Equilibrium and Dynamic Properties of Liquid Crystals Confined in Complex Matrices

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Cover Sheet

FINAL REPORT

EQUILIBRIUM AND DYNAMIC PROPERTIES OF LIQUID CRYSTALS
CONFINED IN COMPLEX MATRICES

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2. OBJECTIVES

The main objectives of the project were as it was described in the proposal. We had concentrated 1) on the theoretical study of fundamental mechanisms of the torque that is acting on the orientation of liquid crystals (LC) in light beams, 2) on the theoretical and experimental study of nonlinear dynamics and catastrophes in the orientational state of LC in light beams, 3) on the possibility to relate the far field patterns that arise due to self-phase modulation of a light beam interacting with a LC to the orientation magnitude and its spatial pattern, 4) on the investigations of dielectric relaxation of confined nematic and smectic liquid crystals by broad-band dielectric spectroscopy, 5) on photon correlation spectroscopy of filled and confined liquid crystals, 6) on the investigations of the influence of confinement on the orientational order and isotropic-nematic phase transition, and 7) on the investigations of influence of confinement and random structure of pores on optical rotatory power of a chiral liquid crystal, 8) investigations of ferroelectric liquid crystals.

3. STATUS OF EFFORT

The final report is entirely based on the research plan that was originally proposed in the Air Force project.

We have studied both theoretically and experimentally the fundamental problems of light interaction with LC and corresponding forces and torque in LC. We are further developing the method of measurement of laser beams in the near field from the far field patterns that are distorted by propagation of the beam through LC. We have obtained important experimental results on the focusing of various beams into the nonlinear cell and retrieval of that information from the nonlinear distortions. Considerable progress is made in the theoretical study of linear and nonlinear propagation of laser beams through tubular waveguides, including the LC-surrounded waveguides. We performed light scattering, photon correlation spectroscopy and broad-band dielectric spectroscopy investigations of confined, filled and dispersed liquid crystals.

The establishment of the Laboratory for Physics of Condensed Matter that includes the Dielectric Spectroscopy Laboratory and Light Scattering and Photon Correlation Spectroscopy Laboratory at UPR is completed.

The UPR group has established collaboration with AFRL/MLPJ, WPAFB the Laser Hardened Materials Branch/the Materials and Manufacturing Directorate, part of the Air Force Research Laboratory.

The results obtained from September 15, 1995 to March 14, 1999 are described in 47 peer reviewed publications and 83 presentations at National and International conferences and seminars.

4. ACCOMPLISHMENTS/NEW FINDINGS

We have obtained a number of important new results in the investigations supported
by the project.

4.1. Study of interaction of laser diode beams with LC

Study of interaction of diode lasers with LC and LC-based complex materials is becoming very important for the following reasons. Presently, the diode lasers occupy the main share in the laser market. The power of laser diodes and their wavelength range is increasing in fast steps. Thus, incorporation of laser diodes in the study of material properties of LC and LCMN as well as the use of LC-based materials for control and analysis of the beams of laser diodes may have wide application potential. Laser diodes are characterized by low spatial coherence of their beams and large divergence. We carried out a series of experiments which proved that, notwithstanding of this circumstance, a rather regular pattern can be produced at the output of the LC, and that this pattern describes the induced phase shift and the strength of interaction just as well as the annular ring system obtained with "good" Gaussian beams. We explored this method to carry out collimation of the diode laser beam. This is a rather complicated process since at least three lenses have to usually be explored in order to get acceptable collimation. Our method, however, proved very advantageous since it visualized the beam profile at the focus, and one could easily judge about the quality of collimation by the symmetry of the far field pattern. By that, the focal spot position could be readily determined as the place where the interaction between the beam and the LC proved to be maximal (maximal divergence of the beam and maximal number of fringes).

4.2. Use of LC-systems for characterization of high power laser beams

One of the novel applications of LC-based materials is characterization of laser beams. Particularly, what is needed to be known in most of applications is the power density (Watts per cm²) and not the total power of the beam. However measurement of the power density of laser beams was carried out in several steps: measurement of the total power of the beam, determination of the waist location and its size. Different techniques were developed to carry out such measurements. All of them have certain advantages and disadvantages. Thus, CCD-based laser beam profiling systems have the advantage of capturing the whole beam at once, but their hypersensitivity, low damage threshold and low resolution makes them unusable, particularly, at the focal spot of high power beams. The systems which allow high resolution measurements and that can be applied to the focal region of high power laser beams attract therefore considerable attention. We developed the new principles of laser beam characterization. Namely, we showed that the use of nonlinear interaction of laser beams with matter may make possible new generation devices which would combine simplicity and low-price of non-electronic beam diagnostic systems with accuracy and quantitative character of electronic schemes. We provided evidence that the new nonlinear-optics-based devices will have unique features which could not be dreamed of in the framework of conventional principles for laser beam characterization. These new principles are based on the circumstance that light beams, especially the beams
of high power lasers, modify properties of materials and, in particular, their refractive index. In many materials, the refractive index changes linearly with the power density of radiation over a wide range of the beam power density. Thus, measurement of the changes in the refractive index profile, or corresponding change in the phase of the beam directly yields the power density profile of the laser beam. Use of LC and LC-based complex materials ensures that the process is essentially non-absorptional, non-resonant, and that in-line non-distorting measurements can be carried out parallel for large number of beams.

4.3. Intrinsic interference and interferograms of laser beams

There exist different ways of registration of orientation of LC. In experiments with laser beams, the most straightforward method makes use the phase modulation of the beam induced by reorientation of LC. Such phase modulation gives rise to diffraction patterns in the far field zone which carries information about the reorientation of the LC. Typically, the beam has Gaussian profile of intensity distribution, and the corresponding pattern is a system of concentric rings, with their number N equal to dF/2p. Thus, in an extremely simple procedure, calculation of the number of rings, one is able to determine dF and, consequently, reorientation magnitude of LC. This method has a good accuracy for large number of rings, and works well when the LC is positioned at the exact focus of the beam. Since many years it was observed that the pattern of rings reveals sometimes a more complicated infrastructure. Understanding of the origin of these complications is essential for correct measurement of the phase shift, and hence, of the orientation magnitude of the LC as well as for correct characterization of the interaction process of light with LC. We studied the conditions when the conventional annular ring system shows an infrastructure, and found out new interesting patterns of light diffraction which accompany the conventional system of rings under certain circumstances. Namely, when LC is placed before or after the focal spot of the beam, the beam possesses an additional linear phase curvature due to the lens, apart from the nonlinear phase introduced by the LC. Propagation of a beam with such a linear + nonlinear phase modulation results in the infrastructure of the "expected" system of rings. We found out that the effect of the linear phase modulation could be compensated to a remarkable degree by a lens placed after the LC. Thus we provided complete understanding of the self-phase modulation patterns which would allow to refine the use of lasers for the study of LC, as well as to use the interaction of laser beams with LC for characterization of the laser beams themselves.

4.4. Fundamental mechanisms of the torque acting on LC in light beams

We have done a remarkable step forward in our efforts to understand the about-100-fold enhancement of the NLC's orientational optical nonlinearity, which has been earlier discovered by other scientists and is presently under intense studies. The fundamental problem with this enhanced nonlinearity is that there is more than sufficient amount of energy deposited into the medium by the laser beam to perform the change of orientation of NLC. In this connection the transfer of mechanical momentum and torque was
suggested as a cause of steady-state non-gravitational convective motion of a liquid (or of an LC) under the illumination by a light beam. The detailed theoretical study revealed, that this phenomenon of the steady convective motion should exist. We have studied the torque deposition into liquids or liquid crystals - the torque that results both in hydrodynamic motion and in the change of orientation of liquid crystals. It was established as a result of the study, that the previously accepted models described the contributions of the spatially inhomogeneous translational momentum deposition, and not the spin angular momentum deposition. In this connection the mechanisms of dye-induced nonlinearities are considered for the creation of such nonlinear optical devices, that yield the response to the interference patterns with a short spatial period, and do not produce the overall deterioration of the beams due to self-focusing.

4.5. Beam Reconstruction and Interpolation with Induced Nonlinearity Gauge (BRIEFING)

We have designed and developed new principle of microscopy, Nonlinear Optical Microscopy. It is related to the measurements of the intensity distribution at a small-size focal waist of a laser beam. Originally, the method, was suggested, developed and USA-patented by our team, aimed to the measurement of laser beam characteristics. It consists of the following. The beam is focused in such a way, that its focal waist illuminates the layer of the LC. As the result of nonlinear phase modulation, the external self-focusing occurs. A single parameter of the far-field pattern is registered: the number of "rings" of that external self-focusing. This number is easily translated into the parameter of interest: peak intensity I_{peak} (W/cm²) at the transverse cross-section of the waist, in assumption that the orientation of the LC is known. In our work, related to the project, we have developed that idea to the Beam Reconstruction by Interpolation of an Electromagnetic Field with an Induced Nonlinearity Gauge. It is based on the possibility to collect much more data; namely, the intensities at all the pixels of the far-field pattern. Second pattern should be collected as well, corresponding to the far-field distribution of intensity in the original beam, without nonlinearity at all. A computational algorithm was suggested and implemented, how to reconstruct three small-scale (essentially microscopic) characteristics of the beam at the waist:

1. Absolute peak intensity I_{peak},

2. Transverse profile of intensity I(r)

3. Transverse profile of the phase of radiation.

In this way the complex field may be found in all the 3-dimensional space with absolute normalization. What is important, this may be done via the registration of the relative intensity profiles only, when it is performed in the far field zone, i.e. with low spatial resolution.

Thus, we have devised a new nonlinear-optical microscopy, where an extremely short focal length (about 100 micrometers) lenses are self-generated in a LC. The severe aberra-
tions of those lenses are accounted for, compensated and even actively exploited by proper computing. Essential advantage of such a microscopy is the possibility to achieve high spatial resolution at the waist without high-quality objective lenses; actually, without external imaging lenses at all. This may particularly be important for "difficult" spectral ranges, as UV or IR. The method is of general importance and can be applied to any other nonlinear optical media.

4.6. Nonlinear interaction of light with moving media

In our preceding work related to the present project, we had discovered that the transverse motion of the LC with respect to the beam has strong influence on the interaction of light with LC. We developed a theory which describes the influence of the motion on the reorientation magnitude of the LC. We have modeled the self-phase modulation patterns that are formed due to the motion. The theory has a new prediction that the character of the dependence of the LC reorientation as a function of the speed of motion changes at a particular speed that depends on the material parameters.

4.7. Linear and nonlinear light propagation through multimode fibers

Various schemes of focusing of light in free space and into a nonlinear optical cell were studied theoretically, including the specific cases of so-called non-diffracting Bessel beams. The use of such beams for energy transmission through a multimode optical waveguide experimentally investigated. Image transmission through multimode waveguides was a part of the theoretical efforts. If such a multimode fiber is surrounded by the nonlinear medium, then the nonlinear effects were shown both to influence the propagation of image, and to reveal the information about the intensity of the beam. Talbot effect of linear-optical image self-reproduction was predicted theoretically for the tubular waveguides and for the whispering gallery modes of round fibers. The phenomenon of azimuthal self-focusing was predicted for such guides and modes, with the perspectives of applications to the all-optical switching.

4.8. Theoretical and experimental study of thermal diffusion effects in systems containing absorbing mobile centers

Thermal diffusion is one of the essential mechanisms that causes redistribution of molecules and nanometer-size particle in laser beams. We examined these processes for solutions of absorbing particles in liquids (Soret-effect).

4.9. Theoretical and experimental study of thermal diffusion effects in systems containing absorbing mobile centers

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solutions of absorbing particles in liquids (Soret-effect). We found experimental evidences that the escape of absorbing centers (particles or molecules) from the laser beam limits the absorption and heat release in the system. For the first time, we have experimentally evaluated the thermal diffusion constants for solution of magnetic nanoparticles.

4.10. Thermodynamic stability of mobile networks

Liquid Crystalline Mobil Networks (LCMN) are complex materials. There are large number of parameters which describe the state of the system: the orientation of LC, the structure of the network, the strength of interaction of the LC with the network, the characteristics of the mobility of the network, boundary conditions imposed both on the network and on the LC. The equilibrium and dynamic properties of LCMN are essentially determined not only by the constituent materials but by the procedures and techniques of preparation as well. We prepared mobile networks with two, hydrophobic and hydrophilic kinds of nanometer-size particles of silica. We observed stronger light scattering in hydrophilic system proving the expectation to get smaller pore size and, therefore, higher degree of chaotization of the LC-orientation. However, the hydrophilic system proved unstable against heating up to phase transition temperature to the isotropic phase of LC. We interpreted such a behavior as follows. Heating destroys the hydrogen bonds since the typical energy of these bonds is rather small and comparable to the thermal energy at room temperature. The freed hydrophilic particles tend to phase separate in the hydrophobic environment (LC). On contrary, the hydrophobic particles, when freed, find themselves suspended in a "natural" hydrophobic environment. These observations and conclusions are very important in the future work: hydrophilic networks ensure denser network, and, therefore, smaller scale of LC reorientation, however, the network is irreversibly destroyed when heated to a sufficiently high temperature. These observations will also be important when choosing LCMN for applications in optical information storage and display purposes, as well as for characterization of laser beams.

4.11. Surface properties of LCMN

A small percentage of silica nano-particles is capable of creating huge surface area in LC, typically, 100 cm²/g. Thus, the network influences strongly on the bulk properties of LC primarily due to interactions at the interfaces of the network and the LC. Most importantly, the network has an orientational influence on the LC. On the other hand, the structure and the orientation of the network itself may depend on its interaction with the substrates of the cell where the LCMN has to be sandwiched for studies and applications. Such a layer would find applications in adaptive optics elements where LC is used to correct large phase aberrations. It should be noted that presently known LC-based composite media can not be used for optical phase modulation purposes since they only can change their scattering properties under external influences. Unlike this, LCMN have the potential of re- writable orienting memory layers which may open new opportunities for optical information storage, display and processing purposes.
4.12. Stability of LC orientation in confined structures

LC in confined structures have been under intensive studies during many years given its fundamental and practical importance. The presence of the network may remarkably affect the bulk equilibrium and dynamic properties of LC. Since the most important parameter describing the state of LC is its orientation, we studied stability of LC orientation in confined structures. We found out that the orientation of LC may become unstable for deformations of the capillaries. We determined the critical radius of curvature for a particular situation. The obtained result is of primary importance since in real systems we may expect distribution of not only sizes but the shapes of the confinements. Thus, the critical dynamics of the system due to presence of the capillaries of critical curvature may influence the properties of complex systems. The obtained results can be used in the design of optical memory elements where the response of the material to external influences is softened and allows effective control with low power consumption.

4.13. The investigations of dielectric relaxation of confined nematic and smectic liquid crystals by broad-band dielectric spectroscopy

Using dielectric spectroscopy in the frequency range $10^{-3}$ Hz-1.5 GHz, we investigated the influence of confinement on the dynamic properties of polar nematic and smectic liquid crystals dispersed in porous matrices with randomly oriented, interconnected pores with pores sizes 1000 Å and 100 Å as well as in cylindrical pores. The confinement has a strong influence on the dielectric properties of LC. The observed dielectric spectra together with two bulk like modes, typical for LC, have some features general for confined organic liquids. The differences between bulk and confined behavior is resulted in the appearance of a low frequency relaxation process ($f \leq 10$ KHz) absent in bulk, a process due to surface layer in the frequency range in between $10^4$ Hz and $10^6$ Hz, a modified bulk-like mode due to the molecular rotation around short axis and a high frequency mode librational motion. A new relaxation process, absent in bulk LC, is the process, with relaxation time $\sim 10^2$ s, origin of which is under question. The main features of these low relaxation processes observed in 1000 Å and 100 Å, absent in bulk, are: (a) these processes are not described by Debye relaxation function, (b) the dielectric strength is very high and (c) these relaxation times are temperature dependent. The existence of this low frequency relaxation process accompanied by huge increase in the dielectric strength suggests that both these facts are results of interfacial polarization arising at pore wall-liquid crystal interface. The structure of thin surface layer of LC on solid surface, in our case pore wall, could be very different from the structure of liquid crystal in bulk. For example, at the interface polar layer may exist. Generally two main different reasons may cause appearance of the polar layer: absorption of ions or dipole polarization due to polar interactions of molecular dipoles with solid surface. Ion absorption in two heterogeneous materials gives rise to dispersion of dielectric permittivity which develops according to the following scenario: for a mixture of two or more components the accumulation of charges
at the interfaces between phases gives rise to polarization which contributes to relaxation if at least one component has nonzero electric conductivity. The phenomenon is known as the Maxwell-Wagner (M-W) effect. The facts that relaxation times are strongly temperature dependent and there exists a spectrum of relaxation times suggests that the first relaxation process is probably not related to M-W effect, but is due to the surface induced polar ordering.

4.14. Dynamics of molecular motion of nematic liquid crystal with negative dielectric anisotropy confined in cylindrical pores

In LCs with negative dielectric anisotropy, if the angle between the molecular dipole and the long axis of molecule is not equal to 90°, two molecular relaxation processes should be observed. These processes are due to the reorientation motion of molecules about their short and long axis. If the alignment in pores is radial, i.e. the molecules are oriented perpendicular to the pore walls, then the influence of the pore wall-LC interface on the properties of the surface layer should be stronger than in the case of axial orientation. In these systems, the difference between the dynamical behavior of the molecules belonging to the surface layer and molecules farthest from the wall should be more clear than for confined alkylcyanobiphenyls.

We have investigated the dielectric properties of p-methoxybenzylidene-p'-n-butylaniline (MBBA), the LC with negative dielectric anisotropy, confined to cylindrical pores of 200 Å diameter and parallel to each other. Broadband dielectric spectroscopy was applied to investigate the dynamical behavior of MBBA in confinement. Both molecular modes due to the molecular rotation around its short and long axis were observed in pores. The confinement results in the modification of the bulk-like modes and of the temperature dependencies of the relaxation times. Two low frequency modes due to relaxation of interfacial polarization (collective mode) and reorientation dynamics of molecules at liquid crystal-pore wall interface (surface mode) were observed. MBBA was supercooled in pores up to 120 degrees below the bulk crystallization temperature. The relaxation time of the surface mode has strong glasslike temperature dependence.

4.15. Glass transition and anomalous broadening of dielectric spectra in deeply supercooled liquid crystal confined to random porous medium

Using broadband dielectric spectroscopy (frequency range: 0.001 Hz - 1.8 GHz) we have investigated the role of disorder, size effects and interface on the dynamical behavior of different dielectric modes in confined liquid crystals. Liquid crystals — alkylcyanobiphenyls — were confined in random porous media with pores of mean sizes equal to 100 Å and 1000 Å. Confinement of liquid crystals to random porous medium with highly developed pore-wall surface area has strong influence on the dynamical behavior of liquid crystal and qualitatively changes its properties. Confinement substantially suppresses crystallization, and therefore liquid crystal in restricted geometry might be supercooled as much as ~ 150 degrees below bulk crystallization temperature. As a re-
sult we observed glass transition in the materials which are non glass formers in bulk. Anomalous broadening of the dielectric spectrum of the third - bulk like - mode due to molecular reorientation motion is observed in deeply supercooled state up to 140 degrees below the bulk crystallization temperature.

4.16 Photon correlation spectroscopy of confined liquid crystals

We used photon correlation spectroscopy to investigate the influence of the confinement and interfaces on the behavior and physical properties of nematic liquid crystals dispersed in porous matrices of different pore geometry and size. We used matrices with randomly oriented, interconnected pores (porous glasses with average pore sizes of 100 Å and 1000 Å) and parallel cylindrical pores (Anopore membranes with pore diameters of 200 Å and 2000 Å).

The photon correlation experiments show significant changes in physical properties of confined liquid crystals and suggest that there is some evidence for glass-like dynamical behavior, although bulk liquid crystals do not have glassy properties neither in anisotropic nor in isotropic phases. Slow relaxational process which does not exist in bulk LC and a broad spectrum of relaxation times (10^{-8} - 10)s appear for LC confined in random and in cylindrical pores. We found that even about 20°C below bulk crystallization temperature the relaxational processes in confined LC were not frozen.

The relaxational processes in confined LC are essentially non-exponential. For confined LC, in the temperature range below nematic - isotropic phase transition temperature, we observed overlapping relaxational processes which could be satisfactorily described by the decay function \( f(q, t) = a_1 \cdot \exp(-t/\tau_1) + a_2 \cdot \exp(-(t/\tau_2)\beta) + a_3 \cdot \exp(-x^2) \), where \( x = ln(t/\tau_0)/ln(\tau_2/\tau_0) \) and \( \tau_0 = 10^{-8}s \). For LC in 100 Å random pores, the third term describing the slow process dominates, whereas for 200 Å and 2000 Å cylindrical pores as well as 1000 Å random pores the contribution from the first and the second terms is more visible.

We suggest that differences in dynamical behavior of confined LC from that in the bulk are mainly due to the existence of the interface.

4.17. Dynamic light scattering of confined liquid crystals in isotropic, nematic, and smectic phases

Dynamic light scattering were performed to study the influence of confinement on the dynamic behavior of liquid crystals (LCs) in isotropic, nematic and smectic-A phases. In isotropic phase the only fast, single exponential decay due to the order parameter fluctuations is observed. While decreasing the temperature, but still above I-N phase transition in pores, the contribution from this decay decreases and second decay due to director fluctuations appears. The existence of this decay is the evidence for the formation of ordered (paranematic) phase preceding I-N transition in confined LCs. In nematic phase the decay due to order parameter fluctuations vanishes, the relaxation due to director fluctuations dominates, and slow process absent in the bulk LC appears. In smectic phase the director
fluctuations are almost frozen.

4.18. Dielectric relaxation in filled nematic liquid crystals

Nematic liquid crystals filled with Aerosil particles are new heterogeneous materials important for different optoelectronic applications. These materials are suspensions of small silica particles, about 10-17 nm in diameter, dispersed in nematic liquid crystals. The particles are known to form a network structure dividing liquid crystal into domains with linear size approximately 250 nm. We used both hydrophilic and hydrophobic particles, filling them with the nematic liquid crystal-5CB.

Broad band dielectric spectroscopy (1 mHz - 1.5 GHz) was applied for the investigation of these materials. Two bulk-like modes due to the rotation of molecules around the short axis and the tumbling motion were observed in filled 5CB. Additionally, a low frequency relaxation process and the dispersion of dielectric permittivity due to conductivity were also observed. The modification of the surface of the particles has stronger influence on the slow process and is less important for the molecular modes. The contribution of the slow process for the hydrophilic sample to the total polarization is greater than for the hydrophobic sample. In addition, the corresponding characteristic frequencies are lower for the case of hydrophilic samples. These facts suggest that the low frequency relaxation is an Aerosil particle-liquid crystal interface related phenomena and the origin of this process maybe explained on the basis of surface induced polarization.

4.19. Static and dynamic light scattering in filled nematic liquid crystal

The new confined liquid crystal system - the nematic liquid crystal filled with dispersed small silica particles - so-called Filled Nematics (FN) attracts attention for intensive study due to the fundamental and practical interest. FN are suspensions of highly dispersed silica in the nematic phase of liquid crystal. The advantage of FN with respect to porous matrices is an ability to control the density of the aerosil network and therefore, the average size of LC domains. The pyrogenic silica - that is obtained by hydrolysis of silicon tetrachloride in an oxygen-hydrogen flame - can form densely packed stable suspensions in which the silica occupies only 2 to 3 percent of the volume. Investigations have shown that the agglomeration of 2-3 volume percent of Aerosil particles in a nematic phase of liquid crystal forms a stable three-dimensional network dividing the liquid crystal into LC domains with a linear size of approximately 2500 Å.

Nematic liquid crystal (5CB) filled with aerosil particles has been investigated by static and dynamic light scattering. The properties of 5CB were found considerably affected by the network which formed by the aerosil particles. The N-I phase transition was found considerably depressed while the nematic phase retains even 20 K below crystallization point of bulk 5CB. It was found from photon correlation spectroscopy that in addition to director fluctuations process in bulk 5CB two additional relaxation processes exist in filled 5CB. The slow relaxation process, with a broad spectrum of relaxation times, is somewhat similar to the slow decay, which is observed in confined nematic liquid crystal.
The middle frequency process was assigned to the director fluctuations in the surface layer formed at the particle-LC interface. The decay function describing this relaxation process is stretched exponential ($\beta \approx 0.7$). The temperature dependence of the relaxation times of the middle frequency obeys the Vogel-Fulcher law. Such a temperature dependence, accompanied by a broad spectrum of relaxation times suggests that the dynamics of the director fluctuations near the Aerosil particle-LC interface is glass-like.

4.20. The investigations of the influence of confinement on the orientational order and isotropic-nematic phase transition

We have studied the orientational order of octylcyanobiphenyl which has both nematic and smectic phases, confined to macroporous (1000 Å pore size) and microporous (100 Å pore size) interconnected glasses. It was found that the weakly first order nematic to isotropic (NI) phase transition is present in the macroporous glass with a nematic phase characterized by a uniform distribution of the director that coexists with an isotropic component. The orientational order is slightly depressed from that of bulk and there is no increase in orientational order due to the smectic-A onset. The order in the microporous glass is similar to that in Vycor: the NI transition is replaced by a continuous evolution of local orientational order. From static light scattering experiments we obtained that the temperature dependence of ($I_{sc}$) in isotropic phase of confined LC is different from that in the bulk. In pores $I_{sc}$ is almost independent of temperature in the temperature range corresponding to the isotropic phase. In the bulk isotropic phase this intensity is temperature dependent and exhibits the mean-field theory critical exponent expected near a second-order transition at a temperature $T^*$ preempted by a first order phase transition at $T_{NI}$, namely: $I_{sc} \sim 1/(T - T^*)$. In determination of phase transition temperature in finite systems the difficulty is that the transition region occupies a finite temperature interval and it is unclear what should be regarded as the transition temperature. The combination of static and dynamic light scattering methods is very useful to determine the phase transition temperature of LC in pores. In dynamic light scattering experiment, only one relaxation process due to fluctuations of order parameter should be observed in isotropic phase. In nematic phase the decay of Intensity/Intensity autocorrelation function is due to director fluctuations. The difference in relaxation times of these two processes is of three orders of magnitude, and it is very easy to identify the nature of relaxation process and the phase correspondingly. We determined the nematic-isotropic phase transition temperature for LC in pores as a temperature below which there is no visible decay due to order parameter fluctuations. These temperatures coincide with temperatures at which rise in the intensity of scattered light (when temperature decreases) finishes.

4.21. The investigations the influence of confinement and random structure of pores on optical rotatory power of a chiral liquid crystal

We made an attempt to investigate the influence of confinement on optical properties of chiral liquid crystal. The optical rotatory power of a chiral liquid crystal in a Vycor-like
glass has been measured as a function of temperature. Unlike the sharp cusp observed near the isotropic - blue phase transition temperature in bulk, an S-shaped dependence of smaller magnitude was observed for the confined system. The observed behavior may be attributed to a combination of surface interactions and finite size effects, which are discussed in terms of an infrared cutoff in the orientational pair correlation function.

4.22. The dynamic properties of confined antiferroelectric liquid crystal

Since the discovery of Antiferroelectric Liquid Crystals (AFLCs) - materials important in display technology - various novel liquid crystalline phases were found in the temperature range between the antiferroelectric SmCA and ferroelectric SmC* phases. These phases were found to be ferrielectric-like. The appearance of these phases seems to be due to the competition between the antiferro- and ferroelectric interactions in adjacent smectic layers that stabilize SmCA and SmC* phases. We investigated the influence of confinement on the dynamic properties and the appearance of ferrielectric phases as determined by photon correlation spectroscopy. The bulk AFLC under investigation (AS573) possesses various ferrielectric and antiferroelectric phases between SmCA and SmC* phases. Dynamic light scattering of the sample was measured in the bulk and in cylindrical pores of two different diameters: 200 Å and 2000 Å. The intensity/intensity autocorrelation function of the bulk sample consists of three relaxation processes, while in the confined liquid crystal the fastest relaxation process (50-250 msec) does not exist. The analysis of the autocorrelation functions and the temperature dependencies of the relaxation times show that the ferrielectric phases (SmCg, AF, FlLC) are not formed in the pores. It was shown that in the smallest pores the electrostatic interactions between the spontaneous polarization of neighboring smectic layers are weaker than in the larger pores and in bulk. This fact stresses the importance of long-range electrostatic interactions for the existence of ferrielectricity. The SmC* - SmA phase transition temperature in the pores is about 4 °C lower than in the bulk sample, while the SmCA - SmC* transition in pores and the SmCA- SmCg transition in bulk are of the same value of temperature. These facts have been explained by the structural aspects of AFLCs in a confined geometry.

4.23. Micro-Raman investigation of pressure-induced transformations in MBBA

The pressure-induced changes in the Raman spectra of a nematic liquid crystal (MBBA) were investigated in the wavenumber range 5-1670 cm⁻¹. With increasing pressure, the Raman spectrum undergoes qualitative changes in a systematic manner and three distinct phase transitions, from nematic to plastic crystal, from plastic to crystalline C₅₆P and from C₅₆P to C₆₅P, are obtained around 0.39, 0.78 and 3.12 GPa respectively. Pressure is found to be an obvious parameter to affect the Raman spectra of MBBA, especially the low-wavenumber phonon modes. The peak wavenumber variation and splitting of various modes with increasing pressure provide evidence of changed intermolecular interactions and conformations of core molecules. The pressure-dependent studies can provide an al-
ternative method to elucidate the polymorphism and the motions of different end groups and core molecules of liquid crystals.

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6. LIST OF PEER-REVIEWED PUBLICATIONS

1. Photon correlation spectroscopy of confined liquid crystals in isotropic, nematic, and smectic phases
   F.M. Aliev, Molecular Crystals and Liquid Crystals, accepted, to be published (1999).

2. Dynamics of molecular motion of nematic liquid crystal confined in cylindrical pores

3. Finite size and interfacial effects in liquid crystals confined to random porous matrices: broadband dielectric spectroscopy investigations
   G.P. Sinha, B. Batalla, and F.M. Aliev, Molecular Crystals and Liquid Crystals, accepted, to be published (1999).

4. The dynamic properties and appearance of the ferrielectric phases in cylindrical pores investigated by photon correlation spectroscopy

5. Dielectric relaxation in filled nematic liquid crystals

6. The dynamic properties of confined antiferroelectric liquid crystal investigated by photon correlation spectroscopy

7. The dynamic properties of 5cb filled with aerosil particles investigated by PCS

8. Dielectric relaxation in a deeply supercooled liquid crystal confined in random porous media
9. Speckle-beams with non-zero vorticity and Poincare-Cartan invariant

10. Use of skew rays in multimode fibers to generate speckle field with nonzero vorticity

11. Slow Dynamics and Glass-Like Behavior of Liquid Crystals Confined in Porous Media

12. Micro-Raman investigation of pressure-induced transformations in MBBA

13. The appearance of ferrielectric phases in a confined liquid crystal investigated by photon correlation spectroscopy

14. Light scattering and photon correlation spectroscopy of filled and confined liquid crystals

15. Dielectric spectroscopy of liquid crystals in smectic, nematic and isotropic phases confined in random porous media

16. Application of broad-band dielectric spectroscopy for investigations of liquid crystal-porous media microcomposites

17. Frequency dependent conductivity and dielectric permittivity of emeraldine base and weakly doped poly-a-toluidine

18. Dielectric spectroscopy of liquid crystals in smectic, nematic and isotropic phases confined in random porous media

19. Application of broad-band dielectric spectroscopy for investigations of liquid crystal-porous media microcomposites
20. Soret feedback in thermal diffusion of suspensions  

21. Surface activated photorefractivity and electro-optic phenomena in liquid crystals  

22. Interaction of light with transversely moving nonlinear medium: Beyond Doppler laser velocimetry  

23. Leakography: visualization of losses in fibers and fiber-optics systems using liquid crystals  

24. BRIEFING: Physical realization and development of beam reconstruction algorithm  
M. Bolshtyansky, B. Zel’dovich, Technical digest of CLEO/QELS’98, paper CThT1.

25. Azimuthal solitons / FWM instability for tubular waveguides and whispering gallery modes  

26. Talbot effect for whispering gallery modes and modes of tubular waveguides  

27. Optical rotatory power of a chiral liquid crystal in a confined geometry  

28. Influence of confinement on dynamics of molecular motion and collective modes of liquid crystal dispersed in pores  

29. Dielectric relaxation of nematic liquid crystal confined in porous matrices  

30. Transfer of momentum and torque from a light beam to a liquid crystal  

31. Stabilization of transmission function: theory for an ultrathin endoscope of one multimode fiber  
32. The decay of unstable orientational states of nematic liquid crystals interacting with a laser field

33. Complex nonlinear optical phenomena in nematic liquid crystals

34. Liquid crystalline behavior of octylcyanobiphenyl confined to submicron size randomly connected porous glasses

35. Dielectric and optical properties of heterogeneous microcomposite materials based on porous matrices and liquid crystals

36. Photon correlation spectroscopy of liquid crystals confined in porous matrices with different structure and pore size

37. Broad-band dielectric spectroscopy of liquid crystals confined in random and cylindrical pores

38. Heterogeneous nanocomposite materials based on liquid crystals and porous media

39. Slow dynamics and glass-like behavior of liquid crystals dispersed in nanoporous media

40. Display Sciences
41. *Influx of ideas from nonlinear optics to liquid crystal display sciences*  

42. *BRIEFING: beam reconstruction by iteration of an electromagnetic field with an induced nonlinearity gauge*  

43. *Characterization of high power laser beams with the aid of nonlinear optical processes*  

44. *Heterogeneous microcomposite materials based on porous matrices and liquid crystals*  

45. *Dynamic light scattering in 5CB confined in disordered porous media*  

46. *Dielectric spectroscopy of nematic liquid crystal confined in random porous matrices*  

47. *Model systems for liquid crystal based dispersed heterogeneous materials*  

7. INTERACTIONS/ TRANSACTIONS

a. Participation/presentations at meetings, conferences, seminars.


33. F.M. Aliev, Confined liquid crystals, October, 1997, University of Puerto Rico, San Juan, PR.


35. F. Aliev, *Dynamical properties of confined liquid crystals*, September 17, 1997, Max Plank Institute, Mainz, Germany.


42. F. Aliiev, *Dynamic behavior and properties of heterogeneous microcomposite materials based on liquid crystals and porous matrices*, Invited talk, International Materials Research Congress, September 1-4, 97, Cancun, Mexico.


55. N.V. Tabiryan, *Liquid Crystal Photonics Principles and Devices*, Seminar at the University of Calabria, Rende (CS), Italy.

56. G.P. Sinha, *Dielectric spectroscopy of confined liquid crystals*, April 17, 1997, University of Puerto Rico, San Juan, PR.


b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories

N.V. Tabiryan is the consultant to Meadowlark Optics, Longmont, Co., on a project funded by Air Force in 1996. Consultations are being provided about complex liquid crystal-based materials (liquid crystals in networks, etc.). Details about the project can
be obtained from Dr. M. Anderson, The Principal Investigator of the Project, or from Dr. T. Bauer, The President of the company by the address: Meadowlark Optics, Longmont, Colorado 80504-9470, Phone (303) 776-4068; fax: (303) 776-5856.

c. Transactions

The group at UPR has performed dielectric spectroscopy investigations of different polymer dispersed liquid crystal materials synthesized at Laser Hardened Materials Branch of Wright-Patterson Air Force Base. These materials are important for variety of switchable transmission and reflection gratings, which have commercial and military applications. The results obtained at UPR are utilized at AFMC Wright-Patterson Air Force Base.

8. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

In our work related to the project, an application for the U.S. Patent has been filed for the new optical principles of image and/or beam transmission through an individual multimode fiber. Twenty claims of that application are now (March 1999) approved by USA Patent Office. New linear and nonlinear effects in tubular waveguides and whispering gallery modes were predicted. The perspectives of their applications, including those for the all-optical switching, are studied. Application to the high-power beam transmission through a multimode waveguide with preservation of angular quality of the beam was demonstrated in a physical experiment. Interpretation of the Poincare-Cartan invariant of Classical Hamiltonian Mechanics was given in terms of the difference between the numbers of right and left optical vortices

In our work related to the project, a U.S. Patent has been obtained for the new, nonlinear optical principles of measurement of laser beams.

Patent


We have invented a new Nonlinear-Optical Microscopy, where an extremely short focal length (of the order of 100 micrometers) lenses are self-generated in a LC. The severe aberrations of those lenses are accounted for, compensated and even actively exploited by proper computing. Essential advantage of such a microscopy is the possibility to achieve high spatial resolution at the waist without high-quality objective lenses; actually, without external imaging lenses at all. This may particularly be important for "difficult" spectral ranges, as UV or IR. The method is of general importance and can be applied to any other nonlinear optical media. Presently, a patent application is under preparation.

Catastrophes and nonlinear dynamic behavior in the orientational state of a nematic liquid crystal has been discovered in the standard geometry of laser beam interaction with
liquid crystals. This observation is a new contribution to the knowledge of fundamental features of light interaction with matter and opens up new possibilities of modelling, study and applications of complex phenomena.

An application for the U.S. Patent has been filed for the new optical principles of image and/or beam transmission through an individual multimode fiber. M. Bolshtyansky, B. Zel'dovich. "Device for image acquisition through multimode fiber." Application by UCF for the USA Patent, May 6, 1997.

New linear and nonlinear effects in tubular waveguides and whispering gallery modes were predicted. The perspectives of their applications, including those for the all-optical switching, are considered.

9. HONORS/AWARDS

B. Ya. Zel'dovich was awarded in 1997 the "Optical Society of America Max Born Award - For outstanding contributions to physical optics, theoretical or experimental - with the citation "For his seminal contributions to the discovery and theoretical understanding of optical phase conjugation."

B. Ya. Zel’dovich was elected in 1998 to the rank of the FELLOW of the Optical Society of America with the citation "For his seminal contributions to the discovery and theoretical understanding of optical phase conjugation, giant nonlinearity of liquid crystals, spin-orbit interaction of a photon, and the up/down asymmetry of light polarization." Note that this covers other fields of optics (underlined above) in comparison with the citation for the previous year's Max Born Award to B. Zel’dovich.

N. V. Tabiryan was elected in 1999 to the rank of the FELLOW of the Optical Society of America for his outstanding contributions to the physics and optics of liquid crystals. The work on the project produced the addition to the knowledge base, that served founding new start-up company: Beam Engineering for Advanced Measurements Co. (BEAM Co.). That knowledge and experience allowed the company to win Phase 1 and Phase 2 SBIR contracts from BMDO for the use of liquid crystals for measuring intensity of laser beams. Another Phase 1 SBIR grant was recently awarded to the company, this time for the high-intensity beam measurements.

F.M. Aliev received 1997 and 1998 Scholarly Productivity Award, for contribution to the development of scientific research in Puerto Rico.

R. Katiyar received 1997 and 1998 Scholarly Productivity Award, for contribution to the development of scientific research in Puerto Rico.