layer normal does not change on application of field parallel to the layers. However the direction of tilt changes resulting in the change of azimuthal angle (\( \phi \)).

This molecular reorientation can collectively takes place in the bulk and the entire macroscopic polarization \( P_s \) is then effective in driving force \( P_s E \). Where \( P_s \) is the spontaneous polarization and response time could be measured with the help of current reversal method.

\[
\tau = \frac{\gamma}{P_s E}
\]

(2.77)

This result was given by Clark and Lagerwall.