Structure and Rheology of Some Bent Core Liquid Crystals

A dissertation submitted
to Kent State University in partial
fulfillment of the requirements for the
Degree of Doctor of Philosophy

by

Christopher Bailey

August 2008
ACKNOWLEDGEMENTS

During my time at Kent State University, I have been fortunate to have received a great deal of support from several people, and I would like to recognize them for their role in the completion of this dissertation. First of all, I would like to recognize my wife, Shereen Bailey, for her love and understanding when I had to sacrifice time with my family to work. I would also like to mention my two beautiful children, Allison and Ethan, who are the loves of my life and brighten my days. I would like to thank the friends that I have had the pleasure of knowing since I came to KSU, in particular John Harden, who has become like a brother to me and I will greatly miss him.

Besides my family and friends, there are several people who made an academic contribution to this dissertation, some of which I will speak about individually. I would like to thank Dr. Peter Palffy-Muhoray for being the person who helped me come to this program and was my advisor for the first two years of my program. It is his passion for physics that has helped instill a similar passion for soft matter physics in me. I would like to acknowledge several professors who have aided my research via discussions and guidance. These professors are; Dr. Eugene Gartland Jr. and Dr. Jonathon Selinger for taking the time to discuss numerical methods, Dr. Ralf Stannarius for his kindness and insightfulness as an advisor when I visited him in Magdeburg, Germany, and Dr. James Gleeson for allowing us to borrow equipment and discussions of our results. I would also like to thank the support staff at the LCI for their help on several areas related to my work. Special thanks goes to Merrill Groom for helping with equipment design and
construction, Liou Qiu and Dr. Oleg Lavrentovich for helping take SEM images, Doug Bryant for helping design and construct liquid crystal cells, Julie Kim and Dr. Quan Li for chemical synthesis. I would like to thank Lynn Fagan, Betty Hilgert, Brenda Decker, Dawn Miller, and Janet Cash for all of their work in keeping the LCI running. Finally, I would like to thank Dr. Antal Jakli for being an excellent advisor to me these last three years. Under his guidance, I have learned a great deal and have accomplished much. I appreciate his kindness and patience with me as we have worked on this project, and have enjoyed his enthusiastic and imaginative approach to science.

I would like to finish by acknowledging the financial support which allowed me to work on this project. In particular I should mention the National Science Foundation (NSF FRG DMS-0456221) and (NSF DMS-0456221), Samsung (Samsung Scholarship), and Kent State University (University Fellowship).
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS .................................................................................................................. iii
LIST OF FIGURES .......................................................................................................................... x
LIST OF TABLES .......................................................................................................................... xxvii

CHAPTER

1 INTRODUCTION ............................................................................................................................... 1
  1.1 A BRIEF HISTORY OF LIQUID CRYSTALS ........................................................................ 1
  1.2 LIQUID CRYSTAL ORDER AND PHASE DESCRIPTIONS .............................................. 2
  1.3 LIQUID CRYSTAL ELASTICITY ...................................................................................... 7
  1.4 EFFECTS OF FRUSTRATIONS ON THE BASIC LIQUID CRYSTAL PHASES ................. 8
  1.5 BENT CORE LIQUID CRYSTALS .................................................................................. 11
REFERENCES ............................................................................................................................. 25

2 THE ROLE OF MOLECULAR SHAPE ON BENT CORE LIQUID CRYSTAL PHASES ........ 31
  2.1 INTRODUCTION .............................................................................................................. 31
  2.2 MOLECULAR MODELING .............................................................................................. 33
  2.3 MOLECULAR MODEL .................................................................................................... 36
  2.4 BIAXIAL LAYER COMPRESSIONS AND ELECTRIC SELF INTERACTIONS .................. 41
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 INTRODUCTION</td>
<td>96</td>
</tr>
<tr>
<td>4.2 MATERIALS</td>
<td>97</td>
</tr>
<tr>
<td>4.3 CHARACTERIZATION OF BENT CORE</td>
<td>97</td>
</tr>
<tr>
<td>4.3.1 EXPERIMENTAL SETUP</td>
<td>100</td>
</tr>
<tr>
<td>4.3.2 RESULTS AND DISCUSSION</td>
<td>100</td>
</tr>
<tr>
<td>4.4 CANTILEVER MEASUREMENTS</td>
<td>107</td>
</tr>
<tr>
<td>4.4.1 EXPERIMENTAL SETUP</td>
<td>107</td>
</tr>
<tr>
<td>4.4.2 RESULTS AND DISCUSSION</td>
<td>107</td>
</tr>
<tr>
<td>4.5 FILAMENT BUNDLE INTERACTIONS AND PROPERTIES</td>
<td>111</td>
</tr>
<tr>
<td>4.5.1 ADHESION FORCES BETWEEN STATIC FILAMENTS</td>
<td>113</td>
</tr>
<tr>
<td>4.5.2 FLOW VISCOSITY BETWEEN FILAMENTS IN CONTACT</td>
<td>115</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>117</td>
</tr>
<tr>
<td>5 DYNAMICS AND ELASTICITY OF BENT CORE FILAMENT BUNDLES</td>
<td>119</td>
</tr>
<tr>
<td>5.1 INTRODUCTION</td>
<td>119</td>
</tr>
<tr>
<td>5.2 MATERIALS</td>
<td>120</td>
</tr>
<tr>
<td>5.3 STATIC BENT CORE FILAMENTS</td>
<td>122</td>
</tr>
<tr>
<td>5.3.1 ANALYSIS AND RESULTS</td>
<td>125</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>5.4</td>
<td>DRIVEN HARMONIC OSCILLATIONS</td>
</tr>
<tr>
<td></td>
<td>IN BENT CORE FILAMENT BUNDLES</td>
</tr>
<tr>
<td>5.4.1</td>
<td>MECHANICAL (SOUND) OSCILLATOR</td>
</tr>
<tr>
<td></td>
<td>EQUATIONS OF MOTION</td>
</tr>
<tr>
<td>5.4.2</td>
<td>MECHANICAL (SOUND) OSCILLATOR</td>
</tr>
<tr>
<td></td>
<td>ANALYSIS AND RESULTS</td>
</tr>
<tr>
<td>5.4.3</td>
<td>ELECTRIC FIELD INTERACTIONS</td>
</tr>
<tr>
<td></td>
<td>WITH BENT CORE FILAMENTS</td>
</tr>
<tr>
<td>5.4.4</td>
<td>ELECTRIC FIELD RESONANCE</td>
</tr>
<tr>
<td></td>
<td>RESULTS AND DISCUSSION</td>
</tr>
<tr>
<td>5.5</td>
<td>DYNAMICS OF FILAMENT RECOIL</td>
</tr>
<tr>
<td>5.5.1</td>
<td>THEORY OF RECOILING FLUID FILAMENTS</td>
</tr>
<tr>
<td>5.5.2</td>
<td>EXPERIMENTAL RESULTS</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
</tr>
<tr>
<td>6</td>
<td>FLOW BEHAVIOR OF BENT CORE LIQUID CRYSTALS</td>
</tr>
<tr>
<td>6.1</td>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>6.2</td>
<td>EXPERIMENTS AND MATERIALS</td>
</tr>
<tr>
<td>6.3</td>
<td>NEMATOCEN RHEOLOGY</td>
</tr>
<tr>
<td>6.4</td>
<td>SMECTOCEN RHEOLOGY</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
</tr>
</tbody>
</table>
APPENDIX

A  NANOLITER RHEOMETRY: TECHNIQUES AND CALIBRATION........ 218
   A.1  INTRODUCTION................................................................. 218
   A.2  DEVICE DESIGN AND GEOMETRY........................................ 220
   A.3  MEASUREMENT OF THE AMPLITUDE OF VIBRATION.............. 221
   A.4  LCR TECHNIQUE............................................................. 224
   A.5  LOCK-IN TECHNIQUE....................................................... 228
   A.6  DETERMINATION OF THE EXPERIMENTAL PARAMETERS... 233
      A.6.1  PIEZOELECTRIC TRANSDUCER CALIBRATION............. 234
      A.6.2  DETERMINATION OF $\phi_0$........................................... 236
      A.6.3  DETERMINATION OF $m_{\text{eff}}$ AND $\phi_1$............... 236
      A.6.4  VISCOSITY COMPARISONS OF 5CB AND 8CB......... 238
   A.7  OPTICAL MEASUREMENT TECHNIQUES.......................... 242

REFERENCES............................................................................ 244
LIST OF FIGURES

1-1  The molecular structures of a) 4-pentyl-4’-cyanobiphenyl (5CB) and b) (4-butylphenyl)-(4-methyl-benzylidene)-amine (MBBA) which are classic examples of rod-like LC mesogens.  c) These materials are typically modeled as a hard cylinder with D_{2\infty} symmetry...................................................... 3

1-2  Examples of the a) Nematic, the b) Smectic (SmA), and the c) Columnar phases (Col_{hd}).  Also labeled are the director \hat{n} and the respective positional order distances d for the smectic and columnar phases........................................ 5

1-3  a) An example of a chiral molecule whose mirror image cannot be superimposed on the original, and the effects of chirality on b) the Nematic (N*) and c) the SmC (SmC*) phase.  Both phases observe a spontaneous helical deformation of the director either perpendicular to the director (N*) or about the cone angle (SmC*).  The effect of chirality on the SmC* phase also induces a spontaneous polarization represented by the arrow which reside parallel to the layers (solid lines).  The bars stuck to the end of the mesogens in the SmC* phase allows one to determine which of the ends of the mesogens are closer to the observer.............................. 10

1-4  Sketch of hypothetical nematic phase of bent-core mesogens......................... 13

1-5  Schematic structure of the ferroelectric SmAPS and the antiferroelectric SmAP_{\lambda} phases.......................................................... 15
1-6 The possible single tilted bent-core smectic structures. Top row: Illustration of the fluid in plane order of the layer polarization, and three dimensional explanation of tilt. Middle row: two dimensional illustration of the four possible situations when only the molecular plane is tilted with respect to the layer normal; Bottom row: two-dimensional illustration of the four possible situations when only the long axis is tilted (leaned) with respect to the layer normal.

1-7 a) The possible double-tilted bent-core smectic structures. Top row: Illustration of the fluid in plane orders of the layer polarization (either uniform or modulated), and three dimensional explanations of tilt. Middle and bottom rows: two dimensional illustrations of the eight possible situations; (b) Graphical explanation of the SmCLP structures in term of two rotation angles \( \theta \) and \( \alpha \).

1-8 Schematic representation of the intercalated layer structures and the nano-segregated version which has the same symmetry as a columnar phase.

2-1 Examples of typical bent-core mesogenic materials with their phase sequences, chemical, steric, and electrostatic structures for the a) B\(_2\), the b) B\(_7'\), and the c) B\(_7\) phases, as obtained by ChemOffice\textsuperscript{®} software package. The extra circles in their model structures represent the unit which frustrates close packing, and the dashed triangle shows the effective region which cannot be occupied by other molecules. d) Also shown is how differences in bump location and size can affect the frustrated structure and their respective phase behavior.
2-2 The geometries of the frustrated packing model. (a): The molecular orientation: \( \hat{n} \) is the director along the long axis, \( \hat{p} \) is the layer polarization axis and \( \hat{k} \) is the layer normal; \( \hat{n} \) tilts in \((\hat{x},\hat{k})\) plane by angle \( \theta \), and the molecular plane makes an angle \( \alpha \) with respect to the \( \hat{y} \) axis. (b): The model molecular dimensions in the \((\hat{n},\hat{p})\) and \((\hat{p},\hat{n})\) planes. (c): Illustration of the excluded volumes (grey areas) for bend and splay deformations. (d) The model of the in-layer polarization splay; (e) The model of the fibers made of B7 and B7' materials illustrating the effects of layer bending………………………………………………………………………………………… 37

2-3 A comparison of the layer thickness between two states where the polarization angle \( \alpha \) differ by \( \pi/2 \). The director tilt in both cases has a value of \( \pi/4 \) and the layer change \( \delta \) is entirely due to the shape biaxiality. We have labeled the primary dimension of the bent core molecule as \( L, d_1, \) and \( d_2 \)…………………………………….. 41

2-4 Suggested structural phase diagram of the B7 and B7' phases as a function of the spontaneous polarization and the polarization angle. Graphical representations of the possible layered structures are shown within the ovals along with their possible locations on the diagram. The directions of increasing \( B_{\text{eff}}, \) temperature, fiber stability, and fiber radius are also included………………………………………….. 48

3-1 The filament geometry used for stability analysis due to longitudinal fluctuations. We have defined several parameters important to analysis, such as the undeformed radius \( r_o \), the deformed radius \( r \), and the perturbation wavelength \( \lambda \)……………….. 56
3-2 Illustrations of the molecular orientation of the molecular long axis $\hat{n}$ and the polarization direction $\hat{p}$ with respect to the smectic layer normal $\hat{k}$. We show the polarization configurations of the SmAP, SmCP, SmCG, and SmLP and their corresponding layer structure.

3-3 The filament geometry used in our stability analysis. The filament has length L, outer radius R, and inner cutoff radius $r_c$, where the smectic properties are assumed to break down. This model shows the layered structure consisting of concentric smectic layers which are essential for filament stability.

3-4 Numerical results of the polarization dependence of filament stability for $c'$ only, $c''$ only, and C. The $c'$ dominates at low polarizations and at large polarizations the $c''$ dominates, however at intermediate polarizations the combination of effects is greater than the sum of its parts.

3-5 Phase diagram which compares the effects of $\lambda_1 = c' \sin \theta_o / \sigma$ to $\lambda_2 = c'' P_o \sin \theta_o / \sigma$ on the stable filament radius, where a) only $P_o$ is varied or b) only $c''$ is varied in the calculation of $\lambda_2$. We also show the stability threshold (dashed line) which occurs at $\lambda_1 + \lambda_2 = 1$.

3-6 The effects of tilt angle on the stable filament radius for various polarizations, $P_o = 10^{-4} \text{C/m}^2$, $P_o = 10^{-3} \text{C/m}^2$, $P_o = 10^{-2} \text{C/m}^2$, and $P_o = 10^{-1} \text{C/m}^2$, when $\alpha_o = 0$. We can see that for all polarizations in the SmAP phase ($\theta_o = 0$) there is no stable filament with $r > r_c$. However there is a definite threshold behavior which is strongly dependent on the polarization. Furthermore, we see that SmCP materials...
with larger polarizations \( (P_o \approx 10^{-2} \text{C/m}^2) \) can form stable filaments, but their radius is below the (MPR) Modified Plateau-Rayleigh instability threshold (solid line), \( R_m \approx 0.1 \mu \text{m} \), which would be unstable to longitudinal fluctuations.

3-7 a) Several plots of stable filament radius versus the value of \( \alpha_o \) at various polarization values, \( P_o = 10^4 \text{C/m}^2 \) (□), \( P_o = 10^3 \text{C/m}^2 \) (▼), \( P_o = 10^2 \text{C/m}^2 \) (+), and \( P_o = 10^1 \text{C/m}^2 \) (○). The bulk \( \alpha_o \) value has a significant effect on the stable filament radius for small polarizations. Larger polarizations also show this effect, however their differences are much more constrained. The largest stable single filaments occur in the SmLP phase (\( \alpha_o = \pi/2 \)) and decreases as we move through the SmCG phase and have a minimum in the SmCP phase. The MPR line (solid line) denotes the threshold below which no filaments are stable. b) The free energy per length for the \( P_o = 10^{-3} \text{C/m}^2 \) case with varying \( \alpha_o \), which shows that the free energy is minimized in the SmLP phase and has an unstable maximum in the SmCP phase.

3-8 A filament cross section (left) composed of a bundle of filaments of various sizes with non-cylindrical smectic layers between them, and the approximate structure (right) of radius \( R_T \) composed of filaments of the average unit radius \( R_o \). We also show the possible structure of a grain boundary which must exist between the filament bundles.

3-9 A graphical representation of the parameterized vector space used to describe the properties of the bent core liquid crystal filaments. This model utilizes a three dimension position vector \( (\vec{r}) \) whose components are functions of the filament...
parameter s and time t. The parameter space that describes the filament is bound
between $0 \leq s \leq s_0$, where $s_0$ is the total length of the unstretched filament. A closer
look at a differential element of the filament of length $ds$, shows that the vector
derivative, $\frac{\partial}{\partial s}$, lies along the filament long axis and is perpendicular to the cross
sectional area $A$.

3-10 Some examples of the forces (blue arrows) on a filament’s cross section generated
by a) axial and b) bending of the filament. We show the neutral plane (dashed red
line) and an exaggerated diagram of the smectic layers and how they compress and
expand due to these distortions.

4-1 The basic molecular structure of the bent core mesogens studied in their filament
forms.

4-2 a) The experimental setup for the static and dynamic measurements which consists
of a microscope connected to a CCD or high speed camera for image collection, a
heat stage with a mount attached to a modified tweezer allowing control of the
tweezer tip spacing. b) The mechanism for tweezer control is the use of a screw
which is run through one side of the tweezer and passes through the other side
which is tapped. This allows control of the distance of the tapped side with respect
to the free side.

4-3 SEM images of several filament in their crystalline phase. In these images we see a)
the flexibility of these filaments, b) the smooth surface texture of a single filament,
c) the tip of a broken filament bundle, and d) a defect structure which forms when a part of a bundle breaks on two ends and recoils to form a bead-like defect.  

4-4 The average filament diameter for the BC1-4 as a function of a) temperature and b) right below transition to the B_7 phase, for varying aliphatic tail lengths ranging from C_7H_{15} to C_{16}H_{33}. The temperature behavior shows a weak dependence which is inversely proportional to the temperature and no dependence on the aliphatic tails.  

4-5 The diameter statistics for BC5 in the B_7 and the B_2 phase along with the best fit curves. We see a clear discrete behavior in the B_7 phase which disappears in B_2 phase. Evidence of bundling can be seen in the B_7 phase when compared to a proposed fiber structure shown at the bottom.  

4-6 a) Experimental setup for the cantilever experiment which consists of a heat stage, a sealed capillary tube attached to a motorized micropositioner, and a stationary cantilever. b) Plot of the weight of different lengths of string as a function of the resulting cantilever deflection as the strings are hung on the cantilever tip. The slope of the best fit line gives a spring constant for the cantilever of 15nN/µm.  

4-7 Data for the bridge radius and force versus time obtained by analyzing video. We inserted images of the process at various times to show the correlations between the fiber radius and the measured force and the video images.  

4-8 Data obtained for the effective surface tension (solid marks) \( \sigma = \frac{F}{\pi R} \) as it develops with time. We also show the radius (hollow marks) for each run so that we can
compare the before and after filament formation. We compare the results of three samples, one in the isotropic phase which does not form a filament and two in the $B_7$ phase where fiber formation is observed.

4-9 Comparison of the filament structure observed under a microscope under 5X and 50X magnification, to the model structure which allows us to determine the adhesion forces between the single and bundle filaments. The structure consists of a single filament spanning two filament bundles (far left). The 50X images show that the single filament is being pulled away from the bundle in the fashion drawn in the upper right corner. By analyzing the force diagram for this static situation, we can determine the adhesion force between filaments and the change in tension.

4-10 Image sequence (10ms per image) of a filament bundle from CB2 whose individual filament units break and proceed to flow by the other filaments in the bundle. The filament bundle before the breaking occurred was about 10$\mu$m and after was around 4.5$\mu$m. We have included arrows and numbers to identify the positions of the four single filaments.

5-1 The basic molecular structure of the bent core mesogens.

5-2 Images of the structures formed during the pulling process for BC5 in the $B_7$ phase. We show the coexistence of the bent filament structures (red circles) and the straight filaments (a) as well as an image of the structures before and after instability occurs (b). By comparing the area between the curved filament region...
with crossed polarizers (c) we clearly see the existence of a thin film spanning the gap. 123

5-3 The model structure for the film connected filaments and the proposed smectic structure which is composed of two edge dislocations and a region of tightly bent smectic layers. This force that holds the centenary shape is the balance between the tension in the filaments (red arrows) and the smectic compression of the film due to the stretching (blue arrows). 124

5-4 The end to end profiles of two filaments highlighted in Figure 5-2a, labeled 1 (circles) and 2 (squares), along with the best fit curve from the above mentioned theory. We have shifted the filament bottoms to align along each other as to fit the data together. 128

5-5 a) The experimental setup for the filament resonance experiments which consists of a heat stage with various ports for accessing the filament under study, a long range microscope connected to a high speed camera, and a micro-positioner capable of pulling and aligning the filament. The experiments which used to oscillate the filament consisted of b) an external speaker pumping sound waves into a port, and c) two electrode (8mm apart) with an applied voltage to oscillate the filaments. 131

5-6 Examples of the maximum amplitude as a function of the frequency, where we have normalized the frequency by $\omega_n$ and the amplitude by the factor $\frac{4f}{\pi \mu m C}$. We show the effects of different dissipation factors which lowers the resonant maximum as the dissipation increases. 136
5-7  a) Filament motion from analysis of high speed video and the Fourier transform which shows a very clear signal at the driving frequency. b) The measured speaker intensity at 25°C in decibels as a function of driving frequency along with the calculated pressure resulting if we use the standard 20µPa reference. 

5-8  The resonant behavior of two BC2 filaments at 153°C compared to the applied speaker pressure. There exist dominant vibrational modes at a) low frequencies (~300Hz) which were not related to the filaments’ shape, and b) high frequencies which were dependent on their shape. The high frequency mode, due to its proximity to the resonance peak of the speaker, was observed by normalizing by the product of the speaker pressure and the filament diameter and fit using the theoretically predicted curve.

5-9  The resonant behavior of two BC5 filaments at 153°C compared to the applied speaker pressure. a) The low frequency mode (~300Hz) which appeared for all of the filaments is not related to the filament behavior but instead with the experimental mounts. b) The high frequency mode is related to the filaments resonance and is fit with the theoretically predicted curves for the maximum displacement.

5-10 The stability diagram as calculated by J.A. Richards which compares the effects of the parameter set (A-2q, q) and ζ on stability of the solution. We see that both the lossy (solid) and lossless (dashed) curves show instabilities as the value of q increases, however the transition shifts to higher q for the lossy system.
5-11 a) The time dependence of the filament displacement before and after applying a 3000 V (0.375V/µm) triangle wave at 23 Hz. We see clear damped harmonic transient behavior region which goes to steady state after about 800ms. b) The Fourier transform of the field off (dashed) and the steady state field on (solid) region. We see one peak in the 0V region which is related to the resonance of the glass holders and multiple peaks when the field is applied

5-12 a) A log-log plot of the amplitude ratio for the $1\omega$ and $2\omega$ coupling to the applied field as compared to the Fourier amplitude ratio $\left(\frac{1}{j^2}\right)$ we see that both curves appear to have the basic trend of the Fourier series but deviate at different frequency ranges. b) By normalizing the coupling ratios by the theoretical ratio and comparing to the amplitude of the 0V Fourier transform, we can see that the deviations are due to a $1\omega$ and $2\omega$ coupling to the filament mount resonance.

5-13 The temperature dependence of the ratio of the $1\omega$ and $2\omega$ coupling amplitudes as a function of temperature for BC5 during heating from the B$_2$ phase. We see that the ratio begins to increase linearly near the B$_2$ to B$_7$ transition temperature (147°C). Above the isotropic transition (164°C) there is a large drop in this ratio as the filament structure becomes unstable.

5-14 Length dependences of the resonance behavior for a) BC5 and b) BC2 at 153°C. We see that both materials resonant range decreases with increasing length in accordance with the theoretical model. In comparison the resonant peaks are much
broader and appear at larger frequencies for a given length for BC2 in comparison to BC5 expected by the columnar type structure of the smectic layers……… 161

5-15 The $1\omega$ resonance spectra for a 6.75 mm filament of BC5 at 153°C along with the resonance fit using Eq. 5.44. We grouped the natural and electric frequencies into a natural frequency $\omega'_n = \sqrt{\omega_n^2 - \alpha_n^2 E_o^2}$ which allows us to then fit the shifts in the resonance peak as a function of electric field to determine $\alpha_n = \frac{\varepsilon_{(e-1)}\pi^2}{\rho_o^2}$ ………… 162

5-16 a) The resonance spectrum of a filament due to a small electric field to minimize the resonance shift which appears to exist near 300Hz (error of the data is around 0.5µm). The electric field dependence of the filament displacement are also shown for different fixed frequencies near the resonance peak. The electric field dependences we show are at b) 200Hz, c) 300Hz, and d) 350Hz along with their approximate fit equations, $\Delta x \approx aE_o \left(1 + bE_o^2\right)$, $\Delta x \approx cE_o \left(1 - dE_o^4\right)$, and $\Delta x \approx eE_o \left(1 - fE_o^2\right)$, respectively……………………………………… 164

5-17 Image sequence of the breaking dynamics for a bent core filament. The image is out of focus initially to allow for the falling filament to pass through the focal plane of the microscope as it breaks for better imaging. This filament diameter was measured to be 6µm and the length is approximately 0.25mm. We can clearly see that the filaments speed is decreasing as it recoils and the modulated wavelength is approximately a constant…………………………………………………………… 171
5-18 The time dependence of the relative displacement of the filament tip and radial
growth (insert) as compared to the behavior predicted by the theory (solid
curves)........................................................................................................ 172

5-19 The average dominant wavelength time dependence for several filaments. The data
at the small times have larger errors due to the low amplitudes involved, however at
larger times a dominate wavelength emerges.............................................. 173

6-1 The base molecular structure of the bow shaped (a) and rod shaped (b) molecules
used in our studies. The specific molecular structures and phase behavior of
materials used in our study is shown in Table 6-1........................................ 181

6-2 Shear rate dependences of the a) viscosities and b) the shear modulus for the series
of bent core nematogens and calamitics in their isotropic phases. All samples were
measured at ~10°C above the nematic transition temperature. The shear moduli for
the calamitics where not shown because they where within the experimental error of
~5Pa............................................................................................................ 184

6-3 We show the shear induced birefringence of BCN1 between crossed polarizers in
the isotropic phase (76.3°C) without shear (top left) and with shear (bottom left).
Graph of transmitted intensity versus shear rate at various temperatures above the
nematic phase are shown (right) along with data fitting using Eq. A.20 in the
Appendix........................................................................................................... 188

6-4 The temperature dependences of the 1ω and 2ω intensity signals for the two
different analyzer/polarizer (AP) configurations for BCN1. We see that the first
and second harmonic signals are maximized for the 0° alignment, suggesting that the birefringence axes are acting along the 45° directions. We also see that the flow birefringence as we approach the nematic transition is dominated by the 2ω effect………………………………………………………………………….. 189

6-5  The temperature dependence of the shear induced birefringence constant as approaches the nematic transition temperature for the bent core nematogens... 191

6-6  The viscoelastic response of BCN1 over two decades of shear rates. We see the presence of two regimes. The first has a constant shear modulus and a shear thinning viscosity, while the second is characterized by a strong relaxation process for both the properties. This suggests that the first regime is probably dominated by permeation while the second shows the effects of shear alignment of the aggregates…………………………………………………………………….. 194

6-7  a) Shear rate dependence of the viscosity and shear modulus for BCN1 in the isotopic (90°C) and the nematic (70°C) phases. b) Temperature dependence of these values at a constant shear rate (517 s⁻¹)……………………………….... 195

6-8  Proposed nanostructures of bent core nematogens in a) the isotropic and b) the nematic phase…………………………………………………………………. 197

6-9  The shear rate dependences of the a) viscosity and b) shear moduli for various bent core smectogens in their isotropic phase. We compare their behavior to the low temperature values of the calamitics………………………………………….. 199
The 2nd harmonic signal from the photodiode as a function the temperature difference from the transition temperature ($T_n$) for very similar shear rates (~2000s$^{-1}$). We compare the behavior of the smectogens to BCN5 which has a similar temperature range and also had a small transition signal. We see a clear difference in behavior between BCN5, the B$_2$ phase (BCS3), and the B$_7$ materials (BCS1, BCS2, and BCS4).

The temperature dependences of a) the viscosities and b) the shear moduli for all of the smectogens. Our temperatures have been adjusted to the isotropic-smectic transition. The shear rates for these smectogens are 71.2s$^{-1}$ (BCS1), 66.5s$^{-1}$ (BCS2), 231s$^{-1}$ (BCS3), and 401s$^{-1}$ (BCS4).

The temperature dependence of the viscoelastic response for BCS2 at various shear rates. We see that the shear thinning is much more prominent in the B$_2$ phase and less so in the B$_7$ phase.

Comparisons of the shear rate dependence of the viscosity for the different phases below the isotropic phase. If we fit these curves with the relationship $\eta = \frac{\beta}{\gamma}$, we see that the exponent $\beta$ for each phase is 0.43 (BCN1) in the nematic phase, 0.78 (BCS2) or 0.63 (BCS4) in the B$_7$ phase, and 0.89 (BCS3) in the B$_2$ phase.

Temperature dependences of several samples at a shear rate of 401s$^{-1}$.

Cross-section of the nL-rheometer consisting of three basic components: a drive system (speaker) (left), a temperature controlled chamber (center), and a piezoelectric transducer to measure the force (right). Measurements are obtained by
driving the speaker at a particular frequency which oscillates a glass rod which enters the chamber. The force of the oscillating rod is transferred to the other rod via the material which is placed between them. This transferred force is measured as current via a piezoelectric crystal and recorded using a lock-in amplifier. An above view of the droplet shows the two glass rods connected with a droplet of 5CB.

A-2  a) Droplet of 5CB (~12nL) at 45°C between two D=125µm diameter glass rods as viewed through an Olympus CX40 inverted microscope. b) A diagram of the same droplet along with the important parameters D (the width of the glass rods), w (the center width), s (the displacement amplitude of the speaker), and L (the distance between the glass rods) that must be measured to calculate the droplet geometry and the shear strain.

A-3  a) Displacement versus voltage at 130Hz and b) the displacement per volts (not RMS) versus frequency in the small voltage regime along with best fits for the glass rod with no fluid attached. The amplitude dependence follows an exponential decay behavior while the frequency dependence for small voltages follows a combination of behaviors due to mechanical dampening and resonance (LRC behavior).

A-4  a) The approximate LCR circuit model for the speaker. b) The measured impedance and phase vs. frequency for the speaker with no fluid at 45°C along with the fit using the circuit approximation.
A-5  Plots of the empty resistance $R_o$ and $C_o$ along with their best fit curves as a function of temperature…………………………………………………………………………………………………… 230

A-6  Graph of the strain rate dependences on the measured stress in units of pC/m$^2$, along with a linear fit for Castor Oil (● and insert) and two silicone fluids manufactured by Clearco Products (■ and ▼) with viscosities of 1, 10, and 60 Pa*s, respectively.  b)  The slopes from part a) as a function of their known viscosity values………………………………………………………………………………………………… 235

A-7  The magnitude and phase of the force when measured for a material in the crystal state.  The phase is a constant $74.9^\circ$ and provides us the value of $\phi_0$.  The slope of the magnitude provides us with the force per volts provided by the speaker….  237

A-8  The $L$ dependence of the elastic (a) and viscous (b) stresses along with their theoretical fits from Eqs. A-18 and A-19.  The resulting values for the average magnitude and phase of the inertial force can be used to calculate the effective mass ($m_{eff}=0.36\pm0.04mg$) and inertial phase shift ($\phi_I=6\pm1^\circ$)………………………. 239

A-9  The temperature dependence of the viscosity ($\eta$) and shear modulus ($G$) for 5CB (a) and 8CB (b).  Our results are in good agreement with those measured by Chemielewski et. al. in the isotropic and nematic phase (■).  We also showed that the shear thinning log behavior discussed in that article, $\eta = (a \log T + b) \dot{\epsilon}^{-0.47}$, still applied in the smectic phase (dashed line), even though we measured at a much larger shear rate……………………………………………………………………………… 241
LIST OF TABLES

1-1 List of several observed bent core liquid crystals................................. 22
3-1 List of physical property values for simulation..................................... 71
4-1 Table of studied mesogens, their structures (Figure 4-1) and phase behavior... 99
5-1 Table of studied mesogens, their structures, and phase behavior............... 121
5-2 Fit parameters and property values from resonance behavior of filaments..... 142
6-1 The molecular structure and phase behavior of the materials studied in our experiments using the diagrams shown in Figure 6-1................................. 182
6-2 Fit parameters for the isotropic viscosity data for bent core nematogens. T is the temperature in Kelvin, $B$, $\gamma_0$, and $\eta_\infty$ are the fitting constants from Eq. 6-2, and $a$ is the apparent particle size as determined using Eq. 6.3 in nanometers............. 186
6-3 Tabulated flow birefringence values of several organic compounds reported in literature, and the values we measured for bent core nematogens............... 192
1.1 A BRIEF HISTORY OF LIQUID CRYSTALS

The history of liquid crystals (LCs) began in the mid-nineteenth century, when strange observations were seen on the covering of nerve cells under the application of polarized light\(^1\). The first scientists to observe LC properties were Rudolph Virchow, C. Mettenheimer, and G. Valentin when they reported interesting anisotropic fluid behaviors in some biological materials; however, none of them realized that they were actually observing a different phase of matter\(^2\). The earliest, but still useful tools for the characterization of LCs, the polarizing microscope and heat stage, were first used by Otto Lehmann\(^2\) to study these strange transitions. In 1888, Friedrich Reinitzer (credited as the discoverer of LCs) working with cholesteryl benzoate, observed two melting points and similar interactions with polarized light as observed by others\(^2\). This and his later works, generated a larger interest into the study of materials which would later be referred to as LCs. Using his polarizing microscope, Otto Lehmann became a leading figure in the study of these new materials and was the first to label them as “Liquid Crystals”\(^2\). In 1922, Georges Freidel established much of the nomenclature such as nematic, smectic,
and cholesteric, which are still used today. Since these early days, the interest in LCs has exploded on both experimental and theoretical fronts. While the experimental side has been motivated by the characterization and discovery of new phases and materials, the theoretical side has attempted to understand the connection between the basic molecular interactions and the resulting phase structures and macroscopic properties.

1.2 LIQUID CRYSTAL ORDER AND PHASE DESCRIPTIONS

The basic unit in LCs is the mesogen, and it is these mesogens which form LC phases which are generally referred to as mesophases. The prefix “meso-“, meaning “in the middle”, references that these phases are between the liquid and solid phase. Some classical examples of LC mesogens are shown in Figure 1-1. The first example (a) is the mesogen typically referred to as 5CB and has many applications in electro-optic displays. The other (b) is commonly called MBBA and is one of the first room temperature nematics and is also the first fully characterized LC mesogen. Classical structural properties of LC molecules had dimensions around 2-4nm in length and 0.1nm in width, resulting in a highly anisotropic shape such as a cigar or a disc. The molecular core can be highly conjugated and is typically much stiffer than the hydrocarbon tails. These structural properties become very important in the formation of LC phases and their macroscopic properties.

The particular LC phase that a mesogen has can be characterized by the order of the phase. The term order refers to the correlation between the orientation or position of one mesogen to another some distance away. A material is said to have orientational
Figure 1-1  The molecular structures of a) 4-pentyl-4'-cyanobiphenyl (5CB) and b) (4-butyl-phenyl)-(4-methyl-benzylidene)-amine (MBBA) which are classic examples of rod-like LC mesogens. c) These materials are typically modeled as a hard cylinder with $D_{2\infty}$ symmetry.
order if any mesogen’s orientation is strongly correlated to the orientation of any other mesogen. Likewise a material is said to have positional order if the position of any mesogen is strongly correlated to the position of any other mesogen. All of the LC phases have orientational order, but the positional order may vary in dimensionality. The amount of order a phase exhibits is typically quantified by the use of order parameters. These order parameters have the property that they must hold the same symmetry of the phase they represent and they are zero when the phase does not exist.

The simplest LC phase is the nematic phase which has orientational order without any positional order (see Figure 1-2a). This phase can be characterized by two order parameters which arise from the orientational correlations of the anisotropic mesogens. The first order parameter, typically called the orientational order parameter, distinguishes the direction of the average molecular alignment (the director)\(^3\). The director, typically written as \( \hat{n} \), is a vector having the special property that \( \hat{n} \cdot \hat{n} = -1 \) far from defects. The second order parameter, called the scalar order parameter, provides information about how well the mesogens are aligned along the director. The scalar order parameter, typically called \( S \), can be calculated by the volume average \( S = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle \) where \( \theta \) is the angle between any particular mesogen in the defined volume and the director axis\(^1\).

Typical values of \( S \) in the nematic phase ranges from 0.3-0.8, but theoretically can range from -0.5 to 1. A value of 1 is associated with 100% perfect alignment along the director, a value of -0.5 is associated with 100% perfect alignment perpendicular to the director, and a value of 0 represents no average (the isotropic phase).
Figure 1-2  Examples of the a) Nematic, the b) Smectic (SmA), and the c) Columnar phases (Col_{hid}). Also labeled are the director $\hat{n}$ and the respective positional order distances $d$ for the smectic and columnar phases.
The next LC phases that we will discuss are the smectics. These mesophases have a wide variety of structures which arise from various combinations of orientational order and one dimensional positional order. These phases typically arise in mesogens with longer flexible tails where there is an energetic advantage to segregate the rigid cores from the flexible tails. This segregation appears as a one dimensional layer spacing that is detectible using X-ray diffraction. This allows one to define the smectic order parameter $\psi$, which describes the quality of the periodic order. This order parameter can be incorporated into the density along the direction of the periodicity $z$ as, $\rho(z) = \rho_o(1 + \psi \cos qz)$, where $q = \frac{2\pi}{d}$ and $d$ is the layer spacing shown in Figure 1-2b. The simplest smectic phase is the smectic A (SmA) phase which results when the periodicity direction is the same as the director direction (see Figure 1-2b). The simplest variation of the SmA phase is the smectic C (SmC) phase, which occurs when the director aligns at an angle, called the tilt angle, to the periodicity direction. While these phases have a one dimensional periodicity, they experience no positional order within the layers, therefore these materials can be considered to be two dimensional fluids. There are several smectic phases more complicated than the SmA and SmC phase, which are commonly grouped together as the hexatic smectic phases. These phases such as the SmB_{HEX}, SmF, and SmI all have the same positional order as in the SmA and SmC, but have additional orientational ordering (called bond orientational order) where the mesogens order into larger groups or clusters.

The final mesophases that we discuss are the columnar phases. These phases are commonly created by disc-shaped mesogens. These mesogens typically have a rigid
center core surrounded by radially arranged flexible tails. These phases tend to separate into stacks or columns of mesogens due to the same incompatibility which separates the smectic phases into layers. These columns form bundles which have a two dimensional structure (see Figure 1-2c) which can be represented by two dimensional form of the positional order parameter. This structure has a periodicity related typically to the molecular size d and depends on the close packing structure of the columns which may form hexagonal packing (Colh), rectangular packing (Colr), and even oblique packing (Colob). The mesogens within the columns can also have different configurations such as disordered (d), tilted (t), or ordered (o) which are analogous to the SmA, SmC, and hexagonal smectics, respectively.

1.3 LIQUID CRYSTAL ELASTICITY

We have spoken about the basic mesophases which exist and the order parameters used to quantify them. However, we have not discussed the cause of the order and effects of distorting them. As we have mentioned, the observed order is driven by interactions between mesogenic molecules which minimizes the free energy of the system. The scalar order parameter free energy density is typically described by the Ginzburg-Landau free energy which holds the temperature information of the order parameter with a gradient term proportional to an elastic constant which we call $K_S^3$. The energy density for S can therefore be written as the following.

$$f_s = \frac{1}{2} a (T - T_s) S^2 - \frac{1}{4} b S^4 + \frac{1}{4} c S^4 + \frac{1}{2} K_S \left( \nabla S \right)^2$$ 1.1
For the director, this orientational elasticity is described by the Frank elastic constants 
\((K_{11}, K_{22}, K_{33}, K_{24})\) which for the nematic phase was first described by Oseen and later
improved on by Frank. The energy density associated with these distortions is shown
below.

\[
\begin{align*}
    f_{\hat{n}} &= \frac{1}{2} K_{11} (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_{22} (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_{33} (\hat{n} \times \nabla \times \hat{n})^2 \\
    &+ \frac{1}{2} K_{24} \nabla \cdot \left( (\nabla \cdot \hat{n}) \hat{n} + \hat{n} \times \nabla \times \hat{n} \right)
\end{align*}
\]

Variations of the smectic and columnar order parameters result in elastic terms associated
with the compressibility of the smectic layers or the columnar columns and are described
by a compressibility modulus \(B\). An example of the energy density for the SmA phase is
listed below,

\[
    f_{\text{SmA}} = \frac{1}{2} K_{11} (\nabla \cdot \hat{n})^2 + \frac{1}{2} B \gamma^2
\]

where \(K_{11}\) is the same elastic constant as described in Eq. 1.2 and \(\gamma\) is the layer strain. For
uniaxial systems with small strains, the layer strain can be assumed to be \(\gamma = \frac{\Delta d}{d}\) where \(d\)
is the undistorted layer spacing and \(\Delta d\) is a small change in layer spacing.

1.4 EFFECTS OF FRUSTRATIONS ON THE BASIC LIQUID CRYSTAL PHASES

The following topic that we discuss deals with the effects of molecular shape
which internally frustrates or spontaneously breaks the natural symmetry of the phases
described above. There are several examples of this effect in liquid crystals and typically
results in the formation of new phases. We first discuss the effects of molecular chirality
on the structure of the liquid crystal phases.
Chirality is defined by the loss of mirror symmetry, i.e. a mirror image of a molecule cannot be superimposed on the original\(^4\). The easiest way to create a chiral mesogen is by having a carbon with four different groups attached to each of its four bonds. This breaks the mirror symmetry, an example of which is shown in Figure 1-3a. If the nematic phase is composed of chiral mesogens then the phase will become a chiral nematic phase (N\(^*\)). This phase is like the nematic phase in that it has orientational order in the absence of positional order; however unlike the nematic phase there is an induced spontaneous twist of the director which has a period length called the pitch (see Figure 1-3b). Similar effects occur in the chiral smectic C phase (SmC\(^*\)) where the introduction of chirality generates a helical rotation of the director about the layer normal (see Figure 1-3c), however unlike the N\(^*\) phase the SmC\(^*\) phase also produces a spontaneous polarization (which has a dipole density which does not average to zero and has an order parameter defined by the polarization vector, \(\vec{P}\)) making it a ferroelectric phase. These effects are believed to be related to the steric interactions requiring a slight angle between neighbors which is biased by the chiral structure of the mesogens\(^3,4\). Other examples of frustrations result from the close packing of rigid cores and flexible tails which may compete with each other. Several numerical studies have shown that this interaction results in interesting phenomena such as the suppression of the nematic phase to form the SmA phase\(^5\) and the induction of the SmC phase over the SmA phase\(^6,7,8\).
Figure 1-3  a) An example of a chiral molecule whose mirror image cannot be superimposed on the original, and the effects of chirality on b) the Nematic (N*) and c) the SmC (SmC*) phase. Both phases observe a spontaneous helical deformation of the director either perpendicular to the director (N*) or about the cone angle (SmC*). The effect of chirality on the SmC* phase also induces a spontaneous polarization represented by the arrow which reside parallel to the layers (solid lines). The bars stuck to the end of the mesogens in the SmC* phase allows one to determine which of the ends of the mesogens are closer to the observer.
In the most extreme cases, a large asymmetry of the rigid core or a large difference in core to tail ratios may generate a modulation of the layer structure and form undulated smectic layers such as in the undulated SmA (USmA) or the undulated SmC (USmC) phase\(^9\). In the most extreme cases, the undulations forms defects which break apart the layers into modulated phases such as the ribbon phases, columnar phases, the \(\text{Sm}\tilde{A}\), or the \(\text{Sm}\tilde{C}\)\(^9\). Similar frustration effects are seen in lyotropic materials in the formation of the ripple phase (gel phase) due to a stiffening of the flexible tails in lyotropic lamellar systems\(^4,10\).

1.5 BENT CORE LIQUID CRYSTALS\(^{11}\)

It has been a little over a decade since it was realized that not only rod-shape (calamitic) or discotic mesogens can form liquid crystals, but bent-core (bow-like or banana-shape) mesogens do, too.\(^{12}\) Although the first synthesis of bent-core liquid crystals (BCLC) was reported more than sixty years ago by Vorländer\(^{13}\), they have not attracted much interest until the synthetic work of Matsunaga et al.\(^{14}\) in the early 1990s. The discovery of the interesting properties of these mesogens has opened up a major new and exciting dimension in the science of thermotropic LCs. Seminal findings, having broad implications for the general field of soft matter physics including the observations of ferroelectricity and spontaneous breaking of chiral symmetry in smectic phases composed of achiral mesogens\(^{15}\). In the following sections, we will discuss the microscopic structures and interactions between bent-core mesogens.
As for the classical mesogens discussed earlier, the bent-core mesogens consist of a rigid, highly conjugated core, and flexible hydrocarbon tails. Bent-core mesogens are typically composed of five aromatic rings with a meta-substituted central ring, various side linkages to the core, and terminal chains at one or both ends. The meta-substitution of the central ring gives an opening angle of approximately 120° and typically are about 5nm long and 0.5nm wide. These mesogens may be symmetric or asymmetric, and the linkages between the aromatic rings may vary in position and size.

One of the major interactions between the bent-core mesogens is their steric close packing, which attempts to fill the space as effectively as possible. This steric requirement when coupled to the bent-shape of the mesogens immediately implies two important features. When translating a bent-core mesogen in the “sea” of the other mesogens, it experiences a periodic interaction due to their molecular kink. This results in a translational symmetry breaking along the long axis of the mesogens (the average direction connecting to the ends of the mesogens) forming temporary smectic-like aggregates. In the case of the nematic phase, this suggests that nematic order is only valid at length scales much larger than these clusters as illustrated in Figure 1-4. The other important feature resulting from close packing is the formation of polar order along the kink direction. Provided that the mesogens have a dipole moment along this direction, then this polar order results in the formation of a spontaneous polarization which is inherently different from that of the SmC* phase where molecular chirality must be coupled to the director tilt as first shown by R.B. Meyer.¹⁶
Figure 1-4  Sketch of hypothetical nematic phase of bent-core mesogens.
This effect is best illustrated in the SmAP phase (Figure 1-5) which is a non-tilted smectic phase with a spontaneous polarization which has only been observed in bent-core LCs.

Due to the previously described shape and close packing requirements of bent-core mesogens, it is convenient to define three orthogonal unit vectors $\hat{n}$, $\hat{m}$, and $\hat{p}$. The vector $\hat{n}$ is the unit vector along the long axis (the director), $\hat{m}$ is normal to the molecular plane, and $\hat{p}$ is along the kink direction which is parallel to the polarization $\vec{P}$. Figure 1-5 shows the situations when $\hat{n}$ is parallel to the smectic layer normal $\hat{k}$. This is similar to the SmA phase of calamitic liquid crystals, except that now the layers are polar. This difference is designated by adding the letter P (for polar) to SmA. In this case one can have two distinct situations, the layer polarization $\vec{P}$ can be either parallel or antiparallel in the subsequent layers corresponding to ferroelectric (SmAP$_S$) or antiferroelectric (SmAP$_A$) subphases. Here we denote the same polarization directions by the subscript S for synchronous and the alternating directions by the subscript A. The symmetry for this set of phases is $C_{2v}$. The situations when the molecular planes are tilted with respect to the layer normal, i.e., when $\hat{m}$ is not perpendicular to $\hat{k}$, are shown in the upper row of Figure 1-6. In this figure, we show the plane determined by the polarization $\vec{P}$ and the layer normal $\hat{k}$ (polar plane), in which case the tilt is illustrated by a bar is stuck on the end of the mesogen which is closest to the observer.
Figure 1-5  Schematic structure of the ferroelectric SmAP$_S$ and the antiferroelectric SmAP$_A$ phases.
Depending on whether the tilt directions between subsequent layers are parallel or antiparallel, one can describe them as being synclinic and anticlinic, respectively. By using the same nomenclature for the SmAP phases we can define two more subscripts to describe the tilt between layers the synclinic (S) or anticlinic (A) configurations. Combining these tilt descriptions with the ferroelectric and antiferroelectric packing configurations discussed earlier, we can arrive at the following four subphases: SmC$_{SP}$, SmC$_{PA}$, SmC$_{PS}$ and SmC$_{AP}$. Such a notation with some variations was introduced by Link et. al.\textsuperscript{17} and is widely used in the literature. Note that the SmCP layers have only a two-fold symmetry axis around $\hat{p}$ (C$_2$ symmetry), i.e. they have the same symmetry as of chiral SmC* materials\textsuperscript{16}. In principle, we can also envision that only the director $\hat{n}$ and $\hat{p}$ are tilted (or leaning) with respect to the layer normal $\hat{k}$. Similarly, the successive smectic layers can be either ferroelectric (with the same direction of polar order) or antiferroelectric (with opposite directions). Likewise, successive layers can be either synclinic (with the same direction of molecular tilt) or anticlinic (with opposite tilt directions). Those situations are illustrated in the bottom row of Figure 1-6. To distinguish from the tilt of the molecular plane (which is denoted by the symbol C to express “clinic”), the tilt of the long axis will be called “leaning” and will be labeled with L. Just as in the SmCP cases, there exists four distinct sub-phases SmL$_{SP}$, SmL$_{AP}$, SmL$_{PS}$ and SmL$_{PS}$ depending on the subsequent tilt and polarization direction combinations. In these phases the polar axes are not parallel to the smectic layers and have C$_s$ symmetry.
Figure 1-6  The possible single tilted bent-core smectic structures. Top row: Illustration of the fluid in plane order of the layer polarization, and three dimensional explanation of tilt. Middle row: two dimensional illustration of the four possible situations when only the molecular plane is tilted with respect to the layer normal; Bottom row: two-dimensional illustration of the four possible situations when only the long axis is tilted (leaned) with respect to the layer normal.
On the same grounds as the previous discussions, one can also imagine that both tilt directions are possible simultaneously\(^{18}\). Those “double–tilted” situations are labeled both with C and L, where the tilt independently can be the parallel or antiparallel to each others. Taking into account that the layer polarizations can either be parallel or antiparallel, we have altogether eight different subphases as illustrated in Figure 1-7. Although in all of these situations the individual layer polarizations are not parallel to the smectic layers, the out of layer components averages out in the anti-leaning structures, and their macroscopic symmetry would be the same as of the SmAP (for anticlinic situations, such as SmCA_LAPA and SmCA_LAPS) or as of SmCP (for synclinic situations, such as SmCS_LAPA and SmCS_LAPS). It is important to note that the SmCLP structures can be equivalently described by a tilt of the molecular plane and a rotation of the layer polarization \(\bar{P}\) about the long axis \(\bar{n}\) by an angle \(\alpha\). If \(\alpha=0\) or \(\pi\) then we have the SmCP case, when \(\alpha=\pi/2\) or \(3\pi/2\) then we obtain the SmLP situations, otherwise we have the SmCLP phase. Double–tilted layers have triclinic symmetry, i.e. they are symmetric only with respect to a 360° rotation around the polar axis \(\bar{P}\) (C\(_1\) symmetry). Such a structure was theoretically predicted by de Gennes\(^{19}\) without a discussion of bent-core materials and was labeled as the SmCG phase where “G” stands for generalized. So far we have considered only those cases where the center of masses of mesogens had periodicity only in one (smectic order), however they may exist in two dimensional periodic structures as well (columnar phases) which are illustrated in Figure 1-8. The situations shown in the upper row of Figure 1-8 assumes an intercalated layer structure. In this case the hydrophobic hydrocarbon chains have to be in close proximity with the aromatic
Figure 1-7  a) The possible double-tilted bent-core smectic structures. Top row: Illustration of the fluid in plane orders of the layer polarization (either uniform or modulated), and three dimensional explanations of tilt. Middle and bottom rows: two dimensional illustrations of the eight possible situations; (b) Graphical explanation of the SmCLP structures in term of two rotation angles $\theta$ and $\alpha$. 

\[ \hat{n} \]

$\hat{k}$

$\hat{p}$

$\hat{p}'$

$\hat{x}$

$\hat{y}$

$\hat{z}$
Figure 1-8  Schematic representation of the intercalated layer structures and the nano-segregated version which has the same symmetry as a columnar phase.
bent cores, which usually are not favored energetically leading to a nano-segregated structure as shown in the bottom row of Figure 1-8.

While the proposed structures in this section are not the only possible phases which are allowed by symmetry, they coincide well with most of the experimentally observed phases. Many of the observations of the smectic and columnar phases of bent-core liquid crystal phases were pioneered by groups in Tokyo\textsuperscript{20}, Boulder\textsuperscript{17}, Berlin\textsuperscript{21}, Halle\textsuperscript{22}, Budapest\textsuperscript{23}, and several other places\textsuperscript{24,25}. In the last several years the research has quickly broadened with very intensive experimental studies carried out all around the world. Activities of this field have been recently reviewed in several papers\textsuperscript{9,26}.

In the first few years of experimental studies seven different bent-core liquid crystal textures were documented and labeled as B\textsubscript{1},…, B\textsubscript{7} according to the chronological order of their observations.\textsuperscript{27} The list of these phases, based on textural observations and X-ray measurements, are summarized in Table 1-1. Since the early time of this nomenclature many of these phases based on textures have been identified in terms of their basic phase symmetries, however others have brought with them more questions than answers.

The B\textsubscript{1} phase is a columnar, non-polar, non-tilted phase corresponding to the structure illustrated in the bottom of Figure 1-8.

The B\textsubscript{2}, which is the most actively studied phase, is identical to the SmCP structures shown in Figure 1-6.

The B\textsubscript{3} phase represents a non-switchable (probably non-polar) non-tilted smectic structure with in-layer positional ordering. Due to the lack of the electro-optical response
it is seldom studied, however some studies indicate the presence of second harmonic generation (SHG activity) and therefore suggests a polar structure\textsuperscript{28}, however these measurements could not be later confirmed.\textsuperscript{29}

Table 1-1  List of several observed bent core liquid crystals.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Polarity</th>
<th>Director tilt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>Columnar</td>
<td>non-polar</td>
<td>non-tilted</td>
</tr>
<tr>
<td>$B_2$ (SmCP)</td>
<td>smectic with no in-layer order</td>
<td>polar</td>
<td>Tilted</td>
</tr>
<tr>
<td>$B_3$ (SmIP)</td>
<td>smectic with hexagonal in-layer order</td>
<td>Polar?</td>
<td>Tilted</td>
</tr>
<tr>
<td>$B_4$</td>
<td>optically active solid</td>
<td>Polar?</td>
<td>non-tilted</td>
</tr>
<tr>
<td>$B_5$</td>
<td>highly viscous SmCP</td>
<td>polar</td>
<td>Tilted</td>
</tr>
<tr>
<td>$B_6$</td>
<td>interdigitated layers</td>
<td>non-polar</td>
<td>non-tilted</td>
</tr>
<tr>
<td>$B_7$</td>
<td>Columnar</td>
<td>polar</td>
<td>Tilted</td>
</tr>
<tr>
<td>$B_7'$</td>
<td>modulated layer structure SmCP\textsuperscript{30} or SmCG</td>
<td>polar</td>
<td>Tilted</td>
</tr>
</tbody>
</table>

The $B_4$ phase has a complicated structure which is still the focus of several current studies. It was in the $B_4$ phase where the first measurements suggesting the existence of optical activity. Currently it is not clear if the structure is some kind of crystal\textsuperscript{31} or a hexatic twist grain boundary (TGB) phase\textsuperscript{32}. X-ray diffraction measurements indicate broader peaks in the wide angle range than in the $B_3$ phase that appears at higher temperatures, which would indicate a less ordered packing in the short range. Freeze fracture electron microscopy studies suggest a structure similar to the lyotropic sponge phase.\textsuperscript{33} Notably this structure is very similar to that proposed for an optically isotropic ferroelectric phase consisting of random SmCA\textsubscript{P5} nanodomains\textsuperscript{34}. 
The B₅ phase was originally assigned to a switchable phase, which appeared below the B₂ phase and showed a somewhat more complex X-ray profile than that of the B₂. However, investigations on freely suspended films showed that it has the same symmetry as of the B₂²⁷ phase, so it appears that there is no need for a separate name.

The B₆ phase is an intercalated smectic structure such as shown in the top left of Figure 1-8 without long range order in the YZ plane. In this phase, the layer periodicity is smaller than half the length of the mesogens. As we mentioned before, this packing makes contacts between the aromatic rigid bent-core and the flexible tails which is not favored for longer tail lengths, explaining why experimentally it is found only in short chain materials.²⁷

The high temperature phase that appears directly below the isotropic phase and forms characteristic helical filaments under cooling³⁶ is denoted as the B₇ phase. Later measurements showed that similar helical structures may appear in several materials with different smectic structures corresponding to at least two distinct phases. The exact phase structure of these materials is still under considerable debate, but there do exist parallels between these phases and the frustrated structures described in section 1.4. The cause of the frustrated layer structure is still unknown, but there are discussions on whether these structures are due to core-tail interactions or core-core interactions. This debate is of high interest to this dissertation and will be mentioned later in Chapter 2.
The SmAP\textsuperscript{37} and nematic\textsuperscript{38} phases were observed well after the B\textsubscript{i} (i=1,…7) nomenclature was introduced and therefore have not been assigned with those symbols. So far there is only one report\textsuperscript{37} of a non-tilted SmAP\textsubscript{A} phase corresponding to the right hand side of Figure 1-5. This phase did not show electro-optical switching while the presence of a large polarization current clearly showed the presence of an antiferroelectric polarization of almost 1000nC/cm\textsuperscript{2}. The nematic phase exhibiting only orientational order are uncommon in bent-core phases probably due to the tendency for smectic ordering as we mentioned above (see Figure 1-4). However, very recently, a number of new bent-core compounds with nematic phases have been synthesized\textsuperscript{38,39,40}, and their physical properties are currently being investigated\textsuperscript{41,42,43}. Light scattering studies in the uniaxial nematic phase\textsuperscript{42}, and recent NMR measurements in the isotropic phase\textsuperscript{44}, reveal drastically slower fluctuations in bent-core compounds than observed in classical rod shaped nematics. This is because their viscosities are about two orders of magnitude larger than classical rod-like materials\textsuperscript{45}. This behavior is also consistent with the cluster concept illustrated in Figure 1-4 and corroborated by recent NMR measurements\textsuperscript{46}. This clustering model has also been helpful in explaining the presence of giant flexoelectric polarizations around three orders of magnitude larger than typical calamitic liquid crystals\textsuperscript{47}. There has also been a surge in theoretical studies\textsuperscript{24,48,49,50} predicting intriguing new thermotropic nematic and isotropic structures which include interesting uniaxial behavior\textsuperscript{42}, field induced biaxiality\textsuperscript{43} and biaxial phases\textsuperscript{51}.
REFERENCES


11. Some figures and text in this section were taken from the following book chapter:


13 D. Vorländer, A. Apel, “Die Richtung der Kohlenstoff-Valenzen in Benzolabkömmlingen (II.).” Berichte der Deutschen Chemischen Gesellschaft, 1101-1109, (1932)


CHAPTER 2

THE ROLE OF MOLECULAR SHAPE ON BENT CORE LIQUID CRYSTAL PHASES

2.1 INTRODUCTION

The introduction of kinks in the shape of liquid crystal mesogens\(^1\) led to an exciting new field in soft matter physics\(^2,3,4\) with a number of new theoretical predictions\(^5\) and experimentally observed nematic\(^6\), smectic and columnar phases.\(^7,8,9,10,11,12\) In spite of a decade of intensive research, the structures of a number of these phases are still not completely clear and most of the phases usually denoted as \(B_1, \ldots, B_7\) according to the chronological order of their discovery. The most active debate concerns the \(B_7\) structures\(^13\), which are most notable for the formation of free-standing fluid filaments\(^14\), banana leaf-shaped domains\(^15\) and helical superstructures\(^16,17,18,19\) including helical filaments\(^20\).

Although many materials with \(B_7\) type textures have been reported in the literature\(^21,22,23\), it remains unclear whether all of these textures have the same phase structure or not. Based on some characteristic differences between their behavior\(^24,25,26,27,28\) we may speak about two different types of \(B_7\) materials. Some of the mesogens, for example, the first \(B_7\) materials\(^16\), have distinct sharp peaks in the low angle
X-ray range\textsuperscript{2} which is characteristic of columnar-like structures. Other B\textsubscript{7} materials, which we denote B\textsubscript{7\prime}, have strong commensurate reflections indicating a layered structure, and small incommensurate satellite peaks which are very close to each other and hard to resolve with normal X-ray techniques.\textsuperscript{29} These satellite peaks were associated with a one dimensional undulation of the smectic layers with a relatively long wavelength, between 10-100nm\textsuperscript{29}, and was attributed to a frustrated in-layer polarization structure in the form of polarization splay domains. Such modulated structures have been the subject of a number of studies\textsuperscript{24,25,26,29,30} and various names, such as SmCP-mod and PM-LU, were used for them. The B\textsubscript{7} materials do not switch electro-optically or show polarization switching for applied electric fields below 40V\textmu m\textsuperscript{-1}, whereas the B\textsubscript{7\prime} materials posses ferroelectric or antiferroelectric\textsuperscript{22} polarization peaks above a threshold of $E > 10V\textmu m\textsuperscript{-1}$ that decreases on cooling\textsuperscript{22,31}, unlike the single tilted SmCP or SmC* phases. Based on these observations and on field-induced polar shifts of transition temperature\textsuperscript{32} it has been suggested that the B\textsubscript{7\prime} materials have $C_1$ symmetry with a double tilted (SmCG)$^5$ structure where the polarization has components in and out of the smectic layers.

In this chapter we will show how frustrations in molecular packing generated by molecular substitutions and electrostatic potentials necessitate a local $C_1$ symmetry and lead to spontaneous polarization splay and layer bending in bent-core liquid crystals\textsuperscript{33}. By calculating the entropic changes due to curvature, we estimate the elastic constants that drive the spontaneous layer bending and polarization splay. We also propose a structural phase diagram which describes how the experimentally observed phase
structures depend on the direction and magnitude of the spontaneous polarization. We finish this chapter with a closer look at the energy terms and discuss the effects of these terms when coupled to biaxial layer compressions and electric self interactions, including any natural length scales which result from this theory.

2.2 MOLECULAR MODELING

We performed simulations of the equilibrium molecular structures and electrostatic potentials using ChemOffice® of virtually all published mesogens\(^2,6,16,18,19,20,21,34,35\) exhibiting the B\(_7\) or B\(_7^*\) phases. From these simulations, we found that only the SmCP phase with C\(_2\) symmetry can be modeled as a bent series of spheres\(^36\) (Figure 2-1a). However all the B\(_7\) mesogens have a single or multiple large steric units attached to the center or outer benzene rings, such as a nitro group\(^34\), which would appear as ‘bumps’ on their model structures (Figure 2-1c). Although the B\(_7^*\) mesogens may have only small units, such as chlorines or fluorines attached to their outer benzene rings, or have no steric inclusions at all\(^35\), one also sees ‘bumps’ in their complex electrostatic potentials generated by the distribution of charges within the chemical structures (Figure 2-1b). One of the interesting things about this behavior is that there is a wide range of variability. This variability can be different depending on the mechanism (steric or electrostatic) but some general trends can be discussed. For the steric interactions, the relative size and location of the bumps are dominating factors. Some examples are shown in Figure 2-1d, where we show the polar packing due to the most
Figure 2-1 Examples of typical bent-core mesogenic materials with their phase sequences, chemical, steric, and electrostatic structures for the a) $B_2^{15}$, the b) $B_7^{35}$, and the c) $B_7^{34}$ phases, as obtained by ChemOffice® software package. The extra circles in their model structures represent the unit which frustrates close packing, and the dashed triangle shows the effective region which cannot be occupied by other molecules. d) Also shown is how differences in bump location and size can affect the frustrated structure and their respective phase behavior.
common steric structures and their respective bump sizes. We also compared these to the packing structure for a B2 molecule with no bumps, which has an effective structure (blue triangle) smaller than the core structure. For the electrostatic structures, the predictability of the inclusions are much more difficult, however there are some guidelines that one may consider. The electrostatic inclusions benefit from the existence of large dipolar units such as Flourines or Chlorines or protruding regions of electron conjugation as in the material of Figure 2-1b. Furthermore, it is also likely that the electrostatic inclusions are weaker than steric inclusions and is related to the lack of a well defined boundary. This typically results in the formation of a low temperature B2 transition due to the increasing importance of steric interactions at lower temperatures which eventually overcomes these weaker electrostatic interactions.

To this point, we have only considered the effects of the rigid core and have ignored any effects due to the flexible tails. We know there are other model types which attempt to describe the B7 phase, in particular the PMLU structure, in terms of distortions of their hydrocarbon tails. This model assumes that it is the tail structure that generates the frustrated packing instead of the core. This type of model has been useful in lyotropic systems for predicting the structures of micelles from their molecular structures and in the formation of the DeVries SmA/SmC phase transition. Although this model may also be applicable in this system, there are a few reasons which we believe can be argued for why this should not the case. First, the temperature range of the B7 phase do not differ significantly from the temperature range of the B2 phase, suggesting that their hydrocarbon tails should not behave much differently. Secondly, the chemical
composition of the flexible tails in the B7 phase is identical to those of the B2 phase, suggesting that there should be no difference in their fundamental behavior. Therefore, the effects of the end tails and the reality that the bumps do not completely fill the entire rigid core are taken into account only by assuming that they favor SmC ordering and polar packing as opposed to anti-polar packing within a layer (an effect which otherwise is not excluded from our simplified packing model). Therefore, based on these molecular observations, we decided to model the molecules as triangular wedges where the triangle represents the molecular side view and the wedge as the molecular cross section (see Figure 2-2b).

2.3 MOLECULAR MODEL

To quantify the effects of frustrated packing, we calculated the curvature dependent excluded volumes and then determined the strength of these interactions by calculating the resulting changes in translational entropy. The important geometrical parameters along with the resulting spontaneous distortions can be seen in Figure 2-2, where we have divided the packing interactions along two orthogonal planes, one perpendicular to the layer normal \( \hat{k} \) (splay plane) and the other within the plane generated by \( \hat{k} \) and \( \hat{n} \) (bend plane). For a given radius of curvature \( r \) describing bend distortions of the polarization direction, the excluded volume \( V_b \) of a single model molecule in the \( (\hat{n}, \hat{p}) \) plane can be given as,
Figure 2-2 The geometries of the frustrated packing model. (a): The molecular orientation: \( \hat{n} \) is the director along the long axis, \( \hat{p} \) is the layer polarization axis and \( \hat{k} \) is the layer normal; \( \hat{n} \) tilts in \( (\hat{x}, \hat{k}) \) plane by angle \( \theta \), and the molecular plane makes an angle \( \alpha \) with respect to the \( \hat{y} \) axis. (b): The model molecular dimensions in the \( (\hat{n}, \hat{p}) \) and \( (\hat{p}, \hat{m}) \) planes. (c): Illustration of the excluded volumes (grey areas) for bend and splay deformations. (d) The model\(^{29}\) of the in-layer polarization splay; (e) The model\(^{14}\) of the fibers made of B\(_7\) and B\(_{7'}\) materials illustrating the effects of layer bending.
Here b is the smallest width of the molecule, L is the molecular length, β is the kink angle, and \( \phi = \tan^{-1}\left(\frac{\tan\beta}{1 + \frac{\beta}{\rho}}\right) \) is the curvature angle (see Figure 2-2b). The excluded volume in the bend plane becomes \( V_b(\hat{n}, \hat{p}) = V_b(\hat{n}, \hat{p}) \cdot \sin^2 \alpha \), which correctly accounts for the projection of the molecule onto the bend plane (see Figure 2-2a). For the splay case, for radius of curvatures \( \rho >> L \), the excluded volume \( V_s \) in the \( \hat{p}, \hat{m} \) plane is:

\[
V_s(\hat{p}, \hat{m}) = L a^2 \left( \tan \left( \frac{\delta}{2} \right) - \tan \left( \frac{\gamma}{2} \right) \right)
\]

where \( \delta \) is the wedge angle (see Figure 2-2b), and \( \gamma \approx \frac{\beta}{\rho} \) is the curvature angle (see Figure 2-2c). From Figure 2-2a, one can see that the correct excluded volume within the smectic layers is the projection of 2.2 determined by

\[
V_s(\hat{x}, \hat{y}) = V_s(\hat{p}, \hat{m}) \cdot \sqrt{\cos^2 \alpha + \cos^2 \theta \sin^2 \alpha}.
\]

It is useful to analyze \( V_s(\hat{k}, \hat{x}) \) and \( V_s(\hat{x}, \hat{y}) \) by comparing the undeformed \((\phi, \gamma \rightarrow 0)\) with the deformed \((\phi, \gamma > 0)\) states. For flat layers, \((\phi \rightarrow 0)\), \(V_b(\hat{k}, \hat{x}) = \frac{1}{2} L^2 b \tan \beta \cdot \sin^2 \alpha\), which has a minimum when \( \alpha = 0 \) (SmCP). However, taking the difference of the excluded volumes of bent and flat layers we find that it is always negative i.e., the bent layers have smaller excluded volumes for any \( \alpha \neq 0 \). It is readily seen for the tightly bent case, which gives

\[
\Delta V_b = V_b(\phi = \beta) - V_b(\phi \rightarrow 0) = \frac{1}{2} L^2 b \left( \beta - \tan \beta \right) \cdot \sin^2 \alpha \quad \text{which for } \alpha \neq 0 \text{ is always negative because } \tan \beta > \beta.
\]

Accordingly, once \( \alpha \) is not zero, a bent layer structure provides closer...
packing of the molecules. Because $\Delta V_\beta$ has a maximum at $\alpha=0$, a flat system becomes unstable for any small perturbation of $\alpha$, thus driving a bend of the layers, which in turn stabilizes $\alpha\neq0$. Considering the difference between the excluded volumes of the splay deformed and uniform states $V_\gamma (\gamma > 0) - V_\gamma (\gamma \to 0) = -1/2 La^2 \rho \cdot \sqrt{\cos^2 \alpha + \cos^2 \theta \sin^2 \alpha}$, we see that it is always negative, but now with a minimum at $\alpha=0$ if $\theta>0$. This means that the effects of layer bend and polarization splay on the polarization angle are competing. A layer bend favors $\alpha=\pi/2$ (SmLP), whereas a polarization splay favors $\alpha=0$ (SmCP). A combination of these two effects therefore sets $0<\alpha<\pi/2$ (SmCG).

In order to estimate the natural length scales of the bend and splay deformations we need to calculate the free energy change arising from the increase in translational entropy $S_{b,s}$, which can be written as,

$$S_{b,s} = -k_B \ln \left(1 - n \Delta V_{b,s}\right) \approx k_B \left(n \Delta V_{b,s}\right)$$

Here $k_B = 1.38 \times 10^{-23} \, J/K$ is the Boltzmann’s constant, $\Delta V_{b,s}$ are the differences between the excluded volumes between the bend/splay deformed and uniform states, and $n$ is the number density of the material. This approximation is valid if $nV_{b,s}<<1$ which is true in our situation for curvatures in the continuum limit. The bend/splay energy densities $f_{b,s}$ then can be estimated by multiplying (-TS_{b,s}) by the number density $n$, thus giving

$$f_b (r) \approx n^2 k_B T \left(V_b (r > 0) - V_b (r \approx \infty)\right) \quad \text{and} \quad f_s (\rho) \approx n^2 k_B T \left(V_s (\rho > 0) - V_s (\rho \approx \infty)\right).$$

In the continuum limit, i.e., when $\rho, r \gg 1/2$ we expand $\Delta V_{b,s}$ up to first order in $r^{-2}$ and $\rho^{-1}$, obtaining the following results.
The extra factor of $\cos^2 \theta$ in 2.4 is due to the fact that $r$ must be rescaled by a factor of $\frac{1}{\cos \theta}$ to correctly account for the molecular tilt in layer bending, and in 2.5 we have written $a = \frac{1}{2} L \tan \beta$. As we show, the energy density can be written in terms of vector operations of the in-layer director $\hat{c}$, the in-layer divergence $(\nabla \cdot \hat{p})$ and out-of-layer curl $(\nabla_\perp \times \hat{p})$ of the polarization direction. By using typical values of the molecular and physical parameters $n = 7.5 \times 10^{26} \text{m}^{-3}$, $T = 425 \text{K}$, $L = 5 \text{nm}$, $b = 1 \text{nm}$, and $\beta = \frac{\pi}{6}$ we calculate that $C = -0.034 \frac{\text{N}}{\text{m}}$ and $K_b = -6.6 \times 10^{-11} \text{N}$. We note that $|K_b|$ is slightly larger than typical Frank elastic constants, and $|C|$ is greater than the measured surface tension $\sigma$, which is $\approx 0.025 \text{N/m}$ in air$^{14,37}$, and $<0.02 \text{N/m}$ in an isotropic melt. Another important observation is that the same polarization splay term can be arrived at in the $(\hat{p}, \hat{m})$ plane suggesting that the polarization splay should have the general form $C(\hat{V} \cdot \hat{p})$. Therefore, this term can promote spontaneous polarization splay in layer and out of layer if the layers are curved.
2.4 BIAXIAL LAYER COMPRESSIONS AND ELECTRIC SELF INTERACTIONS

The spontaneous formation of layer curvature and polarization splay, and the resulting changes in polar angle $\alpha$ which must result, leads one to wonder about the consequences for these distortions. It is known that in SmCP systems the polarization desires a planar orientation, and only by applying a fast, high voltage pulse can one drive the polarization to rotate about the director$^{38}$. This arises because the energy cost for this type of distortion is higher than the elastic distortion energy within the layer, and only by switching the material faster than the viscous stresses will allow can one obtain this distortion. This effect, we believe, is associated with biaxial layer compressions due to small changes in layer spacing caused by molecular reorientations about the director and is shown pictorially in Figure 2-3$^{39}$.

![Figure 2-3](image)

Figure 2-3  A comparison of the layer thickness between two states where the polarization angle $\alpha$ differ by $\pi/2$. The director tilt in both cases has a value of $\pi/4$ and the layer change $\delta$ is entirely due to the shape biaxiality. We have labeled the primary dimension of the bent core molecule as L, $d_1$, and $d_2$. 
The result is a change in the layer spacing which is comparable to the physical width of the molecule. This effect can only occur in systems with biaxial symmetry due to the rotational dependence about the director. This leads us to discuss a more general form for layer compression effects to account for the behavior in bent core smectics. The basic idea is built from the small strain approximation to discuss the layer compression effects due to molecular realignment. The compression free energy density $f_c$ is determined by the layer compression modulus $B$ and the layer strain $\gamma$. For small strains this layer strain can be approximated by the relative change of the stressed layer thickness $d$ divided by the unstressed layer thickness $d_o$ (see Eq. 2.6).

$$f_c = \frac{1}{2} B \gamma^2 \approx \frac{1}{2} B \left( \frac{d - d_o}{d_o} \right)^2$$

2.6

It is in the determination of the stressed and unstressed layer spacing where the molecular orientation becomes important. For a biaxial material, the effective shape of the molecule can be approximated with a generalized ellipsoid. This ellipsoid can be described in general by a 2nd rank tensor whose diagonal values (when in the molecular frame of reference) represent the molecular dimensions $d_1$, $d_2$, and $L$.

$$\vec{D}_{mol} = \begin{pmatrix} d_1 & 0 & 0 \\ 0 & d_2 & 0 \\ 0 & 0 & L \end{pmatrix}$$

2.7

Then by performing various rotation operations in using $\theta$ and $\alpha$ in the $\{\hat{x}, \hat{y}, \hat{k}\}$ coordinate frame (see Figure 2-2a) one can obtain the general shape matrix for a biaxial
material. Then we generate a distance closely related to the layer spacing $d$ by using the following expression.

$$d = (\hat{D} \hat{k}) \cdot \hat{k} = d_1 + (L - d_1) \cos^2 \theta + (d_2 - d_1) \sin^2 \theta \sin^2 \alpha$$

By entering this relationship into the layer strain, $\gamma = \frac{d(a, \theta)}{d_o(a, \theta)} - 1$, where $\theta$ and $\alpha$ and $\theta_o$ and $\alpha_o$ are related to the orientations in the stressed and unstressed configurations, respectively. Then expanding the ratio $\frac{d(a, \theta)}{d_o(a, \theta)}$, for small values of $\frac{d_2 - d_1}{L - d_1}$ and assuming $\frac{d_2}{L - d_1}$ is negligibly small, we obtain the following expansion for the layer strain.

$$\gamma \approx \frac{d_2 - d_1}{L - d_1} \left( \tan^2 \theta \sin^2 \alpha - \frac{d_1}{d_2 - d_1} \sin^2 \alpha_o \right)$$

This strain relationship exhibits a coupling between the tilt and polar angles which must couple to other energy terms to determine which angular variation is preferred. However, is not unreasonable to assume that the uniaxial tilt described by $\theta$ does not vary ($\theta = \theta_o$) while the biaxial distortions due to $\alpha$ could deform, in which case the tangent term can be factored out. By entering this adjusted form of the strain into Eq. 2.6, we obtain the biaxial layer compression energy density.

$$f_c(\alpha) \approx \frac{1}{2} B \left( \frac{d_1 - d_2}{L - d_1} \tan^2 \theta_o \right) \left( \sin^2 \alpha - \sin^2 \alpha_o \right)^2$$

By entering typical values for the molecular dimensions $d_1 = 0.5\text{nm}$, $d_2 = 1.5\text{nm}$, and $L = 5\text{nm}$, and assuming that the tilt angle is $\pi/6$, then the layer compression modulus becomes rescaled by a factor of $5\%$. This means that for a SmC material with a layer compression modulus in the range of $0.1\text{MPa}$, there will be an effective layer
compression modulus, that we will call \( B_c = B \left( \frac{(d_x - d_y)}{(d_x + d_y)} \tan^2 \theta_o \right)^2 \), of approximately 5kPa.

This is experimentally relevant because this value is in excellent agreement with values obtained by Stannarius et. al.\(^{37}\) On a side note, similar terms to the energy density in Eq. 2.10 can be derived from elastic theory as long as they are invariant under

\[
\left( \hat{n}, \hat{k} \right) \leftrightarrow \left( -\hat{n}, -\hat{k} \right)
\]

inversion. One possible candidate takes the form of variations of the square of the layer chirality order parameter, \( \chi = 2 (\hat{r} \times \hat{n} \cdot \hat{p}) (\hat{r} \cdot \hat{n}) = \sin 20 \cos \alpha \)\(^{36}\), form its undistorted state.

\[
f_c'(\alpha) = \frac{1}{2} B_c \left( \chi^2 - \chi_o^2 \right)^2 = \frac{1}{2} B_c \sin^4 2\theta \left( \sin^2 \alpha - \sin^2 \alpha_o \right)^2 \quad 2.11
\]

From Eq. 2.11, we can see that the energy term described in Eq. 2.10 attempts to stabilize the layer chirality when external stresses are applied.

Beyond the simple layer compression modulations due to biaxial rotations, there also exist another consequence of varying the polarization direction. This occurs when local bound charge densities are generated by spontaneous polarization splay \( \rho_B = -\nabla \cdot \vec{P} \).

This results in an elastic energy density of the form,

\[
f_e = (\vec{\nabla} \cdot \vec{P}) \int \frac{(\vec{\nabla} \cdot \vec{P}')}{4\pi \varepsilon_o \varepsilon |\vec{r} - \vec{r}'|} dV' \quad 2.12
\]

where \( \varepsilon \) is the relative dielectric constant and the spontaneous polarization (\( \vec{P} \) and \( \vec{P}' \)) represent the same charge density distribution, however \( \vec{P}' \) is integrated to determine the electric potential spatial distribution. If we assume that the polarization magnitude is a
constant $P_0$, an estimate of the magnitude of $f_E$ (which we will call $B_p = \frac{P_0^2}{\varepsilon_0}$) can be obtained with the following values, $P_o = 100 \frac{\mu C}{cm^2}$, $\varepsilon_o = 8.9 \frac{\mu C^2}{J m}$, and $\varepsilon = 10$, resulting in a value of $B_p \approx 10^4 Pa$.

2.5 NATURAL LENGTH SCALES

From the previous discussions, we determined several elastic energy terms based on a frustrated packing model of bent core molecules. Two of these bulk elastic constants $C$ and $K_b$ were associated with spontaneous splay of the dipolar direction and layer bending $K_b$, respectively, while the other terms, $B_C$ and $B_P$, dealt with the consequences of those spontaneous distortions. Another important observation is that the polarization splay term is inherently a surface term due to Gauss’s law, $\int C(\nabla \cdot \hat{p})dV = \oint C(\hat{p} \cdot d\vec{a})$, therefore the polar direction splay term behaves like a negative surface tension. By comparing the difference of the polarization splay to surface tension ($|C| - \sigma$), the differences of the layer bending and normal Frank elastic constants ($|K_b| - K$), and the combined effects of layer compressions and electric self interactions ($B_{eff} = B_C + B_P$), we can determine three natural length scales for our system. The first is the ratio of the two terms dealing with spontaneous distortions $L_o = \frac{|K_c - K|}{|K - \sigma|}$ and results in a value of approximately 6nm, which is comparable to the molecular length of the molecules. The second length scale is the square root of the spontaneous layer bending
divided by the layer compression term, $\lambda = \sqrt{\frac{k_s-k_f}{\beta_c + \beta_p}}$ which has a value of approximately 60nm, and is similar to the experimentally observed periodicity (10nm < $\lambda$ < 100 nm) of splay domains$^{29}$ (see Figure 2-2d). The final length scale which is the ratio of the surface term compared to the layer compression term, $R_o = \frac{C_O}{\beta_c + \beta_p}$ which has values around 1µm. This is similar to the observed radii of bent core filaments standing in air$^{32}$, and helical filaments formed in isotropic melt$^{20}$ (see Figure 2-2e). The amount of splay in a domain can be estimated from our model, which gives $\Delta \Phi \approx \frac{(\delta - \gamma) \lambda}{b}$. Here $\delta - \gamma$ is the angle between the sides of two neighbor molecules. According to Coleman et al.’s model$^{29}$ (see in Figure 2d), the amount of splay in one domain is twice the tilt angle. The model by Vaupotic et al$^{30}$ finds that it is even smaller, about 10°. Our model gives twice the tilt angle with $\delta - \gamma \sim 1^\circ$, and agrees with Vaupotic et al model with $\delta - \gamma \sim 0.2^\circ$.

As shown above, the steric or electrostatic inclusions not only lead to spontaneous layer bending and polarization splay modulations, but also drive a symmetry reduction from $C_2$ of the SmCP phase to $C_1$ of the SmCG phase characterized with $\alpha > 0$. This means that the splay of an out of layer polarization necessarily induces additional layer bend, which has been observed experimentally.$^{29}$ This coupling results in a wide variety of local molecular and layer configurations which all have the same local symmetry, but their macroscopic behavior depends on the magnitude and the direction of the spontaneous polarization.
2.6 STRUCTURAL DEPENDENCE ON POLARIZATION

A suggested structural phase diagram of the B_7 and B_7' materials as a function of the spontaneous layer polarization P_o (x-axis) and the polarization angle \( \alpha \) (y-axis) is shown in Figure 2-4. The strength of \( B_{\text{eff}} \) increases with \( P_o \) due to \( B_P \), which decreases toward higher temperatures as the polarization decreases. The filament stability increases while the stable fiber radius decreases with increasing \( P_o \) and \( \alpha \). For small \( \alpha \), bilayer type structures may arise to cancel the out-of-layer polarizations and appear as SmCP, as experimentally observed by Bedel et.al.\(^{15} \) in a B_7' material. For intermediate \( \alpha \) and \( P_o \) the effects of the negative C and \( K_b \) begin to overcome the effects of \( B_{\text{eff}} \) leading to small layer bending and a macroscopically observable out-of-layer polarization\(^{35} \). At larger \( \alpha \), pronounced layer undulations occur if \( P_o \) is small, since there \( B_{\text{eff}} \) is small, while for larger \( P_o \) the layers become stiff and break into ribbons, representing the classical columnar type structure\(^{29} \). For the largest \( \alpha \) values, extreme layer stresses or electric self interactions would drive the formation of multiple defect structures and the breaking up of the smectic structure into small smectic domains, which may appear macroscopically as a nematic phase.
Figure 2-4  Suggested structural phase diagram of the $B_7$ and $B_7'$ phases as a function of the spontaneous polarization and the polarization angle. Graphical representations of the possible layered structures are shown within the ovals along with their possible locations on the diagram. The directions of increasing $B_{\text{eff}}$, temperature, fiber stability, and fiber radius are also included.
REFERENCES


CHAPTER 3

THE THEORY OF BENT CORE FILAMENT STABILITY, BUNDLING, AND ELASTICITY

3.1 INTRODUCTION

Non-Newtonian filament formation ranges from natural processes such as silk drawn from spiders and silkworms to synthetic processes used in the production of nylon and polyester fabrics, optical filaments, and even body armor. All of these are stabilized by forming rigidity in the pulling process that opposes the constricting effects of surface tension. This rigidity can have various sources, such as glassy transitions under cooling to the evaporation of solvents or polymerization during the pulling process.

Some of the earliest studies on liquid crystal filaments appeared in columnar liquid crystals and later in smectics with coaxial smectic layering. The study of bent core liquid crystal filaments is fairly new, and much is unknown about their basic structure and properties. The presence of helical filaments growing in the B phase was first reported in 1999, where it was pointed out that polarization might have a crucial role in the formation of the helical filaments. There were also reports that the B phase actually prefers to form stable filaments rather than stable thin films. Characterization of the helical filaments indicated that they were
composed of cylindrically concentric smectic layers and that the helicity was connected to the chiral symmetry breaking of the achiral molecules. Studies of freestanding filaments showed that two bent core liquid crystal phases formed the most stable filaments and were identified to be the B₂ and B₇ phases. The B₇ phase preferred to form single stable filaments in a very narrow size range with radii between 1.5-2µm, while the B₂ phase could only form filaments of much larger radii, which could be associated to bundling of these smaller filament units. Interesting electrical properties of the filaments, such as repulsion and attraction to transverse electrical fields, push/pull attraction of bulk material to longitudinal electric fields, and filament breaking to DC electric field pulses point towards a polar behavior consistent with C₁ symmetry (i.e. polarization components both normal and parallel to the smectic layer normal).

In this chapter we discuss some of the structural properties of bent core filaments. We begin by discussing the Plateau-Rayleigh instability and modifications proposed to describe liquid crystal filaments. We also discuss the failures of these models to describe certain aspects of bent core filament stability. By constructing a free energy per length which includes director distortions, polarization splay, biaxial layer compressions, electric self interactions, and surface tension, we propose the mechanisms behind bent core filament stability. We then extend this result to explain the benefits of filament bundling observed in the SmCP phase. Finally, we develop an elastic theory to treat freestanding filaments as elastic strings which will be used later to describe the motion of vibrating filaments. All results will be discussed and compared to the behavior predicted in Chapter 2 with the assumption of frustrated molecular packing.
3.2 FLUCTUATIONS OF NEWTONIAN FLUID FILAMENTS

The study of Newtonian fluid filaments is a very old and well explained phenomenon. First experimental investigation of fluid filament stability was performed by Joseph Plateau in 1873, when he noticed that streams of Newtonian fluids break apart into a steady stream of droplets with a length approximately three times the diameter\(^{16}\). This result was later determined theoretically by Lord Rayleigh, by comparing the effects of longitudinal fluctuations on the stability of a fluid cylinder due to changes in surface energy. We will reproduce this calculation and then expand on it later to include the effects of bulk elasticity in some liquid crystal phases.

The classic Plateau-Rayleigh model assumed an incompressible fluid cylinder whose energy is described entirely by the surface tension. This cylinder, defined to have an undisturbed radius \(r_0\) and a length \(L\), where a small periodic perturbation of wavelength \(\lambda\) with wave number \(q = \frac{2\pi}{\lambda}\) is applied along the filament is shown in Figure 3-1. The radial disturbance of the surface can be described as \(r(z) = r_0 + \epsilon_1 \cos qz - \epsilon_2\), where \(\epsilon_2\) will be determined by assuming a constant volume.

With the assumption of incompressibility, \(V_D = \pi [r_0^2 - 2r_0 \epsilon_2 + \frac{1}{2} \epsilon_1^2]L + \frac{2\pi n}{q} (r_0 - \epsilon_2) \sin qL + \frac{\pi^2}{4q} \sin 2qL\)

3.1

With the assumption of incompressibility, \(V_D = \pi r_0^2 L = 0\), then we obtain two resulting relationships, \(qL = 2\pi n\) and \(\epsilon_2 = \frac{\epsilon_1}{4n}\), where \(n=1,2,3,\ldots\). By entering these results into the differential surface area element, \(dA_D = 2\pi r \sqrt{1 + \left(\frac{\epsilon_2}{\epsilon_1}\right)^2} dz \approx 2\pi r \left(1 + \frac{1}{2} \left(\frac{\epsilon_2}{\epsilon_1}\right)^2\right) dz\), we get
Figure 3-1 The filament geometry used for stability analysis due to longitudinal fluctuations. We have defined several parameters important to analysis, such as the undeformed radius $r_0$, the deformed radius $r$, and the perturbation wavelength $\lambda$. 
the following increase in surface area by assuming $\varepsilon_1^4 \approx 0$.

$$A_D - 2\pi r_o L \approx \frac{\pi \varepsilon_1^2 L}{2r_o} \left( r_o^2 q^2 - 1 \right)$$

This results in an increase of surface energy due to surface tension $\sigma$ of,

$$\Delta E_s = \sigma \frac{\pi \varepsilon_1^2 L}{2r_o} \left( r_o^2 q^2 - 1 \right)$$

which is always positive, representing an undesired distortion, as long as $r_o^2 q^2 > 1$.

However, if this term becomes negative then the energy of the filament is decreased and the perturbation grows. This results in a maximum length to diameter ratio before the instability begins of

$$\frac{L_{\text{max}}}{2r_o} = \pi$$

which agrees very well with Plateau’s observations.

### 3.3 FLUCTUATIONS OF NON-NEWTONIAN FILAMENTs

Filament stability for non-Newtonian systems results from flow induced elasticity in longitudinal flow or with bulk elasticity in viscoelastic materials. In columnar or smectic liquid crystals, elasticity can arise from compression terms dealing with increasing column density or smectic layer compressions perpendicular to the filament direction\textsuperscript{1,17}. So while the surface tension would try to decrease the filament’s radius, the compression term would resist it. Estimation of the minimum stable filament radius for columnar and smectic liquid crystals were calculated using the Modified Plateau-Rayleigh instability (MPR)\textsuperscript{18} which, by its name, is a modified form of the previously described instability.
The surface energy for the MPR model is the same as the one displayed in Eq. 3.3 however, the presence of a bulk term indicates the need to introduce a radial displacement term described below.

\[ u(x, z) = \frac{x}{r_o} \cos(qz) - \frac{x^2 \varepsilon_1^2}{4r_o} \]  

From this, the bulk elastic energy change (\( \Delta E_B \)) due to the longitudinal fluctuations can be calculated using the following relationship.

\[ \Delta E_B = \int \frac{1}{2} B \left( \frac{\dot{\omega}}{\omega} \right)^2 dV \approx \frac{\pi B \varepsilon_1^2 L}{4} \]  

Therefore, the change in total energy can be determined by the sum of the surface and bulk energies resulting in the following relationship.

\[ \Delta E = \Delta E_s + \Delta E_B = \frac{\pi \varepsilon_1^2 L}{4r_o} \left( 2\sigma r_o^2 q^2 - 2\sigma + Br_o \right) \]  

This results in a maximum length to diameter ratio that is stable to longitudinal fluctuations, \( \frac{L_{\text{max}}}{2r_o} = \frac{\pi}{\sqrt{1 + \frac{\sigma B}{\varepsilon_1^2}}} \), which unlike the results for Newtonian fluid, there exists a size dependence of the instability. More interesting is the fact that if \( r_o > \frac{2\sigma}{B} \), then the filament will be stable to all fluctuations. If we substitute \( \sigma \sim 10^{-2} \text{N/m} \) and \( B \sim 10^5 \text{N/m}^2 \) then we obtain for the minimum stable radius of \( r_{\text{min}} \sim 0.1 \mu\text{m} \). This value is approximately one order smaller than the experimentally observed values and indicates that bent core filaments should be stable to these fluctuations. It was suggested that this discrepancy could be explained by defects which would decrease B, however experiments clearly show that the stable filaments of B7 materials exist in discrete stable diameters (see
Chapter 4) which cannot be explained by this model. This model can only determine a minimum cutoff radius and therefore suggests another mechanism may be necessary to describe the unit size. We believe that the coupling of polarization splay to the layer curvature in SmCG materials may be useful in describing this unit filament size.

3.4 FLUCTUATIONS OF BENT CORE FILAMENTS

We propose a theoretical model that explains the source of bent core liquid crystal filament stability to radial fluctuations and connects this stability to the local symmetry of the smectic phase. Our study probes filament stability on three major bent core phases: the SmAP, the SmCP (B2), and the SmCG (B7). Previous theoretical considerations of these phases were laid out by H.R. Brand, P.E. Cladis, and H. Pleiner in 1998, in which they discussed the symmetries and possible macroscopic consequences of these phases.19 The basic molecular orientations with respect to the undistorted layer normal for these phases are sketched in Figure 3-2 and can be sufficiently described by two angles \( \theta \) and \( \alpha \). In all of the phases, we see three important directions described by the layer normal \( \hat{k} \), the director direction \( \hat{n} \), and the polar direction \( \hat{p} \) which must be perpendicular to the director.

In the SmAP phase, there exists a two-fold symmetry axis along two mirror planes \( (C_{2v}) \). It is a polar phase where the polar direction \( \hat{p} \) is perpendicular to layer normal \( \hat{k} \), which is parallel to the director \( \hat{n} \). SmAP materials show in-plane birefringence and ferroelectric or antiferroelectric type switching.20
Figure 3-2  Illustrations of the molecular orientation of the molecular long axis $\hat{n}$ and the polarization direction $\hat{p}$ with respect to the smectic layer normal $\hat{k}$. We show the polarization configurations of the SmAP, SmCP, SmCG, and SmLP and their corresponding layer structure.
The SmCP phase is also polar parallel to the layer plane, but the molecular plane is tilted with respect to the layer normal. This phase is interesting because of the formation of distinct chiral domains even though the molecules are achiral. The smectic layers have a two fold rotational symmetry (C2) about the polar direction, and the chirality arises from broken mirror symmetry induced by the coupling of layer tilt and polarization.

The SmCG phase has a polarization with component along and perpendicular to the layer normal. This material has the lowest symmetry (C1) of all the polar smectic phases. In our model we will consider the SmCG to be the structure for the B7 phase and we will find that a double tilted structure with $\alpha \neq 0, \pi$ stabilizes the formation of filaments and filaments.

The SmLP phase can be called the “Leaning” smectic phase, and results from the polarization direction lying along the tilt plane $\alpha = \pm \pi/2$ and has $C_s$ symmetry. Although this phase has never been found experimentally it has theoretical importance since this polar orientation provides the largest out-of-layer component for a given layer tilt and may be induced in the previously described phases under the correct conditions.

Regarding their filament stability, experimental investigations showed that SmAP materials do not form stable filaments (unstable); SmCP can form both films and bundles of filaments (metastable), whereas the B7 materials spontaneously form single and bundles of filaments, but they do not form freestanding films (stable).
3.4.1 MODEL GEOMETRY AND APPROACH

We assumed a very simple smectic structure consisting of concentric cylindrical layers running through the entire length of the filament (L) and from the outer radius (R) of the filament to some defect core radius ($r_c$). This very simple model is shown in Figure 3-3, and although not noted in the figure, the cylindrical coordinate system that we will be working in has $\hat{r}$ pointing radially from the filament’s center, $\hat{z}$ along the filament’s long axis, and $\hat{\psi}$ being mutually perpendicular to $\hat{r}$ and $\hat{z}$ such that $\hat{r} \times \hat{\psi} = \hat{z}$. With this coordinate system, we assume that the smectic layer normal lies along the radial coordinate $\hat{r}$.

Although the smectic geometry is simple, we allow the formation of a double tilted SmCG phase characterized by non-zero polar and azimuthal angles $\alpha$ and $\theta$, respectively. For the sake of simplicity, we fix the tilt angle $\theta$ and assume that it cannot be changed. We also assume that the polarization angle $\alpha$ is constant and independent of the radial position, though we allow its uniform variation to minimize the free energy. The azimuth angle around the cone is set to a constant along the $r\psi$-plane for simplicity. With these constraints, we can define the molecular long axis $\hat{n}$ (director), the polarization direction $\hat{p}$, and the molecular plane normal $\hat{m}$ in terms of $\theta$ and $\alpha$.

$$\hat{n} = \cos \theta \hat{r} + \sin \theta \hat{\psi} \quad 3.7$$

$$\hat{p} = \sin \theta \sin \alpha \hat{r} - \cos \theta \sin \alpha \hat{\psi} + \cos \alpha \hat{z} \quad 3.8$$

$$\hat{m} = \sin \theta \cos \alpha \hat{r} - \cos \theta \cos \alpha \hat{\psi} - \sin \alpha \hat{z} \quad 3.9$$
Figure 3-3  The filament geometry used in our stability analysis. The filament has length $L$, outer radius $R$, and inner cutoff radius $r_c$, where the smectic properties are assumed to break down. This model shows the layered structure consisting of concentric smectic layers which are essential for filament stability.
By using \( \hat{r} \), \( \hat{n} \), and \( \hat{p} \), we can define the chiral order parameter \( \chi \) of the layers as,

\[
\chi = 2(\hat{r} \times \hat{n} \cdot \hat{p})(\hat{r} \cdot \hat{n}) = \sin 2\theta \cos \alpha. \tag{21}
\]

The smectic layers have maximum chirality when \( \cos \alpha = \pm 1 \), corresponding to the SmCP phase. For \( 0 < |\chi| < \sin 2\theta \), the layers have \( C_1 \) symmetry (SmCG phase). When \( |\chi| = 0 \), this phase has \( C_s \) symmetry (SmLP phase) and there exists the maximum allowed out of layer polarization.

By taking into account the bulk and surface free energy densities, the total free energy \( F(R, \alpha) \) can be obtained by integrating the free energy density \( f_B(r, \alpha) \) over a cylindrical volume and the surface energy density \( S(\alpha) \) over the surface area.

\[
F(R, \alpha) = 2\pi L \int_{r_c}^R f_B(r, \alpha) r \, dr + 2\pi L S(\alpha) \quad \tag{3.10}
\]

Then by dividing by \( 2\pi L \), we can obtain the free energy per length \( \Phi(R, \alpha) \) as:

\[
\Phi(R, \alpha) = \frac{F(R, \alpha)}{2\pi L} = \int_{r_c}^R f_B(r, \alpha) r \, dr + RS(\alpha) \quad \tag{3.11}
\]

Obviously when the energy minimum occurs at \( R = r_c \), then the bulk terms disappear and the surface term which is governed by surface tension dominates forcing the filament to break. However if the minimum occurs when \( R > r_c \), then the bulk energy may overcome the cost of the surface tension and filament stability can be achieved. Our approach consists of minimizing the free energy per length to determine the minimum polarization angle \( \alpha \) and corresponding filament radius \( R_{\text{min}} \) for different variations of parameters. Below we will discuss the bulk and surface terms considered in the model and their resulting contributions to the free energy per length.
3.4.2 BULK ENERGY TERMS

**Director Distortions**

This energy density accounts for the low energy (Frank Free Energy\(^1\)) director distortions and the spontaneous layer bending term due to the polar contribution discussed in Chapter 2 (Eq. 2.4). Using the one constant approximation for the director distortions \(K\), our energy density takes the following form\(^2\):

\[
f_N(R) = \frac{1}{2} K \left( (\vec{V} \cdot \hat{n})^2 + (\vec{V} \times \hat{n})^2 \right) + \frac{1}{2} K_b \left( \hat{e} \times \vec{V} \times \hat{p} \right)^2 = \frac{1}{2} \left( K + K_b \cos^2 \theta \sin^2 \alpha \right) \frac{1}{r^2} \quad 3.12
\]

The energy density from this term integrates out to have a logarithmic relationship to the core radius \(r_c\) as

\[
\Phi_N(R) = \frac{1}{2} \left( K + K_b \cos^2 \theta \sin^2 \alpha \right) \ln \left( \frac{R}{r_c} \right) \quad 3.13
\]

Below \(r_c\), the director distribution does not matter, and the material is assumed to be either isotropic or a nematic fluid whose director points along the filament and is undistorted. This term can be either positive or negative depending on the behavior of the effective elastic coefficient.

**Spontaneous Polarization Splay**

Spontaneous splay of the polar axis, as discussed in the Chapter 2, may be due to either steric or electrostatic interactions. We attempt to model these two effects by considering two elastic constants, one which is independent of the spontaneous polarization \(c'\) (steric term) and one which is proportional to it \(c''P_o\) (electrostatic).

\[
f_D = c'(\vec{V} \cdot \hat{p}) + c''(\vec{V} \cdot \mathbf{P}) \approx (c' + c''P_o)(\vec{V} \cdot \hat{p}) = C(\vec{V} \cdot \hat{p}) \quad 3.14
\]
If the polarization magnitude $P_o$ is constant, we can define an effective energy constant $C$ which is a linear combination of the two effects. Although we combine $c'$ and $c''$ in the $C$ term, the need to separate these two mechanisms is essential because the elastic $c'$ term is independent of all other energy terms and only drives splay of the molecular kink directions, however the electrostatic $c''$ term is proportional to the macroscopic polarization which is present in other energy terms such as the electric self interactions.

Using the notation provided in Eq. 3.14, we can easily rewrite the dipolar divergence free energy density $f_D$ and free energy per length $\Phi_D$ in terms of the angles $\theta$ and $\alpha$.

$$f_D(r, \alpha) = C\left(\vec{\nabla} \cdot \vec{p}\right) = C\sin \theta \sin \alpha \cdot \frac{1}{r} \quad 3.15$$

$$\Phi_D(R, \alpha) = C\sin \theta \sin \alpha \left(R - r_e\right) \quad 3.16$$

The sign of $C$ can be positive or negative depending on the molecular properties, but Eq. 3.16 can always add negatively to the energy by changing the sign of $\alpha$, so $\Phi_D$ can always oppose the effects of surface tension. Furthermore, $\Phi_D$ is also proportional to the filament radius and has a tilt angle dependence which eliminates this term in the SmAP phase where $\theta=0$.

**Electric Interactions**

This energy density which describes the electric field interactions is shown below,

$$f_E = -\int \vec{D} \cdot d\vec{E} = -\int \left(\varepsilon_o \vec{E} + \vec{P}\right) \cdot d\vec{E}$$

$$f_E = -\frac{1}{2} \varepsilon_o \vec{E} \cdot \vec{E} - \vec{P} \cdot \vec{E} \quad 3.17$$
where \( \varepsilon_0 \) is dielectric permittivity of free space, \( \varepsilon \) is the relative dielectric tensor for the material, and \( \bar{P} \) is the spontaneous polarization. It is important to derive the electric fields resulting from diverging polarizations within the material. Luckily, due to the simple geometry of our model, we are able to calculate these fields by using Gauss’s law inside the filament with the assumption of not free charges.

\[
\oint \left( \varepsilon_0 \varepsilon \bar{E} + \bar{P} \right) \cdot d\bar{A} = 0
\]

\[
\left( \varepsilon_0 \varepsilon_0 \varepsilon \bar{E} + \bar{P} \right) \cdot \hat{r} = 0
\]

\[
\bar{E} \cdot \hat{r} = -\frac{\varepsilon_0}{\varepsilon_0} \varepsilon_0 \left( \sin \theta \sin \alpha \right)
\]

\[
\bar{E} = -\frac{\varepsilon_0}{\varepsilon_0} \varepsilon_0 \sin \theta \sin \alpha \hat{r}
\]

This can be calculated exactly because in all dimensions except the \( \hat{r} \) direction, we assumed that the polarization does not diverge and cannot form electric fields. By plugging this result for the electric field into Eq. 3.17, we are able to obtain the free energy density and free energy per length in terms of \( \theta \) and \( \alpha \).

\[
f_E (r, \alpha) = \frac{\varepsilon_0}{2 \varepsilon_0} \left( \sin \theta \sin \alpha \right)^2
\]

\[
\Phi_E (R, \alpha) = \frac{\varepsilon_0}{4 \varepsilon_0} \left( \sin \theta \sin \alpha \right)^2 \left( R^2 - r_c^2 \right)
\]

The inverse of the relative dielectric tensor appears in both 3.19 and 3.20. This term operates only in the \( \hat{r} \) direction and therefore is reduced to a single element of the inverse tensor. This can be calculated by

\[
\left( \varepsilon_{rr} \right)^{-1} = \frac{1}{\varepsilon_1} (\hat{n} \cdot \hat{r})^2 + \frac{1}{\varepsilon_2} (\hat{m} \cdot \hat{r})^2 + \frac{1}{\varepsilon_3} (\hat{p} \cdot \hat{r})^2
\]

\[
= \frac{1}{\varepsilon_1} \cos^2 \theta + \frac{1}{\varepsilon_2} \sin^2 \theta \cos^2 \alpha + \frac{1}{\varepsilon_3} \sin^2 \theta \sin^2 \alpha
\]
where $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the eigenvalues of the dielectric tensor in the molecular frame of reference.

**Layer Compression**

As discussed in Chapter 2, a natural consequence of polarization distortion is a biaxial layer compression (Eq. 2.10). This energy density takes the form,

$$f_c(\alpha) = \frac{1}{2} B_c \left( \sin^2 \alpha - \sin^2 \alpha_o \right)^2$$  \hspace{1cm} 3.22

and the free energy per length for this term is,

$$\Phi_c(R, \alpha) = \frac{1}{4} B_c \left( \sin^2 \alpha - \sin^2 \alpha_o \right)^2 \left( R^2 - r^2 \right)$$  \hspace{1cm} 3.23

and would oppose the effects of curvature induced by $\Phi_D$. We should note that this term is only valid for small layer deformations. For larger deformations, the layer compression modulus becomes larger (non-linear compressibility).

**3.4.3 SURFACE ENERGY**

The surface term provides an energy cost for creating an interface between two media, in our case air and liquid crystal. Due to possible orientational dependence of the surface energy, we assume an orientational dependent (tensor) form of the surface tension which takes the following form,

$$S = \sigma \cdot \hat{r}$$  \hspace{1cm} 3.24

where $\sigma$ is the tensor form of the surface tension, and $\hat{r}$ is the surface normal for our filament geometry. From this we can rewrite Eq. 3.24 as,
\[ S(\alpha) = \sigma_1 (\hat{n} \cdot \hat{r})^2 + \sigma_2 (\hat{m} \cdot \hat{r})^2 + \sigma_3 (\hat{p} \cdot \hat{r})^2 \]

where \(\sigma_1\), \(\sigma_2\), and \(\sigma_3\) describe the surface tensions if the surface normal was aligned along \(\hat{n}\), \(\hat{m}\), and \(\hat{p}\) respectively. This definition results in the following free energy per length.

\[ \Phi(R, \alpha) = \left( \sigma_1 \cos^2 \theta + \sigma_2 \sin^2 \theta \cos^2 \alpha + \sigma_3 \sin^2 \theta \sin^2 \alpha \right) R \]

3.4.4 DEFECT CORE ENERGY

Due to the existence of the cutoff radius required in this theory, one must examine the possible effects of a defect core on filament stability. We will do this by over-estimating its energy to be compared later on to other terms. By assuming that the filament is in the liquid crystalline phase in thermal equilibrium at temperature \(T \leq T_0\), and the defect core has enough distortion energy to completely melt the liquid crystalline material in the core to the isotropic phase, this core energy can be estimated as,

\[ E_{\text{core}} \leq (n k_b (T_0 - T) + \rho H) V_{\text{core}} \]

where \(n\) is the number density of the molecules, \(k_b\) is Boltzmann’s constant, \(\rho\) is the mass density, and \(H\) is the sum of specific latent heats of the liquid crystal phases to the isotropic phase, and \(V_{\text{core}}\) is the volume of the defect core. Assuming that the defect is a straight line running down the center of the filament, the defect volume can be written as the volume of a cylinder of radius \(r_c\) and length \(L\). By replacing the number density in
Eq. 3.27 by the combination of mass density $\rho$, Avagadro’s number $N_A$, and the molar mass $M$, we can calculate the energy per length $\Phi_{\text{core}}$:

$$\Phi_{\text{core}} < \left(\left(\frac{\rho N_A}{M}\right) k_B (T_o - T) + \rho H\right)\frac{1}{2} r_c^2$$  \hspace{1cm} 3.28

3.4.5 STABILITY RESULTS AND DISCUSSION

Now that we have derived all of the possible energy contributions, we can write the total energy per length as the sum of these components.

$$\Phi_{\text{total}}(R, \alpha) = \Phi_N(R) + \Phi_D(R, \alpha) + \Phi_E(R, \alpha) + \Phi_C(R, \alpha) + \Phi_S(R, \alpha) + \Phi_{\text{core}}$$  \hspace{1cm} 3.29

This free energy has to be minimized for $R$ and $\alpha$ for a given set of property values to find the equilibrium structure. Filament stability requires that the minimum of the energy per length be negative and the radius at this minimum be larger than $r_c$. To simulate the real situations as closely as possible, we have varied the parameters $\theta_o$, $\alpha_o$, $R$, $c'$, $c''$ and $P_o$ and have used reasonable fixed values for the remaining parameters. Both the ranges and the fixed values are provided in Table 3-1.
Table 3-1 List of simulated physical property values

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_o$</td>
<td>Equilibrium Smectic Tilt Angle</td>
<td>$-\pi/2&lt;\theta_o&lt;\pi/2$</td>
</tr>
<tr>
<td>$\alpha_o$</td>
<td>Equilibrium Polarization Angle</td>
<td>$-\pi&lt;\alpha_o&lt;\pi$</td>
</tr>
<tr>
<td>$r_c$</td>
<td>Defect Core Radius</td>
<td>$5\times10^{-9}$m</td>
</tr>
<tr>
<td>R</td>
<td>Outer Filament Radius</td>
<td>$10^8$m&lt;R&lt;10^{-5}$m</td>
</tr>
<tr>
<td>$K_b$</td>
<td>Spontaneous Layer Bending Constant</td>
<td>-66 pN</td>
</tr>
<tr>
<td>K</td>
<td>Director Elastic Constant</td>
<td>10 pN</td>
</tr>
<tr>
<td>$P_o$</td>
<td>Spontaneous Polarization</td>
<td>$10^{-4}$C/m$^2&lt;P_o&lt;10^{-1}$C/m$^2$</td>
</tr>
<tr>
<td>$c'$</td>
<td>Elastic Div. of Dipole Direction Constant</td>
<td>0N/m&gt;$c'&gt;-0.055$N/m</td>
</tr>
<tr>
<td>$c''$</td>
<td>Electric Div. of Dipole Direction Constant</td>
<td>0V&gt;$c'''&gt;-55$V</td>
</tr>
<tr>
<td>B</td>
<td>Layer Compression Modulus</td>
<td>$10^5$Pa</td>
</tr>
<tr>
<td>$d_{2-d_1}$</td>
<td>Approximately the Width to Length Ratio of the Molecule</td>
<td>0.2</td>
</tr>
<tr>
<td>$\varepsilon_1$</td>
<td>Relative Dielectric Constant Along $\hat{n}$</td>
<td>7</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>Relative Dielectric Constant Along $\hat{m}$</td>
<td>10</td>
</tr>
<tr>
<td>$\varepsilon_3$</td>
<td>Relative Dielectric Constant Along $\hat{p}$</td>
<td>12</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>Surface Tension Along $\hat{n}$</td>
<td>0.026 N/m</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>Surface Tension Along $\hat{m}$</td>
<td>0.024 N/m</td>
</tr>
<tr>
<td>$\sigma_3$</td>
<td>Surface Tension Along $\hat{p}$</td>
<td>0.025 N/m</td>
</tr>
</tbody>
</table>
Before proceeding with the numerical calculations we compare $\Phi_{\text{core}}$ with the other terms in Eq. 3.29 using the parameters given in Table 3-1 and by assuming a 1μm radius filament with $\alpha_o=0$, $\alpha=\pi/2$, $\theta_o=\pi/4$, $P_o=10^{-3}\text{C/m}^2$, $c'=0.04\text{N/m}$, $c''P_o=-0.01\text{N/m}$, and a typical molecular weight of 800g/mol. At 10°C below the isotropic–smectic transition with a typical latent heat of 20J/g we find that $\Phi_{\text{core}} \leq 2.51 \times 10^{-10}\text{N}$. On the other hand, we find $\Phi_{\text{total}} = -4.94 \times 10^{-9}\text{N}$ showing that by neglecting the defect term we introduce an error of less than 5%. Since the calculated core energy is an over estimate, it is justified to neglect it in our model. In any case, the core energy would mainly influence the stability transition range and not the stable filament radius. We also note that the director distortion energy per length $\Phi_N = -7.74 \times 10^{-11}\text{N}$ is even smaller than of $\Phi_{\text{core}}$, and can be neglected as well, however it is still included in our calculations. With the remaining terms we would like to analyze the relationships between the total spontaneous polarization $P_o$, the divergence terms $c'$ and $c''$, and the effects of varying $\theta_o$ and $\alpha_o$ on filament stability.

Numerical results were obtained by minimizing the energy per length $\Phi_{\text{total}}$ with respect to $R$ and $\alpha$ via a combination of derivative-free function minimization techniques provided in the Matlab® Optimization Toolbox, such as golden section search and parabolic interpolation combined with unconstrained nonlinear optimization techniques such as the simplex search method. Combining these multiple techniques help to determine a minimum solution to Eq. 3.29, and ensures, but does not guarantee, that these solutions are not local minima or maxima.
Polarization Dependence

Polarization dependences were studied by varying the polarization and calculating the stable filament radius. The first numerical calculation (Figure 3-4) compares the results of three simulations; the first sets \( c'=-0.04 \text{N/m} \) and \( c''=0 \), which probes the behavior of purely steric interactions on filament stability, the second sets \( c''=-11.2\text{V} \) and neglects \( c' \), which probes the effects of purely electrostatic interactions, and the third simulates the general case which uses \( c'=-0.04\text{N/m} \) and \( c''=-11.2\text{V} \) and accounts for both sources of polarization splay. What we see in this graph is that polarization has a tremendous effect on filament stability. The effects of electric self interactions are important in defining the stable filament radius and can be best seen by comparing the \( c' \) only curve which has a decrease in the stable radius as the electric self interaction of \( \Phi_E \) increases. The \( c'' \) curve has a strong stability transition and does not form very large filaments as compared to the \( c' \). However in the general curve, the contributions of both steric and electrostatic interactions greatly enhance the filament radius for intermediate polarization values close to the values for real materials. This behavior suggests that even though the \( c' \) and \( c'' \) are linearly combined, the resulting effect of the two mechanisms can be very different due to the \( c'' \) coupling to other energy terms.

The effects of electric self interactions can be seen more clearly in Figure 3-5, which compares the effects of \( \lambda_1 = c' \sin\theta_o / \sigma \) and \( \lambda_2 = c'' P_o \sin\theta_o / \sigma \) to the simulated stable filament radius (grayscale). What we see is that when \( \lambda_1 + \lambda_2 < 1 \), denoted by the dashed line, then filament stability is not allowed.
Figure 3-4  Numerical results of the polarization dependence of filament stability for $c'$ only, $c''$ only, and C. The $c'$ dominates at low polarizations and at large polarizations the $c''$ dominates, however at intermediate polarizations the combination of effects is greater than the sum of its parts.
Figure 3-5  Phase diagram which compares the effects of $\lambda_1 = \frac{c}{\sigma} \sin \theta_0$ to $\lambda_2 = \frac{c'}{\sigma} \sin \theta_0$ on the stable filament radius, where a) only $P_0$ is varied or b) only $c'$ is varied in the calculation of $\lambda_2$. We show the stability threshold (dashed line) which occurs at $\lambda_1 + \lambda_2 = 1$. 
As you move along increasing $\lambda_2$ in Figure 3-5a, representing an increase in polarization, we see that stability increases outside of the stability threshold and eventually decreases as electric self-interactions begin to dominate the free energy. On the other hand, Figure 3-5b compares the effects when $P_o$ is held constant and the value is $c''$ varied. What we see is that no bias on filament stability which indicates that an important effect in filament stability is electric self-interactions. This occurs because variations of $c'$ or $c''$ only effect the $\phi_D$ term, however when the polarization is varied this effects $\phi_D$ and $\phi_E$, which compete with each other.

**The Angular Dependences**

The angular dependences on filament stability can be studied by varying the layer tilt angle $\theta_o$ or the bulk polarization angle $\alpha_o$. The first case inspects the SmAP/SmCP, transition and the second looks at the SmCP/SmCG/SmLP transitions. By using the property values listed in Table 3-1 and varying only the corresponding bulk angles, we obtain the curves in Figure 3-6 and Figure 3-7, showing the effects of $\theta_o$ and $\alpha_o$ on filament stability, respectively. Both simulations show interesting behavior related to the phase symmetry and the stability of the filaments. The SmAP phase cannot form stable filaments via this mechanism due to a lack of out of layer polarization. This coincides with experimental results, in which we were not able to form filaments of the first SmAP$_A$ material$^{20}$. It is interesting to point out however that the tilt threshold
Figure 3-6  The effects of tilt angle on the stable filament radius for various polarizations, $P_o=10^{-4}\text{C/m}^2$ (●), $P_o=10^{-3}\text{C/m}^2$ (●), $P_o=10^{-2}\text{C/m}^2$ (□), and $P_o=10^{-1}\text{C/m}^2$ (○), when $\alpha_o=0$.

We can see that for all polarizations in the SmAP phase ($\theta_o=0$) there is no stable filament with $r>r_c$. However there is a definite threshold behavior which is strongly dependent on the polarization. Furthermore, we see that SmCP materials with larger polarizations ($P_o\approx 10^{-1}\text{C/m}^2$) can form stable filaments, but their radius is below the (MPR) Modified Plateau-Rayleigh instability threshold (solid line), $R_m\approx 0.1\mu\text{m}$, which would be unstable to longitudinal fluctuations.
Figure 3-7  a) Several plots of stable filament radius versus the value of $\alpha_o$ at various polarization values, $P_o=10^{-4}\text{C/m}^2$ ($\square$), $P_o=10^{-3}\text{C/m}^2$ ($\triangledown$), $P_o=10^{-2}\text{C/m}^2$ ($+$), and $P_o=10^{-1}\text{C/m}^2$ ($\circ$). The bulk $\alpha_o$ value has a significant effect on the stable filament radius for small polarizations. Larger polarizations also show this effect, however their differences are much more constrained. The largest stable single filaments occur in the SmLP phase ($\alpha_o=\pm\pi/2$) and decreases as we move through the SmCG phase and have a minimum in the SmCP phase. The MPR line (dashed line) denotes the threshold below which no filaments are stable. b) The free energy per length for the $P_o = 10^{-3} \text{ C/m}^2$ case with varying $\alpha_o$, which shows that the free energy is minimized in the SmLP phase and has an unstable maximum in the SmCP phase.
decreases with increasing polarization. Therefore if the SmAP phase has a significantly large in-plane polarization, one could stabilize a filament if a molecular tilt could be induced, possibly through shear flow about the $\hat{\psi}$ direction. We also notice that the effect of increasing polarization in all the phases is a decrease in the filament radius, and filaments with large polarizations ($P_o > 5 \times 10^{-2}$ C/m$^2$) have a stable filament radius below the Modified Plateau-Rayleigh Instability limit and would be susceptible to fluctuations. It is important to note that the SmCP phase does not form stable filaments as seen by the maxima for the free energy in Figure 3-7b, but instead must transition to another configuration. This may explain the observations that SmCP filaments exist only in bundles, and not in single form. Since experiments clearly show that B$_7$ filaments are much more stable than B$_2$ (SmCP) filaments, this model is consistent with the possibility that the B$_7$ phase does indeed hold C$_1$ (SmCG type) symmetries.$^{12}$

Finally we would like to derive an analytic free energy for filaments in the regime of large radius $R \gg r_c$, $\alpha = \pi/2$, and only considering the dominating radial dependences. This free energy per length takes the form,

$$\Phi \approx \left( \sigma + C \sin \theta \right) R + \frac{1}{4} \left( \frac{P_o^2 \sin^2 \theta}{\varepsilon \varepsilon_o} + B_c \cos^4 \alpha_o \right) R^2$$

where the first term is due to the surface effects and the second is due to the bulk. By minimizing this energy per length with respect to the radius, we obtain the following result for the stable radius.

$$R_{\text{min}} = \frac{-2(\sigma + C \sin \theta)}{P_o^2 \sin^2 \theta \varepsilon \varepsilon_o + B_c \cos^4 \alpha_o}$$
This result has an overall negative which requires that for realistic positive values of the stable radius that \( C < -\frac{\sigma}{\sin \theta} \). and for reasonable values we can estimate that \( C < -0.04 \text{N/m} \).

By taking the values listed in Table 3-1, we see that Eq. 3.31 results in good agreement with experimental measurements (see Chapter 4) with a value of approximately 2\( \mu \text{m} \).

To summarize, we presented a simple theoretical model assuming constant tilt and azimuth angles of bent-core molecules, but allowed the rotation of the molecular plane with respect to the tilt plane by an angle \( \alpha \) away from the SmCP situation. We showed that non-zero \( \alpha \) values lead to the stability of single fluid filaments. In accordance with the experimental observations, we found good agreement between the minimum stable filament radius and we showed that the director tilt is necessary for filament formation. In all, this study shows that polarization may have significant effects in the structure and behavior of bent core filaments. Since the publication of this work\textsuperscript{23}, efforts have been made to generalize this model by Dan Phillips and Patricia Bauman at Purdue University\textsuperscript{24,25}. Their work has confirmed filament stability similar to the form described above, but has also extended it for filaments with layer undulations as observed by Coleman et. al.\textsuperscript{26}

3.5 BUNDLING OF BENT CORE FILAMENTS

As was discussed earlier, bent core filaments can exist as bundles\textsuperscript{14}, and only the B\textsubscript{7} filaments can form single stable filaments of approximately 2\( \mu \text{m} \) radius (see Chapter 4). As was discussed in the previous sections filament stability is dependent on the
Figure 3-8  A filament cross section (left) composed of a bundle of filaments of various sizes with non-cylindrical smectic layers between them, and the approximate structure (right) of radius $R_T$ composed of filaments of the average unit radius $R_0$. We also show the possible structure of a grain boundary which must exist between the filament bundles.
balance of surface and bulk terms. However, if the bulk is composed of smaller individual filaments, then the balance of bulk to surface effects can be affected. An example of this model is depicted in Figure 3-8, where we describe a random packing of filaments with a distribution of sizes as being composed of a random packing of n filaments of a fixed unit size $R_o$. By redefining the approximate free energy described in Eq. 3.30, we rescale the bulk liquid crystal terms by the number of unit filaments and the surface tension by the square root of the number of the filaments if we neglect the surface tension between filaments.

$$\Phi \approx \sqrt{n} \sigma R_o + n C \sin \theta R_o + \frac{n}{4} \left( \frac{p_o^2 \sin^2 \theta}{\varepsilon \varepsilon_0} + B_c \cos^4 \alpha_o \right) R_o^2$$  \hspace{1cm} 3.32$$

The square root in the surface tension term is an approximation to represent the average radius for a random packing of n filaments, resulting in the relationship between the number of filaments with unit size $R_o$ and the total bundle size $R_t \approx \sqrt{n} R_o$. Then by minimizing this energy with respect to the unit radius $R_o$, we can redefine the relationship for the stable unit filament size to account for bundling.

$$R_o = \frac{-\left( \sigma + \sqrt{n} C \sin \theta \right)}{\frac{p_o^2 \sin^2 \theta}{\varepsilon \varepsilon_0} + B_c \cos^4 \alpha_o}$$  \hspace{1cm} 3.33$$

This suggests that a major advantage for bundling in bent core filaments is an effective reduction of the surface tension. Therefore, when the value of C is near zero such as is expected in the B$_2$ phase, then an adequate bundling of filament structures can stabilize the average filament size if $C < -\frac{\sigma}{\sqrt{n} \sin \theta}$. 
Although, this model is simple and can explain the stability of filament bundles, it is possible that the presence of multiple defects which must exist could drastically increase the bulk energy. Therefore, we will discuss this increase in energy and compare it to the surface energy. In the filament bundles, there must exist unorganized smectic layers which fill the spaces between the individual filament units. These smectic layers must form defects (grain boundaries) to effectively fill these regions, an example of which is drawn in Figure 3-8. By estimating the energy per length for one defect

$$\Phi_{\text{GB}} \approx \frac{\gamma B K}{\kappa}$$

(see Ref. 27), where B is the layer compression modulus, K is a Frank elastic constant, and \(\kappa\) is an average layer curvature, one can estimate the strength of these defects compared to the surface energy. By assuming that n filaments will result in n-1 defects, and by using \(B=0.1\text{MPa}, K=10\text{pN}, \kappa^{-1}=1\mu\text{m}\), and assuming that we have 10 filaments in our bundle, then we get a value of \(\Phi_{\text{GB}} = 9nN\) while the energy of the surface would be \(\Phi_s = \sqrt{n\sigma R_o} \approx 100nN\). This suggests that for reasonably sized filament bundles the effects of defects will result in less than 10% of the value resulting from the increased surface area.

This bundling model of the fluid filaments has an unexpected consequence related to the elasticity of the filaments. In a bundled system, the larger number of filaments will increase the stiffness and the effective compressibility of the bundle. The resulting effective layer compressibility becomes

$$B_{\text{eff}} \approx \frac{\kappa}{2} \left( B_C + \frac{p^2 \sin^2 \theta}{\varepsilon_0} \right)$$

as seen in the denominator of Eq. 3.33, where the square root results from the relative change of the bulk to surface
area with the air. This result and the theory in the next section become important in the analysis of data in Chapter 5.

3.6 FILAMENT ELASTICITY AND THE EQUATIONS OF MOTION

Due to the stability of bent core filaments without flow or the presence of external fields, the treatment of these filaments as structural elastic media becomes important. In situations where large fluid flow can be neglected such as small amplitude oscillations or events happening in very short time scales (see Chapter 5), then this elastic model can be extended to explain the dynamics of these systems. In the case of large flow and significant director or polarization reorientation occurring over long time scales, then this model cannot explain the behavior and a more general formalism should be utilized.

Recent interest in the behavior of smectic filaments has necessitated the development of elastic (our model) and viscous models (see work by A.J. Walker and I.W. Stewart\textsuperscript{28}) to describe the behavior of smectic filaments.

In order to develop a general model capable of describing the elasticity and the mechanical responses of bent core filaments to external fields, we decided to use the Lagrangian formalism because it directly connects the motion of the filaments to the energy terms discussed earlier. To begin this model, we describe a filament as a parameterized vector function using a position vector $\vec{r}$ which is a function of time $t$ and the filament parameter $s$. The filament parameter defines a position along the filament between one end ($s=0$) to the other end ($s=s_o$). The position vector function has the property that at time $t_o$, $\vec{r}(s,t_o)$ describes the filament configuration at that moment in
time, and likewise for a point \( s_0 \), \( \vec{r}(s_0, t) \) describes the trajectory of this position in the filament with time. Furthermore, the vector derivative, \( \vec{r} = \frac{\partial \vec{r}}{\partial t} \), describes the direction pointing along the filaments axis (longitudinal axis) and the stretch within the filament. An example of this description is shown in Figure 3-9, along with the definition of the cross sectional area \( A \) and the differential length \( ds \).

The Lagrangian is a way to describe mathematically the transfer between kinetic and potential energy in a general, coordinate independent manner. This begins by defining the Lagrangian which is composed of the difference between the kinetic and potential energies. The basic Lagrangian per length that we use in this formalism was discussed by Lecker et. al. and is shown below:

\[
L(s, t) = \frac{1}{2} \mu \vec{r}_s \cdot \vec{r}_s - \frac{1}{2} T \left( \vec{r}_s \cdot \vec{r}_s - 1 \right) - \vec{f} \cdot (\vec{r} - \vec{r}_o)
\]

This equation is valid for perfectly flexible and inextensible filaments. The first term is the kinetic energy term where \( \mu \) is the mass per length of the filament. The effect of the inextensible (constant length) approximation is the assumption that \( \vec{r}_s \cdot \vec{r}_s = 1 \) and appears as a Lagrange multiplier whose constant \( T \) represents the local tension in the filament to be determined by the particular problem under study. This approximation, although not explicitly stated, also assumes that the tension is large compared to other extensional forces such as those related to longitudinal strains. The final term deals with the effects of external forces represented as a force per length \( \vec{f} \) which displaces the filament from its initial position at \( \vec{r}_o \). This model, being very useful for building a basic approach to handle string dynamics, it is insufficient and too idealistic for describing the behavior of
Figure 3-9  A graphical representation of the parameterized vector space used to describe the properties of the bent core liquid crystal filaments. This model utilizes a three dimension position vector ($\mathbf{r}$) whose components are functions of the filament parameter $s$ and time $t$. The parameter space that describes the filament is bound between $0 \leq s \leq s_0$, where $s_0$ is the total length of the unstretched filament. A closer look at a differential element of the filament of length $ds$, shows that the vector derivative, $\frac{\mathbf{r}}{\partial s}$, lies along the filament long axis and is perpendicular to the cross sectional area $A$. 
viscoelastic filaments composed of liquid crystals where longitudinal strains can be relevant. We attempt to build onto Eq. 3.34 by first accounting for the elasticity resulting from smectic ordering on the filament dynamics. These considerations result in adding two more energy terms related to the elastic behavior of the filament when exposed to longitudinal and transverse strains,

\[ E_e = \frac{1}{2} Y A (\vec{r} \cdot \vec{r} - 1) + \frac{1}{2} Y I (\vec{r} \cdot \vec{r} - 1) \]

where \( Y \) is Young’s modulus of an elastic material and \( A \) is the cross sectional area. The second term deals with the elastic response to bending of a filament where \( I \) is the second area moment of inertia (for a circular cross section is \( I = \frac{\pi R^4}{4} \)). While Young’s modulus can only describe the elasticity of solids, we will show that a similar relationship can be derived for the bent core filaments composed of concentric cylindrical smectic layers. This occurs because of the smectic layer compressions can be connected to stretching and bending of the filaments in the absence of flow. This derivation begins by considering the bulk energy density term defined by \( \frac{1}{2} B \gamma^2 \) where \( B \) is the layer compression modulus and \( \gamma \) is the layer strain. If we assume that layer compression effects are related to the longitudinal stretching, then the compression strain can be written in terms of the longitudinal strain multiplied by Poisson’s ratio \( (\nu) \). By using this description, we see that the square of the layer strain can be rewritten as,

\[ \gamma = \nu^2 \left( \vec{r} \cdot \vec{r} - 1 + \left( (\vec{r} - \vec{r}) \cdot \vec{r} \right)^2 \right) \]

where the first term deals with extensional effects and the second with bending. The factor of \( \nu \) which converts the longitudinal strain on the filament to radial strain.
second term depicts the effects of layer bending which creates a gradient of longitudinal tension and compression along the bending direction. This gradient can be described as proportional to the displacement from the neutral surface of the filament whose center is defined by \( r_c \) and is inversely proportional to the radius of curvature described by \( r_s \). The neutral surface defines a cross section within the filament where bending induces no longitudinal stress, which in the case of a circular cross section lies in the center of the filament. Furthermore the bending direction can be defined by the vector \( r_{ss} \) whose magnitude is inversely proportional to the radius of curvature. Figure 3-10 depicts the layer distortions (dashed blue lines) resulting from longitudinal forces (blue arrows) generated by stretching or bending and the location of the neutral surface (dashed red line). By integrating the layer compression energy density by the cross sectional area we obtain the following expressions for the energy per length.

\[
E_c = \frac{1}{2} \nu^2 BA (r_s \cdot \vec{r}_s - 1) + \frac{1}{2} \nu^2 BI (r_{ss} \cdot \vec{r}_{ss})
\] 3.37

In an elastic material with volume conservation, the value of Poisson’s ratio would be equal to \( \frac{1}{2} \) which we will assume; however in many real elastic materials this value is slightly lower. With these substitutions, we can rewrite the Lagrangian per length to include these elastic effects.

\[
L = \frac{1}{2} \mu (r_i \cdot \vec{r}_i) - \frac{1}{2} (T + \frac{1}{4} BA) (r_s \cdot \vec{r}_s - 1) - f \cdot (\vec{r} - \vec{r}_o) - \frac{1}{8} BI (r_{ss} \cdot \vec{r}_{ss})
\] 3.38

In this description we grouped the tension and the extensional elasticity together to create an effective tension for a bent core filament. For systems with low curvature \( \left| r_{ss} \right| << s_o^{-1} \), such as small amplitude oscillations, the last term can be neglected. Another effect that
we must include to accurately describe bent core filaments are the effects of viscosity.

Due to the limited dimensionality of smectic fluidity and the structure of the bent core filament (coaxial cylinders), the flow perpendicular to the filament’s long axis can be assumed to be negligible. Along with the assumption of no torsion, the only flow that is of importance lies along the filament’s axis. Therefore we can describe the viscous behavior as being related to asymmetric stretching of the filaments (plug flow). The simplest viscous dissipation term (per length) is shown in Eq. 3.39.

Figure 3-10  Some examples of the forces (blue arrows) on a filament’s cross section generated by a) axial and b) bending of the filament. We show the neutral plane (dashed red line) and an exaggerated diagram of the smectic layers and how they compress and expand due to these distortions.
In this equation, $\eta$ is the viscosity, $A$ is the fluid cross sectional area, $s_o$ is the total length of the filament, and $\frac{\xi}{\tau_o}$ is the shear rates related to longitudinal flow.

To this point we have discussed and developed the Lagrangian and dissipation factor per length which describes the competing energies involved in bent core filament dynamics. In order to derive our equations of motion, we will define the following integral,

$$I = \int_{t_0}^{t} \int_{s_0}^{s} L(t, \vec{r}, \vec{\dot{r}}, \vec{\ddot{r}}, \vec{\tau_{ss}}) dt ds$$

which is referred to as the action. The correct equations of motions can be derived from the action such that $\delta I = 0$, which can be determined using the calculus of variations. The argument we discuss was described in the book *Mathematical Methods for Physics and Engineering* and begins by assuming that there is a functional equation, in our case a position vector solution $\vec{r}_0$, whose derivatives with respect to $t$ and $s$ satisfies the relationship ($\delta I = 0$). Then by using this assumption, we can allow a functional variation from that solution by substituting $\vec{r}(s,t) = \vec{r}_0(s,t) + \alpha \tilde{\beta}(s,t)$, where $\alpha$ is sufficiently small constant and $\tilde{\beta}(s,t)$ is an arbitrary function which varies from the minimum solution. From this relationship we see that we can rewrite all of the partial derivatives which $L$ depends on as derivatives of both $\vec{r}_0$ and $\tilde{\beta}(s,t)$. Furthermore, because $\alpha$ is
sufficiently small we can expand $L$ as a Taylor’s series about the solution at $\vec{r}_0$ with respect to $\alpha$ ignoring higher orders,

$$L(t,\vec{r}) = L(t,\vec{r}_0) + \left( \frac{\partial L}{\partial \vec{r}} \right) \cdot \alpha \vec{\beta}(s,t) + \left( \frac{\partial L}{\partial \vec{r}_i} \right) \cdot \alpha \vec{\beta}_i(s,t) + \left( \frac{\partial L}{\partial \vec{r}_s} \right) \cdot \alpha \vec{\beta}_s(s,t)$$  \hspace{1cm} (3.41)

Then by using integration by parts we see that we can obtain the following relationships for the first and second derivative components of $\vec{\beta}(s,t)$,

$$\frac{\partial L}{\partial \vec{r}_s} \cdot \alpha \vec{\beta}_s = \frac{d}{ds} \left( \frac{\partial L}{\partial \vec{r}_s} \cdot \alpha \vec{\beta}_s \right) - \frac{d}{ds} \left( \frac{\partial L}{\partial \vec{r}_s} \cdot \alpha \vec{\beta}_s \right) - \frac{d}{ds} \left( \frac{\partial L}{\partial \vec{r}_s} \cdot \alpha \vec{\beta}_s \right)$$ \hspace{1cm} (3.42)

$$\frac{\partial L}{\partial \vec{r}_ss} \cdot \alpha \vec{\beta}_ss = \frac{d}{ds} \left( \frac{\partial L}{\partial \vec{r}_ss} \cdot \alpha \vec{\beta}_s \right) - \frac{d}{ds} \left( \frac{\partial L}{\partial \vec{r}_ss} \cdot \alpha \vec{\beta}_s \right) + \frac{d^2}{ds^2} \left( \frac{\partial L}{\partial \vec{r}_ss} \cdot \alpha \vec{\beta}_s \right)$$ \hspace{1cm} (3.43)

where the first time derivative component obeys the same relationship as Eq. 3.42 by substituting $s$ for $t$. In this case, we obtain the following solution for the action from Eq. 3.40.

$$\int_{t_0}^{t_1} \int_{r_0}^{r_1} \left( \frac{\partial L}{\partial \vec{r}} - \frac{d}{dt} \left( \frac{\partial L}{\partial \vec{r}_i} \right) - \frac{d}{ds} \left( \frac{\partial L}{\partial \vec{r}_s} \right) + \frac{d^2}{ds^2} \left( \frac{\partial L}{\partial \vec{r}_ss} \right) \right) \cdot \vec{\beta}(s,t) dt ds$$ \hspace{1cm} (3.44)

The first integral results in the Euler-Lagrange equation provided that this term be zero for all variations of $\vec{\beta}(s,t)$. The second and third integrals are related to boundary and initial conditions, respectively, and if we consider that the initial condition and the boundary points are known (strong anchoring) then $\vec{\beta}(s,t)$ which represents variations
from the known values, must be zero. Therefore we obtain the following Euler-Lagrange equation for a system without dissipation.

\[
\frac{\partial L}{\partial \vec{r}} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\vec{r}}} \right) - \frac{d}{ds}\left(\frac{\partial L}{\partial \ddot{\vec{r}}} \right) + \frac{d^2}{ds^2}\left(\frac{\partial L}{\partial \dddot{\vec{r}}} \right) = 0 \tag{3.45}
\]

This equation is only equal to zero because we have not included the effects of dissipation. In general we can couple the dissipative effects of \( q \) by introducing them in the following manner\(^\text{31}\),

\[
\frac{\partial L}{\partial \vec{r}} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\vec{r}}} \right) - \frac{d}{ds}\left(\frac{\partial L}{\partial \ddot{\vec{r}}} \right) + \frac{d^2}{ds^2}\left(\frac{\partial L}{\partial \dddot{\vec{r}}} \right) = \frac{\partial q}{\partial \vec{r}} \tag{3.46}
\]

thus allowing us to derive the equation of motion for viscoelastic filaments under applied force per length defined by \( \vec{f} \). By entering the Lagrangian shown in Eq. 3.38 and the dissipation per length shown in Eq. 3.39 into Eq. 3.46, we can arrive at the following equation of motion per length of the filament.

\[
\mu \dddot{\vec{r}} + \frac{\eta A}{s_o^2} \vec{r} = \frac{d}{ds}\left((T + \frac{1}{3} BA)\dddot{\vec{r}}\right) - \frac{d^2}{ds^2}\left(\frac{1}{3} BI \dddot{\vec{r}}\right) - \vec{f} \tag{3.47}
\]

This equation will be used in Chapter 5 to describe the dynamic and static behavior of filaments measured in several experiments for analysis purposes.
REFERENCES


CHAPTER 4

EXPERIMENTAL CHARACTERIZATION OF BENT CORE FILAMENT STABILITY

4.1 INTRODUCTION

Classical characterization techniques used on liquid crystalline materials typically assume a thin film with at least an average alignment. Typical techniques such as dielectric spectroscopy, ferroelectric current measurements, dynamic light scattering, and optical characterization under applied fields all require some degree of surface alignment of the material. However, most of the bent core liquid crystal phases such as the $B_7$ phase cannot be aligned in films, resulting in either limiting the characterization to techniques which are insensitive to the alignment or by correcting for the issues caused by bad alignment\textsuperscript{1,2,3}. Fortunately, the desire of the $B_7$ phase to spontaneously form free standing filaments, allows for the consistent formation of large, uniform domains\textsuperscript{4,5}. These freestanding structures have inherent advantages due to their structural stability however there are complications which arise due to device design and analysis which must consider the cylindrical symmetries. The first systematic study of bent core filaments was published in 2003\textsuperscript{6}, where basic structural and electric interactions were considered. Later studies on these filaments included a more in depth structural
characterization using X-ray diffraction and SEM\textsuperscript{7,8}. Static and dynamic studies of bent core filament interactions with DC electric fields lead to physical characterization using damped harmonic resonance\textsuperscript{9,10}.

In this chapter, we probe the mechanical stability of the filaments to better understand the filament structure and formation. We used a variety of techniques ranging from filament statistics to direct force measurements and structural analysis to probe bundling behavior. Results are analyzed and compared to the stability and bundling models described in Chapter 3.

4.2 MATERIALS

We attempted to compare materials with B\textsubscript{7} (B\textsubscript{7'}) and B\textsubscript{2} phases in order to better understand their phase differences. We also chose some materials with very similar molecular structures to study the effects of different molecular designs on filament stability. The basic molecular structure of the materials that we studied can be seen in Figure 4-1. By varying side groups, phenyl linkages, and tail lengths we can obtain a large range of molecular geometries and phase behavior.

4.3 CHARACTERIZATION OF BENT CORE FILAMENT STABILITY

To perform a quantitative investigation of bent core filament stability, we use scanning electron microscopy (SEM) and filament statistics. The filament statistics are obtained by creating multiple filaments and measuring their stable diameters.
Figure 4-1  The basic molecular structure of the bent core mesogens studied in their filament forms.
Table 4-1  Table of studied mesogens, their structures (Figure 4-1) and phase behavior.

<table>
<thead>
<tr>
<th>Name</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>A</th>
<th>B</th>
<th>R₄</th>
<th>R₅</th>
<th>Phase Behavior (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC1</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₇H₁₅O</td>
<td>Cr 85 B₇ 176 Iso</td>
</tr>
<tr>
<td>BC2</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₈H₁₇O</td>
<td>Cr 116 B₇ 177 Iso</td>
</tr>
<tr>
<td>BC3</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₉H₁₉O</td>
<td>Cr (?) B₇ 174 Iso</td>
</tr>
<tr>
<td>BC4</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₁₆H₃₅O</td>
<td>Cr 103 B₇ 175 Iso</td>
</tr>
<tr>
<td>BC5</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>OOC</td>
<td>NCH</td>
<td>F</td>
<td>C₁₀H₂₃O</td>
<td>Cr 110 B₂ 147 B₂₇ 160 Iso</td>
</tr>
</tbody>
</table>
Temperature dependences, the effects of the aliphatic tail lengths, and phase dependent structures are discussed. We find good agreement between the structural model described in Chapter 3 and the experimental results obtained in this study.

4.3.1 EXPERIMENTAL SETUP

The device that we used to pull and hold the filaments is a self closing tweezer with a tapped hole for use with a screw to open and close the tweezer tip. The non-opened end of the tweezers is anchored outside of the heat stage (Instec) with a mount. Figure 4-2 shows this setup and the modified tweezer construction and functionality. Images were obtained using a microscope (Olympus) and a CCD camera connected to a computer.

SEM images were obtained by pulling filaments in our device, cooling to a crystal phase, then placing the filament on a piece of ITO glass. For better SEM images, the filaments were coated with a thin layer of gold using sputtering. SEM images were taken with help from Liou Qiu at the Liquid Crystal Institute characterization facility.

4.3.2 RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) images of filaments and filament bundles can be seen in Figure 4-3, where we show and discuss some interesting structures. The first image shows a filament which has a very ideal cylindrical shape and is very flexible with an approximate radius of curvature of 1-2mm. The second image is of the
Figure 4-2 a) The experimental setup for the static and dynamic measurements which consists of a microscope connected to a CCD or high speed camera for image collection, a heat stage with a mount attached to a modified tweezer allowing control of the tweezer tip spacing. b) The mechanism for tweezer control is the use of a screw which is run through one side of the tweezer and passes through the other side which is tapped. This allows control of the distance of the tapped side with respect to the free side.
broken cross section of the same filament and shows a very smooth surface with no
undulations and a nice circular cross section. The lack of surface undulations, a texture
observed by Coleman et. al.\textsuperscript{1} in bulk, is most likely due to the larger surface tension in air
as compared to in the bulk. The third image is of the cross section of a filament bundle
and one can see a hole in the center which is related to the center filament which broke at
a different position than the outer filaments. This is possible because of the defect
structures which must exist between filaments weakens their crystalline structure. The
final image is of what I call a “bead” defect. This defect forms when part of a filament
bundle breaks on both ends and due to the effects of surface tension retracts into a bead
like shape. What is interesting is that even in the bead shape, the presence of the filament
structure is still observable and looks like a snail shell or a coiled snake on a branch.

Filament statistics were obtained by holding the temperature constant, pulling a
large number of filaments and measuring their diameter. When a sufficiently large
sample number was collected, they were organized into probability graphs of the filament
diameters. We compare the effects of aliphatic tail length and temperature on the average
diameter for the BC1-4 materials (see Figure 4-4a). We see that the effect of the
temperature where the filament is pulled is weak but appears to have an inverse
temperature dependence which obeys the fit, $D = \frac{A}{T^\gamma}$, where $A=359\mu\text{m}^\circ\text{C}$ and
$T_0=276\circ\text{C}$. We also see that the filament diameter dependence on the tail length is
negligible, and suggests the importance of the molecular core interaction on the
formation of filament stability as discussed in Chapter 2. This same result was pointed
out for the local undulated structure by Pociecha et. al. by comparing calculated electron
Figure 4-3 SEM images of several filament in their crystalline phase. In these images we see a) the flexibility of these filaments, b) the smooth surface texture of a single filament, c) the tip of a broken filament bundle, and d) a defect structure which forms when a part of a bundle breaks on two ends and recoils to form a bead-like defect.
density maps and X-ray diffraction pattern for materials with varying tail lengths\textsuperscript{11}. This result is suggestive that the molecular interactions which dominate in the macroscopic filament stability is due to the frustrated packing of the molecular cores.

Figure 4-4b and Figure 4-5 show the probability distribution functions for the diameter of the filaments pulled below the B\textsubscript{7}-Isotropic transition for the materials BC1-4 and below the B\textsubscript{7}-Isotropic and B\textsubscript{2}-B\textsubscript{7} transitions for BC5, respectively. We see that in both situations the probability distribution in the B\textsubscript{7} phase has similar behavior and shows the existence of multiple probability peaks. This behavior can be fit with a superposition of approximately equally separated Gaussian curves whose peaks decrease with increasing diameter. This suggests that there is a unit filament diameter and the peaks correspond to a series of close packing configurations whose structure is suggested in the bottom of Figure 4-5. Evidence of this structure can be seen in Figure 4-3c where we see the broken end of a filament bundle whose center filament has been removed. In the B\textsubscript{2} phase of BC5, we see a much wider size distribution that peaks at larger diameters. This suggests that the unit filament size restriction has disappeared. This is in agreement with our stability model where filament stability is connected to the existence of an out of layer polarization. Therefore, in the B\textsubscript{2} phase with no out of layer polarization, it would be expected that the tendency for a unit size would be eliminated. Instead the B\textsubscript{2} filaments would prefer to bundle to accommodate the increase of free energy by an effective decrease of the surface energy.
Figure 4-4  The average filament diameter for the BC1-4 as a function of a) temperature and b) right below transition to the B7 phase, for varying aliphatic tail lengths ranging from C₇H₁₅ to C₁₆H₃₃. The temperature behavior shows a weak dependence which is inversely proportional to the temperature and no dependence on the aliphatic tails.
Figure 4-5  The diameter statistics for BC5 in the B7 and the B2 phase along with the best fit curves. We see a clear discrete behavior in the B7 phase which disappears in B2 phase. Evidence of bundling can be seen in the B7 phase when compared to a proposed filament structure shown at the bottom.
4.4 CANTILEVER MEASUREMENTS

In this section, we describe how to measure the forces involved when creating a bent core filament using a cantilever as a force detector. Previous measurements like this were performed on static filaments to determine their surface tension which ranged between 20-25mN/m\textsuperscript{8,10}. In this study we will use the cantilever to record the time dependence of the surface tension during the formation process of BC2 and BC4 near the B\textsubscript{7}-Isotropic transition.

4.4.1 EXPERIMENTAL SETUP

The basic experimental setup (Figure 4-6a) for these measurements consists of a heat stage under a microscope where a cantilever is secured and a sealed capillary tube attached to a motorized micro-positioner is moved relative to the cantilever. The cantilever that we use is actually a thin-walled capillary tube used in X-ray diffraction experiments (Wolfgang Muller Glas Technik), which has a 0.1mm diameter with a 10µm thick wall made of glass and is approximately 70mm long. We measured the spring constant of these cantilevers by measuring the resulting deflection due to applying small masses made of various lengths of string at the end, resulting in a spring constant of $k = 0.015 \frac{N}{\mu m}$ (see Figure 4-6b).

4.4.2 RESULTS AND DISCUSSION

Data is obtained by initially bringing the sealed capillary tip in contact with the cantilever tip with the liquid crystal material between them.
Figure 4-6  a) Experimental setup for the cantilever experiment which consists of a heat stage, a sealed capillary tube attached to a motorized micropositioner, and a stationary cantilever.  b) Plot of the weight of different lengths of string as a function of the resulting cantilever deflection as the strings are hung on the cantilever tip. The slope of the best fit line gives a spring constant for the cantilever of 15nN/µm.
The surface tension of the liquid crystal adheres the two tips together, at which point the connected system is moved to deflect the cantilever tip. When the cantilever tip stops moving while the capillary tip does not, then we know that we are near the instability and stop pulling the cantilever. Then by letting the instability develop without the capillary tip in motion, the net acceleration of the cantilever when it pulls away from the capillary is smaller and less likely to break the filaments.

Our measurements begin by comparing the fluid bridge diameter (the smallest distance across the fluid bridge) and the measured force determined by the cantilever deflection for BC4 near the Bγ-Isotropic transition as shown in Figure 4-7. We see that as time progresses, the fluid bridge begins necking and the cantilever moves due to the smaller adhesive force. This results in a further necking of the bridge until a stable filament diameter is achieved, at which the filament diameter and the cantilever diameter stabilizes. This experiment ends when the filament breaks and the cantilever returns to its zero force position. Some interesting observations of this behavior are as follows; (i) the reduction of the bridge diameter always precedes the change in force as detected by the cantilever motion, and (ii) we observe that the proportional changes in the radius and the cantilever force are almost identical. The first observation suggest that prior to the instability, fluid moves away from the center of the bridge to the glass surfaces while still holding a constant adhesive force with the glass. The second observation shows that the surface tension, which is basically determined by the ratio of these two terms \( \sigma = \frac{F}{\pi R} \), is almost a constant in the filament and in the bulk. This behavior is shown in Figure 4-8, where we compare the calculated surface tension \( \sigma = \frac{F}{\pi R} \) as a function of time for BC4.
Figure 4-7  Data for the bridge radius and force versus time obtained by analyzing video. We inserted images of the process at various times to show the correlations between the filament radius and the measured force and the video images.
We also compare this behavior in the isotropic phase which does not form filaments to those in the B7 phase which do form filaments. In both cases, we see that at the beginning of the necking process, there is an increase in the surface tension, probably related to the movement of fluid from the center to the glass surfaces. In the B7 case, this event is followed by a return to the pre-filament value of around 0.018N/m. An interesting point to make is that the surface tension in the isotropic phase is larger by approximately 10% of the value of that in the B7 phase and is probably related to an anisotropic surface tension which aids in the stabilization of the filament structure.

Previous studies of this phenomenon where presented as the mechanism for filament formation in some SmA materials at the SmA-Isotropic transition\textsuperscript{12}. In Figure 4-8, we show the nucleation process for two filaments, both of which show very similar behavior, however run 2 shows a strange phenomenon where the surface tension decreases by 50% before breaking. This is most likely due to a decrease in contact area with the cantilever tip resulting in a decreased in adhesion to the surface.

4.5 FILAMENT BUNDLE INTERACTIONS AND PROPERTIES

Many of the structural studies on filament bundles have been limited to SEM and optical characterizations of the bundle structure\textsuperscript{7,8}. However, little has been said about the physical interactions which take place between individual filaments and the bundle. Our study consists of structural analysis of static and dynamic structures between filament bundles using the experimental setup described in Figure 4-2, and were recorded using images or high speed video. The observed structures typically arose by accident
Figure 4-8  Data obtained for the effective surface tension (solid marks) $\sigma = \frac{F}{2\pi R}$ as it develops with time. We also show the radius (hollow marks) for each run so that we can compare the before and after filament formation. We compare the results of three samples, one in the isotropic phase which does not form a filament and two in the $B_7$ phase where filament formation is observed.
during the creation of filaments for other studies, however due to their interesting properties they were recorded and later analyzed.

4.5.1 ADHESION FORCES BETWEEN STATIC FILAMENTS

The first structure that we study using sample BC3 consists of two approximately parallel filament bundles being bridged in static equilibrium by a thin single filament. An image of this structure is shown in Figure 4-9 along with the proposed force diagram which describes the balance of forces at the filaments connection point. We see that if the single filament bridge is under tension $T_S$ at an angle $\theta$ to the bundle, then the only way that this structure can be in static equilibrium is if there exists an adhesive force $F_A$ normal to the bundle and the tension of the filament at the end which is connected to the bundle $T_B$ must be lower than $T_S$. By summing the forces in the x direction (see Figure 4-9) we can obtain the following relationship for the adhesion force.

$$F_A = T_S \sin \theta$$

By using the value of surface tension measured earlier (~20mN/m) and the information obtained from the image for the single filament radius $R=1.7\mu$m and the deflection angle $\theta=1.2^\circ$. We can instantly determine the adhesive force between the filament and the bundle to be $F_A=4.5$nN, by substituting $T_s = 2\pi R\sigma$. By assuming that the adhesion force is due to the surface tension at the interface then we can see that this force must take the form $F_A = 2\sigma \phi R$, which allows us to determine the contact angle of only $4^\circ$. This suggests that the filament do not deform much when they are in contact.
Figure 4-9  Comparison of the filament structure observed under a microscope under 5X and 50X magnification, to the model structure which allows us to determine the adhesion forces between the single and bundle filaments. The structure consists of a single filament spanning two filament bundles (far left). The 50X images shows that the single filament is being pulled away from the bundle in the fashion drawn in the upper right corner. By analyzing the force diagram for this static situation, we can determine the adhesion force between filaments and the change in tension.
4.5.2 FLOW VISCOSITY BETWEEN FILAMENTS IN CONTACT

This observation was obtained when attempting to use a high speed camera to measure buckling dynamics by breaking filaments made of BC2 (see Chapter 5). The high speed camera (Photron PCI-R2) with a frame rate up to 10,000 fps was borrowed from Dr. James Gleeson from the physics department at Kent State University. The observed behavior consisted of a bundle of filaments whose individual components begin to break and flow by each other. In Figure 4-10, we can see a series of images taken from high speed video that show this flow behavior. The filament bundle at the beginning of the measurement was approximately 10µm in diameter and after four filaments broke the final diameter was about 4.5µm. This is consistent with our bundling approximation of \( R_t \approx \sqrt{nR_o} \) which gives a bundling diameter of 10µm for 5 filaments with a unit diameter of 4.5µm, therefore we can assume that each filament had the same unit radius of \( R_o = 2.25 \mu m \). Analysis of the video showed that the four 500µm long filaments propagated with an average velocity of 5.3mm/s. By assuming that as the filament propagates, a shear stress is generated across the smectic layers which decreases linearly away from the filament contact point resulting in an average terminal velocity \( v \), then we can estimate this viscous force using the following relationship \( F_v = \eta \pi R_o v \) where \( \eta \) is the fluid viscosity, \( R_o \) is the unit filament radius, and \( v \) is the filaments terminal velocity. By matching this viscous force to the filament’s tension determined by the surface tension \( T = 2\pi R_o \sigma \) we can determine the flow viscosity between the filaments to be \( \eta = \frac{2\sigma}{v} \). This results in an estimation of the flow viscosity to be about
8Pas, which is very similar to the values obtained by studying resonance behavior in
Chapter 5.

Figure 4-10  Image sequence (10ms per image) of a filament bundle from CB2 whose
individual filament units break and proceed to flow by the other filaments in the bundle.  
The filament bundle before the breaking occurred was about 10µm and after was around 
4.5µm. We have included arrows and numbers to identify the positions of the four single 
filaments.
REFERENCES


CHAPTER 5

DYNAMICS AND ELASTICITY OF BENT CORE FILAMENT BUNDLES

5.1 INTRODUCTION

The study of string dynamics is an interesting field with numerous applications, many of which deal with the interactions of strings, approximately one dimensional objects, with forces in a three dimensional world. The most fundamental string interactions deal with the motion of filaments under tension and a classic example concerns the study of vibrating strings\(^1\). However there exist many more interesting behaviors which extend far beyond this classical problem. The effects of filaments coupled to viscous systems or the behavior of non-Newtonian fluids have provided a very fruitful field with a wide range of applications in fluid mechanics\(^2,3,4,5,6\), elasticity\(^7,8,9,10\), and biology\(^11,12,13\). With such a wide range of theoretical and experimental interest, there is no wonder that the structural behavior of non-Newtonian fluid filaments has grown in the past few decades. Recent examples of fluid filaments commonly occur in non-Newtonian fluids such as polymers\(^2,5,14\) and liquid crystals\(^15,16,17,18,19\); however it is only in liquid crystals where the existence of freestanding filaments exists without the requirement of flow. For this reason, we attempt to study the dynamics of bent core filaments where flow is negligible.
Using the Lagrangian formalism discussed in Chapter 3, we derived the general dynamic equations for describing their motion. This chapter begins with analysis of filaments bundles shape resulting from being connected to a thin smectic film. Analysis of these results allowed us to determine the biaxial compression modulus for these films. We then moved our discussion to filament dynamics where we studied the response of bent core filaments to oscillating transverse forces and an investigation into buckling instabilities of breaking filaments.

5.2 MATERIALS

The materials that we study are the same materials studied in Chapter 4. For completeness of this chapter we have included the base molecular structure shown in Figure 5-1 and the particular molecular substitutions and phase diagrams shown in Table 5-1. The molecular names that we have used in this chapter follow those described in Chapter 4.
Figure 5-1  The basic molecular structure of the bent core mesogens.

Table 5-1  Table of studied mesogens, their structures, and phase behavior.

<table>
<thead>
<tr>
<th>Name</th>
<th>R_1</th>
<th>R_2</th>
<th>R_3</th>
<th>A</th>
<th>B</th>
<th>R_4</th>
<th>R_5</th>
<th>Phase Behavior (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC2</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₆H₁₃O</td>
<td>Cr 116 B₇ 177 Iso</td>
</tr>
<tr>
<td>BC3</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₉H₁₉O</td>
<td>Cr (?) B₇ 174 Iso</td>
</tr>
<tr>
<td>BC4</td>
<td>H</td>
<td>H</td>
<td>NO₂</td>
<td>OOC</td>
<td>NCH</td>
<td>H</td>
<td>C₁₆H₉₃O</td>
<td>Cr 103 B₇ 175 Iso</td>
</tr>
<tr>
<td>BC5</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>OOC</td>
<td>NCH</td>
<td>F</td>
<td>C₁₀H₂₁O</td>
<td>Cr 110 B₂ 147 B₇ 160 Iso</td>
</tr>
</tbody>
</table>
5.3 STATIC BENT CORE FILAMENTS CONNECTED BY THIN FILMS

The static filament structures that we analyze were observed using the tweezer apparatus described in Chapter 4. The materials BC3 and BC5, where applied between the tweezer tips, heated to their isotropic phase, cooled to the B7 phase, and finally pulled by opening the tweezers with the set screw (see Figure 4-2). We observed that when we pulled multiple filaments at a time, sometimes we would observe that the filaments would bend towards each other for no apparent reason and would straighten spontaneously several minutes later. This behavior was more stable in the BC5 material and could last for several minutes while the BC3 sample would quickly break and return to the straight configuration. The most dramatic effect occurred with the BC3 material when this bending effect was large enough such that the filaments touched. At that moment, the filament adhered to the bottom half of the other filament forming the shape of a ‘y’, and then proceeded to “zip up” creating a single filament bundle. Microscope images of this phenomenon with the much more stable BC5 material can be seen in Figure 5-2, where we show the coexistence of the bent and straight filaments (part a) along with a before and after shot of this effect for two curved sections (part b), and finally the image of the space between the curved filaments between crossed polarizers showing the existence of a birefringent thin film connecting the filaments (part c). From these observations, we can assume that this bending is related to transverse forces being applied to the filament by the thin film. The proposed model for this behavior is that at the beginning of the pulling process the filaments began as part of a larger bundled filament. As the pulling process continued, some of these filaments began to pull away from the larger
Figure 5-2  Images of the structures formed during the pulling process for BC5 in the B7 phase. We show the coexistence of the bent filament structures (red circles) and the straight filaments (a) as well as an image of the structures before and after instability occurs (b). By comparing the area between the curved filament region with crossed polarizers (c) we clearly see the existence of a thin film spanning the gap.
Figure 5-3  The model structure for the film connected filaments and the proposed smectic structure which is composed of two edge dislocations and a region of tightly bent smectic layers. This force that holds the centenary shape is the balance between the tension in the filaments (red arrows) and the smectic compression of the film due to the stretching (blue arrows).
bundle due to their boundary location or the differences in flow of fluid from the source. When this happened, the outer smectic layers or the excess fluid between the filaments would separate into a film being feed by the bulk at the ends. However, when the flow to the film stopped for some reason (possible because all of the excess smectic which was between the filaments was used up), this film would quit growing and the tension in the filament would result in a compressive force on the film. A graphical representation of this idea is shown in Figure 5-3, where the red arrows represent the tension due to the curvature in the filament, and the blue arrows represent the resulting compressive force on the film.

5.3.1 ANALYSIS AND RESULTS

This model begins by using Eq. 3.49 from Chapter 3, with the assumptions of no motion (ignoring time dependences). This results in the following differential equation for the shape of the filament,

\[ 0 = \frac{d}{ds} \left( (T) \hat{r}_s \right) - \tilde{f} \]

which in reality is a set of two differential equations if the filament is assumed to lie in a plane. If we let \( \vec{r} = \vec{x} + s\hat{z} \) where \( x \) defines the transverse axis and \( z \) is the undistorted filaments axis, \( \tilde{f} = f_o \hat{x} \) as the transverse force per length, and assume that

\[ ds = \sqrt{1 + \left( \frac{dz}{dx} \right)^2} \, dz \]

then we obtain the following two equations along the \( z \) and \( x \) directions, respectively.
The first equation shows that the tension is a constant, and the second is the equation for a catenary which was classically used to describe the shape of cables hanging under their own weight. The solution to the differential equation for the displacement $x$ as a function of $z$ is shown below.

$$x = \frac{T}{f_o} \cosh \left( \frac{f_o}{T} z \right) + c$$

The tension $T = \pi D \sigma$ where $D$ is the filaments diameter, is written in terms of the surface tension of the filament, while the transverse force per length $f_o$ is related to the properties of the thin film. When the supply to the film stopped the surface tension of the filament still wants to straighten the filament. This force on the film causes a compression of the smectic layers due to the conservation of volume within the film which is opposed by the layer compression modulus $B$. Accordingly, if the thin film has a thickness $t$, then the force per length caused by the stretched film can be estimated by,

$$f_o \approx \frac{T}{s_o} \varepsilon_{||} = \frac{T}{s_o} \left( \frac{T}{ts_o B} \right)$$

where $s_o$ is the filament undeformed length. We have approximated the films strain parallel to the layer as the ratio of the filaments tension and the force due to the resulting
compression. From this approximation, the solution to the catenary equation can be rewritten as,

\[
\frac{xD}{s_o^2} = \frac{Bt}{\pi\sigma} \cosh \left( \frac{\pi\sigma}{Bt} \left( \frac{zD}{s_o^2} \right) \right) + c
\]

where \(c\) is an arbitrary constant. The ratio of force terms arise in a natural length scale which can be used to rescale the filament’s spatial dimensions by a factor of \(\frac{Bt}{\pi\sigma}\). This relationship can be seen in Figure 5-4, where we have aligned the filament center points to be along each other. By fitting both data sets with the equation shown in Eq. 5.6, we obtain a value \(\frac{Bt}{\pi\sigma} = 0.072\) relating the layer compression modulus and the surface tension. The film thickness was estimated by comparing the transmission color of the birefringent film shown in Figure 5-2c to the Michel-Levi interference chart assuming an in plane birefringence of around 0.1. This results in a layer compression of 5.6 kPa when we use a value of 25mN/m for the surface tension. This is interesting because it is similar to the value reported by Stannarius. et. al.\textsuperscript{21} by measuring the natural frequency of vibrating filaments with small amplitudes and the estimated biaxial layer compression modulus described in Chapter 2.

5.4 DRIVEN HARMONIC OSCILLATIONS IN BENT CORE FILAMENT BUNDLES

In this study, we show how one can measure the mechanical properties of bent core filaments by driving them with external forces. By using the elasticity model derived in the Chapter 3 we can determine their viscous and elastic properties by
Figure 5-4  The end to end profiles of two filaments highlighted in Figure 5-2a, labeled 1 (circles) and 2 (squares), along with the best fit curve from the above mentioned theory. We have shifted the filament bottoms to align along each other as to fit the data together.
measuring their resonant behavior. We used sound waves and alternating electric fields to oscillate the filaments to determine their physical properties. Results will be analyzed using theoretically derived equations of motion and the results compared with our proposed model for the B7 phase.

For these experiments, we used the setup developed at the University of Magdeburg\textsuperscript{21,22} under the guidance of Dr. Ralf Stannarius and his graduate student Alexandru Nemes. This setup consisted of a large heat stage with two glass rods which are connected by a suspended bent core filament. A motorized micro-positioner is used to create and align a filament vertically and in plane with the microscope’s focus. Images obtained with a long range microscope (Questar QM100) were captured with a high speed CCD camera (Citius) capable of capturing up to 10,000 fps. This setup was used in two ways to measure the vibrational behavior of the filaments. First we measured the mechanical response of the filaments to sound waves generated with an external speaker controlled with a TTi 40MHz Arbitrary Waveform Generator (TGA1241) running at 20Vpp. This was done to eliminate any of the issues which arise when dealing with first (Polar) and second (Dielectric) harmonic couplings to the electric field. This problem was studied separately by applying an alternating voltage across two copper plates spaced 8mm apart. To apply a sufficiently large electric field across the copper plates, we also coupled the waveform generator with a 300 times voltage amplifier. This allowed a maximum applied voltage of 6000Vpp which corresponds to an electric field of 0.375V/\textmu m. It should be noted that this electric field is smaller than the typical switching threshold (<5V/\textmu m) that one might expect to reorder the liquid crystal alignment and can
therefore be neglected. The heat stage used in these experiments consisted of a large copper box (8cm X 8cm X 8cm) which was heated and controlled using a digital temperature controller (Jumo). Viewing was made possible with the existence of two windows (~2.5cm in diameter) covered with quartz glass. There also existed four smaller ports (~1.5cm) located along the other four sides of the cube, for accessing the center of the heat stage. In our experiments, one horizontal port was never used and the other was used only in the sound experiments. The vertical ports were accessed by the glass rods in both experiments and were used to pull the filaments. The top glass rod was attached to a Teflon mount which held the glass rod at a fixed position and plugged the top port. The copper plates used in the electric experiments were held in place by a square piece of Teflon that was attached to the top glass rod and was suspended from the top mount. The bottom glass rod ran out of the box and was attached to a xy axes micropositioner and a motorized z axis micropositioner which could be controlled with computer software. A side view of the experimental setup is shown in Figure 5-5 along with the top views of the sound and electrical experiments.
Figure 5-5  a) The experimental setup for the filament resonance experiments which consists of a heat stage with various ports for accessing the filament under study, a long range microscope connected to a high speed camera, and a micro-positioner capable of pulling and aligning the filament. The experiments which used to oscillate the filament consisted of b) an external speaker pumping sound waves into a port, and c) two electrode (8mm apart) with an applied voltage to oscillate the filaments.
5.4.1 MECHANICAL (SOUND) OSCILLATOR EQUATIONS OF MOTION

Using the elasticity theory described in Chapter 3 (Eq. 3.49), we can immediately write the equations of motion for the bent core filament.

\[ \mu \dddot{r} + \frac{\eta A}{s_o^2} \ddot{r} = \frac{d}{ds} \left( \left( T + \frac{1}{4} BA \right) \dddot{r} \right) - \frac{d^2}{ds^2} \left( \frac{1}{4} BI \dddot{r} \right) - \dddot{f} \]  \hspace{1cm} 5.7

By using the approximation of small distortions and assuming that the filament motion will lie in a plane, then we can immediately write the position vector,

\[ \ddot{r}(s,t) = \ddot{x}(s,t) + s \ddot{z}, \] where \( |\ddot{x}| < < s_o \) and \( z \) is the direction of the undistorted filament.

With the approximation of small oscillations then we can immediately ignore the second term on the right hand side due to the approximately constant radius of curvature in the \( x \)-direction. Finally, the driving force per length which causes the filaments motion is due to the oscillating sound waves hitting the filament’s surface. This resulting force per length can be written as, \( \dddot{f} = f_o \cos \omega t \hat{x} \), where \( f_o \) is the product of the pressure waves amplitude and the filament’s diameter \( f_o = 2RP \) and \( \omega \) is the waves frequency. By applying these approximations and driving forces to the filaments equation of motion, we obtain two differential equations for the \( z \) and \( x \) directions.

\[ 0 = \frac{d}{ds} \left( T^* \right) \]  \hspace{1cm} 5.8

\[ \mu x_{ss} + \beta x_s = T^* x_{ss} - f_o \cos \omega t \]  \hspace{1cm} 5.9

where \( \beta = \frac{\eta A}{s_o} \) and \( T^* = T + \frac{1}{4} BA \). From Eq. 5.8, we can see that the tension is a constant determined by boundary conditions. Eq. 5.9 describes the motion of the filament, and is
a partial differential equation which describes a damped driven harmonic oscillator. This
equation can be simplified by assuming that, \( x(s, t) = X(t)(\sin ks + B \cos ks) \), where
\( X(t) \) is the maximum amplitude which holds all of the time behavior, \( b \) is an unknown
constant, and \( k \) is the wave number of the distortion. With fixed boundary conditions
\( x(s = 0) = 0 \) and \( x(s = s_s) = 0 \), we see that \( B = 0 \) and \( k \) must be discretized such that
\( k_n = \frac{\pi n}{s_s} \) and \( n = 1, 3, 5, \ldots \). With the spatial dependence of the filament known, we can
determine the time dependence of the oscillation from the point described by the
maximum amplitude (i.e. \( k_n s_{\text{max}} = \frac{\pi}{2} \)). This equation becomes,
\[
X_n'' + \omega_n^2 X_n + \omega_n^2 X = -\frac{4f_o}{\pi n \mu} \cos \omega t
\]
5.10

where \( \omega_n = \frac{nA}{\mu \omega_0} \), \( \omega_n^2 = \frac{\tau k_n^2}{\mu} \), and the factor of \( \frac{4}{\pi n} \) correctly accounts for the Fourier series
component of driving force corresponding to the \( n \text{th} \) mode. This equation, which is an
inhomogeneous differential equation, will have a homogeneous and particular solution.
The homogeneous solution, which results when \( f_o = 0 \), has three possible solutions which
we list below.
\[
X_h(t) = ae^{-\gamma t} \cos (\omega t - \phi_h)
\]
5.11
\[
X_h(t) = e^{-\gamma t} \left(a \cos \omega t + b \sin \omega t\right)
\]
5.12
\[
X_h(t) = e^{-\gamma t} \left(a e^{i\omega t} + be^{-i\omega t}\right)
\]
5.13
We see that all three solutions decay with time at a time constant, \( \gamma = \frac{\omega}{2} \), this is why these solutions are typically referred to as the transient solutions\(^{23} \). Since our studies typically deal with the steady state motion, we are not concerned with these effects except for their natural decay constant \( \gamma \). The particular solution which is crucial in analyzing our results will be discussed in more detail. The solution to this equation can be obtained by using the substitution \( X_p(t) = a \cos(\omega t - \phi) \), which is very similar to Eq. 5.11 where ‘a’ and \( \phi \) are undetermined constants. The constant ‘a’ represents the amplitude of oscillation and \( \phi \) represents the phase shift between the observed motion and the applied force. By entering this solution into Eq. 5.9, we obtain the following relationship.

\[
-\omega^2 a \cos(\omega t - \phi) - \omega \omega_D a \sin(\omega t - \phi) + \omega_n^2 a \cos(\omega t - \phi) = -\frac{4f_o}{\pi n \mu} \cos \omega t \quad 5.14
\]

This relationship must always hold true, therefore allowing us to solve for ‘a’ and \( \phi \). This solution begins by applying trigonometric identities to separate the time dependence from the phase shift. These substitutions are \( \cos(\omega t - \phi) = \cos(\omega t) \cos \phi + \sin(\omega t) \sin \phi \) and \( \sin(\omega t - \phi) = \sin(\omega t) \cos \phi - \cos(\omega t) \sin \phi \). With these we obtain the following relationships for the \( \cos(\omega t) \) and \( \sin(\omega t) \) components of Eq. 5.14 which must always hold true.

\[
(\omega_n^2 - \omega^2) \cos \phi + \omega \omega_D \omega \sin \phi = \frac{4f_o}{a \pi n \mu} \quad 5.15
\]

\[
(\omega_n^2 - \omega^2) \sin \phi - \omega \omega_D \omega \cos \phi = 0 \quad 5.16
\]
By solving this system of equations we obtain the following relationships for the magnitude $a$, and the phase $\phi$ of the filament’s response.

$$a = \frac{4f_u}{\pi n \mu} \frac{1}{\sqrt{(\omega_n^2 - \omega^2)^2 + (\omega_d \omega)^2}}$$  \hspace{1cm} 5.17$$

$$\tan \phi = \frac{\omega_d \omega}{\omega_n^2 - \omega^2}$$  \hspace{1cm} 5.18$$

Examples of the resulting magnitude are shown in Figure 5-6, where we have normalized the frequency by $\omega_n$ and the amplitude by the factor $\frac{4f_u}{\pi n \mu \omega_n}$. We see that the effect of increased dissipation is a lowering of the resonance peak. This makes sense because the energy loss caused by the dissipation is removed from the available energy used to deflect the filament. The complete solution can be obtained from an infinite series expansion using method of eigenfunction expansion. The full series solution of Eq. 5.9 is shown below,

$$x(s,t) = - \sum_{n=1,3,5,-}^{\infty} \frac{4f_u}{\pi n \mu} \frac{\sin(k_n s) \cos(\omega t - \phi_n)}{\sqrt{(\omega_n^2 - \omega^2)^2 + (\omega_d \omega)^2}}$$  \hspace{1cm} 5.19$$

However, in our experiments we were only interested in the n=1 mode dealing with the simplest vibrational mode.
Figure 5-6  Examples of the maximum amplitude as a function of the frequency, where we have normalized the frequency by $\omega_n$ and the amplitude by the factor $\frac{4f_n}{\pi\mu_0\omega_n^2}$. We show the effects of different dissipation factors which lowers the resonant maximum as the dissipation increases.
5.4.2 MECHANICAL (SOUND) OSCILLATOR ANALYSIS AND RESULTS

By using edge detection code written in Matlab®, we could determine the diameter and position of the filament with time by analyzing the high speed video. This position data was then converted, using Fast Fourier transform routines, into amplitude spectra which was used to determine the first and second harmonic responses of the filament. Examples of this analysis for a filament of BC5 (s₀=2.075mm and D=7.4µm) at 153°C, plotted in Figure 5-7a, clearly show an oscillatory signal at the driving frequencies.

One of the difficulties with this measurement technique is the frequency dependence of the speaker intensity which has its own resonance behavior. The calibration of the speaker intensity was performed by using a RO 203 sound level recorder (Reten Electronic) capable of determining the sound intensity in decibels (dB). The speaker intensity spectrum, measured at room temperature (~25°C), is given in Figure 5-7b along with the conversion to pressure via the following equation.

\[ P = P_{ref} \cdot 10^{\frac{\delta dB}{10}} \]  \hspace{1cm} 5.20

The factor of 20 (instead of 10) in the exponent accounts for the fact that intensity is related to the square of the pressure for ideal gases. The reference root mean squared (rms) pressure at room temperature, \( P_{ref} = 20\mu Pa \), and is the lowest audible pressure and is the reference standard for sound measurements. However, due to the fact that air is an ideal gas which obeys the ideal gas law \( P = mRT \), then as we increase the temperature in the heat stage we would expect an increase in pressure which is proportional to the ratios...
of temperatures in Kelvin. This suggests that at 153°C, the amplitude of the pressure
(not rms) would be 19.5Pa at the resonant peak (~550Hz) which coincides well with the
measured 22Pa obtained separately by Alexandru Nemes in Magdeburg, Germany.

Experimental results for the displacement spectra of BC2 and BC5 at 153°C are
shown for different lengths and diameters in Figure 5-8 and Figure 5-9 respectively, and
will be discussed by separating them into low (<400Hz) and high frequency (>400Hz)
regimes. In the low frequency regime, we see overall behavior which follows closely to
the applied speaker pressure which is expected because of the spring like behavior of the
filament. All of the filaments show a resonant behavior at around 300Hz. This is
unlikely because the resonant behavior should be dependent on the shape of the
filaments, i.e. should decrease as the length increases as seen by the definition of the
resonant frequency, $\omega_n^2 = \left(\frac{2\pi}{k^2} + \frac{\rho}{\pi\rho}\right)k_n^2$. This led to an inspection of the filament mounts
during oscillation, which indeed showed resonance of the mounts and not the filaments
near 300Hz. This means that this resonance behavior can be ignored, leading us to
inspect the oscillation behavior at larger frequencies. One of the major issues with the
larger frequency regime was the presence of a strong speaker resonance near 550Hz.
However, it was observed that the filament’s amplitude near this resonance range differed
from a direct proportionality of the speaker pressure. In fact, the resonant peak was
broader and even shifted to a higher frequency. This suggested the presence of a
Figure 5-7  a) Filament motion from analysis of high speed video and the Fourier transform which shows a very clear signal at the driving frequency. b) The measured speaker intensity at 25°C in decibels as a function of driving frequency along with the calculated pressure resulting if we use the standard 20µPa reference.
Figure 5-8  The resonant behavior of two BC2 filaments at 153°C compared to the applied speaker pressure. There exist dominant vibrational modes at a) low frequencies (~300Hz) which were not related to the filaments’ shape, and b) high frequencies which were dependent on their shape. The high frequency mode, due to its proximity to the resonance peak of the speaker, was observed by normalizing by the product of the speaker pressure and the filament diameter and fit using the theoretically predicted curve.
Figure 5-9  The resonant behavior of two BC5 filaments at 153°C compared to the applied speaker pressure. a) The low frequency mode (~300Hz) which appeared for all of the filaments is not related to the filament behavior but instead with the experimental mounts. b) The high frequency mode is related to the filaments resonance and is fit with the theoretically predicted curves for the maximum displacement.
resonance near the speaker resonance which could be observed by normalizing the spectra by the driving force per length, $f_o$, which is the product of the speaker pressure and the filament diameter. The results, shown in part b of Figure 5-8 and Figure 5-9, illustrate very clearly the presence of resonant peaks which follow the correct $\omega_{n=1}$ trend of increasing length and decreasing resonant frequency. Furthermore, we show good agreement between the theoretical predictions and the experimental data via the fitting of the maximum amplitude from Eq. 5.17 (dashed lines). These best fit curves allowed us to obtain values of the resonant frequency $\omega_{n=1} = \left( \frac{s}{s_0} \right) \sqrt{\frac{2\sigma^*}{\rho k}}$ and the dissipation frequency $\omega_d = \frac{n}{\rho s_0}$ for the two filaments as shown in Table 5-2. From these values, we could determine the apparent surface tension $\sigma^* = \sigma + \frac{\eta \rho}{k}$ and the viscosity $\eta$ by knowing the density of the materials, which we will assume to be 1g/mL. From Table 5-2, we see that the calculated viscosity for both materials is large and constant, while the effective surface tension appears to be dependent on the filament shape which is expected by the theory.

Table 5-2  Fit parameters and property values from resonance behavior of filaments

<table>
<thead>
<tr>
<th>Material</th>
<th>$s_o$ (mm)</th>
<th>D (µm)</th>
<th>$\omega_{n=1}$ (s$^{-1}$)</th>
<th>$\omega_d$ (s$^{-1}$)</th>
<th>$\sigma^*$ (N/m)</th>
<th>$\eta$ (Pa s)</th>
<th>B (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC2</td>
<td>3.54</td>
<td>8.8</td>
<td>3840±30</td>
<td>620±70</td>
<td>0.041±0.004</td>
<td>8±1</td>
<td>29±7</td>
</tr>
<tr>
<td>BC2</td>
<td>4.28</td>
<td>45</td>
<td>3610±10</td>
<td>480±30</td>
<td>0.27±0.01</td>
<td>9±1</td>
<td>87±40</td>
</tr>
<tr>
<td>BC5</td>
<td>3.03</td>
<td>20.5</td>
<td>3950±40</td>
<td>1010±110</td>
<td>0.074±0.006</td>
<td>9±1</td>
<td>38±8</td>
</tr>
<tr>
<td>BC5</td>
<td>4.02</td>
<td>30.3</td>
<td>3440±50</td>
<td>700±110</td>
<td>0.15±0.01</td>
<td>12±2</td>
<td>66±20</td>
</tr>
</tbody>
</table>
The value of the viscosity for BC2 compares well with the value measured in Chapter 4 for the motion of breaking filaments attached to the bundle. From the relationship of the effective surface tension, $\sigma^*$ where 0.025N/m is the actual surface tension, then we can calculate the average layer compression modulus for BC2 and BC5 also shown in Table 5-2. Since the layer compression modulus in these situations are associated with large curvatures, unlike the value of B measured for thin films in Section 5.3.1, we must deal with the effects of polarization splay which generates self interacting electric fields. As discussed in Chapters 3.4, we developed an effective layer compression modulus for the B7 phase, which consists of two parts dealing with biaxial layer compressions and electric self interactions and is proportional to the square root of the number of filaments, N, in the bundle, $B_{\text{eff}} = \sqrt{\frac{N}{2}} \left( B_c + \frac{p^2}{\sigma_o} \right)$. The number of filaments, N, can be estimated by taking the ratio of the cross sectional areas of the filaments to the area of a single filament with a radius of 2µm (A=13µm$^2$). If the curvatures are small as in the thin film situation then the second term becomes insignificant, however for high curvatures as in the filament radius, then B can be dominated by electric self interactions. If we assume that this behavior applies in these measurements and using $B_c = 5.6kPa$ as measured in Section 5.3.1, then we can estimate the out of layer polarization for the filaments. This calculation results in a polarization for the smallest filament in BC2 to be 250nC/cm$^2$ while for the larger bundles we get values of 160nC/cm$^2$ for BC2 and an average of 80nC/cm$^2$ for BC5. An interesting observation is that the polarization shows a decreasing effect due to bundling which might be due to the increasing interstitial volume between filaments with no net alignment ($<P>=0$).
5.4.3 ELECTRIC FIELD INTERACTIONS WITH BENT CORE FILAMENTS

In these experiments, we probed the electric properties of the fluid filaments using alternating electric fields. We begin by discussing the source of the electric interactions which exist for bent core filaments, and use those interactions to modify the elastic model described in Chapter 3. The resulting differential equations show very different behavior than the ones used in the previous section and results from the coexistence of first and second harmonic driving forces. An approximate steady state solution is obtained by assuming a Fourier series solution and is used to analyze the resonance data. We finish our study by discussing how electric fields influence and change the resonance peaks due to an effective decrease in the filaments tension.

The interactions which exist between dielectric\textsuperscript{24} and ferroelectric\textsuperscript{25} materials to applied electric fields have been well documented. These interactions become even more important in liquid crystals, where the elastic energy due to their orientational order can be comparable to those generated by electric fields\textsuperscript{15,26}. In our theoretical discussion of bent core filaments, we proposed that the structure was stabilized by the spontaneous divergence of the polar direction normal to the smectic layers which induces layer bending at curvatures comparable to experimentally observed values. This diverging polarization naturally generates surface and bulk charge densities which can interact with externally applied electric fields. For our filaments, we assume that there are two types of interactions between the filaments and externally applied electric fields related to their charge and dipolar structure. The charge behavior may arise from the presence of unpaired ions which interact with the exposed dipole charges at the air interface. These
interactions introduce a net charge which is proportional to the out of layer polarization component. The dipolar interactions with the electric field typically feel forces only under the presence of field gradients, however due to a connection of the dipole magnitude to the filaments shape we will show that this can also occur under constant electric fields. We will derive the resulting charge and dipole effects for the filaments due to the electric field and their shape.

In order to account for both of these electric field interactions, we will add the following energy terms into the Lagrangian described in Chapter 3. These terms related to the charge and dipole interactions with a uniform electric field are shown below,

$$\frac{dq}{ds} \tilde{E} \cdot (\vec{r} - \vec{r}_s) - \frac{d\tilde{p}}{ds} \cdot \tilde{E}$$

where $\frac{dq}{ds}$ is the charge per length of a filament, $\frac{d\tilde{p}}{ds}$ is the dipole per length, and $\tilde{E}$ is the applied electric field. As discussed before, the dipolar force can only exist in the presence of uniform electric fields if the dipole distribution is distorted. The charge $q$, can be calculated by the surface integral of the out of layer polarization (which is assumed to be proportional to the unpaired ions) and the dipole $\tilde{p}$ can be determined by the first moment of that integral. These integrals are shown below,

$$q = \int \tilde{P} \cdot d\tilde{A}$$

$$\tilde{p} = \int (R\tilde{N}) \tilde{P} \cdot d\tilde{A}$$
where \( \vec{P} \) is the polarization due to spontaneous and induced polarizations, \( d\vec{A} = Rd\theta ds\hat{N} \) is the differential area for a circular cross section where \( \hat{N} \) is the layer normal pointing radially from the filament center, and \( R \) is the filament’s radius. The layer normal for a curved filament becomes more complicated than for a straight filament but can be approximated as,

\[
\hat{N} \approx \hat{N}_o - R\vec{r}_{ss}
\]

where \( \hat{N}_o \) is the undistorted layer normal and \( \vec{r}_{ss} \) is the vector which is inversely proportional to the radius of curvature and points in the direction of the curvature. The polarization vector is composed of spontaneous and induced polarizations. The spontaneous out of layer polarization \( P_\perp \), being proportional to the number of screening ions, is used to determine the strength of the charge interaction with the electric fields. The dielectric mismatch at the surface \( \varepsilon_o (\varepsilon - 1) \) and the electric field perpendicular to the filaments long axis \( \vec{E} \) combine to generate the dipole interaction.

\[
\vec{P} = P_\perp \hat{N} + \frac{1}{2} \varepsilon_o (\varepsilon - 1) \left( \vec{E} - \left( \vec{E} \cdot \vec{r}_s \right) \vec{r}_s \right)
\]

Using this definition of the polarization and the integrals defining the charge and dipole of a filament, we arrive at the following results.

\[
\frac{\partial q}{\partial \xi} = 2\pi R P_\perp \left( 1 + R^2 \gamma \right) - \varepsilon_o (\varepsilon - 1) (\pi R) \vec{E} \cdot (R\vec{r}_{ss})
\]
\[
\frac{\partial \tilde{p}}{\partial s} = -2\pi R^2 P_\perp (R\tilde{r}_s) + \frac{1}{2} \varepsilon_o (\varepsilon - 1) \left( \pi R^2 \right) \left( \tilde{E} - (\tilde{E} \cdot \tilde{r}) \tilde{r}_s \right) + \varepsilon_o (\varepsilon - 1) \left( \pi R^2 \right) \left( \tilde{E} - (\tilde{E} \cdot R\tilde{r}_s) (R\tilde{r}_s) \right)
\]

However, for small curvatures the terms of order \(R\tilde{r}_s\) in the energy can be ignored. This results in \(\frac{\partial \tilde{q}}{\partial s} = 2\pi R P_\perp\) and \(\frac{\partial \tilde{r}}{\partial s} = \frac{1}{2} \varepsilon_o (\varepsilon - 1) \left( \pi R^2 \right) \left( \tilde{E} - (\tilde{E} \cdot \tilde{r}) \tilde{r}_s \right)\) for the charge per length and the dipole per length to be used in Eq. 5.21. By using these definitions and the modified form of the Lagrangian for small curvatures we obtain the following,

\[
L = \frac{1}{2} \mu \left( \tilde{r} \cdot \tilde{r}_s \right) - \frac{1}{2} \left( T + \frac{1}{2} BA \right) \left( \tilde{r} \cdot \tilde{r}_s \right) - 2\pi R P_\perp \tilde{E} \cdot (\tilde{r} - \tilde{r}_o) - \frac{1}{2} \varepsilon_o (\varepsilon - 1) \left( \pi R^2 \right) \left( \tilde{E}^2 - (\tilde{E} \cdot \tilde{r}_s) \right)^2
\]

where we have removed the external force term \(- \tilde{f} \cdot (\tilde{r} - \tilde{r}_o)\) and replaced it with the electric energy per length shown in Eq. 5.21. By using the Euler-Lagrange equation as discussed in Chapter 3, we can determine the following equation of motion.

\[
\mu \tilde{r}_n + \frac{\eta A}{s^2} \tilde{r}_i = \frac{d}{ds} \left( (T + \frac{1}{2} BA) \tilde{r}_s - \varepsilon_o (\varepsilon - 1) A \left( \tilde{E} \cdot \tilde{r}_s \right) \tilde{E} \right) - 2\pi R P_\perp \tilde{E}
\]

By assuming \(\tilde{r} = x\hat{x} + s\hat{z}\) and \(\tilde{E} = E_o \cos \omega t \hat{x}\), then we can obtain the following relationships for the z and x directions.

\[
0 = \frac{d}{ds} (T^*)
\]

\[
\mu x_n + \beta x_i = \left( T^* - 2\alpha E_o^2 \cos^2 \omega t \right) x_{s_s} - \lambda E_o \cos \omega t
\]
In these equations, we have substituted \( \beta = \frac{n}{\varepsilon_0} \), \( T^* = T + \frac{1}{3} B A \), \( \alpha = \frac{1}{2} \varepsilon_0 (\varepsilon - 1) A \), and \( \lambda = 2\pi R P_\perp \). The first equation shows that the effective tension \( T^* \) is a constant, while the second is a more difficult to solve. Unlike the solution for sound, whose coefficients were independent of time, Eq. 5.31 has a time dependent coefficient related to the dielectric interactions of the filament which is coupled to the curvature in the filament.

The first step in solving this equation is to separate the time and spatial dependences as \( x(s, t) = X(t) \sin ks \), where \( X \) is the maximum amplitude which is time dependent and \( k \) is the wave number. With fixed boundary conditions \( x(s = 0) = 0 \) and \( x(s = s_o) = 0 \), \( k \) must be discretized such that \( k_n = \frac{\pi n}{s_o} \) and \( n = 1, 3, 5, \ldots \), which is the same solution as obtained in the sound experiments. The resulting time dependent equation at the maximum amplitude becomes.

\[
\mu X_n + \beta X_t + \left( T^* k_n^2 - 2\alpha k_n^2 \varepsilon_0^2 \cos^2 \omega t \right) X = -\frac{4\lambda}{\pi \varepsilon_0} E_o \cos \omega t \tag{5.32}
\]

If we make the substitutions that \( t^* = \omega t \), \( \zeta = \frac{\beta}{2 \mu_0} \), \( A = \frac{T^* k_n^2}{\mu_0} \), and \( q = \frac{\alpha k_n^2}{2 \mu_0} \varepsilon_0^2 \), then we can rewrite this equation in the form such that the homogeneous solution is the lossy Mathieu equation, \( \ddot{y} + 2\zeta \dot{y} + \left( \omega^2 - 2q \cos 2x \right) y = 0 \), as discussed by J.A. Richards in 1976\textsuperscript{27} (see Figure 5-10). The lossy Mathieu equation is a variation of the classical Mathieu equation, first introduced by Emile Leonard Mathieu in 1868, and has been used to describe the motion of vibrating elliptical drumheads\textsuperscript{28} and parametric resonance\textsuperscript{29}. Parametric resonance occurs when one of the parameters within the differential equation varies periodically with time and is analogous to what occurs when a child is on a swing.
The child generates acceleration by oscillating their center of mass which induces changes in the pendulum's natural frequency. The same type of interaction occurs in our system, where the dielectric interaction can couple to induce motion on the filament. An interesting thing about our system is that the driving force does not couple just to the second harmonic but also has a constant which interferes with the tension of the filament. Another interesting behavior of the Mathieu equation deals with the stability of the solutions (i.e. non-zero or infinite steady state solutions). There are instabilities that arise for different parameter sets of \(A-2q\) and \(q\) and are the major differences between the Mathieu equation and other oscillator equations (see Figure 5-10). The solutions to the Mathieu equation are a set of special functions known as the Mathieu functions. These functions are typically called the Mathieu sine or cosine relating the odd or even functions, respectively. The result of parametric resonance in our system is that even without the presence of a net charge, a stable solution may exist and filament oscillation may occur due entirely to dielectric interactions. An interesting observation is that for a straight filament with no charge, there will be no net force on the filament because of the \(k_n\) dependence of the dielectric force. This means that this interaction must be induced by random fluctuations of the fluid filament.

The particular solution of Eq. 5.32 that we are interested in deals with equations which have a periodic behavior, therefore we will look for a series solution which can be written in terms of trigonometric functions.

\[
X = \sum_{j=1}^{\infty} a_j \cos(j \omega t + \phi_j)
\]  
5.33
Figure 5-10  The stability diagram as calculated by J.A. Richards\textsuperscript{27} for the lossy Mathieu equation (the homogeneous solution to Eq. 5.32), which compares the effects of the parameter set (A-2q, q) and $\zeta$ on stability of the solution. We see that both the lossy (solid) and lossless (dashed) curves show instabilities as the value of q increases, however the transition shifts to higher q for the lossy system.
In this proposed solution, \( a_j \) is the unknown amplitude of mode \( j \) and \( \phi_j \) is the phase of the \( j^{th} \) mode. By substituting this equation into the differential equation, we obtain the following relationship,

\[
\sum_{j=1}^{n} a_j \begin{bmatrix} \left( \omega_n^2 - \omega_c^2 - (j\omega)^2 \right) \cos \left( j\omega t - \phi_j \right) \\ -(j\omega \omega_d) \sin \left( j\omega t - \phi_j \right) \\ -\omega_c^2 \cos(2\omega t) \cos \left( j\omega t - \phi_j \right) \end{bmatrix} = A_o \cos \omega t \tag{5.34}
\]

where we have used the substitutions \( \omega_d = \frac{n A}{\mu^2} \), \( \omega_n^2 = \frac{r^2 \kappa^2}{\mu} \), \( \omega_c^2 = \frac{a_k^2 E_2^2}{\mu} \), and \( A_o = \frac{8 R_p E_2}{n \mu} \).

Applying the same trigonometric identities used in analyzing the sound experiments we can separate the phase from the time dependencies, resulting in the following equation,

\[
\sum_{j=1}^{n} a_j \begin{bmatrix} \left( \omega_n^2 - \omega_c^2 - (j\omega)^2 \right) \cos \phi_j + (j\omega \omega_d) \sin \phi_j \cos \left( j\omega t \right) \\ + \left( \omega_n^2 - \omega_c^2 - (j\omega)^2 \right) \sin \phi_j - (j\omega \omega_d) \cos \phi_j \sin \left( j\omega t \right) \\ -\omega_c^2 \cos(2\omega t) \cos \phi_j + \sin \left( j\omega t \right) \sin \phi_j \end{bmatrix} = A_o \cos \omega t \tag{5.35}
\]

where the first two terms are the same as in the sound theory. However the third term is unique to this equation and results in a coupling of the amplitude and phase between modes. This can be best seen by using the product to sum identities for trigonometric functions which allows us to rewrite the time dependent products in the following form.

\[
\cos(2\omega t) \cos \left( j\omega t \right) = \frac{1}{2} \left[ \cos \left( (j - 2) \omega t \right) + \cos \left( (j + 2) \omega t \right) \right] \tag{5.36}
\]

\[
\cos(2\omega t) \sin \left( j\omega t \right) = \frac{1}{2} \left[ \sin \left( (j + 2) \omega t \right) + \sin \left( (j - 2) \omega t \right) \right] \tag{5.37}
\]
Then by readjusting the indices of the coupling terms so that we can compare the harmonics with the same time dependence, we obtain the following relationship.

\[
\sum_{j=1}^{\infty} a_j \left\{ \left[ (\omega_n^2 - \omega_c^2 - (j\omega)^2) \cos \phi_j + (j\omega \omega_d) \sin \phi_j \right] \cos(j\omega t) \right. \\
\left. + \left[ (\omega_n^2 - \omega_c^2 - (j\omega)^2) \sin \phi_j - (j\omega \omega_d) \cos \phi_j \right] \sin(j\omega t) \right\} \\
- \frac{1}{2} \omega_c^2 \sum_{j=1}^{\infty} a_{j+2} \left[ \cos(j\omega t) \cos \phi_{j+2} + \sin(j\omega t) \sin \phi_{j+2} \right] = 5.38 \\
- \frac{1}{2} \omega_c^2 \sum_{j=1}^{\infty} a_{j-2} \left[ \cos(j\omega t) \cos \phi_{j-2} + \sin(j\omega t) \sin \phi_{j-2} \right] = A_o \cos \omega t
\]

By assuming that the terms dealing with the third mode or greater are negligible, i.e. weak coupling, then we can write out the first few relationships of the expansion. We see that from the 1st mode we get,

\[
a_1 \left[ (\omega_n^2 - \omega_c^2 - \omega^2) \cos \phi_1 + (\omega \omega_d) \sin \phi_1 \right] \\
\left. - \frac{1}{2} \omega_c^2 a_3 \cos \phi_3 - \frac{1}{2} \omega_c^2 a_{-1} \cos \phi_{-1} = A_o \right] = 5.39 \\

a_1 \left[ (\omega_n^2 - \omega_c^2 - \omega^2) \sin \phi_1 - (\omega \omega_d) \cos \phi_1 \right] \\
\left. - \frac{1}{2} \omega_c^2 a_3 \sin \phi_3 - \frac{1}{2} \omega_c^2 a_{-1} \sin \phi_{-1} = 0 \right] = 5.40
\]

and for the 2nd mode,

\[
a_2 \left[ (\omega_n^2 - \omega_c^2 - (2\omega)^2) \cos \phi_2 + (2\omega \omega_d) \sin \phi_2 \right] \\
\left. - \frac{1}{2} \omega_c^2 a_4 \cos \phi_4 - \frac{1}{2} \omega_c^2 a_0 = 0 \right] = 5.41 \\

a_2 \left[ (\omega_n^2 - \omega_c^2 - (2\omega)^2) \sin \phi_2 - (2\omega \omega_d) \cos \phi_2 \right] \\
\left. - \frac{1}{2} \omega_c^2 a_4 \sin \phi_4 = 0 \right] = 5.42
where we have ignored the \( a_{-1} \) constant because it is not a physical mode. The resulting solutions of the undetermined constants for these modes can be seen below.

\[
a_1 = -\frac{\frac{8KP}{n\mu}}{\sqrt{\left(\omega_n^2 - \omega^2 - \frac{\varepsilon_\perp (e^{-1})d_k^2}{\mu} E_o^2\right)^2 + \left(\omega_d \omega\right)^2}}
\]

\[
\tan \phi_1 = \frac{\omega_d \omega}{\omega_n^2 - \omega^2 - \frac{\varepsilon_\perp (e^{-1})d_k^2}{\mu} E_o^2}
\]

\[
a_2 = \frac{a_o \frac{\varepsilon_\perp (e^{-1})d_k^2}{4\mu} E_o^2}{\sqrt{\left(\omega_n^2 - (2\omega)^2 - \frac{\varepsilon_\perp (e^{-1})d_k^2}{\mu} E_o^2\right)^2 + \left(2\omega_o \omega_d\right)^2}}
\]

\[
\tan \phi_2 = \frac{2\omega_o \omega_d}{\omega_n^2 - (2\omega)^2 - \frac{\varepsilon_\perp (e^{-1})d_k^2}{\mu} E_o^2}
\]

These results are what would be expected for a simple superposition of the two electric interactions. For this study the value of \( n=1 \) as in the sound experiments, and the amplitude subscript reference the harmonic vibration with time not position.

5.4.4 ELECTRIC FIELD RESONANCE RESULTS AND DISCUSSION

Experimental work on this project was performed in Magdeburg, Germany during the same time as the sound resonance work. While the sound resonance where a more direct measurement of the elastic response of the filament to driving forces, the application of the external force using a speaker had issues that complicated analysis. Some of these problems were the frequency dependent behavior of the driving pressure...
due to speaker resonances and the strong coupling between the speaker and resonances of 
the filament mounts (glass rods). Both of these experimental issues can be significantly 
reduced by applying electric fields to the sample. We have studied two liquid crystal 
materials which are BC5 and BC2. We chose these materials to probe different aspects 
of the resonance and theory described in Chapter 2. BC5 was chosen because of its two 
phase behavior B7 at high temp and a transition to B2 at lower temperature, which allows 
us to study the phase transition effects on oscillations. BC2 was chosen so that we could 
compare the differences between the B7 and B7 phases. Experiments were preformed by 
either varying the frequency at a constant voltage or by varying the voltage at constant 
frequency.

The first measurements that we would like to discuss dealt with the validity of our 
model. First of all, our models assumed steady state behavior which we tried to ensure 
by waiting approximately 2-4 seconds after turning on the voltage before we took 
measurements. Secondly we assumed a weak coupling between the modes, which we 
will discuss later in our analysis. An example of the transition to the steady state is 
shown in Figure 5-11a for BC5 at 153°C, where we started with 0V until about 200ms 
when we applied a 3000V (0.375V/µm) triangular wave at 23Hz resulting in a transient 
growth of the amplitude until it reached steady state approximately 800ms later. By 
fitting the amplitude of the displacement with time with the function $x_{\text{max}} = a\left(1 + e^{-\frac{t}{\omega_d}}\right)$, 
we can obtain a dampening constant of $\omega_d=240s^{-1}$ and a viscosity of approximately 11Pas 
by using $\omega_d = \frac{\eta}{\rho s_o}$, where $\rho=1000$kg/m$^3$ and $s_o=6.75$mm. This value is very close to the
results obtained from speaker resonance measurements. We also can compare the steady state Fourier transforms (calculated with FFT routines in Matlab\textsuperscript{®}) before and after applying the electric field. The results (see Figure 5-11b) show almost no resonant behavior in the 0V case, except for a peak at about 300Hz which can be associated with the natural frequency of the filament mounts as seen in the sound experiments. We also see a multimode resonant behavior when the electric field is applied. Unlike the sound experiments which had a very large resonance effect related to the sound waves hitting the glass rod, the electric field experiments do not couple as strongly as seen by the apparent lack of a resonant peak in this region when the field is applied. This can be explained by the fact that the sound waves were not confined to the filament region as in the electric field experiments and therefore would impact the mounts as well. This greatly magnifies of the resonant effect of the mounts in the sound experiments when compared to the electric experiments. The multiple mode behavior (up to 11\textsuperscript{th} order) observed in the on state is due to the applied triangular waveform which in terms of a Fourier expansion can be written as \( \frac{x}{x_0} = \sum_{j=1,3,\ldots}^{\infty} \frac{1}{j^2} \sin(j \omega t) \) showing that there are actually multiple driving modes that exist at one time. Furthermore, we see that only odd harmonics should exist if only linear coupling occurs, therefore the even modes must be related to the dielectric coupling to the applied field Eq.5.45. By plotting the amplitude ratios of the odd \( \left( \frac{A_1}{A_j} \right) \) and even \( \left( \frac{A_{2j}}{A_j} \right) \) modes, as compared to the theoretical Fourier expansion \( \left( \frac{1}{j^2} \right) \), we can see that both harmonic couplings basically follow the theoretical trend for the driving signal (see Figure 5-12a). Under further inspection (Figure 5-12b),
Figure 5-11  a) The time dependence of the filament displacement before and after applying a 3000 V (0.375V/µm) triangle wave at 23 Hz. We see clear damped harmonic transient behavior region which goes to steady state after about 800ms. b) The Fourier transform of the field off (dashed) and the steady state field on (solid) region. We see one peak in the 0V region which is related to the resonance of the glass holders and multiple peaks when the field is applied.
we see that the deviations are related to the $1\omega$ and $2\omega$ coupling of the electric fields to vibrations of the filament mounts. These measurements suggest that our model assumptions of small mode coupling were valid and that we should find good agreement between our model and the measured data.

Our next experiment on BC5 probed the phase dependence of the oscillatory amplitude. By applying the same electric field behavior as above, but this time varying the temperature from $136^\circ C$ until the filament became unstable, we could probe the behavior of the B$_2$-B$_7$ phase transition on the filaments motion. We were able to analyze the data by taking the ratio of the $1\omega$ and $2\omega$ signals (i.e. the ratio of Eq.5.43 to Eq.5.45). Far below resonance where $\omega_n >> \omega_d$, the ratio of the $1\omega$ and $2\omega$ signals will reduce to a term which is approximately proportional to $\frac{\alpha_1}{\alpha_2} \propto \frac{P}{\varepsilon_{\perp} (\varepsilon-1)}$. Figure 5-13 shows the temperature dependence of this ratio for BC5 while heating from the B$_2$ phase. We see that in the B$_2$ phase this ratio is less than one suggesting a very small out of layer polarization component. However near the B$_2$ to B$_7$ transition, we see a linear increase of this ratio whose maximum occurs around $163^\circ C$ or near the isotropic transition. Interestingly enough, a similar behavior was observed for the ferroelectric switching threshold measured with this same material as reported by Jakli et al. in 2003$^{30}$. Typically as the temperature decreases the switching threshold increases due to increasing elastic constants, however this material had the opposite effect where the switching threshold decreased. This observation along with birefringence measurements led them to claim that a polarization component existed normal to the smectic layer which decreased under cooling, in agreement with our results.
Figure 5-12 a) A log-log plot of the amplitude ratio for the $1\omega$ and $2\omega$ coupling to the applied field as compared to the Fourier amplitude ratio ($\frac{1}{j}$) we see that both curves appear to have the basic trend of the Fourier series but deviate at different frequency ranges. b) By normalizing the coupling ratios by the theoretical ratio and comparing to the amplitude of the 0V Fourier transform, we can see that the deviations are due to a $1\omega$ and $2\omega$ coupling to the filament mount resonance.
Figure 5-13 The temperature dependence of the ratio of the $1\omega$ and $2\omega$ coupling amplitudes as a function of temperature for BC5 during heating from the $B_2$ phase. We see that the ratio begins to increase linearly near the $B_2$ to $B_7$ transition temperature (147°C). Above the isotropic transition (164°C) there is a large drop in this ratio as the filament structure becomes unstable.
They also reported that there was a second order transition to the B2 phase also in agreement with our observations.

Phase comparisons between BC5 and BC2 can be seen in Figure 5-14a and b, respectively, showing that both materials have similar filament length dependences as seen by the decrease of the resonant frequency with increasing length. However, the differences in resonance behavior of the two materials can be understood by considering the local layer structure of these materials. The material BC2, as discussed earlier has a quasi-columnar structure composed of smectic ribbons separated by multiple defects, while BC5 has a layer undulated structure with very little defects. Therefore, there is no surprise that the resonant peaks for BC2 are broader and shifted to higher frequencies when compared to BC5 materials. The broadness comes from the larger viscosity which is approximately twice that of BC5.

The electric field dependences on filament resonance can be observed in two different ways. First by comparing the effects of increasing electric fields on the resonance spectra, then by studying how the field dependences behave in different regimes of the resonance spectra. An example of the electric field effect on the resonance spectra of BC5 can be seen in Figure 5-15. We see that the amplitude increases and the resonant frequency decreases with increasing field as expected by Eq. 5.43. The inset graph shows the electric field dependence of the resonant frequency allowing us to fit for the mode dependent dielectric polarizability $\alpha_{n=1} = \frac{\varepsilon_n (\varepsilon-1) x^2}{\rho_0^2} = 2 \times 10^{-7} \frac{e^2}{kg m^3}$. Then from our definition of $\alpha_n$ we can estimate the relative dielectric constant by using $s_{0}=6.75$mm,
Figure 5-14 Length dependences of the resonance behavior for a) BC5 and b) BC2 at 153°C. We see that both materials resonant range decreases with increasing length in accordance with the theoretical model. In comparison the resonant peaks are much broader and appear at larger frequencies for a given length for BC2 in comparison to BC5 expected by the columnar type structure of the smectic layers.
Figure 5-15 The $1\omega$ resonance spectra for a 6.75 mm filament of BC5 at 153°C along with the resonance fit using Eq.5.43. We grouped the natural and electric frequencies into a natural frequency $\omega'_n = \sqrt{\omega_n^2 - \alpha_n E_o^2}$ which allows us to then fit the shifts in the resonance peak as a function of electric field to determine $\alpha_n = \frac{\omega^2}{\rho E_o^2}$. 
\( \rho = 1000 \text{kg/m}^3 \), and \( \varepsilon_0 = 8.9 \times 10^{-12} \text{C}^2/(\text{J} \cdot \text{m}) \). The resulting value for the relative dielectric constant is approximately \( \varepsilon = 105 \), which is large but can exist in polar liquid crystals with spatially varying polarizations, as in the case for filaments with an out of layer polarization component.

Finally we would like to discuss the effect of the electric field on the motion of the filament at constant frequency. Assuming that the dielectric effect contributes to small shifts in the resonant behavior, we expand Eq. 5.43 to first order in powers of

\[
\frac{2\left(\epsilon_n^2-\omega^2\right)\epsilon_n\left(\epsilon_n\omega^2\right)^2}{\left(\epsilon_n^2-\omega^2\right)^2 + \left(\epsilon_n\omega\right)^2},
\]

and obtain the following relationship.

\[
a_1 \approx \frac{8 RP \frac{E_n}{\mu}}{\sqrt{\left(\omega_n^2-\omega^2\right)^2 + \left(\omega_n \omega\right)^2}} \left[ 1 + \frac{\left(\omega_n^2-\omega^2\right)\epsilon_n\left(\epsilon_n\omega^2\right)^2}{\left(\omega_n^2-\omega^2\right)^2 + \left(\omega_n \omega\right)^2} - \frac{\epsilon_n^2}{2\left(\omega_n^2-\omega^2\right)^2 + \left(\omega_n \omega\right)^2} \right] 5.47
\]

We can see that if the dielectric term is small or we are far from resonance, \( a_1 \) is proportional to the electric field. However near resonance, the second term in the expansion becomes important adding a cubic term below resonance and subtracting it when above the resonant frequency. Finally when very close to the resonance peak then the second term becomes insignificant and the third term dominates subtracting a quintic power of electric fields. These three regimes can be seen in Figure 5-16, along with the predicted fit behavior.

In summary, by considering the important interactions the filament can have with externally applied electric fields, we were able to construct mathematical model to describe the appropriate equations of motion for the bent core filaments. We have
Figure 5-16 a) The resonance spectrum of a filament due to a small electric field to minimize the resonance shift which appears to exist near 300Hz (error of the data is around 0.5\( \mu \)m). The electric field dependence of the filament displacement are also shown for different fixed frequencies near the resonance peak. The electric field dependences we show are at b) 200Hz, c) 300Hz, and d) 350Hz along with their approximate fit equations, \( \Delta x \approx aE_o \left(1 + bE_o^2\right) \), \( \Delta x \approx cE_o \left(1 - dE_o^4\right) \), and \( \Delta x \approx aE_o \left(1 - bE_o^2\right) \), respectively.
measured resonance behavior in an attempt to determine some of the electrical properties of the filaments. We have shown that BC5 has a polar transition when heating which corresponds to the $B_2$ to $B_7$ transition, which can be explained with the SmCG model described in Chapters 2 and 3. By analyzing the shifts in resonance peaks due to applied fields, we could determine the dielectric constant near that frequency. Finally, we probed the effects of electric fields on the oscillation amplitudes at different resonance regimes and found good agreement with our model.

5.5 DYNAMICS OF FILAMENT RECOIL

Buckling instabilities in elastic materials have been well studied in several different materials ranging from metals to rubbers\textsuperscript{32}. The first person to study this phenomenon in beams was Euler (1744) who noted that beams in compression would remain straight until a critical load was achieved in which case the beam would buckle\textsuperscript{33}. In 1944, Love further showed that the only stable mode is the fundamental buckling mode described by Euler\textsuperscript{34}. In later studies on beams where a compressive stress much larger than the Euler threshold was suddenly applied, it was noted that the instability developed dynamically and a particular characteristic wavelength would result\textsuperscript{35}. In 2006, Vermorel et. al., revisited the problem of buckling instabilities of soft materials (rubber bands) and found interesting behavior associated with buckling and motion of compressive waves down the filament\textsuperscript{32}. They also studied the effects of buckling dynamics of rubber bands submerged in fluids and found that the buckling instability behavior became more dominating with higher viscosity. Other studies of the viscous
effects on buckling dynamics were discussed by Wolgemuth et. al. in an attempt to better understand the dynamic behavior of cellular flagella and DNA replication\textsuperscript{12}. The study of buckling instabilities in fluid filaments pose a new and exciting field of exploration, however the inability to stabilize freestanding fluid filaments to this point restricted one to study only fluid jets of complex fluids. One such study by Shin et. al., discussed the importance of a buckling instability of the fluid jet during the electrospinning of polymeric filaments\textsuperscript{5}.

Here we probe the first buckling instability in a freestanding fluid filament, and describe the dynamics in terms of our Lagrangian model. Our experimental setup is the same used in Chapter 4 (see Figure 4-2) except a high speed camera (Photron PCI-R2, borrowed from Dr. James Gleeson) was attached to the microscope. The buckling occurs very quickly (within a few milliseconds) and relate to an entirely different type of motion as expected from the resonance measurements. Images of the buckling instability for BC2 is seen in Figure 5-17, where the filament is initially straight before rupture, then recoils into a wavy (most likely a helical) structure, as the tip of the filament propagates towards the other end. By analyzing the images of this coiling process and comparing these results to our model we can determine the bending modulus and viscosity of the filaments. Before presenting the experimental results we will derive the dynamic behavior of the coil amplitude and the filament tip.
5.5.1 THEORY OF RECOILING FLUID FILAMENTS

The dynamics of a filament which is attached at one end but free on the other, can be obtained from a differential equation which is similar to the Euler-Bernoulli description of bending waves\(^32\).

\[
\mu \ddot{r} + \frac{\eta A}{s_o^2} \dot{r} + d\left(T \ddot{r} \right) + \frac{1}{4} BI \dddot{r} = 0 \quad 5.48
\]

Here \(\dot{r}\) is the position along the filament, \(\mu\) is the mass per length, \(\eta\) is the viscosity, \(A\) is the cross sectional area, \(s_o\) is the length of the filament, \(T\) is the tension, \(B\) is the compressibility of the smectic layers, and \(I\) is the area moment of inertia. The third term sign has been changed, because without a boundary to support the fluid filament from both ends the surface tension will act as a compressive force on the filament. For small amplitudes of the deflection, the position vector is \(\hat{r} \approx R \cos ks \hat{x} + R \sin ks \hat{y} + s \hat{z}\), where \(R\) is a function of time and \(k\) is a constant mode number. By entering this into Eq. 5.48, we obtain the following relationships for the deflection of the filament in the \(x\), \(y\), and \(z\) directions.

\[
\left( R'' + \frac{\eta}{\rho s_o} R' + \frac{BI}{4 \mu} k^2 \left( k^2 - \frac{4 T}{M} \right) R \right) \cos ks \frac{\partial r}{\partial t} + \frac{kr}{\mu} \sin ks = 0 \quad 5.49
\]

\[
\left( R'' + \frac{\eta}{\rho s_o} R' + \frac{BI}{4 \mu} k^2 \left( k^2 - \frac{4 T}{M} \right) R \right) \sin ks \frac{\partial r}{\partial t} + \frac{kr}{\mu} \cos ks = 0 \quad 5.50
\]

\[
\frac{\partial T}{\partial s} = 0 \quad 5.51
\]

These result in a single differential equation that describes the behavior of \(R\) as a function of time.
By assuming the solution in the form, \( R = r_o \left(1 - e^{-at}\right) \), we result in two relationships for \( \alpha \) and \( k \) that must hold our solution to solve Eq. 5.52.

\[
\alpha^2 - \left( \frac{\eta}{\rho s_o^2} \right) \alpha = - \left( \frac{Blk^2}{4\mu} \right) \left( k^2 - \frac{4T}{Bl} \right)
\]

When we perform some algebra, we get

\[
\left( \frac{Blk^2}{4\mu} \right) \left( k^2 - \frac{4T}{Bl} \right) = 0
\]

These result in the non-trivial solutions of \( \alpha = \frac{\eta}{\rho s_o^2} \) and \( k = 2\sqrt{\frac{T}{Bl}} \) for the decay time and the stable mode number respectively. Finally by using these results, we can approximate the filament tip displacement \( \delta = s_o - z(s_o) \) which is derived from the following integral relationship.

\[
\delta(t) = s_o - z(s_o) = s_o - \int_0^s \sqrt{1 - \left( \left( \frac{\partial x}{\partial s} \right)^2 + \left( \frac{\partial y}{\partial s} \right)^2 \right)} \, ds
\]

Due to the relationship, \( \left( \frac{\partial x}{\partial s} \right)^2 + \left( \frac{\partial y}{\partial s} \right)^2 = r_o^2 k^2 \left(1 - e^{-at}\right)^2 \), which is independent of \( s \), we can determine the tip displacement and the radial growth for small values of \( r_o^2 k^2 \) as shown below.

\[
\delta(t) \approx \frac{1}{2} s_o r_o^2 k^2 \left(1 - e^{-at}\right)^2
\]

\[
r(t) = r_o \left(1 - e^{-at}\right)
\]
5.5.2 EXPERIMENTAL RESULTS

Experimental data was obtained by taking high speed video (1000 frames per second) and determining the filament profile for a particular frame by recording the different pixel locations which determine the filament shape. Then by analyzing these positions, we could determine the tip position, the dominate buckling wavelength, and the buckling amplitude with time. We did this for several filaments of BC2 near the isotropic transition, and have plotted their relative tip displacements and radial growth with time as shown in Figure 5-18. We also fit the scaled curves with the dynamic behavior predicted in Eqs. 5.56 and 5.57. The resulting curves provide values of the time constant $\alpha$ to be $0.71 \text{ms}^{-1}$ for the tip displacement variation, and $1.26 \text{ms}^{-1}$ for the radial distribution. Although our theory predicts that the decay rate should be equal, we should point out that the theory was only valid for small displacements and therefore at best is only an approximation of the observed tip displacement behavior. By entering these numbers into the definition of $\alpha = \frac{\sigma}{\rho \eta s_o}$, along with the mass density $\rho = 10^3 \text{kg/m}^3$ and the length of the filament $s_o = 2.5 \text{mm}$, we estimate the viscosity to range between 5-8 Pas which is similar to the values determined with other techniques. The wavelength data (see Figure 5-19) shows a large wavelength near the beginning but quickly chooses a constant value. This wavelength is measured to be $90 \mu\text{m}$ which corresponds to a mode number of $k = 6.98 \times 10^4 \text{m}^{-1}$. By entering this into the relationship for the compression modulus, $B = \frac{32\sigma}{R_o k^2}$, along with the values $\sigma = 25 \text{mN/m}$ and $R_o = 3.5 \mu\text{m}$ for the surface tension and filament radius, respectively, we obtain a value for the bulk modulus to be
3.83MPa, which is much greater than the values obtained in the resonance measurements.

One possibility for this discrepancy could result from large normal stresses due to the motion which drives the smectic layer strain past the biaxial regime and into the normal compression regime. In which case the measured value are in the correct range for typical SmC materials.
Figure 5-17 Image sequence of the breaking dynamics for a bent core filament. The image is out of focus initially to allow for the falling filament to pass through the focal plane of the microscope as it breaks for better imaging. This filament diameter was measured to be 6µm and the length is approximately 0.25mm. We can clearly see that the filaments speed is decreasing as it recoils and the modulated wavelength is approximately a constant.
Figure 5-18 The time dependence of the relative displacement of the filament tip and radial growth (insert) as compared to the behavior predicted by the theory (solid curves).
Figure 5-19 The average dominant wavelength time dependence for several filaments.

The data at the small times have larger errors due to the low amplitudes involved, however at larger times a dominate wavelength emerges.
REFERENCES


28 E. Mathieu, “Memoire sur Le Mouvement Vibratoire d’une Membrane de forme Elliptique”, Journal des Mathematiques Pures et Appliquees, 137-203, (1868)


33 L. Euler, Opera Omnia I, pp. 231-297, Lausanne, (1744)


CHAPTER 6

FLOW BEHAVIOR OF BENT CORE LIQUID CRYSTALS

6.1 INTRODUCTION

The dynamic properties of complex or ordered fluids can provide much information about their microscopic structures and interactions between the fluid components. These properties are typically characterized by applying external stresses and measuring the resulting response. In modeling these responses, one tries to relate how the applied external stresses change the balance between conserved quantities (energy, momentum, and mass) and the un-conserved, dissipative quantities such as viscosity. In complex or ordered fluids, the microscopic structure of the fluid changes under the applied stresses and therefore the viscous and/or elastic behavior of the material becomes rate dependent which is called non-Newtonian behavior. Examples of this type of interaction occur regularly in polymer melts, foams, mixtures, slurries, and liquid crystals.

In liquid crystals, there are interactions caused by orientational or positional order which exist outside of the effects of inertia and viscous dissipation. These extra interactions relax slowly and are caused by hydrodynamic variables, and a typical
example in liquid crystals is the orientational order parameter (director)\(^3\). The result of the director is that the shear stresses can couple to the director field resulting in director deformations (flow alignment) and even turbulent behavior (tumbling)\(^3\). This picture becomes even more complicated when there are large differences in molecular diffusion times along (\(t_∥\)) or perpendicular (\(t_⊥\)) to the director. This type of behavior is common in lamellar systems such as cholesterics (\(\frac{t_∥}{t_⊥} << 1\)) or smectics (\(\frac{t_∥}{t_⊥} >> 1\)) at low shear rates. In the case of cholesterics, this large time scale difference arises from the periodicity of the pitch which requires a rotation as the material flows along the helical axis. In the case of smectics, the large time scale results from the energy barrier required to move molecules between smectic layers. This idea was first proposed by Helfrich and is referred to as permeation\(^4\). In general these additional flow properties are non-trivial and become even more complicated in systems like bent-core liquid crystals where there are multiple hydrodynamic modes related to rotations of the director and polarization, and the coupling of those effects to the smectic order.

Viscosity measurements of bent-core materials have been almost a completely untouched field. Much of the early data focused entirely on the rotational viscosities of the B\(2\) phase and were obtained by measuring ferroelectric switching times\(^5,6,7\). Later works on this subject showed interesting behavior where the polarization could be switched about the smectic layer normal or about the director\(^8\), and was theoretically connected to an anisotropic viscosity due to biaxial order. Viscous behavior in bent core nematics related to the director fluctuations have been determined by using dynamic light scattering\(^9\) or observing relaxation times while magnetically switching an aligned
sample\textsuperscript{10}. All of these measurements provide estimates of the rotational viscosity which range in order of 0.1-3 Pas.

Flow viscosity measurements for any of the bent core phases are almost completely unknown and therefore leave an interesting question, why? The answer is most likely related to the amount of available material which is typically synthesized (~100mg or ~ 100µL), which does not supply enough material for typical viscosity measurements (~1mL). One prior study on a bent-core nematic used electro-rotation of a glass rod to measure the flow viscosity by balancing the electric torque on a glass rod spacer to the viscous drag on the rotating cylinder\textsuperscript{11}. The results of these studies provided values of the viscosity in the isotropic and nematic phase which ranged from 20 to 250 Pas, much larger than the previously observed rotational viscosities. This behavior was associated to the presence of smectic aggregates which form a weakly organized, frustrated packing structure.

In our studies, we used the nanoliter viscometer discussed in the Appendix to characterize the rheological properties of several bent core liquid crystals. We studied the unaligned viscoelastic responses in the bent core isotropic, nematic, B\textsubscript{2}, and the B\textsubscript{7} phases. In this chapter, we will characterize their shear rate and temperature dependencies and discuss their flow induced optical properties. Our results will be discussed and compared to those obtained with several rod-like mesogens which exhibit the nematic and SmA phases. They suggest that the steric packing and the frustrations thereof are extremely important in determining the observed viscoelastic behavior of these bent core materials.
6.2 EXPERIMENTS AND MATERIALS

The experimental setup for this study uses the same device and setups described in the Appendix. We performed a series of measurements on each of our materials, consisting of shear rate dependences at a constant temperature, temperature dependencies at various shear rates, and optical measurements (flow birefringence) as a function of temperature.

The materials that we use consist of bent core and rod shaped molecules whose basic shapes are shown in Figure 6-1 along with their specific structures and phase diagrams provided in Table 6-1. When we discuss our results we will group these materials into several general categories, the calamitics (5CB and 8CB), the bent core nematogens (BCN1-5), and the bent core smectogens (BCS1-4). Within each of the bent core mesogens we have various tail lengths, tail substitutions, side group linkages, phenyl linkages of the core, and various observed phases. Some of these relationships will be discussed and general trends discussed.
Figure 6-1 The base molecular structure of the bow shaped (a) and rod shaped (b) molecules used in our studies. The specific molecular structures and phase behavior of materials used in our study is shown in Table 6-1.
Table 6-1  The molecular structure and phase behavior of the materials studied in our experiments using the diagrams shown in Figure 6-1.

<table>
<thead>
<tr>
<th>Name</th>
<th>$R_1$ ($R_{1}^\prime$)</th>
<th>$R_2$ ($R_{2}^\prime$)</th>
<th>$R_3$</th>
<th>A</th>
<th>B</th>
<th>$R_4$</th>
<th>$R_5$</th>
<th>Phase Behavior (Cooling, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CB</td>
<td>(CN) (C$<em>{7}$H$</em>{11}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 24 Nem 36 Iso</td>
</tr>
<tr>
<td>8CB</td>
<td>(CN) (C$<em>{8}$H$</em>{17}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 22 SmA 34 Nem 41 Iso</td>
</tr>
<tr>
<td>BCN1</td>
<td>Cl H H COO COO H O(CH$<em>{2}$)$</em>{6}$C$<em>{2}$H$</em>{2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 56 Nem 71 Iso</td>
</tr>
<tr>
<td>BCN2</td>
<td>Cl H H COO COO H OC$<em>{11}$H$</em>{23}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 58 Nem 87 Iso</td>
</tr>
<tr>
<td>BCN3</td>
<td>Cl Cl H COO - H O(CH$<em>{2}$)$</em>{6}$C$<em>{2}$H$</em>{2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 60 Nem 94 Iso</td>
</tr>
<tr>
<td>BCN4</td>
<td>Cl Cl H COO - H O(CH$<em>{2}$)$</em>{7}$C$<em>{2}$H$</em>{2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 64 Nem 98 Iso</td>
</tr>
<tr>
<td>BCN5</td>
<td>Cl Cl H COO - H OC$<em>{17}$H$</em>{17}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 75 Nem 115 Iso</td>
</tr>
<tr>
<td>BCS1</td>
<td>H H NO$<em>{2}$ COO NCH H OC$</em>{17}$H$_{17}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 116 B$_{7}$ 177 Iso</td>
</tr>
<tr>
<td>BCS2</td>
<td>H H H COO NCH H SC$<em>{10}$H$</em>{21}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 99 SmCP 128 B$_{7}$ 140 Iso</td>
</tr>
<tr>
<td>BCS3</td>
<td>H Cl H COO NCH H OC$<em>{12}$H$</em>{29}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 68 B$_{2}$ 127 Iso</td>
</tr>
<tr>
<td>BCS4</td>
<td>H H NO$<em>{2}$ COO - H O(CH$</em>{2}$)$<em>{4}$C$</em>{2}$H$_{2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr$<em>{1}$ 34.3 Cr$</em>{2}$ 109.7 B$_{7}$ 118.0 Iso</td>
</tr>
</tbody>
</table>
6.3 NEMATOGEN RHEOLOGY

The first study that we report is the shear rate dependences of the flow viscosity ($\eta$) and the shear modulus ($G$) for the calamitics and bent core nematogens* (Figure 6-2) in the isotropic phase. We find that the calamitics behave as expected, in that they have no observable shear rate dependences (Newtonian behavior) and insignificant values for $G$ which are not shown. The bent core nematogens have a strikingly different behavior. The first observation is that the magnitudes of the viscosities are larger than the calamitics (typically an order of magnitude). We also see that the behavior is very non-Newtonian and the materials are viscoelastic. The shear modulus decreases with increasing shear rate for all of the bent core nematogens (BCN) and follows a power law of the form,

$$G = \frac{g}{\gamma^\beta} \quad 6.1$$

where $g$ and $\beta$ are fitting constants. While $g$ is different for each sample, the value of $\beta$ is similar and has an average value of 0.76. This type of shear rate dependence suggests that the BCN materials have an elastic structure even in their isotropic fluid phase. For the viscosity behavior, we fit the data with a relaxation relationship of the form,

$$\eta(\gamma) = \frac{B}{\gamma^2 + \gamma_o^2 + \eta_\infty} \quad 6.2$$

where $B$ is a constant, $\gamma_o$ is a characteristic shear rate, and $\eta_\infty$ represents the high shear rate viscosity. This model is very similar to the dielectric relaxation processes, commonly called Debye relaxation\textsuperscript{12}, where molecular motions (related to interactions

* Nematogen: A material that forms the nematic phase directly below the isotropic phase.
Figure 6-2  Shear rate dependences of the a) viscosities and b) the shear modulus for the series of bent core nematogens and calamitics in their isotropic phases. All samples were measured at ~10°C above the nematic transition temperature. The shear moduli for the calamitics were not shown because they were within the experimental error of ~5Pa.
between dipoles and electric fields) are unable to follow an applied alternating electric field due to their finite viscosity. Based on the orders of magnitude increase in the viscosity, we conclude that in our system the molecules are replaced with anisotropic aggregates, and the electric torques with the applied shear stress. This aggregate model for these materials was first used to explain unusual pretransitional fluctuations of the nematic order parameter measured by magnetic and dynamic light scattering measurements. By drawing from the Debye model, we can estimate the average size of these aggregates in the isotropic phase by assuming that the aggregates are in motion due to thermal energy \( (k_B T) \) and these rotating “particles” dissipate the energy due to viscosity \( (\eta_\infty) \). This analogy can be used to approximate the effective aggregate size ‘a’ shown below.

\[
a = \sqrt[3]{\frac{k_B T}{4\pi \eta_\infty \gamma_0}}
\]

The results of this equation and the fitting parameters obtained in Figure 6-2a using Eq. 6.2 are tabulated in Table 6-2. These predict an aggregate size in the range of 10-20nm, which is in good agreement with small angle X-ray scattering data for BCN5 in the isotropic phase which shows a smectic correlation length of approximately a 4-5 smectic layers (~22nm).

From this data, we can also draw some insight into the effects of molecular structure on the average aggregate size. It looks from Figure 6-2 that the largest effect is the result of replacing a rigid unsaturated carbon-carbon bond with a more flexible saturated bond at the end of the hydrocarbon tail. This causes an increase in apparent
Table 6-2  Fit parameters for the isotropic viscosity data for bent core nematogens. $T$ is the temperature in Kelvin, $B$, $\gamma_o$, and $\eta_\infty$ are the fitting constants from Eq. 6.2, and $a$ is the apparent particle size as determined using Eq. 6.3 in nanometers.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T$ (K)</th>
<th>$B$ (Pa s$^{-1}$)</th>
<th>$\gamma_o$ (s$^{-1}$)</th>
<th>$\eta_\infty$ (Pa s)</th>
<th>$a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCN1</td>
<td>363</td>
<td>$1.1 \times 10^6$</td>
<td>1200</td>
<td>0.25</td>
<td>11</td>
</tr>
<tr>
<td>BCN2</td>
<td>368</td>
<td>$3.5 \times 10^5$</td>
<td>870</td>
<td>0.10</td>
<td>17</td>
</tr>
<tr>
<td>BCN3</td>
<td>378</td>
<td>$3.5 \times 10^6$</td>
<td>6600</td>
<td>0.03</td>
<td>13</td>
</tr>
<tr>
<td>BCN4</td>
<td>378</td>
<td>$6.6 \times 10^5$</td>
<td>2800</td>
<td>0.03</td>
<td>17</td>
</tr>
<tr>
<td>BCN5</td>
<td>398</td>
<td>$3.0 \times 10^5$</td>
<td>3200</td>
<td>0.015</td>
<td>21</td>
</tr>
</tbody>
</table>
aggregate size by 55% for the one chlorine materials (BCN1 and BCN2) and by 62% for
the two chlorine materials (BC3 and BC5). The next comparison that we can make is the
effect of increasing the tail length which shows a 31% increase in aggregate size when
increasing the number of carbons from 8 to 9 (BC4 and BC3). These observations
suggest, at least qualitatively, that an increase in tail flexibility results in an increase in
aggregate size.

Further evidence of this aggregate behavior can be seen by measuring the flow
birefringence of these samples. By using the methods described in the Appendix, we
were able to measure the birefringence as a function of shear rate at different
temperatures above the nematic phase transition. An example of the data obtained for
BCN1 is shown in Figure 6-3, where we show the effects of increasing shear
birefringence as the material approaches its nematic transition. The observed behavior
was first predicted by De Gennes\textsuperscript{14} and results in the following relationship where $A$ is
the leading term in the Landau free energy and $\eta$ is the flow viscosity.

\[
\Delta n(T, \gamma) = \frac{2\pi}{\eta(T)\gamma} |\gamma|
\]

Another interesting result is that this term is proportional to the absolute value of the
shear rate meaning that the measured birefringence should follow the second harmonic of
the applied shear. This behavior can be easily checked with the lock-in amplifier which
clearly shows that the $2\omega$ effect does in fact dominate above the nematic transition (see
Figure 6-4). The lock-in also allows us to measure the extension angles where these
effects occur, in our case at 45° to the shear direction.
Figure 6-3  We show the shear induced birefringence of BCN1 between crossed polarizers in the isotropic phase (76.3°C) without shear (top left) and with shear (bottom left). Graph of transmitted intensity versus shear rate at various temperatures above the nematic phase are shown (right) along with data fitting using Eq. A.20 in the Appendix.
Figure 6-4  The temperature dependences of the $1\omega$ and $2\omega$ intensity signals for the two different analyzer/polarizer (AP) configurations for BCN1. We see that the first and second harmonic signals are maximized for the $0^\circ$ alignment, suggesting that the birefringence axes are acting along the $45^\circ$ directions. We also see that the flow birefringence as we approach the nematic transition is dominated by the $2\omega$ effect.
Results on all of the samples with measurable signals are plotted in Figure 6-5. By fitting this data with \[ \frac{d(\Delta n)}{dT} = \frac{2\eta}{d(T-T^*)} = 2\eta C \] which is the derivative of Eq. 6.4 we see that we obtain good agreement with the theory. The results of the fits shown in Figure 6-5 are tabulated and compared with other materials in Table 6-3. The values of the flow birefringence coefficients \((2C\eta)\) are reported at 1°C above the nematic transition so that temperature effects can be scaled out and a viscosity value could be determined from our measurements. The flow birefringence coefficients for our samples are very large (orders of magnitudes larger than in calamitics) and compare most closely to the wormlike micelle solution (CTAB & KBr)\(^{17}\) and the side chain liquid crystal polymer (SCLCP)\(^{19}\) melt. We note that both of these systems consist of macromolecular structures which aid in the generation of a large shear induced birefringence, similar to the proposed aggregate model. Where these two systems differ from the bent core nematogens is in the inverse energy coefficient \(C\) as calculated by dividing out the viscosity of the material. We see that the value for \(C\) in the SCLCP is comparable to that of 5CB suggesting that the large flow birefringence is mainly determined by the polymer network distorting under the applied stress thereby aligning the mesogenic units attached to the backbone. The behavior for the bent core nematogens shows a completely different story having \(C\) values 20-70 times larger than 5CB. This is in agreement with measurements by Wiant et. al. where the leading Landau term which is the inverse of \(C\), was found to be 30 times smaller in BCN1 than typical calamitics\(^9\).

To finish our study on bent core nematogens, we take a look at the low shear rate (<500s\(^{-1}\)) regime of BCN1 and the temperature dependence of this phase as
Figure 6-5  The temperature dependence of the shear induced birefringence constant as
approaches the nematic transition temperature for the bent core nematogens.
Table 6-3 Tabulated flow birefringence values of several organic compounds reported in literature, and the values we measured for bent core nematogens.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (T-T*) (°C)</th>
<th>2Cη (ns)</th>
<th>η (Pa s)</th>
<th>C (10^-7 Pa^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene¹⁵</td>
<td>30</td>
<td>5×10^-4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5CB¹⁶</td>
<td>40 (4.7)</td>
<td>6.5</td>
<td>0.028</td>
<td>5.64</td>
</tr>
<tr>
<td>BCN1</td>
<td>72.7 (1)</td>
<td>109,000</td>
<td>2.3</td>
<td>237</td>
</tr>
<tr>
<td>BCN2</td>
<td>86.2 (1)</td>
<td>68,000</td>
<td>0.8</td>
<td>425</td>
</tr>
<tr>
<td>BCN3</td>
<td>92.3 (1)</td>
<td>4655</td>
<td>0.45</td>
<td>103</td>
</tr>
<tr>
<td>BCN4</td>
<td>97.1 (1)</td>
<td>8360</td>
<td>0.3</td>
<td>139</td>
</tr>
<tr>
<td>CTAB &amp; KBr¹⁷</td>
<td>30 (-)</td>
<td>1,300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PMMA/Toluene¹⁸</td>
<td>25 (-)</td>
<td>4.5</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>SCLCP¹⁹ (isotropic melt) (Mw = 85,800 g/mol)</td>
<td>128 (6)</td>
<td>144,000</td>
<td>~150</td>
<td>4.6</td>
</tr>
</tbody>
</table>
it transitions to the nematic phase. Figure 6-6 shows the presence of two regimes which have two different flow behaviors. In the first regime, the shear modulus is almost constant while the viscosity shows a strong shear thinning behavior. Due to the low shear rates, this behavior may be dominated by the permeation behavior of molecules through the frustrated aggregate network. In the higher shear rate regime, we see that the shear modulus and the viscosity observe the same relaxation process suggesting that the shear stresses in this regime are large enough to destroy or align the aggregates. The temperature dependences of the viscosity and shear modulus are shown in Figure 6-7 for the isotropic and nematic phases. For both properties we see an overall increase in the nematic phase and an apparent loss of the relaxation process observed in the isotropic phase. A closer look at the temperature dependence of these properties shown in part b), suggests that while the value at 70°C is larger than the value at 90°C, there is an overall decrease in the viscosity and bulk modulus of around 10% at the phase transition to the nematic phase. This agrees with the expected behavior if the aggregates align in the transition to the nematic phase as shown in Figure 6-8a and b.

As discussed in Chapter 2, frustrations in molecular packing of bent core smectics can result in structural instabilities which can buckle or even break apart the smectic structure. In the most extreme cases, we proposed that these frustrated structures could disassociate and form free floating clusters of smectic domains surrounded by a non-smectic phase (see Figure 2-4), and it is this model that we believe can explain the
Figure 6-6 The viscoelastic response of BCN1 over two decades of shear rates. We see the presence of two regimes. The first has a constant shear modulus and a shear thinning viscosity, while the second is characterized by a strong relaxation process for both the properties. This suggests that the first regime is probably dominated by permeation while the second shows the effects of shear alignment of the aggregates.
Figure 6-7  a) Shear rate dependence of the viscosity and shear modulus for BCN1 in the isotopic (90°C) and the nematic (70°C) phases.  b) Temperature dependence of these values at a constant shear rate (517 s⁻¹).
observed strange rheological behavior. Although these measurements alone are not sufficient enough to prove this model, we can still discuss some of our observations and compare to the proposed frustrated packing model. The bent core nematogens all have a single or double Chlorine atom attached to their central phenyl ring, whose size is approximately 1/3 the size of the phenyl group. These Chlorines would act as large bumps which could frustrate the local molecular packing. This suggests that these bent core nematogens would be excellent candidates for a SmCG configuration. This argument is further strengthened by our comparisons of the average aggregate size to the tail flexibility, which suggests that more flexibility increases the aggregate size. It appears that the result of more tail flexibility may help to overcome the rigid core frustrations by allowing the molecules to have more “wiggle room” within a smectic layer.
Figure 6-8  Proposed nanostructures of bent core nematogens in a) the isotropic and b) the nematic phase.
6.4 SMECTOGEN RHEOLOGY

In the previous section we discussed some of the interesting flow behavior of bent core nematogens. The most interesting behavior occurred in the isotropic phase where we measured phenomenon which can be related to the formation of smectic aggregates. In our study of bent core smectogens† we begin by considering their isotropic phase behavior in comparison to some of the bent core nematogens. Figure 6-9 shows the viscosity and shear modulus for some of our smectogens and compares them to the calamitics in their isotropic phase. We can see that the viscosity for the smectogens is closer to the values of BCN5 rather than BCN1 most likely because the smectogens temperature range is closer to that of BCN5. In any case, all of the smectogens have similarities in their general flow behavior to that of the nematogens, suggesting the presence of smectic aggregates in their isotropic phase, too. The behavior of the B2 material (BCS3) is the most similar to the nematogens, while the B7† materials (BCS2 and BCS4) show a peak in their viscosity at a particular shear rate. We note that similar shear rate dependencies exist in surfactant solutions which form wormlike micelles²⁰,²¹,²², which supports the similarities of their structure. These systems, which are lyotropic phases and therefore are strongly dependent on the concentration of the constituent molecules, show viscosities which range from 0.001Pas (water) to 60Pas, and have shear moduli which range from 0.01 to 10Pa. These are in fair agreement with our observed property values.

† Smectogen: A material that forms smectic phase directly below the isotropic phase.
Figure 6-9  The shear rate dependences of the a) viscosity and b) shear moduli for various bent core smectogens in their isotropic phase.  We compare their behavior to the low temperature values of the calamitics.
Due to the presence of this aggregate behavior in the smectogens, it is important to see if large flow birefringence effects exist in these materials as well. We attempted to measure this behavior with the same methods used for the nematogens, however the signals were small or comparable to the background noise. Therefore we decided to measure the flow birefringence of these smectogens by using a lock-in amplifier connected to the photodiode. This allowed us to remove the effects of background noise and measure the effects related to the flow birefringence (2nd harmonic effects). The results of these measurements are shown in Figure 6-10, where we compare the high temperature nematogen (BCN5) and our smectogen series. The pretransitional effects of BCN5 are similar to the other nematogens however all of the smectogens behave differently. The material BCS3 has no 2nd harmonic signal in the isotropic phase which increases when cooled to the B2 phase, and is consistent with director switching about the cone angle. In the B7 materials, only small signals exist near the transition which most likely is related to the nucleation of the phase, however no director switching effects occur in the smectic phase. From these results we can suggest two things; either the isotropic aggregates in the smectogens are much smaller or less concentrated than the nematogens.

The viscosities and shear moduli of the smectogens as a function of temperature can be seen in Figure 6-11, where we have adjusted their transition temperatures so their basic behaviors can be compared. We first see that BCS1, which has a classical B7 structure composed of smectic ribbons, has a much larger (more than an order of magnitude) viscosity and shear modulus. While some of this may be related to
Figure 6-10 The 2\textsuperscript{nd} harmonic signal from the photodiode as a function the temperature difference from the transition temperature ($T_{tr}$) for very similar shear rates ($\sim 2000\text{s}^{-1}$). We compare the behavior of the smectogens to BCN5 which has a similar temperature range and also had a small transition signal. We see a clear difference in behavior between BCN5, the B\textsubscript{2} phase (BCS3), and the B\textsubscript{7} materials (BCS1, BCS2, and BCS4).
the different shear rates of these samples, it can not explain the differences between BCS1 and BCS2 which have similar shear rates. In all of the B7 samples (BCS1,2 and 4), we see that there exists a maximum viscoelastic response approximately 4°C below the transition to the B7 phase. This behavior does not exist in the BCS3 sample which does not have a B7 phase. It is likely that this behavior is related to the helical filament growth which forms in the B7 phase, creating an unorganized smectic structure with many defects, and it is only later when these filaments join to form larger smectic domains does the viscoelastic behavior decrease. It is also interesting that the drop in viscoelastic response from this maximum is characteristic of the phase. For BCS1 this drop is only 9% of the peak value, while for BCS2 and BCS4 this drop is around 25% showing a less frustrated structure for the latter two phases. The shear rate behavior of the smectic phases can be seen in Figure 6-12 for BCS2 which has a B7' and B2 phase under cooling, and in Figure 6-13 where we compare the shear rate behavior at the peak viscoelastic point for some of the smectogens. In Figure 6-12 we see that shear thinning effects occur in each of the phases, however the effect is most drastic in the B2 phase where a more classic smectic structure exists. In the B7 phase, we see a peak in viscoelastic behavior as seen in Figure 6-11 and we also see that a threshold shear rate (100s$^{-1} < \gamma_{th} < 500s^{-1}$) exists which does not appear in the B2 phase. Notably, the shear thinning in the B7 phase is less effective even above 100s$^{-1}$ which can be seen in Figure 6-13, where we show the shear rate dependences of nematogens and smectogens a few degrees below the isotropic transition.
Figure 6-11  The temperature dependences of a) the viscosities and b) the shear moduli for all of the smectogens. Our temperatures have been adjusted to the isotropic-smectic transition. The shear rates for these smectogens are 71.2 s\(^{-1}\) (BCS1), 66.5 s\(^{-1}\) (BCS2), 231 s\(^{-1}\) (BCS3), and 401 s\(^{-1}\) (BCS4).
Figure 6-12 The temperature dependence of the viscoelastic response for BCS2 at various shear rates. We see that the shear thinning is much more prominent in the B₂ phase and less so in the B₇ phase.
We see that by fitting the data with a power law behavior \( \eta = \frac{\dot{\gamma}^\beta}{\gamma} \) we can compare the shear thinning strength with the exponent \( \beta \). The results of this fitting show that the weakest shear thinning behavior \( \beta=0.43 \) occurs in the nematic phase, while the B\(_7\) phases are next with \( \beta=0.63 \) (BCS2) or 0.78 (BCS4), while the strongest shear thinning occurs for the B\(_2\) phase with \( \beta=0.89 \). This can be interpreted as larger internal frustrations due to molecular packing may suppress their shear thinning properties.

The final comparison that we will make is shown in Figure 6-14, where we show the temperature dependences for several bent core materials for a shear rate of 401s\(^{-1}\). We see that viscosity behavior in BCN1 which had the largest viscosity behavior of the nematogens follows roughly with the viscosity behavior of the BCS3 in the B\(_2\) phase and the peak value in BCS2 in the B\(_7\) phase. This behavior is likely due to permeation of bent core molecules through the smectic layers which exist in all of these phases to some degree.
Figure 6-13  Comparisons of the shear rate dependence of the viscosity for the different phases below the isotropic phase. If we fit these curves with the relationship $\eta = \frac{\beta}{\gamma^\alpha}$, we see that the exponent $\beta$ for each phase is 0.43 (BCN1) in the nematic phase, 0.78 (BCS2) or 0.63 (BCS4) in the $B_7'$ phase, and 0.89 (BCS3) in the $B_2$ phase.
Figure 6-14  Temperature dependences of several samples at a shear rate of 401 s$^{-1}$.
REFERENCES


18 R. dell’Erba, Polymer, 42, 2655-2663 (2001)


CHAPTER 7

SUMMARY AND DISCUSSION

This dissertation investigated the role of steric interactions between bent core mesogens and how these affect their structural and dynamic properties. We began this dissertation with a general discussion of liquid crystals and the fundamental interactions which drive macroscopic order. We discussed the effects of steric interactions between rod shaped molecules and their influences on liquid crystalline order. By expanding this discussion to bent core liquid crystals, we discussed the role that shape has on the structure and symmetry of their liquid crystal phases. For more information about this subject, please refer to the book chapter co-authored by Dr. Antal Jakli, John Harden, and I.¹

In chapter 2, we built on this idea of steric packing by considering the effects of frustrated packing on the properties of bent core smectic phases. We studied how fundamental changes in molecular structures of bent core mesogens may disturb the local packing structure and result in spontaneous polarization splay and layer bending. When these two spontaneous distortions are coupled to smectic ordering, we show that an instability results which necessitates a local SmCG structure with C₁ symmetry. When

these elastic constants caused by the frustrated packing are compared to biaxial layer compressions and polarization self-interactions, we obtain natural length scales which compares well to experimentally observed layer undulations and freestanding fluid filaments. We finished this chapter by considering the effects of polarization magnitude and direction on these frustrated smectic layers and proposed a phase diagram which describes several frustrated structures and compared them with structures reported in literature. This work was already published in Physical Review Letters in 2007.

In chapter 3, we discussed and developed various theories related to the stability of liquid filaments. We began by discussing the instabilities related to fluid bridges or streams and described the effects of liquid crystalline behavior on these instabilities. We considered observations of bent core filaments and discussed the inability of these theories to explain the unit fiber size, filament bundling, and their phase dependence on filament stability. We showed that all of these behaviors could be understood by considering the effects of surface tension, spontaneous polarization splay, biaxial layer compressions, and electric self interactions. A simple model considering filament bundles that we derived suggests that these structures may result from the fact that the increase of surface energy caused by increasing the filament size is smaller than the energy gained from the bulk, increasing the stability of bent core filaments. This model helps explain the stability of B₂ filaments which only form bundles, while the B₇ filaments can form both bundles and single filaments. We also discussed the stiffening of fluid bundles and estimated their effective layer compression modulus which is

---

dependent on the bundled structure. We finished by building a Lagrangian model to
describe the viscoelastic behavior of bent core filaments where flow is small which
allowed us to derive the equations of motion which were later used to study the elasticity
of these filaments. Some of this work has already been published in Physical Review E
in 2007\textsuperscript{3}.

In chapter 4, we experimentally quantified some of the properties of bent core
filaments. Our study began with a statistical analysis of filament diameters\textsuperscript{4} and we
showed that the average filament diameter was very insensitive to the aliphatic tail
length, suggesting that the fiber stability is caused by the rigid core-core interactions as
predicted by our model in Chapter 2. The results showed the existence of a unit filament
size which existed in the B\textsubscript{7} phase but was lost in the B\textsubscript{2} phase to a broader distribution
related to fiber bundles. Our next study focused on the dynamics of filament formation
as measured by a cantilever to determine the filaments tension as the process unfolds.
Our results indicated that the filaments tension is similar to that of the bulk material and
compares well to other experimentally determined values. We also showed that the
surface tension in the B\textsubscript{7} phase was approximately 10\% less than that in the isotropic
phase and suggested that this resulted from the surface tension anisotropy. Finally we
obtained information about the filament-filament interactions which occur in bundles.
The first study was preformed on a static structure where a single filament bridged two
bundles in static equilibrium. Analysis of the connection angle and the filament size led
us to estimate the adhesion forces between filaments in a bundle. The final study dealt

\textsuperscript{3} C.A. Bailey, E.C. Gartland Jr., and A. Jakli, Phys. Rev. E, 75, 3, 031701, 2007
\textsuperscript{4} C.A. Bailey, "Bent core fibers: stability, structure and polarization", ILCC 2006, Keystone, CO
with the viscous flow of a filament bundle as individual filaments broke and propagated down the bundle. Measurements of the average terminal velocity and filament diameter allowed us to estimate the viscosity of the filaments.

Chapter 5 consisted of several experiments whose analysis was made possible by the equations of motion derived in chapter 3. These experiments consisted of filaments whose equilibrium shape was distorted by the influence of external forces. Our first study was preformed on filaments which were deformed by the presence of a thin film which connected them. It was shown that the films stress was related to the effects of surface tension and the lack of flow into the film, and from our analysis we could determine the biaxial compression modulus of the thin film which compared well with small amplitude oscillations due to the filaments natural frequency. Studies on the filaments using oscillating forces provided information of the mechanical and electric properties of these filaments. The driving forces that we used were created with sound waves due to a speaker or by applying a voltage across two parallel capacitor plates. The sound experiments could be analyzed by a simple damped harmonic oscillator equation, but the data was complicated by the presence of speaker resonances. The electric field experiments resulted in more complicated interactions due to charge and dielectric interactions with the electric fields. The effect of dielectric forces resulted in a constant and second harmonic interaction which affected the behavior of the first harmonic signal. This interaction allowed us to approximate the dielectric constant and the electric field effects near and far from resonance. Analysis of the effective compression modulus allowed us to estimate the polarization normal to the smectic layers which seemed
reasonable for these materials. Finally, we showed that the ratio of the first harmonic to second harmonic signals was large in the B$_7$ phase and became small in the B$_2$ phase. This was associated to screening ions near the filaments surface which was proportional to the out of layer polarization and is consistent with the SmCG model we proposed in chapter 2.

In chapter 6 we discussed the basic flow properties of bent core liquid crystalline materials using our nanoliter viscometer. Our study focused on two categories of bent core liquid crystals which we characterize as nematogens and smectogens. Both phases showed non-Newtonian behavior in the isotropic phase which was connected to the formation of smectic aggregates. The aggregate size was indirectly measured by the viscosity dependence on shear rate in the isotropic phase of several nematogens. By drawing an analogy between this system and Debye relaxation in dielectrics, we could estimate the aggregates sizes which compared well to correlation lengths measured using X-ray scattering. The study of smectogens and nematogens in their liquid crystal phases showed interesting shear thinning behavior which was most effective in the B$_2$ phase, then the B$_7$ phase, and finally the nematic phase. It was suggested that frustrations in the local smectic structures could explain this behavior in that the most frustrated structure (nematics) would show the slowest shear alignment properties. Interesting effects in the B$_7$ phase showed the presence of a maximum viscoelastic response a few degrees below the isotropic transition which did not exist in the B$_2$ phase. This was associated with

---

entanglement of the helical filament structures which nucleate in the B7 materials.

Finally, we discussed some of the optical effects of applying shear stresses (flow birefringence) which showed a significant effect in the nematogens but were not observable in the smectogens. This suggests that the aggregates which exist in the smectogens are either much smaller or exist in lower numbers than in the nematogens.

In the Appendix, we described a novel device for measuring the viscoelastic behavior of non-Newtonian fluids using very small amounts of material (~10nL)\(^6\). We developed techniques for our device which allows easy calibration and calculation of the viscosity and shear modulus for various shear rates. Unlike many methods which require larger amounts of material or the use of indirect measurement of the shear stresses, our method directly measures the force and phase shift of a fluid sample allowing us the ability to expand this device beyond simple viscosity measurements (a property not capable in almost all small volume viscometers). Due to our measurement techniques, we could reduce the sensitivity of our device by playing with the applied frequency, contact area, displacement amplitude, etc. Furthermore we could use resonance measurements along with an impedance analyzer to determine viscoelastic properties at the resonant frequency of the speaker, a region not accessible with the lock-in techniques. This duel mode operation allowed us to perform a wide variety of viscoelastic measurements. We also showed how optical properties, such as flow birefringence could be measured with our device via the use of a microscope while applying shear.

The larger scope of this study was to better understand the role steric interactions play in the microscopic and macroscopic structures of these materials. The studies reported in this dissertation probed mainly the elasticity and structural properties of these materials. An extension of this study, for which I had less involvement, was performed by Dr. G.G. Nair using mixtures of bent core nematogens with rod shaped molecules. The goal was to decrease the strong steric interactions between the bent core mesogens and lower the transition temperatures. The results of this study were both interesting and unexpected due to the formation of a low temperature anticlinic SmC phase which existed even below room temperature. This mixture also showed fast biaxial switching below a millisecond without ferroelectric switching. This study is currently in waiting for publication in Advanced Materials sometime in 2008.

Other studies, which will be extensions of this work, consist of taking advantage of the cylindrical symmetries of the freestanding filaments and manipulating their physical properties. One of these studies, whose preliminary results were obtained by collaborative efforts between Dr. Istvan Janossy, Dr. Antal Jakli, Jake Fontana and I, suggest that the bent core filaments may be used as fluid optical waveguides. Some interesting observations of this project show that waveguiding occurs in both the crystal and B\textsubscript{7} phase. This will be further studied by Jake Fontana in his trip to the Research Institute for Solid State Physics in Budapest, Hungary during the summer of 2008.

\footnote{G.G. Nair, C. Bailey, S. Taushanoff, K. Fodor-Csorba, A. Vajda, Z. Varga, A. Bota, and A. Jakli, “Electrically tunable color using mixtures of bent core and rod shaped molecules”, accepted for publication in Advanced Materials, 2008}
Another study will consist of manipulating the elastic properties of these filaments by mixing with reactive monomers or nanoparticles. Preliminary results of this project were performed by me in Magdeburg, Germany where I mixed a low concentration of carbon nanotubes with bent core liquid crystals exhibiting the B7 phase. These measured resonance behavior suggested a stiffening of the filaments, but the data was distorted due to the resonance of the speaker and therefore was not included in this study. Further studies will be investigated by Nicholas Diorio in collaboration with Ralf Stannarius in Magdeburg, Germany.

In all, I have learned a great deal about the properties of bent core liquid crystals. During my guidance under Dr. Antal Jakli, I have been involved on all levels of the research process. I have helped write books and articles for publications and presented at several conferences. I have built experimental setups of all shapes and sizes for my work and others, and have designed software for data analysis and acquisition using MatLab® and LabView®. I have work on theoretical studies in collaboration with applied mathematicians, and have worked with pure experimental physicists. I have found this dissertation experience very fulfilling and I would again like to extend a thank you to all who were involved.
A.1 INTRODUCTION

Rheological studies have been found useful in several important arenas from medical diagnostics and biological sciences of cellular and tissue functions, the manufacturing of inks, paints and varnishes, to obtaining better understanding of basic non-Newtonian materials such as polymers, and liquid crystalline materials\textsuperscript{1,2,3,4,5}. However, some of these fields rely on a limited amount of material, especially in the biological fields (typically on the order of a few mL)\textsuperscript{1}. Therefore, recent technological needs have driven a renewed interest in both shrinking the scale of rheological techniques and the amount of material needed to perform such measurements\textsuperscript{1}. Classical small volume rheological techniques can be generalized into three basic categories which are capillary, rotational, and falling/rolling ball viscometers\textsuperscript{6}. While some success has been made in the shrinking the size scale of the latter two, they still rely on amounts of material on the order of a mL\textsuperscript{1}. Much more successful attempts have been made in shrinking the size of the capillary methods, mainly due to successes of micro-fabrication techniques in creating micro-fluidic channels. These methods have reported successful viscosity
measurements using material volumes in the order of a µL^{2,3} down to about twenty nL^7. However these methods are typically only valid for Newtonian flow regimes and low viscosities^2, which limits their use as a general rheological tool. Some improvements on this technique have allowed greater viscosity range (1cP<\eta<100cP), but is still limited to Newtonian behavior^3. Many classical rheometers used to measure complex viscoelastic properties relied on oscillatory motion to induce shear stresses on a fluid. This technique has been applied to several micro-viscometer techniques based on resonance properties of cantilevers^8 or piezoelectric crystals^1,9. For most of these techniques the detector has to be submerged in a container of material^8, and only one method using quartz crystals can measure rheological properties of around 10µL of material^1. This method, however, resonated between 5-10MHz, resulting in very large shear rates, usually well above typical non-Newtonian behavior transitions. In summary, although there have been numerous attempts at developing rheometers capable of measuring material properties with very small volumes, there has not yet been one flexible enough to perform generalized measurements over a wide range of material types and regimes.

Due to our interest to perform viscoelastic studies on bent core liquid crystals, we built a device that would require very small amounts of material (typically 10 nL) and would work over a wide viscoelastic regime.
A.2 DEVICE DESIGN AND GEOMETRY

In designing the nL-rheometer, we wanted to allow for accurate temperature control and optical measurements in parallel with the viscoelasticity measurements. This was obtained by building a device that is compact, thermally insulated and has a large viewing window for use with a microscope. This window allows us to visually inspect and make measurements of the droplet shape. Figure A-1 shows a diagram of the device along with labels of its major components. On the left is the drive system, which in our case is a speaker but in general could be any electromotive actuator. The center component is a temperature controlled chamber where the sample is placed between the two optical fibers. We used optical fibers because they are not thermally or electrically conductive, and because they allow a very controlled shape. On the right is the sensing device, for example a piezoelectric transducer that converts the mechanical force into an electric signal.

Two basic force measurements techniques are possible with this setup. The first method uses a 1920 Precision LCR meter (Quadtech) to measure shifts of the resonant frequencies caused by the presence of the fluid. The second method uses a 7265 DSP lock-in amplifier (EG&G Instruments) attached to the piezoelectric crystal to measure the force transferred from the drive system through the fluid. We chose these two techniques because the lock-in techniques is good for obtaining general viscoelastic measurements, however the LCR technique is more suited for quick viscosity measurements where varying parameters is not required. Figure A-2 shows the above view image of a fluid bridge of 5CB through an Olympus CK40 inverted microscope between two optical
fibers. Also included is a diagram of the droplet showing the important experimental parameters used in the calculation of the fluid geometry and shear strain. The diameter $D$ (125 µm) of the glass rods was used as the length scale in our analysis. The droplet waist $w$, the distance between the fibers $L_0$, and the oscillation amplitude $s$ were all experimentally measurable quantities by analyzing images of the droplet. Due to the surface tension, the material somewhat overlaps the optical fiber, therefore the distance between the fibers measured experimentally ($L_0$) and that used in the analysis ($L=L_0+\delta$) differ slightly by the extrapolation length $\delta$. In general, $\delta$ must be a fitting parameter; however we do know that, theoretically, $\delta$ lies between zero and the radius of the fiber. These parameters can be used to calculate the effective cross sectional area $A$ and droplet volume $V$ shown in Eq. A.1.

$$A \approx \frac{2}{3} wD = \pi r^2 \quad \text{and} \quad V \approx AL \quad \text{for large } L \quad \text{A.1}$$

A.3 MEASURMENT OF THE AMPLITUDE OF VIBRATION

Measurements of the voltage and frequency dependencies of $s$ are needed to correctly characterize the strain behavior. The displacement calibration curves used in our studies are shown in Figure A-3 for a constant frequency ($f=130$ Hz) with a varying voltage (part a), and the frequency dependence of the amplitude per volts for small displacements (part b). The voltage dependence of the speaker amplitude arises from a competition of electric and elastic forces on the speaker head. The strong resonant behavior makes it difficult to measure the forces using lock-in techniques near resonance. If we use a speaker for driving this technique, we must stay below 200 Hz where the
Figure A-1  Cross-section of the nL-rheometer consisting of three basic components: a drive system (speaker) (left), a temperature controlled chamber (center), and a piezoelectric transducer to measure the force (right). Measurements are obtained by driving the speaker at a particular frequency which oscillates a glass rod which enters the chamber. The force of the oscillating rod is transferred to the other rod via the material which is placed between them. This transferred force is measured as current via a piezoelectric crystal and recorded using a lock-in amplifier. An above view of the droplet shows the two glass rods connected with a droplet of 5CB.
Figure A-2  a) Droplet of 5CB (~12nL) at 45°C between two D=125µm diameter glass rods as viewed through an Olympus CX40 inverted microscope. b) A diagram of the same droplet along with the important parameters D (the width of the glass rods), w (the center width), s (the displacement amplitude of the speaker), and L (the distance between the glass rods) that must be measured to calculate the droplet geometry and the shear strain.
frequency behavior is constant. However, by measuring changes of the speaker
resonance due to the presence of the fluid we can still determine the viscous properties of
the fluid. This method does not allow us to vary the shear rate and is insensitive to elastic
forces. Therefore we will only show the validity of this technique but will not use it in
the next chapter when analyzing bent core materials. The second method uses direct
measurement of the force with a piezoelectric transducer allowing strain rate and
temperature sweeps. In order to avoid issues with resonance, we do not use frequency
sweeps, but instead we vary the distance between rods (L) to vary the strain rate. This
method is by far faster and easier to couple to temperature and optical measurements.

A.4 LCR TECHNIQUE

This method does not require the piezoelectric sensors, and relies on the
dependence of the resonant frequency of the drive system. Impedance measurements
along with circuit analysis were used to determine the viscous and elastic behavior for the
test material.

The viscosity determination relies on the fact that at resonance all of the electric power is
being dissipated. Therefore if one assumes that changes in resonance can be caused by
the presence of the fluid, then we are able to measure the extra power being dissipated by
that fluid by measuring the shift in the resonance frequency. Mathematically this
statement can be written as,
Figure A-3  a) Displacement versus voltage at 130Hz and b) the displacement per volts (not RMS) versus frequency in the small voltage regime along with best fits for the glass rod with no fluid attached. The amplitude dependence follows an exponential decay behavior while the frequency dependence for small voltages follows a combination of behaviors due to mechanical dampening and resonance (LRC behavior). 

\[ 2s = a^*(1 - \exp(-V/b)) \]

\[ a = 5.25 \times 10^{-4}, \ b = 3.18 \]
where the subscripts $f$ and $o$ represent the setup with or without the fluid, respectively. The dissipation factor can be written as $Q(\omega) = \frac{1}{2} \eta AL \left( \frac{\omega}{L} \right)^2$ (units of Watts) and the electric power $P = \frac{V_r^2}{2\pi}$ (where $R$ is the electric resistance and $V_r$ is the RMS voltage). In the range where the displacement $s$ is proportional to the voltage (see Figure A-3), we obtain the following relationship for the viscosity which is related to the change in the inverse of the resistance of material.

As in the measurements for viscosity, we can approach the elasticity in a similar way. If we calculate the average power (rate of change of energy averaged over one period $T$) of a spring system with spring constant $k$ and oscillatory displacement $x(\omega) = se^{i\omega}$, we can obtain the following.

What is interesting about Eq. A.4, is that by assuming that the displacement is proportional to the voltage then we can write the inverse of the effective impedance as,

which is identical to the impedance due to capacitance. Therefore the elasticity due to a fluid element can be calculated in a similar manner as done for the dissipation in Eq. A.3 resulting in the following relationship.
Therefore, shifts in capacitance can be explained by changes in elasticity of the system. This is less accurate than the viscous term because of the elasticity of the speaker membrane also plays a significant role, which in many cases will be several orders of magnitude larger than the capacitances due to fluid elasticity. An estimation of the elasticity term, using the surface tension (~20mN/m) for \( k \) and \( s=70\mu m \) at 1V, gives an estimate in the range of 100pF compared to the values sited in Figure A-5 on the range of 100\( \mu F \), therefore placing the percent changes of the capacitance due to the fluid element well below the resolution of the LCR device (0.1% of reading).

The LCR meter can measure the impedance of the speaker which has both phase and magnitude information. Therefore, if we use an appropriate electrical model for our speaker system, then we should be able to calculate the dissipative resistance related to the frictional losses in the system and the capacitance related to the elasticity. The effective circuit that we used to describe the speaker and to fit the measured data is shown in Figure A-4. The equations used in the fit of the magnitude and phases are shown below,

\[
|Z(\omega)| = \sqrt{\left( R_l + \frac{R}{1 + (\frac{\omega}{\omega_0})^2}\right)^2 + \left( \frac{R(\frac{\omega}{\omega_0} - \frac{\omega_0}{\omega})}{1 + (\frac{\omega}{\omega_0})^2}\right)^2} \quad \text{A.7}
\]

\[
\psi(\omega) = \tan^{-1}\left( \frac{\frac{\omega}{\omega_0} - \frac{\omega_0}{\omega}}{1 + (\frac{\omega}{\omega_0})^2}\right) \quad \text{A.8}
\]
where $R$ is the resistance of interest, $R_l$ is the lead resistance, $\omega_1 = \frac{1}{RC}$, and $\omega_2 = \frac{R}{L}$ are the characteristic angular frequencies due to the capacitance $C$ and inductance $L$. It is also important to note that the resonance frequency, $\omega_r = \sqrt{\omega_1 \omega_2} = \frac{1}{\sqrt{LC}}$, is determined by the geometric mean of these two natural frequencies. Below is the temperature dependence of the empty resistance $R_o$ and capacitance $C_o$ between 25ºC and 45ºC. To summarize, we have described how, by using Eqs. A.3 and A.6 combined with circuit analysis, we can determine the viscosity and elasticity (if large enough) as a function of temperature.

A.5 LOCK-IN TECHNIQUE

This method uses a piezoelectric transducer attached to a glass rod to measure the charges (current) induced by forces applied via the fluid coupling to the speaker. When this current is measured with a lock-in amplifier it can allow direct force measurements with the sensitivity related to the sensitivity of the lock-in amplifier (~fA). In our case, this sensitivity is dependent on the frequency and give the following relationship to the minimum measurable force, $F_{\text{min}} \approx \frac{10 \mu N \cdot Hz}{f}$. Outside of this equipment limit, the force from the fluid can also be controlled experimentally through manipulating the geometry of the glass rods. This results in a very flexible device for measure the fluid properties over many orders of magnitude (we have measured viscosities between 0.01Pa*s to 100Pa*s).

The basic theoretical model for this measurement technique can be derived by comparing the bulk and kinetic energy terms to the viscous dissipation term. The easiest method for dealing with this system is by using the Lagrangian function to describe the mechanics.
Figure A-4  a) The approximate LCR circuit model for the speaker.  b) The measured impedance and phase vs. frequency for the speaker with no fluid at 45°C along with the fit using the circuit approximation.
Figure A-5 Plots of the empty resistance $R_o$ and $C_o$ along with their best fit curves as a function of temperature.
The simplest Lagrangian which describes a material’s elasticity ‘Lm’ is shown below.

\[ L_m = \frac{1}{2} mL^2 \dot{\varepsilon}^2 - \frac{1}{2} G A L \varepsilon^2 + F \varepsilon \]  

A.9

In this expression \( \varepsilon \) is the shear strain and \( \dot{\varepsilon} \) (which will also be referred to as \( \gamma \) when the ‘dot’ notation is unavailable) is the shear rate. The first term is the kinetic energy of the material, and the second term combines the potential energies from elasticity (\( G \) is the elastic shear modulus) and the last term is the energy associated with the drive system.

The negative in front of \( F \) denotes that the energy is added to the system. For a purely elastic material, the variational derivative of Eq. A.9 with respect to \( \varepsilon \) and \( \dot{\varepsilon} \) will result in the natural equation of motion. However, in viscoelastic materials, the variational derivative equation changes to include dissipative effects (non-conserved forces)\(^{10}\). This equation takes the form shown in Eq. A.10, where \( Q = \frac{1}{2} \eta A L \dot{\varepsilon}^2 \) is the dissipated power due to viscosity and the right hand side is the rate of decrease of the Lagrangian.

\[
\frac{\partial L_m}{\partial \varepsilon} - \frac{d}{dt} \left( \frac{\partial L_m}{\partial \dot{\varepsilon}} \right) = \frac{\partial Q}{\partial \dot{\varepsilon}} 
\]  

A.10

This relationship results in the following equation for the shear force applied to the material.

\[ F = mL\ddot{\varepsilon} + GA \varepsilon + \eta \dot{A} \dot{\varepsilon} \]  

A.11

With the assumptions that the cross sectional area \( A \) is constant and using the following relationships for periodic force \( F = F_o e^{j\omega t} \) and strain \( \varepsilon = \frac{1}{L} e^{j\omega t} \), we can obtain the force relationship shown below.

\[
F_o = -m\omega^2 s + \left( \frac{G}{\omega^2} + i\eta \right) A \left( \frac{\omega}{L} \right) 
\]  

A.12
In this solution, we notice that the force \( F_o \) has two components related to inertial forces and the viscoelastic behavior of the material.

Experimentally, however, there exist measurable inertial forces related to things other than the fluid element. These effects could be related to vibrational modes of the glass rods which we haven’t been considered. These effects can be taken into account by defining an effective mass \( m_{eff} \). The consequence of this substitution is that the phase of the effective inertial term is no longer required to be in phase with either component of the viscoelastic force. This adjustment to Eq. A.12 generates the following relationship for the magnitude and phase of the measured force.

\[
|F_o| = \sqrt{(GA \frac{\omega}{\varphi} + m_{eff} \omega^2 s \cos \phi_1)^2 + (\eta A \frac{\omega}{\varphi} + m_{eff} \omega^2 s \sin \phi_1)^2}
\]

\[
\phi = \phi_0 + \tan^{-1}\left(\frac{\eta A \frac{\omega}{\varphi} + m_{eff} \omega^2 s \sin \phi_1}{GA \frac{\omega}{\varphi} + m_{eff} \omega^2 s \cos \phi_1}\right)
\]

The two phase shifts, \( \phi_0 \) and \( \phi_1 \), are related to the effects of lag from the motion of the drive system to the applied voltage (would be \( \sim 90^\circ \) for a lossless speaker) and shifts in the inertial term due to \( m_{eff} \), respectively. Some advantages of using the above definitions are:

1) If \( m_{eff} \) is much greater than the mass of the test material \( m \) (\( \sim 10^{-2} \) mg), then \( m_{eff} \) and \( \phi_1 \) can be considered to be experimental constants.

2) Since \( \phi_0 \) is related solely to the drive system, it can also be considered an experimental constant.
By using this notation, we can now determine the properties of $G$ and $\eta$ by measuring the magnitude and phase of the force, the geometrical parameters of the droplet, and the voltage dependence and frequency of the applied displacement.

\begin{align*}
G &= \left( \frac{L}{4s} \right) \left( F_0 \cos (\phi - \phi_0) - (m_{\text{eff}} \omega^2 s) \cos \phi_1 \right) \quad \text{A.15} \\
\eta &= \left( \frac{L}{4s} \right) \left( F_0 \sin (\phi - \phi_0) - (m_{\text{eff}} \omega^2 s) \sin \phi_1 \right) \quad \text{A.16}
\end{align*}

With these equations along with device calibration, which will be discussed in the next section, one can determine the viscoelastic properties of a wide range of materials with very small volumes.

A.6 DETERMINATION OF THE EXPERIMENTAL PARAMETERS

This section will show how calibration of the device was obtained by measuring of several materials. We will break this analysis up into several parts to describe each section in full. We begin with the calibration of the piezoelectric constant by measuring several silicone fluids with known viscosities. Then determine the value of $\phi_0$ by measuring the stress-strain curve of a liquid crystal material in its crystal state, and measure the values of $\phi_1$ and $m_{\text{eff}}$ by using several calamitic liquid crystals in their isotropic phase. Finally, we use these constants, to determine the viscosity and shear modulus as a function of temperature for 5CB and 8CB and compare to published results measured with a classical rheometer.
A.6.1 PIEZOELECTRIC TRANSDUCER CALIBRATION

Calibration of the piezoelectric transducer is a necessary step mainly because there is no guarantee of 100% efficiency of force transfer. This conversion is crucial because it determines the value of \( F_0 \) thru the following relationship.

\[
F_0 = \frac{\sqrt{2} I_r}{2\pi f d_{zz}}
\]  
\hspace{100pt} A.17

In Eq. A.17, the factor of \( \sqrt{2} \) comes from converting the RMS current \( I_r \) measured by the lock-in amplifier to its true value; \( f \) is the frequency needed to convert the current to the electric charge generated by the force and \( d_{zz} \) is the piezoelectric coefficient (in units of pC/N) which converts the measured charge to force. The easiest way to determine the piezoelectric coefficient is to take materials with known viscosities and measure their response to shear rate. Then by comparing the measured viscosities to the known ones, we can determine the piezoelectric coefficient. Examples of this calibration are shown in Figure A-6 for a castor oil and two silicone fluids. The first graph shows the response of the measured induced charge divided by the droplet cross sectional area (shears stress) as a function of shear rate. We see that all of the samples show good linear behavior except the 60 Pa s sample whose value begins to shear thin at around \( \gamma = 90s^{-1} \). This shear thinning range is similar to the range reported for this material by their manufacturer, Clearco Products\textsuperscript{11}. Finally, plotting the slope of the stress-strain curve as a function of known viscosities, we can fit for the piezoelectric coefficient \( d_{zz} = 160 \pm 10 \text{ pC/N} \).
Figure A-6  Graph of the strain rate dependences on the measured stress in units of pC/m², along with a linear fit for Castor Oil (● and insert) and two silicone fluids manufactured by Clearco Products (■ and ▼) with viscosities of 1, 10, and 60 Pa*s, respectively.  b) The slopes from part a) as a function of their known viscosity values.
A.6.2 DETERMINATION OF $\phi_0$

The experiment to determine $\phi_0$ is fairly straightforward. It consists of measuring the force and phase for a material in the crystal state. This works, because if you look at Eq. A.14 and assume that the shear modulus $G$ is much greater than any other effects then the relationship reduces to $\phi = \phi_0$. This effect is best shown in Figure A-7, where we measured the force and phase of a material in the crystal state at room temperature. This graph clearly shows a constant phase and a linear proportionality of the force to the applied voltage. The measured force is the maximum force allowed by the speaker and not due to the shear modulus of the crystal. This is known because the crystal fused the two glass rods no displacement was observed, suggesting a direct coupling between the speaker and the piezoelectric crystal.

A.6.3 DETERMINATION OF $m_{\text{eff}}$ AND $\phi_1$

This is the last set of constants that need to be determined before general material characterization can begin. For these we measured several calamitic nematic materials in their isotropic phase, and analyzed the remainder of the forces involved. Applying isotropic Newtonian fluid behavior ($G=0$) into Eq. A.13, we can calculate the in and out of phase components of the shear stress ($\tau = F/A$). The resulting relationships are shown below for the elastic (in phase) and viscous (out of phase) components.
Figure A-7  The magnitude and phase of the force when measured for a material in the crystal state. The phase is a constant 74.9° and provides us the value of \( \phi_0 \). The slope of the magnitude provides us with the force per volts provided by the speaker.
Interestingly, the stress due to inertia is independent of $L$, therefore allowing us the ability to distinguish it from the viscous term which in inversely proportional to $L$. Figure A-8 shows the $L$ dependence of the measured elastic (a) and viscous (b) stresses along with the theoretical fits for several liquid crystal materials in the isotropic phase. The liquid crystal samples that we studied were 5CB (4’-Pentyl-biphenyl-4-carbonitrile) at 45°C, 8CB (4’-Octyl-biphenyl-4-carbonitile) at 45°C, and 6OO8 (4-n-octyloxyphenyl-4-n-hexyloxybenzoate) at 90°C.

Using this technique we could determine the values of the effective mass and the inertial phase shift which are $m_{\text{eff}} = 0.36 \pm 0.04\text{mg}$ and $\phi_i = 6 \pm 1^\circ$, respectively.

Interestingly, the uncertainty for $m_{\text{eff}}$ is comparable to the mass of the fluid element (~0.01mg) which allows us to use this as an experimental constant. The uncertainty in the effective mass translates in our measurements to an error of the shear modulus $G$ and viscosity $\eta$ of 2 Pa and 2 mPa s, respectively.

A.6.4 VISCOsITY COMPARISONS OF 5CB AND 8CB

Now that we have calibrated the device we can begin to characterize the viscosity behavior of unknown materials. We measured the viscosity dependence with temperature
Figure A-8  The $L$ dependence of the elastic (a) and viscous (b) stresses along with their theoretical fits from Eqs. A.18 and A.19. The resulting values for the average magnitude and phase of the inertial force can be used to calculate the effective mass ($m_{\text{eff}}=0.36\pm0.04mg$) and inertial phase shift ($\phi_i=6\pm1''$).
of the well studied mesogens of 5CB and 8CB. We chose them because we can easily compare these measurements with previously obtained results. The article which we will refer was written in Rheologica Acta by Chmielewski et. al. in 1984\textsuperscript{12}. In this article, they studied the non-aligned apparent viscosity of several biphenyl liquid crystals using a “Rheotest-2” viscometer. This viscometer uses a set of coaxial cylinders whose gap can be filled with about 1mL of fluid. We also show the viscosity measurements for 5CB using the LCR technique to compare with measurements obtained from the lock-in technique. By comparing our results with theirs, we show how accurate our method is even though we used five orders of magnitude less material (~7nL). Furthermore, we show that the shear thinning behavior, proposed in their article, of the viscosity with temperature, $\eta = (a \log T + b) \dot{\varepsilon}^{-0.47}$, still holds even for much larger shear rates. In our studies we used a shear rate of $\dot{\varepsilon} = 8620s^{-1}$ compared to their 1300s$^{-1}$ maximum shear rate. Although the behavior of their shear thinning fit worked, our best fit parameters were smaller than their reported values. The values of $G$ in our measurements were less than 10Pa which could be explained by small changes in surface tension due to shear. Our approximation of $G$ can be estimated as a ratio of the surface tension difference between the glass rods and the air interface to the effective diameter of the droplet which gives a value of $G \approx \frac{\Delta \sigma}{D} = \frac{2 \times 10^{-3} \sqrt{\varepsilon}}{4 \times 10^{-3} m} = 5Pa$. Interestingly, we can see that across the isotropic to nematic transition for both materials the value of $G$ decreases, while at the nematic to SmA transition for 8CB the value increases. This effect could be due to surface
Figure A-9  The temperature dependence of the viscosity ($\eta$) and shear modulus ($G$) for 5CB (a) and 8CB (b). Our results are in good agreement with those measured by Chemielewski et. al. in the isotropic and nematic phase ($\blacksquare$). We also showed that the shear thinning log behavior discussed in that article, $\eta = (a \log T + b) \dot{\varepsilon}^{-0.47}$, still applied in the smectic phase (dashed line), even though we measured at a much larger shear rate.
anchoring in the nematic case or the inability to accommodate the anchoring in the smectic case.

A.7 OPTICAL MEASUREMENT TECHNIQUES

To this point, we have focused on the measurement of shear stresses to compute the viscoelastic properties of a material. However, due to our devices design, we are also able to place the material under a polarizing microscope for simultaneous optical measurements during shear. This allows us to perform flow birefringence measurements while still performing the classical force measurements discussed in previous sections. The experimental setup consists of using an Olympus CX40 inverted polarizing microscope along with our device. We use crossed polarizers where one of the polarizer axes aligned along the shear direction (along s) or at 45° to it. Intensity measurements were preformed with a photodiode using both DC and lockin voltage measurements. DC measurements were preformed with an HP34401A multi-meter connected to a computer for timed data acquisition. The 1st and 2nd harmonic measurements were obtained with an 7265 DSP lock-in amplifier (EG&G Instruments) and where used to analyze the mechanism of shear induced birefringence. The theory used to measure the birefringence of our samples, is show in Eq. A.20, where $d$ is he thickness of the sample ($\sim D$), $\lambda$ is the wavelength being studied, and $\Delta n$ is the birefringence of the sample. For small birefringences, the wavelength for white light can be approximated by the average value which is being studied ($\lambda = 600nm$) and problems associated with $\Delta n$ created phase shifts larger than $\pi/2$ can be ignored.
The results of this setup will be described in Chapter 7 on studies done on bent core liquid crystals.
REFERENCES

1. A. Saluja and D.S. Kalonia; AAPS PharmSciTech 2004; 5 (3) Art. 47  


7. N. Srivastava and M.A. Burns; Lab Chip 6, 744-751 (2006)


11. Product information is published on their company website at 