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 quasi long range translational order within the layers [1]. The inherent fluid-layer structure and low vapor pressure of smectic liquid crystals enable 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 condensed phase 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 liquid crystal 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 profile [6] and have been used to show that the interlayer interactions in antiferroelectric tilted smectics do not extend significantly beyond nearest neighbors [7].

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 ap-
plied fields and surfaces. Effects arising from weak ordering are significantly enhanced in ultrathin free films and filaments wherein the intermolecular coupling is effectively 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 position of the study of freely suspended liquid crystal structures as one of most exciting and fruitful areas of complex fluid physics. In addition, several potentially interesting microgravity free film experiments have been identified.

2. - Work Carried Out under NASA Grant NAG3-1846

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 NAG3-1846 are listed in Section 3 and indicated by a Publication Number [P#] when cited. Results are reported in the following project areas, which were outlined in the NAG3-1846 proposal:

- Generation and exploration of freely suspended liquid crystal bubbles.
- Exploration of the role of curvature in determination of film structure.
- Study of the in-plane layer structure of freely suspended liquid crystal films.
- Molecular dynamics computer simulation of smectic film layer structure.

2.1 - HIGHLIGHTS OF WORK CARRIED OUT UNDER NASA GRANT NAG3-1846

Bent core (banana-shaped) molecules: Pasteur's experiment in a fluid
- discovery of the spontaneous formation of macroscopic domains of a chiral phase in a fluid smectic of achiral banana-shaped molecules.
- observation of chiral domains in two- and three-layer films of achiral banana-shaped molecules.
- demonstration that the chiral phase ground state is antiferroelectric.

Generation and manipulation of smectic liquid crystal bubbles
- development of techniques for inflating and holding smectic liquid crystal bubbles.
- measurement of the gas permeability of few layer thick liquid crystal films.
- generation of dense island arrays on few layer thick films.

Bent core (banana-shaped) molecules: Discovery of freely suspended smectic filaments
- nested cylinder layer geometry.
- observation of a compression-induced buckling instability to a helical structure.

Study of (+1, -1) topological pair annihilation and defect-island interaction
- the simplest liquid crystal defect dynamical process.
- apparent defect mobility decreases with separation, whereas theory predicts an increase.
- analysis of thermal fluctuation effects.

Determination of in-plane polarization in tilted smectic films
- first unambiguous evidence for single layer alternation of polarization direction in antiferroelectric smectics.
- first observation of fracture of the orientation field in a liquid crystal via coupling of surface polarization to in-plane electric field.
- observation of ferroelectric ordering of the surface polarization of the tilted surface layers of an un-tilted (smectic A) film.

Study of tilted smectic films in a rotating in-plane electric field
- winding of orientational solitons.
- theoretical modeling of soliton velocity.
- modulation of soliton width by orientational elastic anisotropy.
- relaxation of ring patterns to determine orientational diffusion coefficient.

Atomistic molecular dynamics simulation of smectic structure
- development of a state-of-the-art force field for liquid crystal simulation.
- simulation of the layer structure of untitled (smectic A) and tilted (smectic C) phases.
- study of nanosegregation in smectic layered solvents, including discovery of photo-induced nanophase segregation.
We have made a major discovery in condensed matter science, finding macroscopic chiral domains in a fluid phase of achiral molecules. Our observation follows a line of study of the relationship between macroscopic and molecular chirality that was begun by Pasteur in 1848. He found that crystals of a molecularly chiral salt of "racemic acid" existed in left and right handed forms - the left and right handed molecules spontaneously segregating into macroscopically left and right-handed chiral crystals respectively. Subsequently there have been many observations of coexisting domains of opposite handedness crystallized from molecules which are chiral as well as achiral in isotropic solution (achiral molecules). In the latter cases the molecules adopt chiral conformations which pack more effectively than achiral conformations. However, in the 150 years since Pasteur, all observations of such spontaneous chiral segregation have been made in crystal phases. Ours is the first such observation in a fluid. These results appeared in Science in December, 1997 and were the subject of a Science "Research News" article, shown in the right, in March, 1998. The molecules which form the SmCP_A, first synthesized in Japan in 1994 by Matsunaga, are "bow" or "banana"-shaped as a result of their bent core. Their highest temperature smectic phase was first identified as a SmC, but then, by the Tokyo Tech (Takezoe) group in 1996, as SmA with the possibility of polar ordering. Using samples of the Matsunaga and Takezoe compounds, we were able to show that the phase was indeed tilted (SmC). Moreover, our experiments, in particular those on freely suspended films, revealed an amazing feature of this phase missed in the earlier work: the spontaneous breaking of achiral symmetry. This achiral symmetry breaking results from the combined effect of the two distinct intralayer broken symmetries shown in Figure 1: polar ordering of the molecular bows (with their arrows pointing in a particular direction, clearly a consequence of the bent shape), and molecular tilt (rotation about the arrows). This discovery indicates that a rich variety of novel structures and phases will be available from these more complex molecular shapes.

Generation and manipulation of smectic liquid crystal bubbles

The inherent fluid-layer structure and low vapor pressure of smectic liquid crystals enable 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. Our initial studies were complicated by a geometry requiring very slow filling during the critical period when the bubble reaches its minimum radius of curvature as a hemispherical cap at the end of the hypodermic needle. Analysis of this problem indicated that we needed to minimize the gas volume behind the bubble and with this change we were able to generate smec-
Island Pore

Figure 2: Schematic film profiles for islands and pores. The change in layer number is achieved by dislocations.

By filling the bubble with a permeant gas, such as helium, and monitoring the time rate of change of bubble radius. The gas permeability of films which are only a few molecular layers thick and its dependence on film thickness have never been measured but are fundamental properties. The helium permeability of liquid crystal bubbles was measured by filling them with helium and observing the decrease of radius as the helium diffuses out through the film. This permeation is fairly spectacular: a two layer thick, 2 centimeter diameter bubble filled with 1 atm helium and surrounded by air will deflate by the leakage of helium through the film in about 10 seconds. The radius vs. time data was employed to determine helium permeability, which is about 1000 He atoms/sec/LC molecule for a two layer film. One of the techniques was to detach bubbles from the needle and levitate them. However, gas rapidly leaks via permeation out of few layer thick bubbles, reducing their radius with time. Thus experiments were carried out with the bubbles still attached to the needle.

A second class of experiments performed focused on the behavior of island arrays on bubbles. Islands are pancake-like stacks of extra layers on an otherwise uniform thickness film, as shown in Figure 3. Islands are of interest as statistical mechanical and dynamical objects because of their very small mass ($10^{12}$ gm for a 10 µm diameter island), and coupling to the 2 dimensional fluid film. Swirling the bubble with an air jet generates a two-dimensional foam of islands which is quite stable against island aggregation, which takes place very slowly. The islands respond in a polar way to applied electric field, indicating that they are either charged or significantly more polarizable than the surrounding film. In a microgravity environment the Perrin length, $k_BT/mg$ 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. Interactions between islands can be controlled by charging the sphere.

Bent core (banana-shaped) molecules: Discovery of freely suspended smectic filaments

We have for many years endeavored to make filaments of smectic liquid crystals having the nested cylindrical layer structure shown in Figure 4, a geometry that would enable a variety of experiments on smectics that have highly curved, defect-free layers. These efforts failed until recent experiments

tic bubble films very easily. Two distinct experiments were carried out: measurement of gas permeability of the liquid film; and formation of arrays of smectic islands.

Freely suspended liquid crystal films offer a truly unique opportunity for the study of the permeability of ultrathin fluid films. The tethered bubble (or tube) appears to be an ideal geometry for studying the gas permeability of liquid crystal films by filling the bubble with a permeant gas, such as helium, and monitoring the time rate of change of bubble radius. The gas permeability of films which are only a few molecular layers thick and its dependence on film thickness have never been measured but are fundamental properties. The helium permeability of liquid crystal bubbles was measured by filling them with helium and observing the decrease of radius as the helium diffuses out through the film. This permeation is fairly spectacular: a two layer thick, 2 centimeter diameter bubble filled with 1 atm helium and surrounded by air will deflate by the leakage of helium through the film in about 10 seconds. The radius vs. time data was employed to determine helium permeability, which is about 1000 He atoms/sec/LC molecule for a two layer film. One of the techniques was to detach bubbles from the needle and levitate them. However, gas rapidly leaks via permeation out of few layer thick bubbles, reducing their radius with time. Thus experiments were carried out with the bubbles still attached to the needle.

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Figure 4: Freely suspended filaments in a transverse electric field. Filaments are observed in reflected light with crossed polarizers, the optic axis being parallel to the axis of the filaments. In some filaments (in this case the top filament) a $\pi$ reorientation of the optic axis is trapped as is indicated by the arrow in the microphotographs. This reorientation moves at a constant velocity along the length of the filament when an electric field is applied normal to the filament, moving from one end of the filament to the other with one sign of field and vice-versa. The diameter of the filament is 13 µm while its length is over 2 mm.
done with films of a chiral homolog [P9] of the bent-core molecule in Figure 1. Attempts to make films by the usual spreading technique yielded freely suspended filaments up to several millimeters long and 2-20 \( \mu \text{m} \) in diameter. These filaments were locally uniform in width, with the width changing via discrete jumps. Some filaments were lath-shaped and could be wound into a helix by pulling the filament between a pin and cup and rotating the pin. The filament responded to an electric field applied normal to its axis. Such filaments offer exciting possibilities for study of the spontaneously chiral phases formed by bent-core molecules. They are highly ordered single domain preparations, making them ideal for high resolution x-ray study of the chiral phase structure.

**Study of (+1, -1) topological defect pair annihilation in 2 and 3 layer films**

We have 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 reflected light microscopy. Figure 5a 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 \( \frac{dr}{dt} \) as a function of \( r \). These data are shown in Figure 5b. 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 \( \frac{1}{r} \) force. This predicts that at a given separation the rate of approach, \( \frac{dr}{dt} \), should behave as \( \frac{1}{r} \) and \( r\frac{dr}{dt} = \text{constant} \). However our experiments show a clearly different behavior, with \( \frac{dr}{dt} \sim \frac{1}{r}\log(r) \). 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).

**Determination of in-plane polarization in tilted smectic films [P1, P4, P5, P6, P9, P12, P15]**

We have obtained a very beautiful result in freely suspended films of the antiferroelectric liquid crystal material MHPOBC, obtaining the first unambiguous evidence for longitudinal ferroelectricity in a liquid crystal and, at the same time, developing a technique for distinguishing ferroelectric from antiferroelectric ground states in tilted smectic phases. Figure 6 sketches the experiment, showing a
portion of a freely suspended film, incident and reflected light to probe the orientation of the molecular tilt direction in the film plane, electrodes for applying an electric field in the film plane, and sections of the film where it is two and three layers thick. Where the film has an even number of layers the surface induced polarizations give a net polarization in the direction of the molecular tilt, and the single layer transverse polarizations due to chirality cancel. As a result, in an applied electric field the tilt direction aligns parallel to the field. However, where the film is an odd number of layers thick the surface polarizations cancel but the transverse polarizations do not, adding to give the net polarization of a single layer. Figure 6 shows the molecules and the longitudinal and transverse polarizations in the two cases. Figure 7 shows the orientation of the resulting polarization and tilt direction in an applied field, with the tilt direction, indicated by a "T", normal to the polarization, indicated by an "→", for an odd number of layers, and parallel to the polarization for an even number of layers. With appropriate optics the two tilt orientations can be visualized as black and bright in reflected light (Figure 7a). The image in Figure 7b shows a reflected light micrograph of such a film in an applied field. This discovery will enable the first measurement of longitudinal polarization and a detailed comparison of longitudinal and transverse liquid crystal polarizations.

We have used this technique in a variety of ways, establishing that the ground state of the bent core phases is antiferroelectric [P9,P12], and showing that the so-called "thresholdless antiferroelectric" tilted smectic phase is actually a ferroelectric smectic C [P4,P5].

This work has also been extended to exploit electric field coupling to ferroelectric surface ordering in achiral freely suspended films [P1,P6]. In a smectic C film the molecules are tilted, yielding ferroelectric order at the surface. The uniform tilt through the film yields opposite polarization on the two surfaces. With the application of an electric field these polarizations flip to be along the field, some regions going clockwise and others counterclockwise. Such opposite rotation produces line defects where the polarization rotates rapidly through π radians (π-walls). The π-walls form an interesting pattern on the surface of the film. There are two sets of weakly interacting walls, one set on each surface, shown in Figure 8. This interesting observation will enable...
us to measure the surface polarization and elastic coefficients. This line of research has yielded two novel liquid crystal phenomena. By applying a sufficiently large electric field we can apply a torque to the orientation field that is sufficiently large to fracture it [P1], yielding, in a smectic C film [where the molecule tilts are synclinic (in the same direction) in adjacent layers], a single interface where the molecules tilt in opposite directions, as illustrated in Figure 9. This interface is metastable, persisting for several minutes once the field is removed, showing that there is a metastable minimum at the anticlinic orientation in the interlayer orientational potential energy.

Additionally, we have found that the tilt orientations on the film surface become anticlinic at high temperatures where the film interior is smectic A (molecules not tilted) [P6]. Thus, the tilted surface layers on the two sides of an untilted film interact to favor opposite orientation. A variety of possible explanations for this effect have been considered, including van der Waals interactions and fluctuation confinement, but at present it is a complete mystery.

**Study of tilted smectic films in a rotating in-plane electric field [P2]**

The combination of fluidity and local anisotropy which characterizes ferroelectric smectic C* films is effectively probed by application of an in-plane electric field. Particularly interesting is the response when the field rotates in the film plane. In this case the tilt direction reorients along with the field in the film center but is pinned with fixed orientation at the film edge, necessitating the formation of an orientational soliton with each $2\pi$ rotation of the field. The solitons reflect the film shape, forming rings on a circular film. The characteristic spacing of the soliton depends on the applied field strength, as shown in Figure 10. The solitons move toward the film center with a velocity that increases with applied field strength.

With the field removed the ring patterns provide a useful probe of the liquid crystal elastic anisotropy, the rings being wider in regions where the deformation having the larger elastic constant is dominant (Figure 11). The orientational diffusion constant can be measured by observation of the relaxation of the ring pattern once the field is set to zero. See Figure 12.

**Figure 10:** Soliton rings formed by a rotating electric field. As the field rotates each soliton moves toward the film center with a velocity that varies with $E$ as $1/E^2$. From [P2].

**Figure 11:** A fully developed ring pattern with the field removed involves both splay and bend of the orientation field. The splay elastic constant is larger, making the rings wider in the splay regions. In films with large polarization this situation is reversed, with the bend regions being broader. From [P2].
The computational component of this research focuses on improving our understanding of liquid crystal nanophysics via direct atomistic simulation of molecular organization in smectics, in particular the layering in smectics and the behavior of solutes in smectic films. During the past several years we have developed a variety of effective computational tools for the simulation of molecularly realistic liquid crystal models, and have begun to apply them to understanding smectic structure [P7]. These tools include a hybrid ab initio/empirical force field specifically designed for modeling liquid crystalline materials and special simulation techniques (multiple-timestep molecular dynamics, hybrid Monte Carlo, particle-mesh Ewald method) enabling efficient configuration-space and conformational sampling. A highly accurate force field is required because the self-organization of soft materials such as LCs is governed by the interplay of a variety of subtle energetic and entropic effects, which must be adequately quantified.

These methods have been applied to the study of solute distribution in a smectic phase, under conditions where the shape of the solute molecules, in this case the azo dye 7AB, can be changed from linear (trans) to bent (cis) optically. We find a distinctive photoinduced nanosegregation, the 7AB intercalating between and expanding the layers upon trans to cis isomerization. Quantitative agreement with measured layer expansion indicates that the simulation accuracy is adequate for a variety of films-related problems.

Figure 12: (left) Schematic of the nanometer scale organization of the azo dye 7AB in a smectic solvent. (right) Mass density profiles along the layer normal for 8CB (open circles) for a trans-7AB/8CB mixture (a) and for a cis 7AB/8CB mixture (b). In the trans state the TAB locates preferentially in the smectic layers, whereas in the cis state it nanosegregates between the layers. The calculated layer expansion which results matches that found in experiments. From [P7].
3. - Publications and Presentations Resulting from Research Supported by NASA Grant NAG3-1846

Publications


Presentations


[C12] "Longitudinal and transverse ferro-electricity in freely suspended films of an antiferroelectric liquid crystal," D.R. Link, J.E. Maclennan, and N.A. Clark, Sixth International Conference on Ferroelectric Liquid Crystals, Brest, France (1997).


Invited conference presentations


Ph.D. theses

REFERENCES CITED