FINAL REPORT

NAG3-2457 - STRUCTURE AND DYNAMICS OF FREELY SUSPENDED LIQUID CRYSTALS

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SUMMARY OF RESEARCH

1 - BACKGROUND AND RESEARCH THEMES

Smectic liquid crystals are phases of rod shaped molecules organized into one dimensionally (1D) periodic arrays of layers, each layer being between one and two molecular lengths thick. In the least ordered smectic phases, the smectics A and C, each layer is a two dimensional (2D) liquid. Additionally there are a variety of more ordered smectic phases having hexatic short range translational order or 2D crystalline or quasi long range translational order within the layers [1]. The inherent fluid-layer structure and low vapor pressure of smectic liquid crystals enables the long term stabilization of freely suspended, single component, layered fluid films as thin as 30Å, a single molecular layer [2,3,4]. The layering forces the films to be an integral number of smectic layers thick, quantizing their thickness in layer units and forcing a film of a particular number of layers to be physically homogeneous with respect to its layer structure over its entire area. Optical reflectivity enables the precise determination of the number of layers [4].

These ultrathin freely suspended liquid crystal films are structures of fundamental interest in condensed matter and fluid physics. They are the thinnest known stable fluid structures and have the largest surface-to-volume ratio of any stable fluid preparation, making them ideal for the study of the effects of reduced dimensionality on phase behavior and on fluctuation and interface phenomena. Their low vapor pressure and quantized thickness enable the effective use of microgravity to extend the study of basic capillary phenomena to ultrathin fluid films.

Freely suspended films have been a wellspring of new LC physics. They have been used to provide unique experimental conditions for the study of condensed phase transitions in two dimensions. They are the only system in which the hexatic has been unambiguously identified as a phase of matter [1], and the only physical system in which fluctuations of a 2D XY system and Kosterlitz Thouless phase transition has been observed [4] and 2D XY quasi long range order verified [5]. Smectic films have enabled the precise determination of smectic layer electron density and positional fluctuation profiles [6] and have been used to show that the interlayer interactions in antiferroelectric tilted smectics do not extend significantly beyond nearest neighbors [7]. Freely suspended films played a pivotal role in the recent discovery of macroscopic chiral-polar ordering in fluids of achiral molecules [8].
The interactions which are operative in liquid crystals are generally weak in comparison to those in crystalline phases, leading to the facile manipulation of the order in liquid crystals by external agents such as applied fields and surfaces. Effects arising from weak ordering are significantly enhanced in ultrathin free films and filaments, in which the intermolecular coupling is effectively further reduced by loss of neighbors.

Over the past four years this research, which we now detail, has produced a host of exciting new discoveries and unexpected results, maintaining the study of freely suspended liquid crystal structures as one of most exciting and fruitful areas of complex fluid physics. In addition, a class of experiments on the behavior of 1D interfaces in 2D films have been pursued with results that point to potentially quite interesting effects in microgravity.

2 - WORK CARRIED OUT UNDER NASA GRANT NAG3-2457

In this Section we detail the work carried out over the past four years under this Grant. Publications resulting from the support of NASA Grant NAG3-2457 are listed in Section 3 and indicated by a Publication Number [P#] when cited. Results are reported in the following areas, which were outlined in the NAG3-2457 proposal:

- Generation and exploration of freely suspended liquid crystal bubbles
- Use of planar freely suspended films to probe the structure of liquid crystal phases
- Computer simulation of smectic film layer structure.

2.1 - HIGHLIGHTS OF WORK CARRIED OUT UNDER NASA GRANT NAG3-2457

**Bent-Core (Banana-Shaped) Molecules**
- Discovery in freely suspended films of the least symmetric fluid: a triclinic fluid layered smectic.
- Visualized polarization modulation (PM) in freely suspended films.
- Established the structure of the B7: PM in a bulk condensed phase
- Observed PM/undulated layer structure in freely suspended filaments.

**Generation and Manipulation of Smectic Liquid Crystal Bubbles**
- Illumination techniques for observing smectic bubbles.
- Use of gas jets to drive bubble flow and island generation.
- Observation of island coarsening and aggregation.
- Electric field application to smectic bubbles.
- Optical tweezer trapping of islands on smectic bubbles.
- Optical tweezer trapping of polyballs on smectic bubbles.
- Laser generation of pores in smectic bubbles.

**Study of (+1, -1) Topological Pair Annihilation**
- Development of a defect tracking algorithm.
- Determination of in-plane ordering in tilted smectic films.
- 2D smectic and nematic (apolar) order in bola-amphiphile films.
- Molecular resolution AFM of free films transferred to substrates.
- Bilayer-by-bilayer antiferroelectric ordering in achiral polymers.

**Computer Simulation Of Smectic Structure**
- Molecular “out-of-layer” fluctuations favor synclinic ordering.
- Atomistic simulation of anticlinic tilted smectic phases.
- Atomistic simulation of SmA 8CB, showing dipolar correlations.

![Figure 1](image-url)
2.2 - DETAILS OF WORK CARRIED OUT UNDER NASA GRANT NAG3-2457

2.2.1 - Tethered Smectic Spheres: Generation and Manipulation of Smectic Liquid Crystal Bubbles

The inherent fluid-layer structure and low vapor pressure of smectic liquid crystals enables the long term stabilization of freely suspended, single component, layered fluid films as thin as 30Å, a single molecular layer. Stable spherical films of low vapor pressure fluid are potentially quite interesting and useful for a variety of studies of the flow and fluctuation properties of thin fluid films. The formation and manipulation of smectic bubbles has thus been a focus of our work. A particular advantage of bubbles is that they have a large area-to-boundary ratio, reducing transfer of material in and out of the film. We have developed an apparatus, with components sketched in Figure 2, that enables us to inflate bubbles, observe them optically at low and high resolution, and manipulate them with flow and electric field in our laboratory. Bubbles are inflated using a computer-controlled syringe. This chamber is attached to the x-y stage of a Leica DMRXA2 microscope, which is used for high resolution viewing of the tops of bubbles. All observation is in reflected light, since reflectivity R is very sensitive to N, the number of layers in the film (R = N^2). Low resolution observation of the entire bubble is carried out also in reflection with a macro-video camera and a hemisphere of the bubble diffusely illuminated from all directions, a requirement for observing the whole hemisphere.

Figure 3: Schematic film profiles for islands and pores. We propose to simulate the structure mediating the changes in layer number.

Figure 4: Islands rapidly moving by enable visualization of the extensional flow of the bubble surface generated by the gas jets in Figure 2d. The inset shows islands transiently trapped in the velocity null at the center and one being stretched by the flow. The result of this process is the island emulsion of Figure 1.

These bubbles offer unique opportunities for the study of ultrathin fluid films. As an example we show in Figures 1 & 4 some early results on generating two dimensional (2D) emulsions (arrays of islands) or foams (arrays of pores) on smectic films and observing their structure and dynamics. Islands are pancake-like stacks of extra layers on an otherwise uniform thickness film, as sketched in Figure 3, and pores the complementary holes. Islands are of interest as statistical mechanical and dynamical objects because of their very small mass (10^{-12} g) for a 10 µm diameter island), and coupling to the 2D fluid film.

Figure 2d shows the setup for generating island emulsions. The bubble is inflated and a pair of opposing sub-millimeter diameter hypodermic needles connected to pressurized gas are located within 100 microns of being tangent to the smectic sphere. These gas jets
induce pure extensional, in-plane flow at a point on the bubble, as shown in Figure 4, with a shear rate of \( \sim 100 \text{ sec}^{-1} \), which generates a two-dimensional array of islands as shown in Figure 1. The overall generation mechanism is not completely determined but one important process is illustrated in the inset of Figure 4, which shows an island being pulled apart in the extensional flow. The emulsion in Figure 1 is in the smectic C (SmC) phase, and is stabilized by the elastic energy of the "c-director field", which is the azimuthal orientation field of the local plane of tilt of the molecules in the SmC. The c-director field is visualized by the “T” symbol, where the bar indicates the end of the tilted molecules closest to the reader. The boundary of an island imposes a \( 2\pi \) reorientation of \( c \) as it is circumnavigated, trapping a +1 (2\pi) strength topological defect inside and a -1 strength defect outside, as indicated in Figure 1c. This condition generates short range repulsion and longer range attraction between the islands. Figure 1b shows the evolution of the emulsion on the top of the sphere where we can currently do high resolution imaging, showing that the density decreases as the islands sediment to the lower part of the bubble, and that at lower density the evolved state is a system of island chains stabilized by topological charge alternation (+1 -1 +1 -1 +1 ...). In a microgravity environment the Perrin length, \( k_B T/mg \) for an island will be large compared to the bubble size, meaning that in this case the islands will be thermally dispersed over the bubble surface and sedimentation will not occur.

2.2.2 - Chiral Phases from Achiral Bent-Core (Banana-Shaped) Molecules

Structure of the B7 Phase: Freely Suspended Films of a Polarization Modulated Smectic - Our discovery in 1997 of macroscopic chiral domains in a fluid phase of achiral molecules [8] led to a variety of new freely suspended film projects during this Grant period directed toward developing and understanding new banana phases and structures. Of these, none has been more interesting and important than coming to a realization of the structure of the B7 phase. This work began with the study of MHOBOW, shown in Figure 6 and discussed in Figures 5 and 8-10. MHOBOW was designed with a methylheptyloxy cabonyl tail to be SmCsPF, the homochiral ferroelectric variant of the assembly of tilted chiral layers to form the SmCP phases shown in Figure 6. This design was, in fact, successful, with electric field application to MHOBOW revealing electro-optics familiar from chiral ferroelectric smectics [P17]. However, before the field was applied MHOBOW looked nothing like the other SmCPs, growing from the isotropic as helical filaments and exhibiting amazing optical textures, similar to those found in the other four materials shown in Figure 6. In fact, these materials seemed so different that they were denoted as an-
other phase, the B7. Early attempts to make freely suspended films of these materials failed, yielding only filaments. The filaments proved interesting however, with x-ray diffraction studies showing that they had multiple closely-spaced lamellar reflections, shown in Figure 8, indicating a basic nested cylinder structure with some sort of in-plane modulation. One of the major breaks in understanding the B7 was our development of a drawing method for MHOBOW that after five years of trying finally yielded freely suspended films. The fundamental technique for studying tilted smectic freely suspended films is Depolarized Reflected Light Microscopy (DRLM), shown in Figure 7, whereby the in-film-plane projection of the azimuthal orientation of the tilt can be visualized. DRLM images of a typical few-layer thick MHOBOW film are shown in Figure 9. Freshly drawn films exhibit a distinctive 2D smectic texture, providing direct evidence for a 1D layering-like modulation of the 2D layer structure in the B7. The x-ray diffraction of MHOBOW showed that the spacing between the lamellar sub-peaks decreased with time, indicating that the modulation wavelength was increasing with time. MHOBOW has a CHN linkage that is susceptible to hydrolysis into molecular sub-fragments, and in the films the presence of these impurities eventually increases the modulation wavelength until it is resolvable optically. This serendipitous feature enabled us to show that the basic driving mechanism for the in-plane periodicity was modulation of the polarization, sketched in Figure 10. This type of modulation reflects the inherent desire of any vector field describing ordering to splay locally, but is typically suppressed by the energetic cost of the defects (magenta lines in Figure 10) which are required if the majority of space is to be filled with one sign of splay. In the bent-core SmC$_6$P$_1$ system, the driving is strong enough that polarization modulation is achieved.
Smectic C\textsubscript{g} Phases: Freely Suspended Films of Layers with Triclinic Point Group Symmetry - We have found unambiguous evidence in freely suspended films that a simple bis-alkoxy "bow-shaped" molecule with the resorcyliadene aniline core [9] (NORABOW, Figure 11) exhibits a symmetry breaking rotation about the molecular "bowstring" sketched in Figure 12, such that the local layer symmetry is triclinic, with the polarization in the plane of the layers neither parallel nor perpendicular to the average optic axis projected onto the film plane, as it is in the SmCPs of Figure 6. The layers in Figure 12 thus possesses the long-sought chiral general smectic C (SmCPG) symmetry, a reduced-symmetry version of the general smectic C phase suggested by de Gennes in his 1976 monograph. The DRLM evidence for this in NORABOW is shown in Figure 11. Here an area of a 5-10 layer thick film is illuminated obliquely (orange arrow) and viewed in depolarized reflected light with a slightly uncrossed analyzer and an in-plane field is applied (left images) and reversed (right images). In SmCP materials, field reversal produces pairs of images with the same sign of contrast between the trapped 2\pi loops and the background. However, in NORABOW a variety of domains with different contrast switching are simultaneously observed, indicating that at least some of them must be SmCPG. This phase is the first example of a LC with triclinic point group symmetry. This material also exhibits...
unusual and potentially useful analog electro-optics, with susceptibility as large as the best electroclinic materials known and very large changes in birefringence. It may be that these interesting and unusual properties are related to a tendency for the resorcylidene aniline groups to form both intramolecular and intermolecular hydrogen bonds, effectively producing H-bonded sheets within the layers.

2.2.3 - Bola-Amphiphiles: Freely Suspended Films with 2D Nematic and Smectic Ordering

C. Tschierske of the University of Halle has pioneered the development of bola-amphiphiles, small molecules (biphenyl derivatives) which have hydrogen bonding groups at the ends of the core where the usual liquid crystals have aliphatic tails [10]. The bola-amphiphiles have an aliphatic tail connected to the side of the core. These materials form layered lamellar phases where the core long axes lie parallel to the lamellae, offering the possibility of significant 2D ordering in the layer plane. We have made the first freely suspended films of such materials and are using the film technique to complement Tschierske’s x-ray and bulk textural methods to determine phase structure. Although in the beginning it was not clear whether such materials would even make freely suspended films, it turned out that it was possible and quite interesting. The nature of the 2D in-plane ordering is clearly discernible from the film textures in Figure 13, which shows two fluid phases: a lower temperature phase which exhibits a 2D focal conic texture indicative of in-plane smectic ordering, and a higher temperature phase which is a 2D nematic, exhibiting orientation fluctuations reminiscent of the c-director fluctuations in freely suspended smectic C films. It is important to note that the in-plane director field in the present case is nonpolar, i.e. it can support \( \pi \) disclination points, several of which are evident in Figure 13, whereas the polar smectic field has topological defects of even multiples of \( \pi \) only.

2.2.4 - Study of \((+1, -1)\) Topological Defect Pair Annihilation in 3 Layer Films

We studied the attraction and annihilation of pairs of opposite strength topological defects in two layer thick freely suspended smectic C films. These are generated in quenches (from the smectic C to the smectic A and back), by collapse of a free film bubble from spherical to planar shape, which generates many defects. The defects annihilate in pairs until there are only two left. These last two are observed via DRLM. Figure 14 shows a typical pair of annihilating defects. For each such event, the separation, \( r \), vs. time is measured and data for a series of events is used to find the average collapse rate \( dr/dt \) as a function of \( r \). The results are surprising. Current theoretical models of the annihilation process assume that the defects undergo diffusive Brownian motion while attracting via a two dimensional Coulomb \( (1/r) \) force. This predicts that at a given separation the rate of approach, \( dr/dt \), should behave as \( 1/r \) so that \( r(dr/dt) = \) constant. However, our experiments show a clearly different behavior, with \( dr/dt \sim (1/r)\log(r) \). This observation indicates that the current theoretical understanding of the fluctuation behavior of topological defects is flawed, a problem of fundamental interest with wide ranging
implications in statistical physics (for example, in describing the physics of vortex motion in superconductors and the kinetics of the early universe). During this past Grant period we developed an IDL program that extracts defect position from video records. This will greatly enhance the efficiency of our data collection in further exploring this effect.

2.2.4 - Computer Simulation

The phase behavior of the tilted smectic phases observed in freely suspended films has made it clear that many surprises are in store in the study of the interlayer organization of smectics. Thus, the recent experiments of Huang and co-workers elucidating the three, four, and higher layer periodic structures in MHPBOBC homologs [11], our collaborative discovery of non-coplanar tilts in few layer films of a high polarization smectic C [P16], our observation of an anticlinic minimum in the interlayer energy in synclinic DOBAMBC [P24], the finding of anticlinic surface layer ordering in the tilted surface of smectic A films [P24], and the amazing polymorphism of the bent-core phases made possible by changes of clinicity and polarity [8,17] all represent features unexpected, or at best poorly understood, on the basis of current understanding of layer interactions in smectics. Thus such layer interactions have been a focus of the simulation program, an approach that is well suited to developing new understanding of these interactions which appear to depend in delicate ways on the details of the layer interfaces. The following projects have been carried out during the last Grant period:

**Atomic Simulation of Anticlinic Ordering in MHPBOBC** - One of the more interesting questions in the physics of tilted smectics is the origin of the anticlinic ordering in the classic antiferroelectric material MHPBOBC (Figures 15, 16 [12]) and its homologs and derivatives that share the methylheptyloxy carbonyl (MHOC) tail, for example MHOBOW in Figure 4. In

![Figure 16: Bulk atomistic simulation of MHPBOC in the antiferroelectric phase showing its anticlinic molecular tilt in adjacent layers. This simulation shows that the MHOC tail lies generally parallel to the layers (see Figure 15), leading to reduced out-of-layer fluctuations and anticlinic, rather than synclinic, ordering.](image)

**Figure 17:** Helmholtz free energy as a function of the cosine of the tilt angle for synclinic (black) and anticlinic (red) States of the hard spherocylinder system. Also shown is the free energy as a function of tilt angle (inset) for both states, and several representative configurations of the system. This energy difference favoring the synclinic state with increasing tilt is explicitly due to out-of-layer fluctuations. If they are suppressed by an additional potential, the synclinic and anticlinic curves become essentially identical.

![Figure 17: Helmholtz free energy as a function of the cosine of the tilt angle for synclinic (black) and anticlinic (red) States of the hard spherocylinder system. Also shown is the free energy as a function of tilt angle (inset) for both states, and several representative configurations of the system. This energy difference favoring the synclinic state with increasing tilt is explicitly due to out-of-layer fluctuations. If they are suppressed by an additional potential, the synclinic and anticlinic curves become essentially identical.](image)
order to address this question and provide a basis for design of other bent core systems we carried out simulations of MHPOBC directed toward understanding the organization of the tails in anticlinic phases. Figure 16 shows a typical configuration in the antiferroelectric phase. Although not evident from this picture, statistical analysis (Figure 15) shows that the MHOC tail is bent by ~90° so that it is nearly parallel to the layers. This orientation of the tail makes it energetically more costly for molecules to fluctuate out of a layer and penetrate a neighboring layer, an event that favors synclinic ordering. Thus we expect that of out-of-layer fluctuations would favor synclinic ordering, which we explicitly demonstrated in the hard spherocylinder model, discussed next.

**Demonstration that Out-of-Layer Fluctuations Favor Synclinic Ordering** - The overwhelming majority of tilted smectic liquid crystals exhibit synclinic (SmC) ordering (a uniform tilt direction in all smectic layers) rather than anticlinic (SmCA) ordering (a tilt direction that alternates from layer to layer). We have recently proposed that polar molecular-scale fluctuations of the interfacial between smectic layers provide a general entropic mechanism favoring synclinic ordering, and have presented evidence from simulations of the hard spherocylinder system in support of this hypothesis [Plo]. We find that the entropy of the synclinic state of \( L/D = 5 \) spherocylinders is higher than the entropy of the anticlinic state for large tilt angles, and show that this entropy difference can be directly traced to molecular-scale fluctuations of the layer interface (Figure 17). This entropic mechanism may be suppressed in materials exhibiting anticlinic ordering due to a bent molecular conformational preference that quenches interface fluctuations.

**Simulations of Interface Clinicity and Ordering in Bent-Core Systems** - Bent-core molecules may effectively be thought of as bilayer smectic systems in which every odd layer interface is chemically fixed to be a certain angle. The polymorphism of the SmCP class of smectic liquid crystals (Figure 6) arises from what happens at the even interfaces. We have begun to explore layer interfaces in bent-core systems by carrying out Monte Carlo simulations of a minimal hard spherocylinder dimer model to investigate the role of excluded volume interactions in determining the phase behavior of bent-core materials and to probe the molecular origins of polar and chiral symmetry breaking. We show in Figure 18 the phase diagram of hard spherocylinder dimers of length/diameter ratio 5 as a function of pressure or density and dimer opening angle \( \psi \). With decreasing \( \psi \), a transition from a nonpolar to a polar smectic A phase is observed near \( \psi = 167° \), and the nematic phase becomes thermodynamically unstable for \( \psi < 135° \). Free energy calculations indicate that the antipolar smectic A (SmAP_A) phase is more stable than the polar smectic A phase (SmAP_T). No chiral smectic or biaxial nematic phases were found.

Recent experiments indicate that doping low concentrations of bent-core molecules into calamitic smectic solvents can induce anticlinic and biaxial smectic phases [13]. We have carried out Monte Carlo simulations of mixtures of rodlike molecules (hard spherocylinders with length to breadth ratio \( L_{rod}/D = 5 \)) and bow-shaped molecules (hard spherocylinder dimers with length to breadth ratio \( L_{bow}/D = 5 \) or 2.5 and opening angle \( \psi \)). We find that a low concentration (3%) of \( L_{bow}/D = 5 \) dimers induces anticlinic (SmC_A) ordering in an untitled smectic (SmA) phase for \( 100° \leq \psi < 150° \) (see Figure 19). For \( L_{bow}/D = 2.5 \), no tilted phases are induced. However, with decreasing \( \psi \) we observe a sharp transition from intralamellar nanophase segregation (bow-shaped molecules segregated within smectic layers) to interlamellar nanophase segregation (bow-shaped molecules concentrated between smectic layers) near \( \psi = 150° \).
3.1 - Publications


3.2 - Presentations


"LONGITUDINAL POLARIZATION IN FREELY-SUSPENDED LIQUID CRYSTAL FILMS," J.E. Maclennan, D.R. Link, and N.A. Clark, 7th International Conference on Ferroelectric Liquid Crystals, Darmstadt, Germany (1999).

"MOLECULAR ORIGINS OF ANTICLINIC ORDERING IN TILTED SMECTICS," M.A. Glaser, and N.A. Clark, 7th International Conference on Ferroelectric Liquid Crystals, Darmstadt, Germany (1999).


3.3 - Invited conference presentations


3.4 - Ph.D. Theses

[T1] "EFFECTS OF SPONTANEOUS POLARIZATION ON THE STRUCTURE AND DYNAMIC PROPERTIES OF FERROELECTRIC LIQUID CRYSTALS," David Coleman, Department of Physics, University of Colorado (2002).
4 - REFERENCES CITED