The Optics of Thermotropic Liquid Crystals

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Nonlinear Optics of Liquid Crystals

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6.1 Introduction

One of the most spectacular nonlinear optical effects in liquid crystals (LC) can be observed when a continuous laser beam is incident normally on a homeotropically aligned nematic LC film. At low laser intensities the beam passes through the film without much distortion. When the intensity is increased beyond a characteristic value, the transmitted beam profile suddenly starts to change. A sequence of concentric luminous rings moves out from the center, expanding slowly. Depending on the intensity, the transmitted beam can finally appear as a large pattern exhibiting as many as a hundred rings, as shown in Figure 6.1. An impressive view indeed! This beautiful phenomenon, known as optical Fredericksz transition, was discovered in 1980 [1]. Although nonlinear optical effects in LC had been first studied in the early 1970s [2–5], this phenomenon was responsible for the ensuing rapid growth in the field.

In this brief review chapter, we limit our discussion to those non-linear optical effects discovered after 1980, based on the unique properties of LC molecules to reorient collectively under the influence of an external field. The focus of attention will be on the ability of an intense optical field (coherent laser light) to induce significant director reorientation and the exploration of associated phenomena in the mesomorphic phases. For isotropic fluids the optical field only reorients individual molecules leading to rather weak non-linear optical effects. By contrast with LC the cooperative molecular effect is strong and quite low intensity laser beams may have a significant effect. Several reviews [6–10] of this still developing area of research exist and we refer the interested reader to these for a more extensive coverage of the material presented in this chapter.

6.2 Optical Nonlinearities of Liquid Crystals

Liquid crystals are composed of strongly anisotropic molecules. They exhibit peculiar “mesomorphic” phases in a range of temperatures between the ordinary solid and liquid

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phases [11,12]. In these mesophases, the molecules are correlated to assume an average orientation, thus spontaneously breaking the full rotational symmetry of a liquid. This molecular orientation can be easily changed and controlled by weak external fields, a feature which makes LC useful for electro-optical applications, displays, etc., and unique for their unusually strong optical nonlinearities.

In contrast to the ordinary optical Kerr effect resulting from individual molecular reorientation, observed in isotropic liquids, the correlated molecular reorientation (CMR) yields a huge optical nonlinearity for LC. A refractive index change of $\sim 0.1$ can be obtained with a light intensity of only $10\, \text{W cm}^{-2}$. Unfortunately, because it involves collective motion of the molecules, the response of this giant nonlinearity is extremely slow, often of the order of seconds, which is a major drawback for many applications.

Optically-induced CMR was first considered theoretically in [13] and later experimentally demonstrated in [1,14–17]. Let us discuss CMR in a nematic film more explicitly. The

local optical dielectric tensor of a nematic can be written as

$$
\epsilon_{ij} = \epsilon_{ij}^0 + \epsilon_1 \mathbf{s}_i \mathbf{s}_j,
$$

(6.1)

where $\epsilon_1 = \eta_1^2$ and $\epsilon_0 = \epsilon_\parallel + \epsilon_\perp = \eta_0^2$ are the optical dielectric constants for electric fields perpendicular and parallel, respectively, to the director $\mathbf{s}$ describing the molecular orientation. $\delta$ is the unit matrix, $\epsilon_1$ is the dielectric anisotropy which is about 0.6 and always positive, and $\eta_0$ and $\eta_1$ are the ordinary and extraordinary refractive indices, respectively.

If a reorientation of $\mathbf{s}$ is induced by an external field, the principal axes of $\epsilon_{ij}$ rotate accordingly, resulting in a change of the refractive index and/or birefringence axis seen by a light wave propagating in a given direction.

The free-energy density for the interaction of light with the nematic LC is given by

$$
F_c = -\frac{\kappa_0}{8\pi} (\mathbf{E} \cdot \mathbf{E})^2
$$

(6.2)

where $\mathbf{E}$ is the optical electric field and the angular brackets denote the average over an optical cycle. To minimize this free energy, $\mathbf{s}$ must reorient parallel to the electric field (remember that $\epsilon_1$ is positive). Taking the derivative of equation (6.2) with respect to the angles which specify $\mathbf{s}$ yields the optical torque acting on $\mathbf{s}$.

$$
\tau_0 = \frac{\kappa_0}{4\pi} (\mathbf{E} \times \mathbf{E})
$$

(6.3)

In a single domain nematic film, $\mathbf{s}$ is usually determined only by the boundary surfaces, at which a preferred orientation of $\mathbf{s}$ exists. This boundary constraint, called ‘anchoring’, is usually quite strong and not easily changed by light. Therefore, to be reoriented in the bulk, $\mathbf{s}$ must undergo a spatial variation from the surface to the bulk. The elastic free-energy density for the deformation is

$$
F_d = \frac{1}{2}K_{11}(\nabla \cdot \mathbf{s})^2 + \frac{1}{2}K_{22}(\nabla \times \mathbf{s})^2 + \frac{1}{2}K_{33}(\nabla \times \nabla \times \mathbf{s})
$$

(6.4)

where $K_{11}, K_{22}$, and $K_{33}$ are three Frank ‘elastic’ constants [11,12]. The functional derivative of the total energy $F_{\gamma} + F_d$ with respect to a local change of $\mathbf{s}$ yields the elastic torque $\tau$, acting on $\mathbf{s}$. As an estimate, a reorientation of $\mathbf{s}$ by an angle $\theta$ across a distance $l$ generates an elastic torque of the order of $K_\theta l^2$, where the elastic constant $K$ is typically about $10^{-6}\, \text{erg cm}^{-2}$. The elastic torque is an internal torque that acts to balance the external optical torque in equilibrium. Therefore the longer $l$ is, the easier is the reorientation, and the larger is the optical nonlinearity. In real cases, $l$ is usually either the shortest thickness of the LC film, or the beam transverse dimensions. Consider a nematic film of 100 $\mu\text{m}$ thickness. An extraordinary plane-wave of intensity $I = 10\, \text{W cm}^{-2}$ in an optimal geometry (see Section 6.1) can induce in the film a maximum reorientation angle of $\theta = 5\, \text{mrad}$, corresponding to an average refractive index change of $\delta n \approx 10^{-3}$. The coefficient $n_2 = 3n_0^2 l$ is $\approx 10^{-4}\, \text{cm}^{-1}\text{W}^{-1}$, about 10 orders of magnitudes larger than that of the Kerr effect for ordinary liquids.

For the discussion of reorientation dynamics of $\mathbf{s}$, an effective torque $\tau$, describing the effect of viscosity must also be included in the torque balance. It can be usually approximated by

$$
\tau_v = -\gamma_1 \frac{\partial \mathbf{s}}{\partial t}
$$

(6.5)
where \( \gamma_1 \) is an orientational viscosity coefficient. The complete torque balance

\[ \tau_1 + \tau_2 + \tau_3 = 0 \]  

(6.6)

then yields the dynamic equation of motion for the reorientation of \( s \). The explicit form of this equation is a parabolic nonlinear differential equation of first order in the time derivative and second order in the spatial derivatives of \( s \). A dimensional analysis shows that the relaxation time of \( s \) is given by the ratio \( \gamma_1 I^2 / K \), usually of order of seconds, which is 11 or 12 order of magnitudes longer than that of ordinary liquids. The strong dependence of both the coefficient \( n_t \) and the response time on the characteristic length \( I \) is a consequence of the nonlocality of the CMR process, in connection to the elastic torque.

In cholesterics, \( F_4 \) acquires a new term that describes the spontaneous helical configuration of \( s \). This term is usually significantly stronger than the others in equation (6.4), and makes the optical reorientation more difficult. In smectics, there is a layer structure which is coupled to \( s \). In smectic As the coupling forces \( s \) to be normal to the layers, and when \( s \) is changed the layers must be displaced. This makes the reorientation much harder than in nematics. In smectic Cs, \( s \) is tilted away from the layer normal, and is free to rotate in a cone around it (except for the necessity to overcome the small elastic deformation energy, present because of the boundary constraints). Therefore strong CMR and optical nonlinearity comparable to those of nematics are possible.

It was recently discovered that when a nematic LC is doped with a small amount (less than 1% by weight) of certain absorbing dye, the medium can possess a strongly enhanced optical nonlinearity due to CMR [18,19]. The enhancement can be as big as 100 or more, while the response time seems to remain unchanged. Analysis of the experimental data suggests that the expression for the optical torque in equation (6.3) is still valid, at least approximately, but the dielectric anisotropy must be replaced by a much larger \( \zeta \) [19–21]. A novel feature is that, unlike \( n_t \), \( \zeta \) can be both positive and negative; in the latter case, \( s \) tends to be perpendicular to \( E \) instead of parallel [21]. It is noted that the dielectric anisotropy \( n_t \) in the dye-doped LC is essentially unchanged. Obviously, the optical torque in the doped LC cannot be related to the dielectric anisotropy. The most intriguing aspect of the phenomenon is its generality: many dyes work, as long as they absorb at the laser wavelength and can be dissolved in the LC host.

A plausible explanation of the dye-assisted CMR has been presented in [20,22]: dye molecules are anisotropic. In a nematic, they are preferentially oriented along the director \( s \), through interaction with the oriented LC molecules. Under continuous laser illumination, part of the dye molecules are excited. The probability of excitation depends on the orientation of the dye molecules; those oriented closer to the optical field \( E \) (assuming linear polarization) are more likely excited. If we assume that the orientational interaction between the dye molecules and the neighboring LC molecules is not the same for dye molecules in the ground state and in the excited state, then a net torque acting on the LC director \( s \) should result. The functional dependence of this dye-induced torque on \( s \) and \( E \) is actually dictated by symmetry considerations. To the lowest order in the electric field, the new torque has a form just like that of \( \tau_1 \), in equation (6.3). A model calculation can provide an explicit expression for \( \zeta \) as a function of relevant parameters [22]. The theoretical estimates of the effects seem to be compatible with the observations.

Laser absorption in LC can also affect the orientation of \( s \) in some other ways. For example, laser heating can create thermal gradients or induce flow, which are coupled to the director fields. It can also change the elastic constants, and consequently modulate \( n_t \) in nematics, or the helical pitch in cholesterics, or the tilt angle of \( s \) and the layer normal in smectic Cs [7]. Photo-induced conformation change of dopant molecules in the bulk or surfactants that determine the surface alignment has also been suggested for CMR of an LC bulk [23].

Besides the orientation of the director \( s \), laser heating can also affect the orientational order parameter \( S \) of LC in a mesophase. The dependence of \( S \) on the temperature can be fairly strong, especially closer to the nematic–isotropic transition. Laser-induced refractive index change \( \delta n \) occurs because both refractive indices \( n_2 \) and \( n_3 \) (in particular their difference) are functions of \( S \). The magnitude and the response time of the effect depend not only on light absorption, but also on thermal conduction and diffusion. The latter can be sensitive to the geometry and thermal properties of the container. For a 100 nm SCB film sandwiched between temperature-controlled windows, the coefficient \( n_t = 6nI \) is of the order of \( 10^{-11} \) cm\(^2\) W\(^{-1}\), and the response time is about 10 ms. The first observation of this effect was reported in [5]. More recent studies, including the interplay of this effect and CMR were reported in [16–27].

If ultrashort laser pulses are used, CMR of LC is obviously too slow to respond. However, individual molecules in the correlated bundles can still be reoriented as their response time is of the order of hundreds of picoseconds. As a result, the order parameter \( S \) or, more generally, the orientational distribution of the LC molecules around \( s \) is changed. In this case, \( n_t \) is of order of \( 10^{-11} \) cm\(^2\) W\(^{-1}\). It is interesting to note that in the isotropic phase LC behave like ordinary liquids, but when the isotropic–nematic transition is approached, molecular correlation begins to set in and \( n_t \) develops a component that exhibits a strong pretransitional enhancement, in both the amplitude and the response time. The enhancement diverges as \((T - T^*)^{-1}\), where \( T^* \) is a temperature slightly (\( \sim 1 \) K) below the transition temperature. The first observations of these pretransitional effects were reported in [2–4]. Recently, it was discovered that also this single-molecule orientational nonlinearity can be strongly enhanced when the LC is dye-doped [28,29].

Optical nonlinearities of LC can also come from vibrational, electronic, and electrodielectric contributions, but they are basically the same as and therefore not necessarily stronger than in ordinary organic liquids. A brief discussion of the second-order electronic nonlinearities of LC, described by the susceptibility tensor \( \chi^{(2)} \) is however in order. It is well known that, for materials with inversion symmetry, \( \chi^{(2)} \) vanishes in the electric-dipole approximation. This is true for fluids in general, but for chiral LC in the ferroelectric smectic C* phase, the inversion symmetry is actually broken, with the appearance of a polar ordering of molecules in a direction perpendicular to \( s \) and to the smectic layer normal. The polar order is evidenced by the presence of a spontaneous electric polarization. With proper choice of molecules \( \chi^{(2)} \) of smectic C* LC can be very large, comparable to those of conventional inorganic nonlinear-optical crystals. The largest reported to date is \( \chi^{(2)} = 5 \) pm V\(^{-1}\) [30]. A recent review on the nonlinear optical properties of ferroelectric LC appears in [31].

A large \( \chi^{(2)} \) may also exist at an LC interface, if one or more monolayers of LC are polar-oriented by effect of the interaction with the substrate. Optical second harmonic or sum-frequency generation from the interface can then be readily detected and have been used to investigate the complex phenomenon of surface anchoring [32–37].

### 6.3 Nonlinear Optics Effects

We now review various nonlinear optical effects in LC. We shall only discuss those arising from CMR since most of the others are qualitatively the same as in other materials. In proper geometries and for low light intensity, even nonlinear optical effects resulting from CMR...
are similar to those in a medium with an intensity-dependent refractive index. They include intensity-dependent phase retardation, four-wave mixing, stimulated light scattering, self-focusing or defocusing, bistability in the presence of external feedback, etc. [38]. There are also effects which have little or no analogy in other materials. The most unusual ones are the optical Fréedericksz transition, intrinsic bistability, and several static and dynamical effects related to director reorientation change of light polarization in the LC medium. In these phenomena, the vectorial and nonlocal nature of the material response is important and the effects are often so highly nonlinear that they are beyond the perturbation limit.

### 6.3.1 Intensity-dependent Phase Retardation

An incoming linearly-polarized laser field can reorient the director $s(r)$ of the LC in the plane of polarization, and change the refractive index seen by the wave. The refractive index change in turn affects the propagating beam properties. The simplest case is that of an extraordinary plane wave obliquely incident on a transparent nematic film, prepared in the homeotropic alignment ($s$ normal to the film). For very weak laser intensity, such that the reorientation of $s$ is negligible, the laser beam propagating in the film sees an effective refractive index

$$\tilde{n} = \sqrt{n_s^2 \sin^2 \alpha + n_e^2 \cos^2 \alpha}$$

(6.7)

where $\alpha$ is the angle between $s$ and the wavevector (see inset in Figure 6.2). If the laser intensity $I$ is small but sufficient to reorient $s$ by a small angle $\theta(r)$ in the plane of the beam polarization, then the dynamical equation (6.6) can be linearized, and reduced to the form

$$-\gamma_1 \frac{\partial \theta}{\partial t} + K \Delta \theta = -\frac{\epsilon_s \tilde{n} \sin \alpha}{n_e^2} \frac{\partial \phi}{\partial z}$$

(6.8)

Here, we have assumed $K_{11} = K_{22} = K_{33} = K$, for simplicity, and $I$ is defined as the $z$-component of the Poynting vector. For strong homeotropic anchoring, the boundary conditions are $\theta(z = 0) = \theta(z = l) = 0$, where $l$ is the film thickness. The stationary solution of equation (6.8) is then given by

$$\theta(z) = \frac{e_n \tilde{n} \sin \alpha}{2n_e^2 K} I(z - l).$$

(6.9)

This reorientation leads to a first-order refractive index change

$$\delta n(z) = \frac{\partial \tilde{n}}{\partial \alpha} \frac{\partial \alpha}{\partial \theta} \delta(z) = \frac{e_n \tilde{n} \sin \alpha \cos \alpha}{n_e^2} \theta(z)$$

(6.10)

and an intensity-dependent phase retardation across the film

$$\phi = \frac{2 \pi}{\lambda \cos \alpha} \int_0^l \delta n(z) \, dz = \frac{\pi \epsilon_s \delta n \sin^2 \alpha}{6n_e^2 \epsilon_k K} l$$

(6.11)

where $\lambda$ is the laser wavelength in vacuum. Equation (6.11) however breaks down at large $I$, as shown in Figure 6.2. Note that $\phi$ is positive in transparent nematics, but in dye-doped absorbing nematics, $\epsilon_s^2$ in equation (6.11) is replaced by $\epsilon_s \chi$, which can be positive or negative. In a typical transparent nematic film, with $l = 100 \mu m$ and $\alpha = 30^\circ$, a phase retardation of $2\pi$ is achieved with an intensity as low as $30 \ W/cm^2$, or less. This phase retardation can be easily measured using an interferometer or a polarimeter, or using the effects of self-focusing or self-defraction, as will be described in Section 6.33. The first experiments to demonstrate self-induced phase retardation were reported in [11,14,17]. Studies of self-induced phase retardation in wave-guides filled with nematic LC have been recently reported [39-41].

### 6.3.2 Optical Fréedericksz Transition

Equation (6.3) shows that the optical torque on the director $s$ vanishes when the optical field $E$ is parallel or perpendicular to $s$. In transparent LC, since the anisotropy $\epsilon_s$ is positive, the torque always tends to align $s$ parallel to $E$. When $s$ and $E$ are perpendicular, any small fluctuation of $s$ away from equilibrium results in a finite torque on $s$ that would like to amplify the fluctuation. If the optical torque is smaller than the elastic torque, the fluctuation is damped, and the original state remains stable. But if the intensity is above a threshold value $I_{th}$, then the optical torque can overcome the elastic one, and $s$ will be reoriented. This effect is analogous to the Fréedericksz transition induced by static electric or magnetic fields.

Consider for example the same system discussed in the previous section, when the laser beam is normally incident ($\alpha = 0$). In this case, $\alpha$ on the right-hand side of equation (6.8) should be replaced by $\theta$, and, in the limit of small $\theta$, we have $\sin 2\theta = 2\theta$. The stable stationary solution of equation (6.8) is then

$$\theta(z) = 0 \quad \text{for} \quad l < I_{th}$$

$$\theta(z) = \frac{\epsilon_s \tilde{n} \sin \alpha}{I_{th}} \quad \text{for} \quad l = I_{th}$$

(6.12)

where

$$I_{th} = \frac{\pi n_e^2 \epsilon_k}{\epsilon_s \tilde{n} \sin^2 \alpha}$$

(6.13)
The coefficient $A$ is arbitrary, but the arbitrariness is removed when the nonlinear terms are included in equation (6.6). If $I$ is just above $I_t$, the solution approximately still takes the form of equation (6.12), with $A \propto \pm \sqrt{I - I_t}$. Therefore at $I = I_t$ there is a second-order transition from $\vartheta = 0$ to one of the two symmetrical solutions of $\vartheta = \pm \sqrt{I - I_t} \sin (\pi/4)$. A refractive index change of $\delta n \times \nabla \times I - I_t$ and the resulting optical phase retardation $\delta \times I - I_t$ are then obtained. This phase retardation can be studied by means of the associated self-focusing and diffraction effect, as will be described in the next section. An example is shown in Figure 6.2 (circles and solid curve). We note in passing that the optical Fröhlich transition can also occur with circular or elliptical laser polarization, although the threshold is higher.

For $l = 100$ $\mu$m, $I_n$ is typically of the order of $1$ kW cm$^{-2}$. The threshold can be lowered by biasing the film with a destabilizing electric or magnetic field. In this way it is possible to have a large self phase retardation for extremely low laser powers. In different experiments, it is possible to observe a first-order transition, instead of second-order, accompanied by hysteresis and bistability. This occurs for example when the input light polarization is circular, or when a stabilizing magnetic field is applied to the medium. These cases will be discussed in more detail in Sections 6.3.4 and 6.3.8, in connection with optical bistability.

Besides the first works on the observation of optical Fröhlich transition [1,17], we also refer the readers to [7,42–45] for more details.

### 6.3.3 Self-focusing and Self-diffraction

When a laser beam traverses a nematic LC film, its transverse intensity profile $I(\rho)$ induces a refractive index change $\delta n(\rho, z)$ in the medium and leads to a spatial self-phase modulation $\phi(\rho)$ of the emerging beam, as described in the previous two sections. Normally, unless the beam radius is large, $\phi(\rho)$ does not follow the intensity profile $I(\rho)$, mainly because of transverse elastic coupling of the distortion in the medium [46]. In any case, $\phi(\rho)$ still has a bell-like profile like $I(\rho)$. Thus, the light emerging from the LC sample has a curved wave front, as shown in Figure 6.3. A ray propagating normal to the wave front at $\rho$, makes an angle

$$\psi = \arctan \left[ \frac{\Delta}{2\pi} \frac{\mathrm{d} \phi}{\mathrm{d} \rho} \right]$$

with the input beam axis. Since the retardation $\phi(\rho)$ is positive, the rays are all converging, yielding a self-focused laser beam [47,48]. Self-defocusing is possible in absorbing LC, if the phase retardation is negative [21].

Beyond the focus, the beam expands again. Then, in the far-field, a large spatial phase modulation of the wave front should produce a multiple-ring diffraction pattern, as described in Section 6.1 [49–51]. The rings can be understood as the result of interference between waves propagating in the same direction. Figure 6.3 shows that there are always two points on the bell curve of $\phi(\rho)$ where the slopes $\mathrm{d} \phi/\mathrm{d} \rho$ are the same. The waves generated at these two points propagate in the same direction and interfere in the far-field. The interference is constructive or destructive depending on the phase difference between the two waves, namely, $2n\pi$ for maximum constructive interference and $(2n + 1)\pi$ for maximum destructive interference, with $n$ being a positive integer. The interference rings result from cylindrical symmetry of the beam. It is easily seen that the total number of bright rings should be given by the nearest integer to, but smaller than, $\phi(0)/2\pi$. A more rigorous treatment of this effect, based on diffraction theory, can be found in [52].

### 6.3.4 Optical Bistability

Optical bistability refers to the case of an optical system having two possible equilibrium states of output for the same light input. Which output state the system prefers depends on the history of the input signal, and the response shows hysteresis. This effect has potential applications in memory devices, optical switches, and others.

Optical bistability is the result of sufficient feedback to the input/output loop of a system. It can occur, for example, in a Fabry–Perot cavity filled with a medium characterized by an intensity-dependent refractive index, such as LC. In fact, with a nematic LC in the cavity, the effect can be readily observed at very low laser intensities [53,56] (see Figure 6.4). Optical bistability in LC can also be obtained in a geometry with a single mirror providing the feedback, and the transverse self-phase-modulation is exploited [33,57,58].

Contrary to other nonlinear materials, LC driven by optical-field-induced reorientation can provide an intrinsic feedback that leads to optical bistability, without any external feedback. One example is provided by the optical Fröhlich transition described in Section 6.3.2, with the addition of a magnetic field strengthening the stability of the initial undistorted state [59]. The threshold intensity of light is then increased and the transition is made sharper. With increasing magnetic field, the transition finally becomes first order, which is a form of bistability. Instead of a magnetic field, one can use an electric field or a second laser beam to induce the same effect [60]. Intrinsic optical bistability can also be observed in nematics doped with a small amount of a chiral agent, to make them weakly cholesteric [61,62]. Other examples of intrinsic optical bistability or even multistability can be found in connection with polarization changes of a laser beam propagating in LC [63–66]. The observation of mirrorless bistability in polymer-dispersed LC has also been reported [67].

### 6.3.5 Optical Transistor

We consider here a system in which the intensity of a weak laser beam controls the modulation of a strong laser beam. A nematic LC film can be used to obtain this effect, by setting the linearly polarized strong beam close to the threshold intensity in the optical...
Freedericksz transition geometry ($E$ normal to $s$), and the weak beam in an oblique incidence geometry [68]. The strong beam can reorient the LC sample with the weak beam that initiates the reorientation without a threshold. The degree of reorientation then depends strongly on the intensity of the weak beam. As a result, a small intensity modulation on the weak beam can lead to a large phase modulation on the output strong beam. This phase modulation can then be converted into an intensity modulation on the strong beam output (see Figure 6.5).

### 6.3.6 Four-wave Mixing

Following the previous discussion, the optical torque on the director $s$ can be expressed as

$$
\theta = \frac{\epsilon_0}{4\pi} \sum_{i=1}^{2} (s \times A_i)(s \cdot A_i^*) + \frac{\epsilon_0}{4\pi} [(s \times A_1)(s \cdot A_2^*) e^{i\varphi - \Delta}] + \text{c.c.,}
$$

with $q = k_1 - k_2$ and $\Delta = \omega_1 - \omega_2$. The interference of the two waves is described by the terms in the square brackets. It is seen that, in this case, interference is possible even if the polarizations of the two waves are orthogonal.

In response to the torque, $s$ is reoriented and a refractive index grating with wavevector $q$ and frequency $\Delta$ is created. The details of the response are, as usual, sensitive to the geometry. Consider, for example, two $p$-polarized waves in a homeotropic nematic film. In the weak intensity limit, equation (6.8) can be used to describe the reorientation. Neglecting the effect of boundary conditions, the grating of reorientation angle $\vartheta$ is given by

$$
\vartheta = \frac{\epsilon_0}{4\pi} \sin(\beta_1 + \beta_2) A_1 A_2^* e^{i(q r - \Delta)} + \text{c.c.,}
$$

where $\beta$ is the angle between $A_i$ and $s$. One finds that the modulation depth of the grating increases for increasing $q$, because the elastic torque $\tau_0 \sim K q^2$ acts against the reorientation. Moreover, the depth decreases for increasing $\Delta$ because of the damping effect of the viscosity torque $\tau = \gamma_1 \Delta$. The $\beta$-grating results in a refractive index grating which can diffract a third incoming wave to yield the four-wave mixing output.

We consider three special cases of four-wave mixing in LC here.

#### 6.3.6.1 Degenerate Four-wave Mixing and Phase Conjugation

Four-wave mixing is degenerate when $\Delta = \omega_1 - \omega_2 = 0$ and the grating is stationary. Experiments on this effect were reported in [15,69–74]. If two of the three input waves are counter-propagating, i.e. $k_1 = -k_2$, then it can be shown that the output has an amplitude

![Figure 6.5](image)

Figure 6.5 Strong-beam output power $I_{out}$ versus weak-beam power $I_{in}$ for strong-beam input power $I_{in} = 48$ mW (solid circles) and $I_{in} = 42$ mW (open circles).
6.3.6.2 Stimulated Light Scattering (Two-wave Mixing)

Two waves interfering to create a material grating can also scatter from the grating into each other. This can be regarded as a special case of four-wave mixing. If the grating refractive-index amplitude is complex, then energy can be exchanged between the two waves. Traditionally, such a process is known as stimulated light scattering, but more recently is also called two-wave mixing. As seen in equation (6.17), this is the case in LC if \( \Delta \neq 0 \). The maximum energy transfer between the two waves is realized when \( \Delta = \pm 1/\tau \), where \( \tau = \gamma_1/Kq^2 \) is the time constant of the LC grating relaxation.

Theory and experiments on stimulated light scattering by reorientation of s in LC were reported in [13, 15, 77–83].

In the smectic A phase, reorientation of s is coupled with the displacement of the smectic plane. The corresponding coupled equations of motions describe a set of mixed orientational travelling waves, known as ‘second sound’ waves in LC (which behave somewhat like transverse phonons) [12]. Stimulated light scattering by second sound waves in smectic A has been proposed in [84].

6.3.6.3 Twist Grating and Mutual Phase Retardation

A homogeneously aligned nematic film (s parallel to the film) acts like a waveplate. A normally incident wave, linearly polarized at 45° from s, sets up a polarization grating in the film, with \( q = 2\pi(n_0 - n_s)/\lambda \), which in turn induces a twist-reorientation grating of s, as shown in Figure 6.7. The problem can be considered as coupling of an ordinary wave and an extraordinary wave via the orientational grating. While energy transfer between the two waves is absent because the frequency difference \( \Delta \) is zero, the coupling can affect the phase retardations experienced by each component wave. Thus, the phase retardation of one wave may depend on the intensity of the other [7]. If finite beam-size effects are considered, phenomena like mutual-focusing are also possible. It should be noticed that in this geometry, in the lowest order, the first and one of the other two terms of equation (6.16) vanish, indicating that the optical torque depends only on the interference of the two waves. It also follows that the phase retardation of one wave depends only on the intensity of the other wave.

6.3.7 Optical Pattern Formation

An optical pattern here refers to a two-dimensional ordered pattern in the light transverse intensity profile of a beam. It is possible that a beam with an initially smooth transverse profile can spontaneously break into a transverse structure with spatial modulation, after

Figure 6.6 Experimental geometry (a), and diffracted beam powers of various orders (b) for degenerate four-wave mixing producing a 71 \( \mu \)m grating (n is the director, H is a magnetic field used to bias the director orientation and optimize the efficiency).
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passing through a nonlinear medium. A simple geometry to observe pattern formation in LC is that described in Section 6.3.1, with the addition of a mirror at a small distance after the sample, which reflects the beam back in the sample [85–88]. When the intensity is increased above a characteristic threshold, a transverse structure starts to emerge, with light clustering into spots arranged in a geometrical fashion. Typically, the final stable structure is hexagonal, as shown in Figure 6.8, but also rolls, squares, or even pentagons and triangles have been observed [89,90].

The observation can be explained by the well known Talbot effect, which describes periodic conversion of transverse phase modulation to amplitude modulation and vice versa of an optical wave propagating in free space [87,88]. Consider a plane wave propagating along z, and having at $z=0$ a transverse phase modulation with wavenumber $q$. After a distance $z_T = 8\pi^2/(\lambda q^2)$, known as the Talbot length, the transverse phase modulation is reproduced exactly. In between, at $z = z_T/4$, the transverse phase modulation is completely converted to amplitude modulation, with the same wavenumber $q$. The wave is again phase-modulated and amplitude-modulated at $z = z_T/2$ and $3z_T/4$, respectively, although with a change in sign (or a 180° phase shift). Let us now consider a laser beam propagating into an LC film. Any small inhomogeneous fluctuation in the director orientation induces a transverse phase modulation in the transmitted beam. This phase-modulated beam then propagates in air from the sample to the mirror and back to the sample, for a total distance $2d$. If $2d = \left(\frac{1}{2} + m\right)z_T$, where $m$ is a non-negative integer, then the beam reflected from the mirror has the phase modulation completely converted to intensity modulation as it reaches the film. For any given $d$, this condition will be satisfied by all modulation components having

$$q = q_m = \frac{\pi^2(1 + 4m)}{\lambda d} \quad (6.18)$$

The intensity modulation, in turn, because of self-phase retardation, can induce a phase modulation of the beam in the medium. This new phase modulation is exactly in phase with the initial phase modulation. The mirror therefore acts as a positive feedback enhancing the overall modulation on the transmitted beam from the film. The pattern appears only when the laser intensity is above a characteristic threshold, at which the positive feedback becomes larger than the elastic torque $-Kq^2$. Note that only the magnitude, but not the direction, of $q$ is fixed by equation (6.18). If only one direction is modulated, one has the so-called ‘rolls’ pattern. However, the nonlinear competition between modulations in different directions usually settles on a set of ‘compatible’ modes arranged with well defined reciprocal angles. This then leads to the ordered geometric structures, such as the hexagons, appearing as stable patterns.

6.3.8 Interplay Between Beam Polarization and Director Reorientation

The most unusual optical effects observed in LC arise from strong coupling between the director $s$ and the beam polarization. The polarization affects the optical torque inducing the reorientation, and the latter in turn affects the former via the altered birefringence. One example is the case of twist-grating four-wave mixing in a homogeneously-aligned nematic film, described in Section 6.3.6. Even more interesting examples can be found with the case of homeotropic alignment. Assume that, after the initial light-induced reorientation, the director is tilted from the surface normal and is specified by the angles $\delta(x)$ and $\varphi(x)$. While the polar angle $\vartheta$ between $s$ and $Z$ is constrained by the elastic torque, the azimuthal angle $\varphi$ is not, because at the boundaries its value is undetermined. For this reason it can be easily made to vary in time through interaction between $s$ and the optical field. The result can be understood in terms of angular momentum exchange between light and the LC medium, as will be illustrated by the following examples.

6.3.8.1 Optical-field-induced Director Rotation (Self-induced Stimulated Light Scattering)

Consider a circularly polarized beam normally incident on a homeotropic nematic LC film. When the intensity is above the threshold for optical Fredericksz transition, $s$ begins to be reoriented, usually in a $\varphi$ direction determined by some residual asymmetry in the system. Afterwards, the sample becomes birefringent and the polarization of the light

Figure 6.8 Hexagonal pattern spontaneously assumed by a laser beam going through an LC film in the presence of a feedback-mirror.
propagating in the film changes accordingly. If the light emerges elliptically polarized, then a net angular momentum along \( z \) must have been deposited in the sample. The angular momentum lost by the light per unit time can be written in the form \((e_m - e_{om})I/\omega\), where \( e \) is the ellipticity of the light polarization. With the help of the wave equations for light propagation and of equation (6.3) it can be shown that this angular momentum is indeed equal to the total optical torque along \( z \), \( \int z \tau_\varphi \, dz \), as expected. This torque forces the molecules to rotate around the \( z \)-axis, as shown in Figure 6.9. The rotation as a whole is opposed only by the viscous torque \( \tau_\varphi \), because of the absence of boundary constraints. The following equation for the rotation of \( s \) in \( \varphi \) can be derived from integration of equation (6.6):

\[
\frac{I}{\omega} (e_m - e_{om}) = \gamma_1 \int \frac{\Delta \varphi}{\Delta t} \sin^2 \varphi \, dz
\]

(6.19)

As anticipated, the elastic torque does not appear in equation (6.19). Moreover, the sign of the left side of the equation is determined by the sign of \( e_m \), since in general \( |e_{om}| \ll 1 \). Therefore the sign of \( \Delta \varphi/\Delta t \) (which is approximately independent of \( z \)) is also determined by that of \( e_m \). This implies that the rotation must continue always in the same direction, as determined by the helicity of the input light.

Since the birefringence axes, defined by \( \varphi \), are constantly rotating, the polarization ellipse of the emerging light must rotate at the same rate. The rotation speed \( \Omega = \Delta \varphi/\Delta t \) is a complicated function of the intensity \( I \), and it is typically of the order of \( 10^3 \) Hz. From the optical point of view, the effect can be regarded as an unusual kind of stimulated light scattering, by the ‘Goldstone mode’ \( \varphi \) of the LC, where the circularly polarized input light is scattered into circularly polarized light of the opposite handedness, and simultaneously shifted in frequency by \( 2\Omega \). Since the frequency shift depends on the light intensity, the effect can be called ‘self-induced’ stimulated scattering. Its observation and theoretical study was reported in [66,91,92].

### 6.3.8.2 Phase Retardation Locking and Multistability

These effects take place when the input light is linearly polarized, but it becomes elliptically polarized in the sample. For this to happen, it is necessary that the reorientation is not in the polarization plane of the input light. When a plane wave at normal incidence is considered, a theoretical study shows that \( s \) should spontaneously rotate out of the polarization plane, when the light intensity is above a second threshold beyond the Fréedericksz transition [63]. If the light emerges elliptically polarized, the molecules are put in rotation, because of the angular momentum transfer associated with the polarization change. The rotation will stop only if the total phase retardation \( \phi = m\pi \), since in this case the emerging light is again linearly polarized, and the angular momentum transfer vanishes. A detailed analysis [63] shows that only if \( m \) is odd, the combined system of light and LC is stable. The self-induced optical retardation therefore appears ‘quantized’. For a given intensity, several reoriented states can be simultaneously stable (multistability). If the intensity is changed slowly while the system is in one of these states, the system follows adiabatically the state evolution. However, since the change must be continuous, the phase retardation cannot jump and remains locked to its ‘quantum’ value, as long as it is stable.

Thus far, these striking predictions have not been well confirmed by experiments, although some observations may have indicated the existence of such effects [64,65]. The reason is undoubtedly connected to the intensity variation over a finite laser-beam cross-section, which has been ignored in the theoretical analysis.

Similar polarization effects exhibiting optical bistability have also been studied in chiral-doped nematics, as reported in [61,62].

### 6.3.8.3 Complex Nonlinear Dynamical Effects

Besides the two ‘simpler’ limit cases of circular and linear polarizations of the input beam, a variety of complex nonlinear dynamical effects can also be observed with elliptical polarization, depending on the beam intensity \( I \) and input ellipticity \( e_m \). They include libration, rotation, and nutation of the director and the associated variations of the output beam polarization, as shown in Figure 6.10. The first study of these dynamical effects was reported in [93].

Another input configuration that can give rise to spontaneous oscillations and other

![Figure 6.10](image-url) Diagrams of various dynamic regimes in the \( (l, \chi) \) plane, where \( e_{om} = \sin 2\chi \).
(a) Experimental observations: squares, circles, and triangles denote distorted-equilibrium, persistent oscillation, and precession-nutation states, respectively. Open (solid) symbols refer to states obtained with increasing (decreasing) laser intensity. (b) Theoretical simulations: U, D, O, and P refer to undistorted, distorted-equilibrium, persistent oscillation, and precession-nutation regimes, respectively. Solid lines describe boundaries between different dynamic regimes. The dashed line describes the boundary at which \( P \) switches back to U, D, or O as the pump intensity decreases.
nonlinear dynamical effects has the laser beam obliquely incident at a small angle (few degrees) on a homeotropic nematic film, and its polarization perpendicular to the incidence plane. With $s$ and $E$ initially orthogonal, this is a configuration that can give rise to the optical Fredericksz transition. When the laser intensity is above the threshold for transition, the initial reorientation of $s$ makes $E$ neither parallel nor perpendicular to the birefringence axis (defined by $s$), and therefore the beam polarization in the sample changes accordingly to elliptical. The ensuing reorientation process and the variation of the beam polarization then become dynamical. The observation of periodic oscillatory regimes similar to the case with normally incident, elliptically polarized input beam, was reported in [94,95]. A theoretical study was reported in [96]. At higher laser intensities, the system undergoes a sequence of transitions to different periodic or quasiperiodic regimes, finally ending in deterministic chaos [97]. This effect is still unexplained.

6.4 Conclusions

The major part of the fundamental physics of nonlinear optics in LC is already well understood. The very strong coupling between the director and the laser field through the director reorientation mechanism gives rise to extremely high optical nonlinearities for some LC media. This makes LC rather unique as nonlinear optical materials. Besides from the common well-known nonlinear optical effects, a number of new nonlinear optical phenomena have been found to exist only in LC. They are so highly nonlinear that the usual perturbation approaches to understand nonlinear optical effects are no longer valid. As a result, the full complexity of such problems is still beyond our grasp. More work is needed to further our understanding and explore many remaining possibilities in this interesting area of research.

Acknowledgements

I. M. gratefully acknowledges a fellowship from Università ‘Federico II’ di Napoli, Italy. This work was supported by National Science Foundation Grant No. DMR-9025106.

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