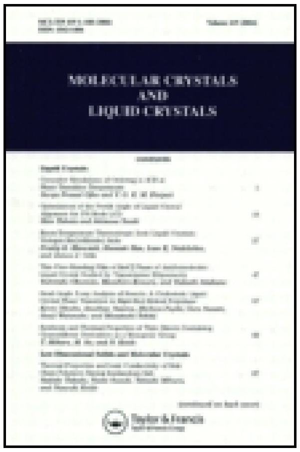


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 20 Apr 2011.

To cite this article: H. L. Ong , R. B. Meyer , A. J. Hurd , A. J. Karn , S. M. Arakelian , Y. R. Shen , P. N. Sanda , D. B. Dove , S. A. Jansen & R. Hoffmann (1990): Progress in Linear Optics, Non-Linear Optics and Surface Alignment of Liquid Crystals, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 179:1, 365-375

To link to this article: http://dx.doi.org/10.1080/00268949008055381

*Mol. Cryst. Liq. Cryst.*, 1990, Vol. 179, pp. 365–375
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Printed in the United States of America



# PROGRESS IN LINEAR OPTICS, NON-LINEAR OPTICS AND SURFACE ALIGNMENT OF LIQUID CRYSTALS

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Abstract We first discuss the progress in linear optics, in particular, the formulation and application of geometrical-optics approximation and its generalization. We then discuss the progress in non-linear optics, in particular, the enhancement of a first-order Freedericksz transition and intrinsic optical bistability in homeotropic and parallel oriented nematic liquid crystal cells. Finally, we discuss the liquid crystal alignment and surface effects on field-induced Freedericksz transition.

## I. INTRODUCTION

An essential requirement for the existence of liquid crystal (LC) is that the molecule must be highly geometrically anisotropic, usually long and relatively narrow. A direct consequence of the ordered arrangement of the anisotropic molecules is the intrinsic anisotropy of mechanical, electrical, magnetic and optical properties. LCs are excellent systems for studying electro-optics, magneto-optics, non-linear optics and field-induced transition, since the experimental geometries can be well defined by the appropriate surface condition and the LC orientation can easily be modified by an external field. The LC orientational response to the external perturbation is a collective effect and is usually extremely large. In the paper, we report some of our recent progress in the studies of the LC's optical properties, optical-field-induced and enhanced reorientation effects, and surface alignment effects.

We first discuss, in the next section, a general method using the geometrical-optics approximation (GOA) for finding the approximate solution for the optical field in a layered-inhomogeneous general LC structure with arbitrary angle of incidence. The results are then applied to study the LC optical properties. We discuss in Sec. III the enhancement and observation of a first-order Freedericksz transition and intrinsic optical bistability (OB) in nematic LCs (NLCs). The prediction that a first-order Freedericksz transition can always be enhanced in homeotropic and parallel oriented NLC cells has been confirmed experimentally. Finally, we discuss in Sec. IV the LC alignment and surface effects on the field-induced Freedericksz transition. Variable oblique LC alignment has been obtained experimentally from homogeneous and also inhomogeneous surfaces composed of homeotropic and parallel alignment agents. We show that surface interactions can induce bistable and multistable transitions, and obtain the general criteria for the existence of a first-order Freedericksz transition. We also discuss electronic structure calculations of the alignment properties of 5CB on smooth Cr, Cu and Au metal surfaces, and show that the chemical bonding can play an important role in the LC surface alignment.

## II. LINEAR OPTICS

### A. GEOMETRICAL-OPTICS APPROXIMATION

Approximate solutions, such as the GOA, the phase-integral method and the method of perturbation theory, are of significance in the study of wave propagation in inhomogeneous media.[1] It has been shown by Luneberg and by Kline that the GOA is an asymptotic solution of Maxwell's equations[2,3] and for slowly varying inhomogeneous isotopic media, the GOA and its extension are most suitable.[1]

We first studied the wave propagation in a layered-inhomogeneous planar anisotropic LC structure, in which the ordinary and extraordinary waves are decoupled for a wave incident in the plane containing the LC director. Using the GOA, we obtained the zeroth-order and first-order approximation solutions and hence the GOA validation criterion for the extraordinary wave propagation in the inhomogeneous planar anisotropic structure.[4,5] By considering the conditions for which the GOA is an exact solution, we also obtained a theorem regarding the conditions for nonreflecting structures in layered-inhomogeneous uniaxial media.[6] The results and their extensions can be summarized as a few GOA laws and theorems.[7]

### B. GENERALIZED GEOMETRICAL-OPTICS APPROXIMATION

The ordinary and extraordinary waves are coupled in non-planar media and for a planar medium with wave incident in the plane not containing the LC director. To include the coupling of the two waves, we recently defined a new basis using the ordinary and extraordinary waves and formulated a new generalized GOA (GGOA).[8,9] We obtained a general analytic solution for the optical fields in the general inhomogeneous anisotropic media with arbitrary angle of incidence. The GGOA can be reduced to two other major optics models: the Jones 2 x 2 matrix and the Stokes vector representations.

### C. APPLICATIONS

The GOA has been successfully used to study the wave propagation in a spatially inhomogeneous planar NLC, such as a periodically bent NLC[4,10], a hybrid oriented NLC cell,[5] and an absorbing planar Guest-Host nematic LC display.[11] Excellent agreement between the GOA calculation, the exact calculation, and the experimental data was demonstrated. The GOA has also been used to study the optical-field-induced molecular reorientation[12–15] and bistability in NLCs,[16,17] which will be discussed in the next section. The GGOA was applied to study the optical properties of planar and non-planar oriented LC media and LC displays, including the Guest-Host nematics, twisted nematic, general single and double layer supertwisted nematic LC displays, and helical cholesteric and smectic-C liquid crystals.[8,9,18–20] The GOA has also been used to study the purely optical-field-induced twist Freedericksz transition in nematic and smectic LCs by Santamato *et al.*[21–24]

## III. NON-LINEAR OPTICS

### A. OPTICAL-FIELD-INDUCED FIRST-ORDER FREEDERICKSZ TRANSITION IN HOMEOTROPIC ORIENTED NEMATICS

The study of LC optical nonlinearities via optical-field-induced molecular reorientation is of particular interest because among fluids, LCs have the largest optical-field-induced refractive index changes. The reorientation torque produced by a cw laser on LCs can result in an extremely strong collective molecular reorientation and large associated nonlinear effects.[12–15]

Our studies showed that for a homeotropic oriented NLC with large optical and elastic anistropies, the transition can be first order and hence intrinsically optically bistable.[16,17,25] This characteristic distinctly differs from the dc-field-induced Freedericksz transition which is always a second-order transition with rigid surface condition. By examining material data, we found that OB with a relatively narrow bistable width could occur in three NLCs: PAA (p-azoxyanisole), $m_3$, $m_5$.[26] Tabiryan *et al.* and we showed that with an additional magnetic field or electric field, OB can always be enhanced or suppressed and hence can be seen in all existing NLCs.[14,16,17,25-31] The enhancement of the optical-field-induced first-order transition from a second-order transition by an additional magnetic field has been observed experimentally by Prof. Shen's group and provides the first observation of a first-order Freedericksz transition and intrinsic OB in NLCs.[32] The electric-field-enhanced, optical-field-induced first-order Freedericksz transition in NLC has also been observed by Prof. Chen's group recently.[33]

### B. OPTICAL-FIELD-ENHANCED FIRST-ORDER FREEDERICKSZ TRANSITION IN PARALLEL ORIENTED NEMATICS

We also studied the external field effects on the Freedericksz transition in a planar parallel oriented NLC cells.[34,35] In this geometry, the dc-field-induced transition is always second order, with or without an additional dc field. However, with an additional optical field, it is possible to obtain a dc-field-induced first-order transition from an otherwise second-order transition. Recently, Prof. Chen's group reported the first observation of the optical field enhanced, electric-field-induced first-order Freedericksz transition in a parallel oriented NLC.[36,37]

## IV. SURFACE EFFECTS

### A. ALIGNMENT BY INHOMOGENEOUS SURFACES

In spite of the great effort being devoted to the study of alignment of LCs, the diagnosis and the conditioning of surfaces, and studies of molecular interaction with, and alignment by surface, remain among the least understood areas of LC physics. In 1978, Meyer suggested that a controlled inhomogeneous surface might allow experimental means to measure the basis parameters describing LC alignment.[38] We presented experimental results showing that the interaction between the LCs and inhomogeneous surfaces leads to oblique alignment and confirms the Meyer prediction.[39]

Experimentally, we have constructed inhomogeneous surfaces with parallel and homeotropic orientations. Both random and periodic patterns were generated by vapor deposition of metal; random structures of metal islands were made by controlling the thickness of evaporated metal and the periodic structures were made by deposition through a mask. We developed three methods for generating the inhomogeneous surfaces. The inhomogeneous surfaces are essentially flat and contain some patterns of known materials having different alignment properties for the LC used. The competition between the orienting forces in neighboring regions of the sample surface leads to spatially varying structures in the LC director at the surface, which dies out in the interior of the sample in a boundary layer whose thickness is comparable to the fundamental wavelength of the surface pattern. The resulting equilibrium mean orientation and mean anchoring energy can be controlled by varying the properties of the surface pattern. We showed experimentally that variable alignment ranging from parallel to homeotropic orientations can be obtained for the nematic 6CB (4-cyano-4'hexylibiphenyl) by inhomogeneous surfaces.

## B. MULTISTABLE AND OBLIQUE ALIGNMENT BY HOMOGENEOUS SURFACES

We studied the effects of a homogeneous, short-range, arbitrary strength interfacial potential on the dc and optical field-induced Freedericksz transition and obtained the exact solution.[40] We found that the function $G(\theta_m)$ which gives the field $G$ needed to maintain the NLC state with a given $\theta_m$ is a single-valued function of $\theta_m$ but is not necessary monotonic, i.e., it can assume the same value for different $\theta_m$, where $\theta_m$ denotes the maximum deformation angle in the cell, as compared to its initial orientation. The transition is second order if $G$ is a monotonic function of $\theta_m$. However, if the function of $G(\theta_m)$ has one of more locally extremal values at some intermediate angles between 0 and $\pi/2$, then several first-order transitions accompanied by hysteresis loops could occur at these angles. We obtained the general criteria for the existence of a first-order transition and showed that surface interactions could induce bistable and multistable transitions. We also clarified the description of saturation field and saturation-state maintenance field that were incorrectly discussed by others.[41] Our general results agreed with the results reported by Becker, *et al.*, where they showed that electric-field-induced bistable and multistable transitions can be obtained with some surface potential for a twisted NLC.[42,43]

We suggested three simple experimental methods for manifesting the effects of finite anchoring on the Freedericksz transition. We also suggested three simple empirical approaches, for which one may observe the multistable transition. In one method, we suggested that by mixing two silane solutions, each giving different alignment when used alone (either parallel or homeotropic) to the same NLC at the same temperature.[40] This empirical approach has been used to obtain variable oblique LC alignment from otherwise homeotropic or parallel alignment agents.[44-47] Becker *et al.*[45] reported that high pretilt angles have been obtained in the range of 20° to 40°, by adequate combinations of rubbed low pretilt alignment polymer surfaces and surfactants that are normally used for homeotropic orientation.[44] In 1987, Filas and Patel[45] reported the mixture of two different silanes (one for homeotropic and the other for parallel alignment), and Matsumoto *et al.*[46] also reported the mixture of polyimide (parallel) and chromium salt (homeotropic) for aligning NLCs with oblique alignment ranging from parallel to homeotropic orientations. Recently, Fukuro and Kobayashi reported a remarkable chemical synthesis of a series of special polyimides comprising of an ordinary long-chain polymer (for parallel alignment) and the other is an extra chemically attached hydrocarbon branch with a finite length (for homeotropic alignment).[47] The special polyimides were used to align NLCs with a stable pretilt angle from a few degrees up to 30 degrees by a rubbing technique. The high pretilt alignment method is particular useful for the highly multiplexed supertwisted nematic displays.[48,49] It is hoped that the field-induced multistable transition could be observed in NLCs in the near future.

## C. ALIGNMENT BY METAL SURFACES

We studied the role of surface bonding interactions on the alignment properties in the bulk phase by comparative studies of the induced alignment for 5CB (4′-n-pentyl-4-cyanobiphenyl) bordered by various flat metal surfaces from both experimental and theoretical approaches.[50,51] The results show that chemical bonding is an important factor in the LC's surface alignment.

Experimentally, homeotropic induced alignment was observed for 5CB with Cu and Ag boundary layers, whereas parallel alignment was observed for Cr and Au.[52] The alignment results are discussed for the cases of Cu, Cr, and Au in relation to the differences in chemical bonding interactions at the surfaces for parallel versus homeotropic adsorbate orientations. In order to gain insight on the chemical origins of preferred surface anchoring configurations, simplified molecular orbital calculations were first performed on hypothetical organometallic complexes consisting of a fragment of the 5CB, cyanobenzene, interacting with isolated metal atoms at several bonding locations.[50] We also performed a more realistic calculation by extending the interface to two dimensions by applying periodic boundary conditions and with the use of the extended Hückel/tight binding method for a layer of cyanobenzene upon a two-layer slab of the metal.[51] Both calculations gave the correct alignment for Cr (parallel) and Cu (homeotropic). For Au, parallel alignment is observed, whereas the homeotropic alignment is favored by the molecular orbital calculation and the parallel configuration is correctly predicted when the surface electronic wavefunctions are utilized in the slab calculation. The results showed that chemical bonding effects play a deciding role on the alignment of liquid crystals on flat metal surfaces.



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52. We also performed the alignment experiment with flat Ag, Au, Cr, and Cu surfaces different LC materials, such as 6CB, E7 (a nematic mixture) and MBBA [N-(p-methoxybenzylidene-p-butylaniline)] The same alignment results as those of 5CB are obtained.