Chapter 2

SUPPRESSION OF DIRECTOR FLUCTUATIONS AS A NEW NONLINEARITY

A timeless knowledge it shall bring to Mind,

Its aim to life, to Ignorance to close.

Sri Aurobindo in Savitri, -p 258

2.1 Introduction

An integral part of the nonlinear optics of liquid crystals is to describe the underlying processes responsible for the nonlinear optical effects. Director reorientation and thermal indexing [1, 2, 3] have been identified as two of the nonlinear optical processes possible in these systems. Both these processes result in a nonlinear coefficient of the order of 10^{-2} which is six to eight orders of magnitude higher than that found in even a highly nonlinear material like CS_2. It is for this reason that these nonlinearities in liquid crystals are referred to as 'giant optical nonlinearities' in the literature.

Liquid crystals appear turbid due to the macroscopic thermal fluctuations in the nematic director. P. G. de Gennes first pointed out that an external static magnetic field can suppress these director fluctuations by exerting a torque on the director through the diamagnetic anisotropy [4]. We know that the electric field of the laser exerts a torque on the director through the dielectric anisotropy. It is therefore natural to expect the suppression of director fluctuations even in a suitably polarised laser field [2]. We point out here that laser induced suppression of the director fluctuations can lead to considerable optical nonlinearities in liquid crystals [5]. This nonlinearity is entirely different from that due to director reorientation and it also affects the orientational order parameter in liquid crystals. Its magnitude is not so large as that due to director reorientation but is still much larger than the classical optical Kerr nonlinearity found in crystals and liquids. Further, on its own it not only results in most of the familiar nonlinear effects like self-focusing but also leads to some new effects. To highlight this process we consider situations wherein the usual process of director reorientation is strictly absent.

It is well known that a majority of liquid crystals are transparent and they absorb only in the deep ultraviolet ($\lambda < 2500\dot{A}$). Hence, the light absorption is negligible in the visible part of the spectrum. Therefore we do not consider the laser absorption and its associated thermal effects in this chapter.

2.2 Laser Induced Suppression of Director Fluctuations

At a finite temperature, in a liquid crystal, there are always thermal fluctuations in the director. These thermal fluctuations can be reduced by lowering the temperature but this may often lead to the disappearance of the liquid crystalline phase. We can consider other means of suppressing the director fluctuations. It was pointed out long ago by de Gennes[4] that the director fluctuations in a nematic liquid crystal can be suppressed by a static magnetic field applied along the director. Expectedly, this enhances the dielectric anisotropy, the increase being proportional to the strength of the applied field. One of the consequences of the reduction in director fluctuation is that the orientational order parameter of the system increases. Due to an increase in this order parameter we find a decrease in light scattering from nematics. This prediction was experimentally verified later by Malraison et. al. [6]. A similar process also operates in cholesterics. In this case the enhancement in dielectric anisotropy

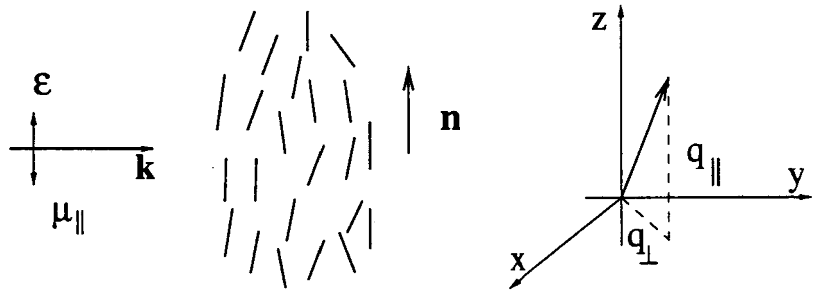

Figure 2.1: *The geometry for the suppression of the director fluctuations.*

implies an increase in the twist elastic constant. Hence, the cholesteric pitch increases. This was experimentally established by Belyaev et. al. [7]. These authors observed a *red shift* in the Bragg band of a cholesteric, with negative dielectric anisotropy, by the application of a static electric field along the twist axis. Naturally, suppression of director fluctuations can be expected even in the electric field of an intense laser beam. We first address ourselves to this effect in non-absorbing nematic and cholesteric liquid crystals.

2.2.1 Nematics

We consider an aligned nematic sample with the undisturbed director parallel to the z-axis i.e., $\mathbf{n}_\circ = (0,\ 0,\ \mathbf{1})$ as shown in the figure 2.1.

Following de Gennes it is easy to work out the director fluctuations, of a wavevector **q**, in a linearly polarised laser beam. The fluctuations of the director at any point is described by small, non-zero components $n_x(\mathbf{r}), n_y(\mathbf{r})$. The elastic distortion energy density in terms of these components is:

$$\begin{aligned} \mathcal{F}_{elastic} &= \mathcal{F}_\circ + \frac{1}{2}K_1\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)^2 \\ &+ K_2\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x}\right)^2 \\ &+ K_3\left[\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right] \end{aligned} \tag{2.1}$$

where K_1, K_2, K_3 are the splay, twist and bend elastic constants. In addition when the electric field of the laser beam is acting along the director (i.e., **z-axis)** the optical dielectric energy density is then:

$$\mathcal{F}_{optical} = \frac{1}{16\pi}\epsilon_a\mathcal{E}^2\left(n_x^2 + n_y^2\right) \tag{2.2}$$

It is convenient to go over to q-space to analyse these director fluctuations whose Fourier components are

$$n_x(\mathbf{q}) = \int n_x(\mathbf{r})exp(i\mathbf{q}\cdot\mathbf{r}),\ etc \tag{2.3}$$

In terms of these Fourier components the net free-energy density $= \mathcal{F}_{elastic} + \mathcal{F}_{optical}$ becomes

$$\mathcal{F} = \mathcal{F}_\circ + \frac{\Omega^{-1}}{2}\Sigma_q[K_1|n_x(\mathbf{q})q_x + n_y(\mathbf{q})q_y|^2 \tag{2.4}$$

$$+ K_2|n_y(\mathbf{q})q_y - n_y(\mathbf{q})q_x|^2 \tag{2.5}$$

$$+ (K_3q_z^2 + \epsilon_a\mathcal{E}^2)(|n_x(\mathbf{q})|^2 + |n_y(\mathbf{q})|^2)] \tag{2.6}$$

For a given q it is convenient to diagonalise the above quadratic form. The two components n_1 and n_2, that diagonalises 3 has components along the unit vectors $\mathbf{e_1}$ and $\mathbf{e_2}$. The vector $\mathbf{e_2}$ is normal to q while $\mathbf{e_1}$ is normal to $\mathbf{e_2}$. In terms of n_1 and n_2 the free-energy density becomes:

$$\mathcal{F} = \mathcal{F}_\circ + \frac{\Omega^{-1}}{2}\Sigma_q\ \Sigma_{j=1,2}|n_j(q)|^2\left(K_3q_{||}^2 + K_jq_\perp^2 + \epsilon_a\mathcal{E}^2/8\pi\right) \tag{2.7}$$

where $q_{||} = q_z$ is the component parallel to the director, while $\mathbf{q}_\perp = \mathbf{q}\cdot\mathbf{e_1}$ is the normal component.

In the above expression for $\mathcal{F}$ the various degrees of freedom in the system are decoupled. We apply the equipartition theorem for each degree of freedom according to which at thermal equilibrium, the average free-energy for each degree of freedom is $\frac{1}{2}k_BT$. Thus

$$\left\langle n_j^2(q)\right\rangle = (\Omega k_BT)/(K_3q_{||}^2 + K_jq_\perp^2 + \epsilon_a\mathcal{E}^2/8\pi) \quad j = 1,2 \tag{2.8}$$

In the one constant approximation where all the elastic constants are equal ($K_1 = K_2 = K_3 \equiv$ K), the two modes are identical. Thus we get

$$\left\langle n_x^2(q)\right\rangle = \left\langle n_y^2(q)\right\rangle = \frac{k_BT}{K\left(q^2 + \xi^{-2}\right)} \tag{2.9}$$

where ξ is the coherence length defined as $\xi = \frac{8\pi cK}{\epsilon_a} I$. In real space equation (2.9) becomes:

$$\begin{aligned} \left\langle n_x^2 \right\rangle = \left\langle n_y^2 \right\rangle &= \frac{k_B T}{2\pi^2 K}\left[\frac{1}{l} - \frac{\pi}{2\xi}\right] \\ \left\langle n_z^2 \right\rangle &= 1 - 2\left\langle n_x^2 \right\rangle \end{aligned} \tag{2.10}$$

Here l is of molecular dimensions, c is the velocity of light, K is the curvature elastic constant, **I** is the intensity of a laser beam,

ϵ_a is the optical dielectric anisotropy, T is the absolute temperature, and k_B is the Boltzmann's constant. From equation (2.10) we can easily calculate the modified optical dielectric constant parallel and perpendicular to the director and they are given by:

$$\begin{aligned} \left\langle \epsilon_{\parallel} \right\rangle &= \epsilon_{\parallel}^{\circ} - \frac{2k_B T}{\pi K l} + \frac{\epsilon_a^{\frac{3}{2}} k_B T}{2\sqrt{16\pi^3 c K^3}}\sqrt{I} \\ \left\langle \epsilon_{\perp} \right\rangle &= \epsilon_{\perp}^{\circ} + \frac{k_B T}{\pi K l} - \frac{\epsilon_a^{\frac{3}{2}} k_B T}{4\sqrt{16\pi^3 c K^3}}\sqrt{I} \end{aligned} \tag{2.11}$$

where $\epsilon_{\parallel}^{\circ}$ and $\epsilon_{\perp}^{\circ}$ are the optical dielectric constants along and perpendicular to the director in the absence of director fluctuations. Thus in the presence of a laser beam the correction term is dependent on the *square root* of its intensity. Further, though the third term linearly increases with T, yet at any temperature the second term is greater than the third term. Hence, an increase of temperature always reduces this dielectric constant. These and similar considerations apply to smectic liquid crystals as well. As described in chapter 1, smectic *A* liquid crystals have molecules arranged in layers with their preferred direction of alignment along the layer normal. In this system only splay fluctuations in the director are suppressed by the laser. On the other hand in smectic *C* liquid crystals, the molecules are again arranged in layers but the director is at an angle to the layer normal. Here the in-plane fluctuations of the c-director, which is the projection of the director on to·the layers, are suppressed by the laser field when its electric vector is along the c-director.

2.2.2 Cholesterics

Next we consider the same effect in a cholesteric liquid crystal which can be looked upon as a nematic uniformly twisted along a direction perpendicular to the nematic director. The corresponding distortion free-energy density is thus similar to the distortion free-energy density of the nematic as was discussed in chapter 1. We consider a situation with the laser beam propagating along the helix axis and with a wavelength $\lambda \ll \Delta\mu P$. In this limit, known as the Mauguin limit, the eigenwaves, as discussed in chapter 1, have their electric vectors either parallel or perpendicular to the local director. We consider the eigenstate for which the electric vector is parallel to the local director everywhere. This can be easily realised experimentally. In this geometry the electric vector follows the director twist inherent in the cholesteric.

In cholesteric liquid crystals for the wavevectors **q** parallel to the twist axis there are two independent modes of director fluctuations viz.,(i) the in-plane fluctuations, also called the twist mode, and (ii) the out-of-plane fluctuations also called the umbrella mode [8]. These modes correspond to the independent degrees of freedom and the theorem of equipartition can be invoked here. In the twist mode the director perturbations can be written as:

$$\begin{aligned} n_x &= \cos(q_\circ z + \delta n_t) \approx n_x^\circ - \delta n_t \sin(q_\circ z) \\ n_y &= \sin(q_\circ z + \delta n_t) \approx n_y^\circ + \delta n_t \cos(q_\circ z) \\ n_z &= 0 \end{aligned} \tag{2.12}$$

with $\delta n_t = \delta n_\phi \; exp(iqz)$ and $q_\circ$ is the wavevector of the helix and is defined as $q_\circ = 2\pi/P$ where **P** is the pitch of the helix. The mean square of the amplitude is given by:

$$\left\langle \delta n_\phi^2(q) \right\rangle = \frac{k_B T}{K(q^2 + \xi^{-2})} \tag{2.13}$$

In the second mode, i.e., the umbrella mode, the director perturbations can be written as:

$$n_x = \cos(q_\circ z) + \cos(\delta n_u) \approx n_x^\circ \tag{2.14}$$

$$n_y = \sin(q_\circ z) + \cos(\delta n_u) \approx n_y^\circ$$
$$n_z = \sin(\delta n_u) \approx \delta n_u$$

with $\delta n_u =$ bn, $exp(iqz)$. Then

$$\left\langle \delta n_z^2(q) \right\rangle = \frac{k_B T}{K(q^2 + q_\circ^2 + \xi^{-2})} \tag{2.15}$$

We note that the ***twist*** *mode* is similar to a mode in a nematic but in the *umbrella mode* the fluctuations are sensitive to the pitch P. In the same geometry in the case of smectic C liquid crystals only the suppression of in-plane fluctuations in the c-director are relevant. This is given by equation (2.9) or (2.13).

2.2.3 Estimation of the nonlinear coefficient

It is important to estimate the magnitude of this effect before we embark upon its implications. From the statistical theory of the nematic state we know that the change AS in the orientational order parameter, $\Delta\epsilon_a$ in the optical dielectric anisotropy and AK in the elastic constants are related to S,ϵ_a,&K by $\frac{\Delta S}{S} = \frac{\Delta \epsilon_a}{\epsilon_a} = \frac{\Delta K}{2K}$. Assuming, K = 10^{-12} Newton, T = 300 K, ell = 2.89, $\epsilon_\perp$ = 2.25 and the laser intensity of **I** = 10^5 ***kW/m***^{2}(10 kW/cm^2), we find that the relative change in ϵ_a or K is of the order of 10^{-4}. Thus the correction to the optical dielectric constant is quite high. Only an applied magnetic field as high as 10^5 G can effect the same amount of change in ϵ_a or K. Further, at these intensities the optical nonlinearity is greater by three orders of magnitude compared to the normal Kerr effect in isotropic phase of liquid crystals [9]. It is thus meaningful to work out the nonlinear optical effects due to this process.

2.3 Nonlinear Optical Effects in Nematics

2.3.1 Self-focusing and self-divergence

We first consider effects of laser suppression of the director fluctuations in a nematic. Let the sample be illuminated by a parallel beam of linearly polarised light with electric field parallel to the nematic director. Further, the beam has, say, an intensity

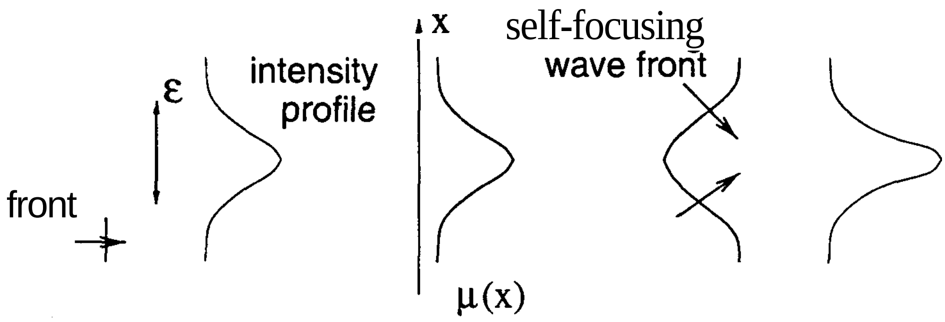

Figure **2.2:** *Figure shows the plane wavefront being self-focused due to the induced refractive index profile (also shown in the figure).*

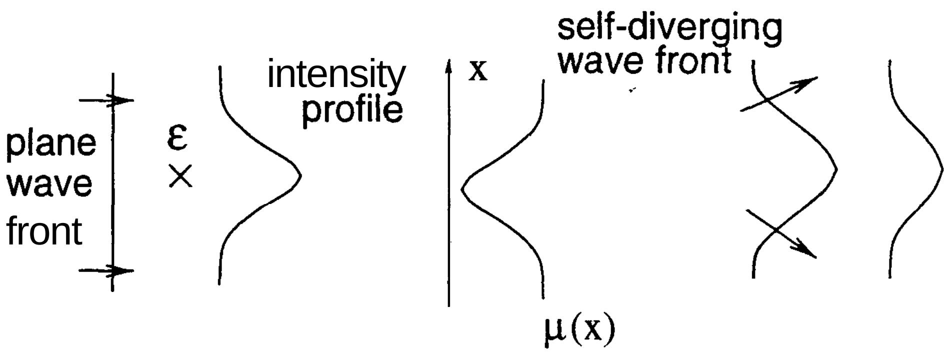

Figure **2.3:** *Figure shows the self-divergence of the plane wavefront due to the induced refractive index profile (also shown in the figure).*

profile with a central peak. As a consequence of the suppression of the director fluctuations, the refractive index along the director increases in proportion to the local electric field strength while it decreases in a direction perpendicular to the director (see equation (2.11)). Thus for this polarisation the medium acquires a greater refractive index at the center of the beam than at its periphery.

Hence, the incident plane wavefront gets distorted to a concave shape so that the beam is self-focused on propagation through the medium as shown in figure **2.2.** It is easy to show that we get self-focusing in many other geometries and even when ϵ_a is negative. We get a very interesting result when a partially polarised light beam is incident on the medium. It is well known that a partially polarised light can be decomposed into two completely polarised orthogonal but incoherent beams. Let the more intense component have its electric vector parallel to the director. The weak incoherent orthogonal component is ineffective in suppressing the director fluctuations.

Then for a parallel beam with a central peak intensity profile the refractive index for the intense component is again a profile with a central peak. Hence, this component is self-focused on propagation through the medium. On the other hand, the refractive index profile for the orthogonal incoherent electric field will have a central dip. Therefore, this lateral component exhibits self-divergence as it propagates through the ,medium. The second effect is depicted in figure **2.3.**

2.3.2 Self-iridescence

We now work out the effects of the boundary in the case of a finite sample. We assume the laser beam to propagate normal to the boundary with its electric vector parallel to the director. The geometry is shown in figure **2.4.**

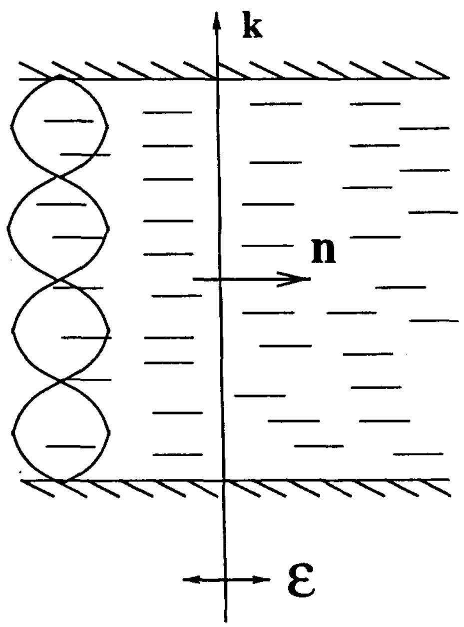

Figure 2.4: *Figure shows the confined nematic with its director parallel to the boundaries. Also shown is the standing wave intensity pattern.*

The rear boundary reflects part of the incident light. The reflected light interferes with the forward propagating light. This sets up a standing wave inside the medium. The intensity of the standing wave at the antinodes is four times the incident intensity of the reflected component and zero at the nodes. **As** the intensity of incident light increases the intensities at the antinodes also increase. When the intensity is sufficiently high the director fluctuations are considerably suppressed at the antinodes leading to a change in refractive index. Thus we get a periodic change in the refractive index due to a periodic variation in the intensity of the standing wave. The induced periodicity is $\lambda/2\mu$. Thus it satisfies the Bragg condition for reflection of the incident wave. This process further increases the reflected component. When the intensity of the laser beam is increased further the suppression of fluctuation becomes all the more effective and the Bragg reflection from the induced periodic structure increases leading to an almost complete reflection of the incident laser beam, if the sample size is comparable to the penetration depth of the Bragg reflected wave. This phenomenon can be termed as *self – iridescence*. It must be stated here that the standing wave induced periodicity through usual Kerr nonlinearity has been studied theoretically in the isotropic phase of cholesterics near the isotropic-cholesteric transition by Ye *et.al.* [10]. Though they propose a helical structure induced by counter propagating circular polarised light beams, yet they have not realised the importance of this inevitable self-iridescence discussed here. In fact this process will completely wipe out the effect predicted by these authors.

2.3.3 Light scattering

We now consider the effect of laser induced suppression of the director fluctuations on light scattering. The scattering of light due to the director fluctuations is a well studied subject [4]. The propagation of light is sensitive to changes in the dielectric tensor ϵ_{ij} due to changes in the orientation of the director. Hence the propagation of light is sensitive to the director fluctuations also. To calculate the scattering cross-section first we find the dipole moments induced by the ingoing radiation field $E_{in}(\mathbf{r}) = \mathrm{E}\ \mathbf{i}\ exp(i\mathbf{k}\,.\,\mathbf{r})$, where E is the amplitude, $\mathbf{i}$ is the unit vector specifying the polarisation and k is the wavevector of the incident beam:

$$\mathbf{P}(\mathbf{r}) = 1/(4\pi)(\epsilon(\mathbf{r}) - \mathbf{1})\ E_{in}(\mathbf{r}) \tag{2.16}$$

where $\mathbf{1}$ represents a unit tensor. The outgoing field is obtained by summing all the contributions above over the volume of the sample. After going through some simple calculations and projecting the total outgoing field amplitude onto the final polarisation direction f we obtain:

$$\mathbf{f} \cdot \mathbf{E_{out}}(\mathbf{r}') = (E/R)\, exp(i\,\mathbf{k}\,.\,r')\, a \tag{2.17}$$

where $R = (\mathbf{r} - \mathbf{r}')$ and a, is given by

$$\omega^2/4\pi c^2 \int_{(\Omega)} \{\mathbf{f} \cdot (\epsilon(\mathbf{r}) - \mathbf{1}).\mathbf{i}\}\, exp(i\,\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}$$

$$\mathbf{q} = \mathbf{k}_\circ - \mathbf{k}$$

α is known as the scattering amplitude. In terms of the Fourier components the scattering amplitude can be also written as

$$\alpha = (\omega^2/4\pi c^2)\, \mathbf{i} \cdot \epsilon(\mathbf{q}) \cdot \mathbf{f}$$

The differential cross-section per unit solid angle of the outgoing beam around the outgoing direction is

$$\sigma = \left\langle |\alpha|^2 \right\rangle$$

where the < > denote as usual the thermal average.

We now calculate the contribution to $\epsilon(\mathbf{q})$ due to the orientational fluctuations. Letting the fluctuations $\delta\mathbf{n} = \mathbf{n} - \mathbf{n}_\circ = (n_x, n_y, 0)$, and expanding ϵ to first order in $\delta\mathbf{n}$ we get:

$$\mathbf{f} \cdot \epsilon \cdot \mathbf{i} = \mathbf{f} \cdot \langle\epsilon\rangle \cdot \mathbf{i} + \epsilon_a(\mathbf{f} \cdot \delta\mathbf{n})(\mathbf{n}_\circ \cdot \mathbf{i}) + \epsilon_a(\mathbf{f} \cdot \delta\mathbf{n}_\circ)(\delta\mathbf{n} \cdot \mathbf{i}) \tag{2.18}$$

Again, in the one elastic constant approximation, we find for the scattering cross-section as:

$$\sigma = 2\left(\epsilon_a\omega^2/4\pi c^2\right)^2 \left\langle |\delta n(\mathbf{q})|^2 \right\rangle (i_j f_z + i_z f_j)^2 \tag{2.19}$$

where j represents the directions of either of the two permitted normal modes of the director fluctuations.

If we consider the presence of an electric field of the laser beam polarised parallel to the director and selecting an outgoing field orthogonal to initial polarisation, the scattering cross-section can be obtained using equation (2.10). We get

$$\sigma(q) = \Omega\left(\frac{\epsilon_a^2\pi^2}{\lambda^4}\right) \frac{k_B T}{Kq^2 + \epsilon_a I/c} \tag{2.20}$$

with positive ϵ_a. It is obvious from this equation that the scattering cross-section is reduced on increase of the laser intensity. For a q $\approx 10^7\ cm^{-1}$ and an intensity of about **10** kW/cm^2 the scattering cross-section is reduced by as much as **25%.** This in turn should lead to an increase in transmitted intensity for polarisation parallel to the director.

2.4 Nonlinear Optical Effects in Cholesterics

2.4.1 Unwindingofthe structure

Now we discuss the nonlinear optical effects to be expected in cholesteric liquid crystals. Let a linearly polarised light in the Mauguin limit be incident on the structure along the helix axis as shown in figure 2.5. We consider the mode for which the

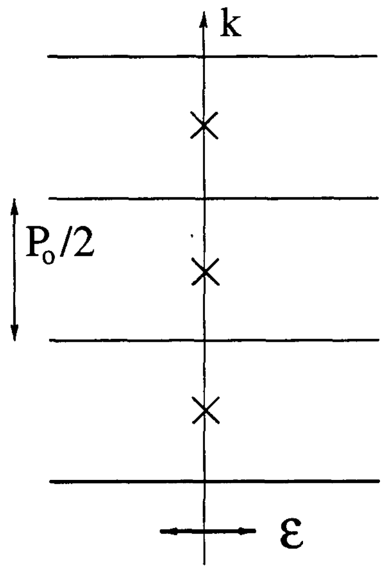

Figure 2.5: *Laser beam propagating along the helix axis. P_o is the pitch of the cholesteric.*

electric field is parallel to the local director and hence the director fluctuations are suppressed globally. This increases the order parameter locally everywhere which in turn increases the twist elastic constant. But cholesteric pitch is linearly proportional to K_2. Hence even the pitch increases as the intensity increases. We get a linear increase in pitch with the square root of intensity, the slope of which is $4P_o k_B T\sqrt{\epsilon_a/(8\pi cK)}/(S_o\pi K)$, where P_o is the uniform pitch and S_o is the zero field

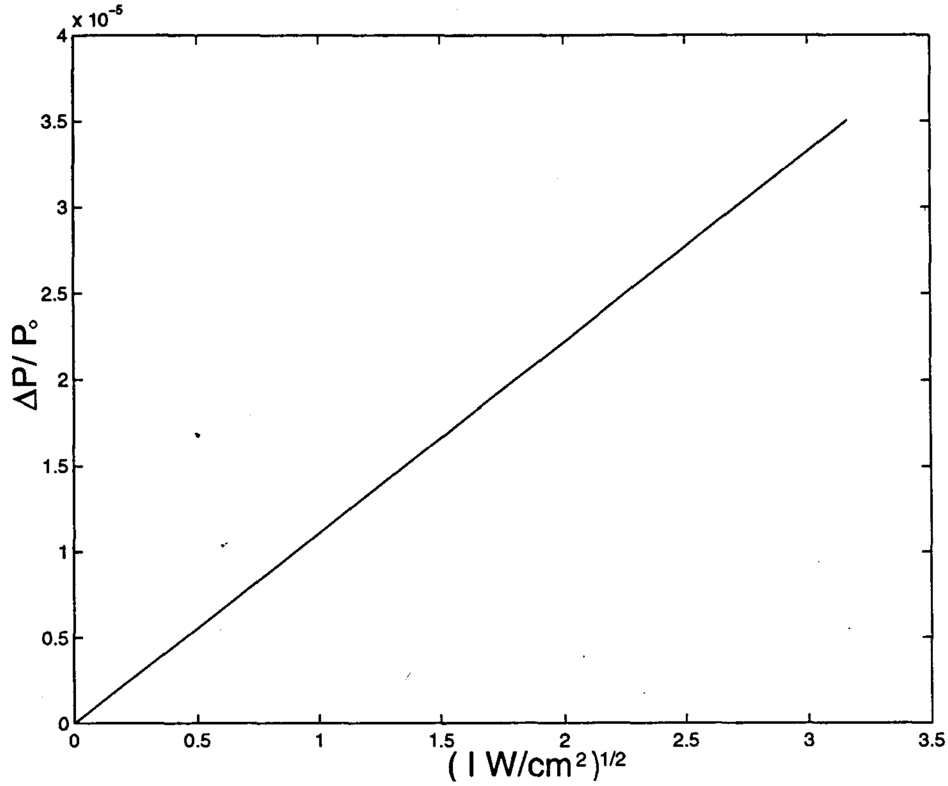

Figure 2.6: *Figure showing the variation of pitch as a function of the laser intensity.*

order parameter.

A typical calculation is shown in figure 2.6. As a result of this effect the azimuth of the electric field vector of the emergent beam will be different from that when the laser is absent or the intensity is very low. As the laser intensity is increased, say to $\mathbf{I} = 10^5$ $kW/m^2(10kW/cm^2)$ the azimuth changes by 1° to **2".** This change is easy to detect by optical techniques. It is not difficult to see that we can get in this limit all the effects like self-focusing, self-divergence, self-iridescence predicted in the case of nematic liquid crystals. The only difference is that as we go along the twist axis the local electric vector twists with the director.

2.4.2 Effect of a standing wave

In the standing wave geometry, but still in the Mauguin limit the electric field suppresses the director fluctuations at the antinodes. Again it is periodic with the period equal to half the wavelength of light inside the medium. As the field is more at the antinodes the pitch of the cholesteric increases much more in these regions. Thus we

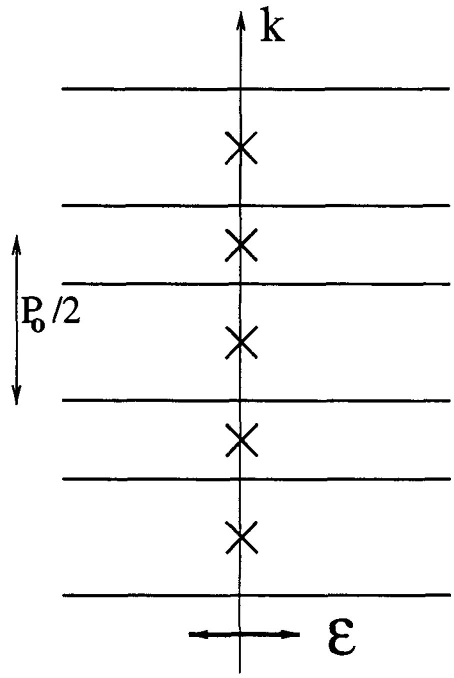

Figure **2.7:** *The modulation of pitch as a function of the laser intensity is shown schematically. There are alternating regions with high and low twist. The pitch is large at the antinodes.*

find a modulation of the twist in the presence of standing wave. This modulation is non-uniform and is on a scale of the wavelength of light. The figure 2.7 depicts the effect schematically.

2.4.3 Self-induced oscillations in the Bragg mode

If the wavelength of incident light is comparable to the optical period $\lambda_o(= \mu P)$ of the cholesteric then we get Bragg reflection at normal incidence for a circularly polarised wave of the same sense as the helix. This phenomenon is due to coherent constructive interference between the waves reflected from the different regions of the cholesterics. This reflection takes place in a band of width of $P\Delta\mu$ centered at λ_o. Inside the Bragg band we get a linearly polarised standing wave. At the long wavelength edge of the Bragg band, the standing wave will have its electric vector parallel to the director while at the short wavelength edge it is perpendicular to the director[11]. Inside the band the electric field decays over a finite length called the penetration depth. We consider here the long wavelength edge only. Due to local but nonuniform suppression of the director fluctuations there is a non-uniform change in pitch. This leads to a phase mismatch between the waves reflected from different regions of the cholesteric. Hence, the strength at the antinodes of the standing wave reduces with a consequent increase in the transmitted intensity. When the field inside the medium is thus reduced the structure relaxes towards the original uniform structure resulting again in an enhancement of the Bragg reflected wave. This process repeats indefinitely leading to *temporal oscillations* in the twist of the structure and the transmitted intensity.

2.4.4 Long wavelength limit in diffraction mode

When a laser beam of wavelength $\lambda \gg \mu P$ is propagating perpendicular to twist axis as shown in figure 2.8 with its electric vector parallel to the twist axis, we get a different result. Here we assume the boundary to anchor the twist axis. In-plane

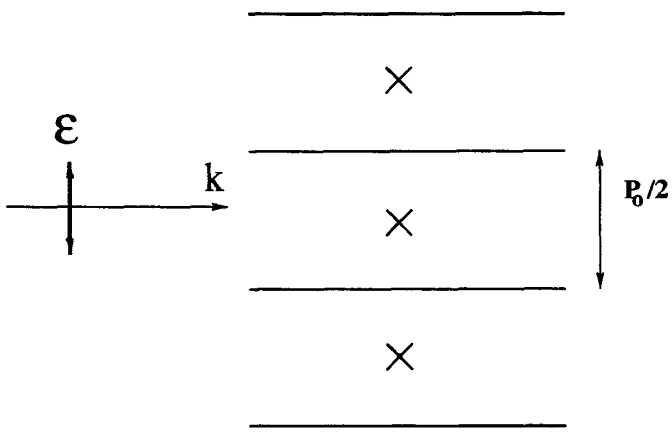

Figure 2.8: *Figure showing the geometry when the laser beam is propagating perpendicular to the twist axis. The electric vector is parallel to the twist axis.*

director fluctuations are unaffected because all orientations of the director in this mode are perpendicular to the field. Thus the amplitude of the fluctuations is given by:

$$\left\langle \delta n_{\phi}^{2}(q) \right\rangle = \frac{k_B T}{K q^2} \tag{2.21}$$

and the out-of-plane director fluctuations are enhanced. This is due to the fact that the dielectric free-energy would be reduced if orientation of the director is parallel to the director and the fluctuation amplitude becomes:

$$\left\langle \delta n_z^2(q) \right\rangle = \frac{k_B T}{K(q^2 - \xi^{-2})} \tag{2.22}$$

Hence, the twist elastic constant decreases leading to a decrease in the pitch of the structure.

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Chapter 3

NEW NONLINEARITY DUE TO CHANGE IN TILT ORDER PARAMETER IN SMECTICS

A passage she cut through from Night to Light,
And searched for an ungrasped Omniscience.
Sri Aurobindo in Savitri, -p 245

3.1 Introduction

The nonlinear optical processes like director reorientation and thermal indexing operate even in smectic liquid crystals [1, 2, 3]. The director reorientation is understood here as the reorienting torque acting on the c-director of the smectic C phase. Ong and Young have studied this process in detail [4]. Yet, in smectic liquid crystals there can be an entirely different nonlinear process. The laser beam can change the molecular tilt with respect to the layer normal [5]. The refractive index change due to this effect grows linearly with intensity. This process will be very dominant near a smectic A to chiral or achiral smectic C phase transition. In these liquid crystals this process will have to be considered along with the process of laser suppression of in-plane c-director fluctuations discussed in chapter 2. This former process may enhance or bring down the effects due to the latter. We.consider in this chapter the consequences of this nonlinearity. We also consider chiral smectics near a chiral smectic C to smectic A transition where the pitch variation with intensity need not be monotonic [6].

3.2 Laser Induced Tilt as a New Nonlinear Optical Process

We assume the laser beam to be propagating in a smectic C liquid crystal, perpendicular to the layers with its electric vector along the c-director. Then the laser field not only suppresses the in-plane fluctuations of the c-director but it also affects the tilt angle *8,* of the molecules relative to the layer normal. The dielectric free-energy density is given by $\epsilon_a(\mathbf{n}\,.\,\mathcal{E})^2/16\pi$, where $\mathbf{n}$ describes the local orientation of the molecule. Near the transition the tilt angle, θ is the order parameter and is of small amplitude. To second order in *8* we can approximate the dielectric energy as $\epsilon_a I\theta^2/16\pi c$. The free-energy density in terms of the tilt order parameter, θ near the smectic $\boldsymbol{A}$ to smectic C transition is given by [7]:

$$\mathcal{F}_{AC} = \mathcal{F}_\circ + \alpha_1\,\theta^2 - \alpha'' I\theta^2 + \alpha_2\,\theta^4 + higher\ order\ terms \\ +coupling\ \ terms \tag{3.1}$$

Here $\alpha_1 = \alpha_\circ(T - T_{AC})$, and $\alpha_2(> 0)$ are phenomenological constants in the free-energy density, $\alpha'' = \epsilon_a/16\pi c$, and ϵ_a is the dielectric anisotropy. Thus the laser intensity affects the tilt order parameter 6. It may be pointed out here that in smectic C liquid crystals in the same geometry, when the electric field is at an angle to the c-director we get c-director reorientation. Ong and others have worked out the nonlinear optics due to this process [4]. But they have ignored the laser induced change in θ which is important near a transition point and must be considered along with the c-director reorientation. The tilt angle θ may increase or decrease depending upon the sign of ϵ_a and the polarisation of the laser beam. For example, for propagation perpendicular to layers with positive ϵ_a and the electric field parallel to c-director, θ increases while for propagation along the c-director with electric field perpendicular to the layers, 6 decreases. Figure *3.1* illustrates the essentials of these processes clearly. When 6 changes we expect corresponding changes in the curvature

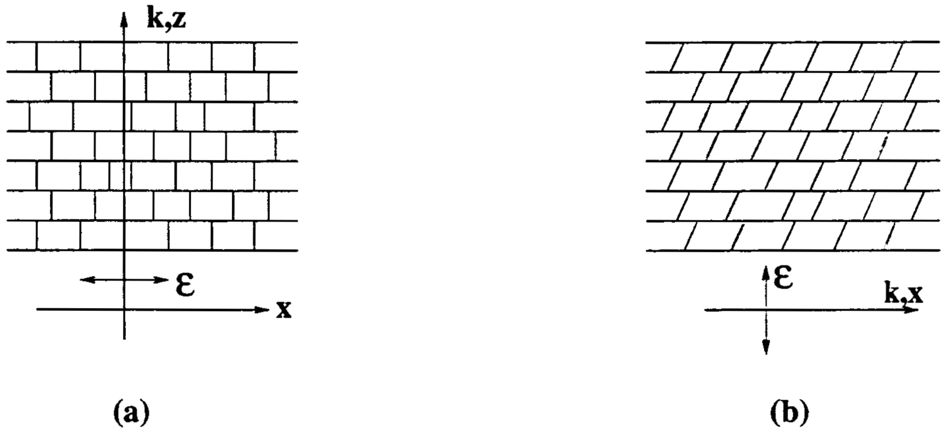

Figure *3.1: Figure shows the two geometries for the laser induced tilt order parameter as a new nonlinear process. In figure (a) the laser is propagating parallel to the layer normal in smectic A phase. In figure (b) laser propagates through a smectic C phase parallel to the layers. In the first geometry induced tilt increases while in the second case the induced tilt decreases*

elastic coefficients for the $\boldsymbol{c}$ vector field and the optical dielectric components of the medium. A laser beam propagating in such a medium in turn gets affected and we study in this chapter some nonlinear optical effects due to this process.

3.3 Estimation of the Nonlinear Coefficient

The relative changes in the curvature elastic constants, and the optical dielectric constant are related to the relative change in the tilt angle as $\frac{\Delta K}{K} = \frac{\Delta\epsilon}{\epsilon} = \frac{2\Delta\theta}{\theta} = \epsilon_a I/8\pi c\alpha_2\theta^2$. The change $\Delta\theta$ is very large near the phase transition point at which 8 is small. In the absence of a laser field at a temperature $T > T_{AC}$, the state with $8 = 0$ is of minimum energy and the medium is in the smectic A phase. At this same temperature let a linearly polarised laser beam propagate along the layer normal (see figure *3.1)*. It is easy to see that at a certain threshold intensity given by $I_{th} = 16\pi c\alpha_\circ(T - T_{AC})/\epsilon_a$, the coefficient of θ^2 term vanishes. At this intensity we get a transition from smectic $\boldsymbol{A}$ to smectic C state. Beyond this intensity we get a non-zero value of θ. For $\alpha_1 = 0.1, \alpha_2 = 0.2$, I_{th} is of the order of $5 \,.\, 10^3\ kW/m^2 (0.5\ kW/cm^2)$. This corresponds to a nonlinear coefficient of the order of 10^{-6} which is comparable to that obtained in the process of director reorientation. In comparison, this is six orders higher than what we find in the so called highly nonlinear materials like for example CS_2. Thus we obtain here a *giant optical nonlinearity*. At twice the threshold intensity the induced tilt θ is as high as 30°! If the medium is made of chiral molecules or has chiral dopants, we get at any non-zero θ a chiral smectic C. In some chiral smectic C, the tilt angle and the pitch are decoupled while in others they are coupled. In the second case a given θ corresponds to a unique pitch. We note that we can get all the effects already referred to in nematic and cholesterics, but here they will be due to suppression of c-director fluctuations. We point out now the existence of some new nonlinear optical effects due to this new process of tilt change in a laser field.

3.4 Nonlinear Optical Effects

3.4.1 New periodic structures

We take up next a smectic *A* (i.e., at T > T_{CA}) with light propagating perpendicular to the layers. Figure 3.2 depicts this situation. Then in the standing wave geometry,

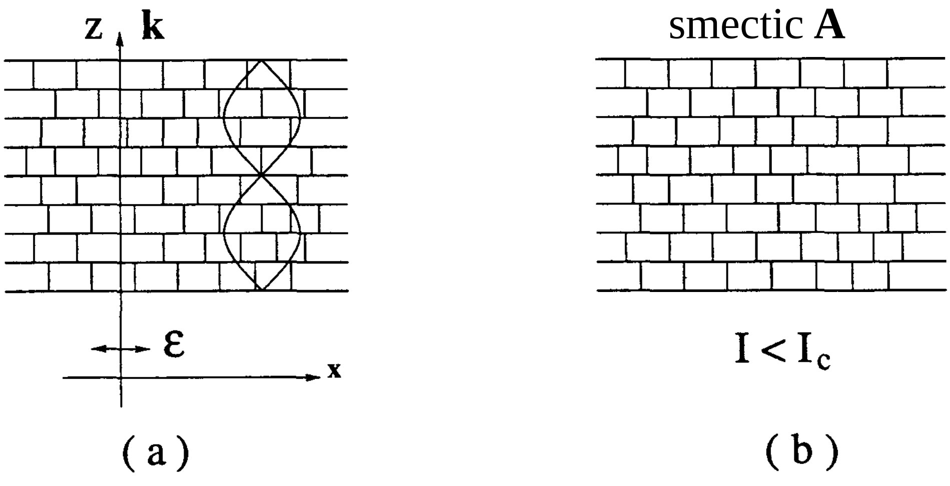

Figure 3.2: *(a) Smectic A liquid crystal in the standing wave geometry. The laser beam propagates parallel to the layer normal and the electric vector is parallel to the layers. (b) When the intensity of the laser beam at the antinode is below the threshold intensity for the smectic A to achiral or chiral smectic C transition we get only smectic A.*

the electric field is periodic inside the medium. Therefore we expect a periodic variation in the director tilt. It has already been said that the director is tilted only in the regions of field strength above a threshold. Thus we get smectic *A* and smectic *C* type blocks to alternate along the direction of propagation. This can happen even when the incident intensity is only slightly greater than one-fourth of the threshold intensity since at the antinodes it will be equal to the threshold intensity. Just above this intensity; the thickness of the smectic *A* blocks will be much more than that of smectic C. With increasing intensity the smectic *C* block thickness increases and at very high intensities it becomes much more than that of smectic *A* blocks. A possible evolution of the structure is depicted schematically in figure **3.2** and figure **3.3.** Very much the same can be expected in smectic *A* which has a low temperature

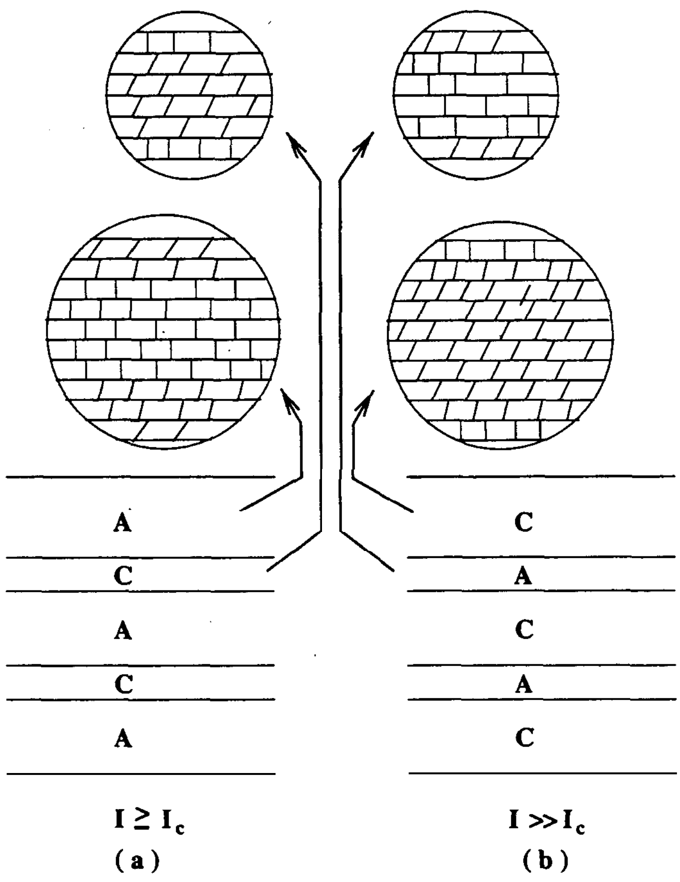

Figure **3.3:** *(a) Smectic A and smectic C blocks when the intensity of the laser beam is just above the threshold for smectic A to smectic C transition. The smectic A block is much thicker than the smectic C block. The tilt in the smectic C block is non-uniform. (b) Smectic A and smectic C blocks when the intensity is very high. The smectic C block is now thicker than the the smectic A block. In both cases the tilt is non-uniform in smectic C block. Insets show the smectic layers in A* **and** *C regions.*

chiral smectic C phase. If the pitch is very large and so coupled to tilt angle that it varies inversely with the tilt angle then above a threshold intensity we will be in the Mauguin limit. Thus we obtain thick smectic ***A*** blocks alternating with thin chiral smectic C blocks as shown in figure **3.3** but with smectic C blocks replaced by chiral smectic C blocks. This structure is rather reminiscent of the twist grain boundary

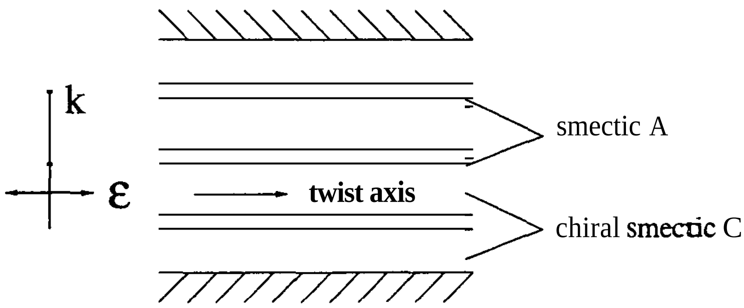

Figure **3.4:** *The figure shows the laser beam propagating through a chiral smectic C perpendicular to the twist axis and parallel to the smectic layers. The electric vector is perpendicular to the layers. We get smectic A regions at the antinodes when beam is very intense.*

phases. With increase of intensity thickness of the chiral smectic C blocks increases. Now let us consider again a chiral smectic C (near the chiral smectic C - smectic ***A*** transition) with the incident light, whose wavelength is very large compared to the pitch, propagating parallel to the layers with polarisation parallel to the twist axis. In this situation the incident polarisation is an eigenmode. Then in the standing wave geometry we obtain periodic variation of the tilt angle, along the layers leading to a novel two dimensional periodic structure. At high intensities this periodic structure consists of alternating smectic ***A*** and chiral smectic C blocks in a direction perpendicular to the inherent twist axis. This structure has been schematically shown in figure **3.4**

3.4.2 Chiral smectic C

We study next a chiral smectic C in which the tilt angle and the pitch are decoupled. Let a linearly polarised light propagate along the twist axis in the Mauguin limit, such that the electric field is locally in the plane of the molecular tilt as shown in figure **3.1.** An increase in the laser intensity leads to an increase in the tilt angle. In smectic C or chiral smectic C the elastic constants for the elastic deformations of the c-director (which is like **n** of a neamtic) increases like θ^2. Hence, increase of laser intensity increases the effective twist elastic constant k_2. Therefore: the pitch which is proportional to k_2 also increases. In this sense this process is no different from the effect due to suppression of the director fluctuations considered in the case of cholesterics. For **I** $= 10^4$ kW/m^2(1 kW/cm^2) the relative change in the elastic

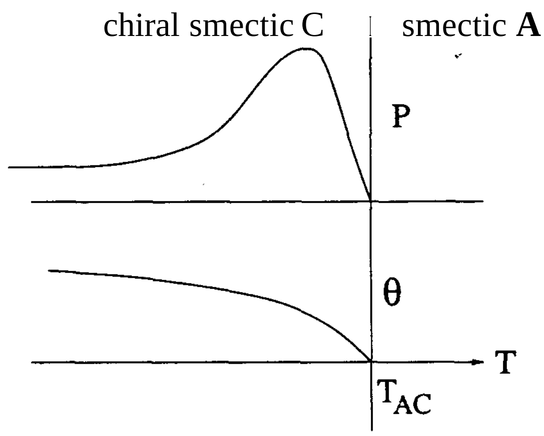

Figure **3.5:** *Figure shows schematically the pitch P* and *the tilt angle θ variation near a smectic A to chiral smectic C transition.*

constant k_2 due to change in 9 is of the order of 0.6 which is quite high compared to 10^{-4} due to suppression of the c-director fluctuations. The resulting change in the refractive index is of the order of 10^{-3}. Hence: pitch changes are very large. In some chiral smectic C's, 8 and the pitch are coupled, as the transition to smectic ***A*** is approached the pitch increases to start with, reaches a maximum and then sharply falls to zero at the transition point as shown in figure **3.5** [6]. But the tilt angle 8 monotonically decreases to zero as the transition point is approached (see figure **3.5).** If we assume that the tilt angle and the pitch are coupled in this fashion then we obtain an interesting behaviour in the Mauguin limit. Increase of laser intensity increases the tilt angle. This may either increase or decrease the pitch depending upon the inherent tilt angle and pitch at a given temperature.

3.4.3 Effect of third harmonic generation

In smectic liquid crystals the symmetry allows the generation of a third harmonic polarisation **[2]** in the geometry shown in figure 3.1 (a). The electric vector of third harmonic can be parallel to that of the fundamental. Invariably, there will not be a perfect phase matching between the fundamental and the harmonic due to optical dispersion. Hence, the torque on the molecule is different at these two wavelengths. Generally, at the harmonic ϵ_a will be higher leading to higher torques. If the smectic is near a smectic A to chiral or achiral smectic C transition then a sufficiently intense electric field of the third harmonic induces a tilt as discussed earlier. The tilt will be periodic and the period is given by $\pi/(k_{3\omega} - k_\omega)$, where the k, and $k_{3\omega}$ are the wavevectors for the fundamental and the third harmonic respectively.

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