Tilt Angle and Birefringence of Smectic Liquid Crystal Materials

A Senior Project

presented to

the Faculty of the Physics Department

California Polytechnic State University, San Luis Obispo

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science Physics
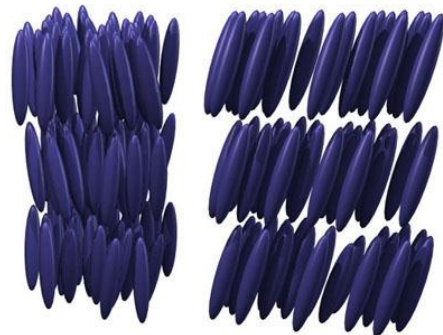
by

Taylor Van Winkle

June, 2013

Introduction

The science of physics is defined as the study of matter and energy. The coexisting relation between the two is in the definition of states of matter. Each separate matter state represents a different and important landmark in the ordering of the molecules that make up any substance. All of us know of the main three observed states of matter that exist in our immediate world; Solid, Liquid, and Gas. Solids, as we know, are comprised of well ordered molecules in crystalline lattice structures, held together by bonds formed between the molecules. Once the particles gain enough energy (normally heat) to break out of the bonds, they slip past one another with ease and lose their positional order. Thus producing the flowing motion.

The line that separates these two phases from each other is not a thin one, but rather a broad spectrum of different states. Within this spectrum lies the fundamental idea behind Liquid Crystals. These special substances are an example of a well ordered liquid that exists between the solid and liquid phases. They are made up of small rod like molecules that are fluid like liquids but also exhibit an overall order about them. Their order comes from their unique shape. They have a long axis that gives them the appearance of an elongated ellipse with small loose end chains. These molecules may exhibit different liquid crystal phases that change with temperature just as the more well known phases do. The main phases we will examine within the liquid crystal phases are denoted as Nematic and Smectic. Within the Nematic phase, liquid crystal molecules are in random motion and are fluid with no positional order, throughout the

substance. Although they are in random positional placements, they still all tend to point in a general direction known as the director. Their positional randomness is obviously more reminiscent of a liquid rather than a solid, which is why they occur at higher temperatures (i.e. closer to the liquid phase). The Smectic phase occurs at lower temperatures than the Nematic and this is evident by its key feature. The fluid Smectic phases are ordered into distinct layers of liquid crystal molecules. As before in the nematic phase, the liquid crystals still poses their orientational order but gain positional order in one dimension, creating layers in which ordering is fluid. The smectic A (SmA) phase is the phase closest to the nematic (see Figure 1A). The liquid crystal molecules in the SmA phase on average point in the direction of the director which points perpendicular to the layers of the substance. The smectic C (SmC) phase is observed as we lower the temperature farther and the director, that was previously normal to the layers, tilts away from the normal by the tilt angle alpha (see Figure 1A). This process of tilting to the side makes an
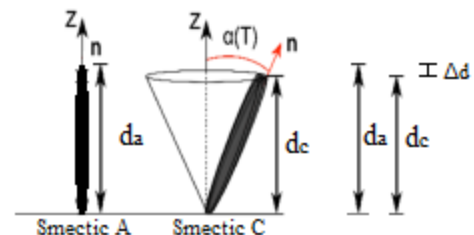

Figure 1A: Typical Smectic A -> Smectic C transition.

effective shrinking in the layer of molecules, Δd, as shown in Figure 1. This layer shrinkage is given by $\cos(\alpha(T - T_{AC}))$ where T is the temperature of the sample and T_{AC} is the transition temperature at which the sample goes from smectic A to smectic C. This layer shrinkage can be as high as 11% in some crystals. (Yoon et al.)

The liquid crystals we used in our experiments, were of a special type known as De Vries liquid crystals, which exhibit a different behavior when transitioning from SmA to SmC. In the De Vries model, the layer shrinkage from SmA to SmC is less that 1%. This astounding result may be
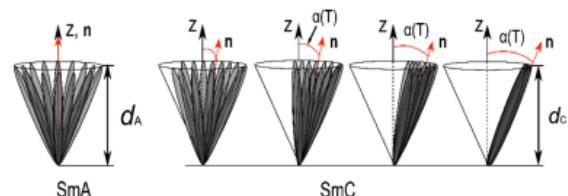

Figure 1B: Diffuse-cone model: Shows how tilt of molecules remains the same while uniform tilt angle changes.

described by the diffuse cone model described in figure 1B. In the SmA phase, the molecules start out with an average tilt already, but are randomly oriented along the tilt cone. This randomness leads to an overall degeneracy of their azimuthal directors so that the average director n points parallel to the layer normal in the Z direction. As the De Vries liquid crystal cools and transitions to the SmC phase, it loses its azimuthal degeneracy. The loss of degeneracy aligns the molecules along a specific azimuthal direction, thus, generating a director tilt without having layer shrinkage.(Yoon et al.). This lack of layer shrinkage makes De Vries liquid crystals a practical choice in manufacturing products. It allows us to put them into screens and eliminate defects due to layer shrinkage of regular smectic liquid crystals as the liquid crystals reorient. Because of this practicality, De Vries crystals have been a major topic of study in the scientific world.

Due to the differences in the size of the molecules axis, light traveling through them is altered. As light passes through the molecule in the direction of the smaller axis it is almost unaltered because the thickness is so small, whereas when light passes through on the longer axis, the light takes more time to get through the thicker material than the shorter side. Because the longer axis slows down the light passing through more than the shorter axis we call the long axis the slow axis and the small axis the fast axis. Because these different orientations produce different effects on the light we can view the different axis as different indices of refractionn_{fast}, and n_{slow}. The differences of these indices of refraction is known as the Birefringence. The birefringence makes the molecules refract light rays differently depending on the direction of oscillation of the light and the direction of incidence onto the molecules. We

can use the phenomenon of birefringence as a helpful tool in determining the orientation and

order of the crystals in the substance. This idea is elaborated on further in the analysis.

Experimental Design

The main goal of our experiment was to measure the

optical properties of the liquid crystal as a function of

temperature stimulus in a polarized microscope.

First we examined how the Liquid Crystals

orientational order changed as we varied the temperature.

As stated above, the order of Liquid Crystals is

proportional to the birefringence of the substance. As the

director tilts in the SmC phase, the light intensity changes

in the polarized microscope. We measured the light

intensity as a function of the temperature. The

experimental setup (see Figure 2), used a small electric oven

placed on a microscope. We then placed samples of liquid

crystal material into the microscope slides and placed the slide

Figure 3: Oven along with a liquid crystal sample. A) Liquid crystal sample. B) Optical viewing port.

A) A camera to capture intensity measurements as temperature is varied. B/E) Polarizers used to orient the light in a particular way and cut out certain light orientations. C) An oven used to control the temperature of the liquid crystal samples. D) Rotating stage to re-orient the molecules with respect to the polarizers.

in the oven (see Figure 3), which had a small hole in the top for viewing. The birefringent

response of the liquid crystals happens when linearly polarized light enters the material and is

split between the fast axis and the slow axis. To achieve the linear polarization we placed a

polarizer over the microscope lamp below the sample. We also placed a polarizer above the

sample below the eyepiece to act as an analyzer. By setting the polarizer and analyzer to

different respective angles to each other, we observed how the liquid crystals effected the transmitted light, and altered the polarization of different incident polarized angles (Figure 4).The process used is taken from an article published in a liquid crystal journal about high resolution temperature scanning techniques for optical studies of liquid crystal phase transitions.(Saipa)

This setup allowed us to physically view the liquid crystals as they changed with temperature as well as find the light intensity of the specific area being measured. To find the light intensity, we used a camera to measure grayscale intensity. So using this camera, we measured the intensities of four different combinations of polarizer angles and sample angles (see Figure 5). Two measurements came from an orientation with the bottom polarizer parallel to the smectic layer normal of the sample. One with the analyzer(upper polarizer) parallel to the polarizer

Figure 4

Light enters in through the first polaroid and is altered by the liquid crystal and then, is again filtered by another polaroid.

and one with analyzer normal to the polarizer. We then changed the orientation of the liquid crystal smectic layer normal to be at a forty five degree angle with respect to the polarizer and measured the intensity for the analyzer being again parallel and then perpendicular to the polarizer.
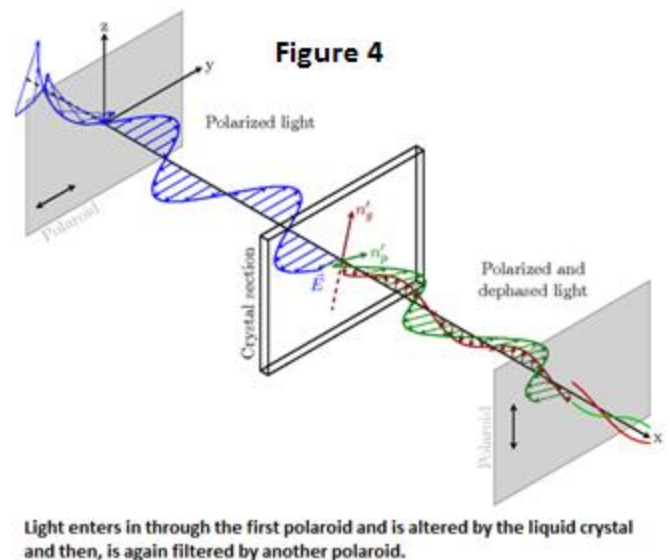
The changing orientations of the polarizer with respect to the analyzer required a degree of repeatability to be able to have consistent measurements. This was reliant on our ability to orient the polarizer and analyzer in the exact same way for each measurement we took. Previous experiments done with this setup had proven to have less acceptable data due to this inaccuracy. If the angle of the polarizer to analyzer was off, we would get an incorrect intensity reading that would throw off our calculations later on. Our solution was to use
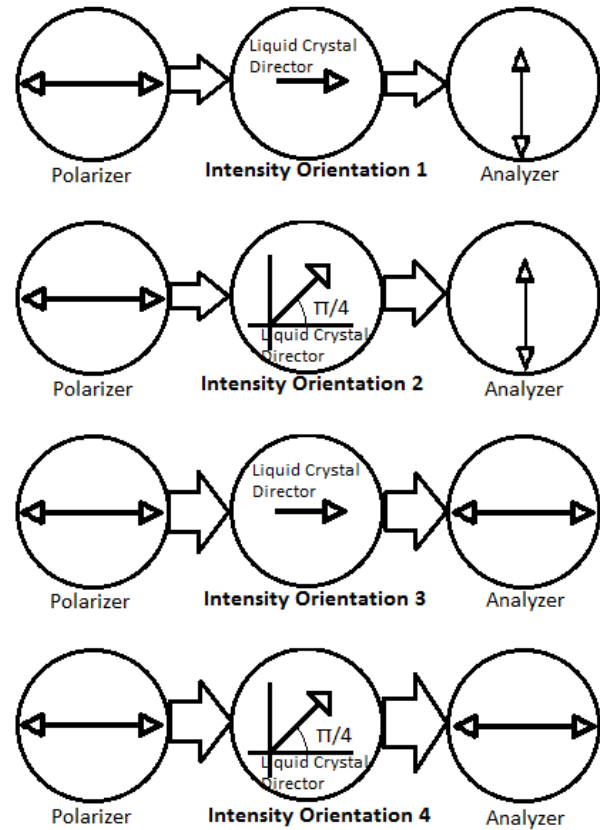

Figure 5: Polaroid orientations in relation to liquid crystal director.

analyzer fashioned in such a way that it fit snugly into one orientation in the microscope. In previous experiments, this meant that we would have to adjust the lower polarizer by hand and adjust it to where we thought it should go. In our new design, we machined a new orientation into our analyzer so that we could place it into the microscope at two different distinct angles normal to each other. This small addition to the experiment helped us achieve a higher level of accuracy by ensuring that the polarizer and analyzer were set at exactly the angles normal and parallel to each other, when needed. It also eliminated the guesswork of trying to figure out where the lower polarizer was supposed to be.

We then combined the four measured intensity equations and used a relation from the article (Saipa) (shown in the analysis) to find the birefringence of the molecules within the

sample as a function of temperature. From the birefringence graph, we could then determine the order of the molecules.

Analysis and Results

The research we were conducting on the liquid crystals, was to examine the birefringence due to temperature of the De Vries liquid crystal known as 8422. Our experiment was to heat the samples of liquid crystals in an oven and then slowly cool them over time while recording changes in intensities. We then use the relation for the Intensity of light as a function of tilt angle, and polarizer/analyzer angle. From the (Saipa) article we have:

$$I = I_0[cos^2(\chi) - sin(2\phi)\sin(2(\phi - \chi))\sin^2\left(\frac{\pi d \Delta n}{\lambda}\right)]$$

where χ is the angle between the polarizer and analyzer, and ϕ is the angle between the polarizer and the liquid crystal layer normal. We then isolated the four unique situations described in the experimental design, setting the polarizer angles to $\phi = \theta$ and $\chi = \frac{\pi}{2}$ for intensity orientation I1, $\phi = \frac{\pi}{4} + \theta$ and $\chi = \frac{\pi}{2}$ for I2, $\phi = \theta$ and $\chi = 0$ for I3, and $\phi = \frac{\pi}{4} + \theta$ and $\chi = 0$ for I4. By orienting the polarizers and sample to these angles, we reduce the Intensity equation into four distinct outcomes of:

$$I_1 = I_0 sin^2(2\theta)sin^2(\frac{\pi d \Delta n}{\lambda})$$

$$I_2 = I_0 cos^2(2\theta)sin^2(\frac{\pi d \Delta n}{\lambda})$$

$$I_3 = I_0 \left(1 - sin^2(2\theta) sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \right)$$

$$I_4 = I_0 \left(1 - cos^2(2\theta) sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \right)$$

For our experiments, we read the intensity data from the camera in the microscope into a Mat Lab program that first interpolated the intensity data as a function of time into intensity data as a function of temperature.
We did this by recording the temperature of the samples alongside the intensity measurements. By interpolating these two datasets, we obtained our Intensities as a function of Temperature as shown in Figure 6. Due to temperature inaccuracies, the horizontal position of data was
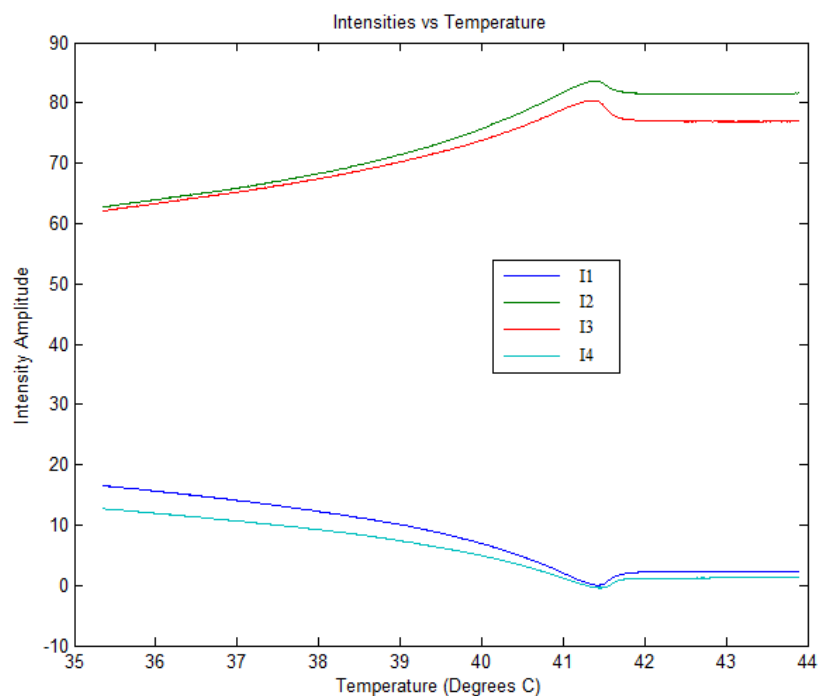

Figure 6: Intensities vs Temperature of I1, I2, I3, and I4.

shifted such that the phase transition occurred at the same measured temperature in all experiments. Our results were a bit interesting in that around the transition temperature we observed a large shift in the Intensities in all of the curves.

From these Intensity functions of temperature, we are able to back calculate the birefingence Δn and the tilt angle θ, as a function of temperature. To do this, we must relate the intensities in the following way:

$$\tau_1 = \frac{I_1}{I_0} = \frac{I_1}{I_1+I_3} = sin^2(2\theta)sin^2(\frac{\pi d \Delta n}{\lambda})$$

$$\tau_2 = \frac{I_2}{I_0} = \frac{I_2}{I_2+I_4} = cos^2(2\theta)sin^2(\frac{\pi d \Delta n}{\lambda})$$

then taking the ratio of

$$\frac{\tau_1}{\tau_2} = tan^2(2\theta)$$

we obtain our tilt angle as

$$\theta = \frac{1}{2}\tan(\frac{\tau_1}{\tau_2})^{\frac{1}{2}}.$$

We then examine the sum of

$$\tau_1 + \tau_2 = sin^2(\frac{\pi d \Delta n}{\lambda})$$

giving us the birefringence as a function of the intensities

$$\Delta n = \frac{\lambda}{\pi d}\arcsin(\tau_1 + \tau_2)^{\frac{1}{2}}.$$

From our equations, we are able to solve for the tilt angle in radians as a function of temperature in degrees Celsius as shown in figure 7. From our predicted theory, the tilt angle and the intensity I1 in SmA phase should be zero. Due to the unexpected minimum in the I1 intensity at the phase transition, the SmA tilt angle was nonzero. From our second equation, we can graph the birefingence as a function of temperature as well (Figure 8). We fit the birefringence graph above and below the phase transition and found the transition

temperature at the intersection of the two curves at 41.4°C. We then apply this to the Tilt angle graph to get the tilt angle as a function of the reduced temperature:
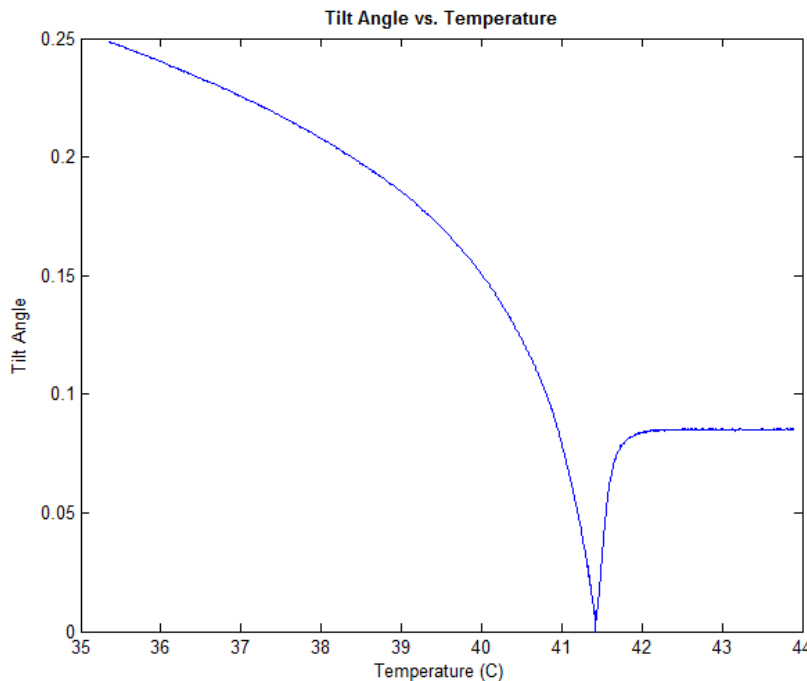

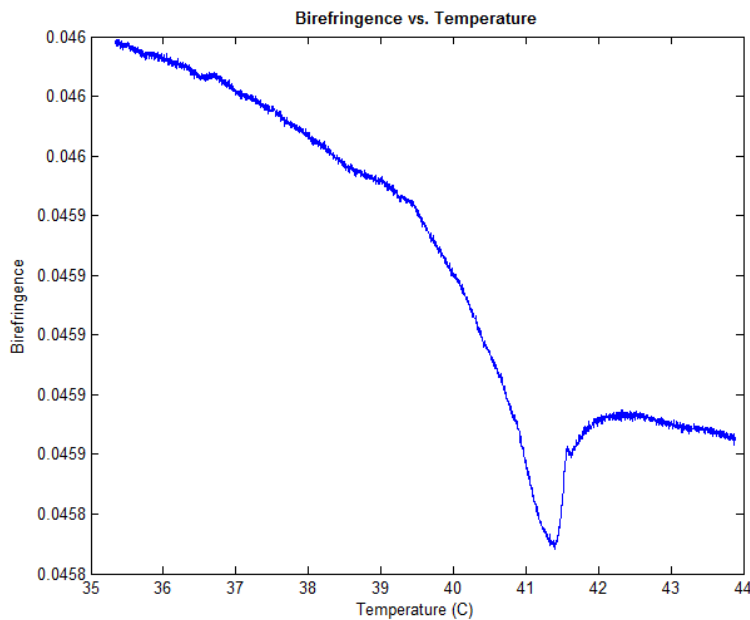**Figure 7**: Tilt angle of the molecules as a function of temperature.

Figure 8: Birefringence as a function of Temperature. We clearly see the critical point in the graph around 41.3 Celsius as our transition from SmA to SmC.

$$t = \frac{(T - T_{AC})}{T_{AC}}.$$

using this equation for reduced temperature where t is the reduced temperature, T is the temperature in degrees Celsius, and T_{AC} is the transition temperature, we reduce our tilt angle and center it on the transition temperature given in figure 9. We then expect, from the article published by Dr. Fernsler(Fernsler et al.), the tilt angle as a function of reduced temperature can be shown to be

$$\theta = \theta_0 |t|^\beta$$

Where β is defined as a critical

exponent. This function only describes the left hand of the graph in the SmC phase. Thus we

examined a small portion just after the transition from t = $-5.64x10^{-5}$ or about zero to t = -.0069. This corresponded to a theta difference from about .01 to .0629. The phase transition theory describes the tilt behavior near the transition temperature, hence our evaluation of a restricted temperature range. We then exploit the fact that this equation is a power law and take the natural logarithm of both sides. The equation then transforms into the linear equation

$$\ln(\theta) = \ln(\theta_0) + \beta\ln(|t|).$$

We then plotted the log log plot of $\ln(|t|)$ vs $\ln(\theta)$ shown in figure 10. Once we had the log log plot of reduced temperature vs Tilt angle on that small interval, we applied a linear fit to find the exponent β as shown in the equation above. Our linear fit gave us an equation of $.4912 * \ln(|t|) - 0.42$ which would give us a critical exponent of .4912 ± .0238. This result is consistent with the theory provided in (Fernsler et al.)of an expected critical exponent of around .5 for a second-order, continuous mean field phase transition. This critical exponent is a common way to express the order of a phase transition.
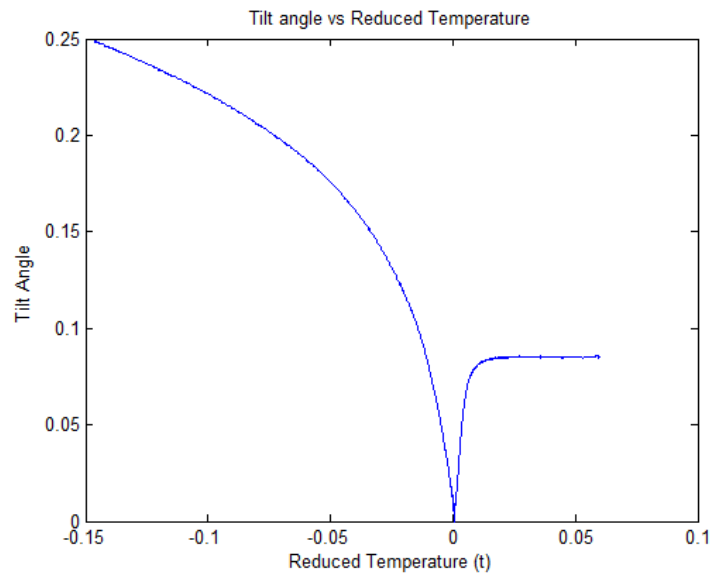

Figure 9: Tilt angle vs Reduced Temperature
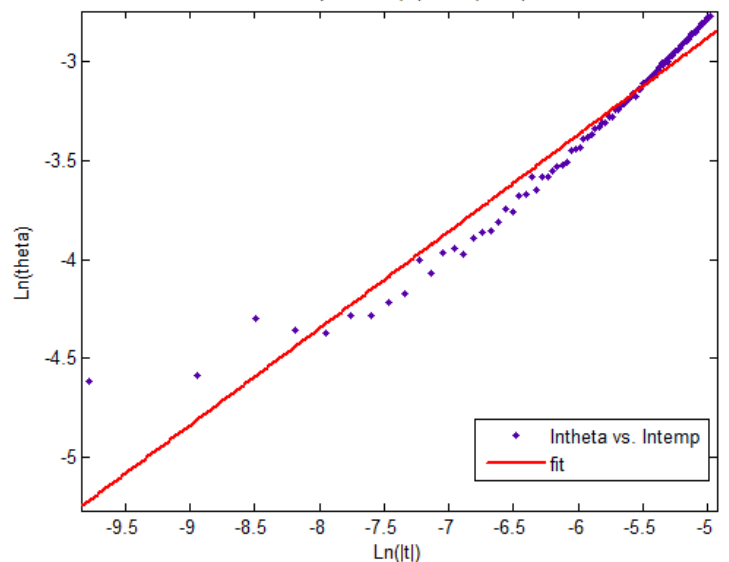

Figure 10: Ln(|t|) vs Ln(theta) fitted to a linear curve to find the critical exponent Beta

Conclusion

Our experiment was clearly indicative of the theory provided in the Fernsler article.

Given that our calculated value of the critical exponent followed the theory so closely, I would

say that our modifications seemed to strengthen our results. The change of the polarizer to a

multi-fixed position rather than physically adjusting the angles by hand produced a higher

resolution data set. This data set, as stated, was consistent with the theory, with the exception

of the expectation that the tilt angle be before the SmA SmC transition be flat. This was quite

surprising to see such a large reduction in the tilt angle just before the transition. This obviously

stems from the dips in the intensity curves I1, I2, I3, and I4. The reasons for the dips in intensity

could be due to sample degradation over time. Nevertheless, the data still yielded acceptable

values for the second-order phase transition, and birefringence. Although our theory suggested

a value for beta as .25, which varied from our experiment, we were still able to find the

birefringence of these materials quite accurately. Future investigations might be warranted as

to the nature of the intensity dips at the transition temperature, but overall the mean field

theory was upheld.

Fernsler, Jonathan et al. "Birefringence Suppression Near the Smectic A–smectic C Phase

    Transition in de Vries-type Liquid Crystals." *Liquid Crystals* 39.10 (2012): 1204–1215.

    Taylor and Francis+NEJM. Web. 4 June 2013.

Saipa. "A High Resolution Temperature Scanning Technique for Optical Studies of Liquid Crystal

    Phase Transitions." 29.3 (2012): 347–353. Print.

Yoon, HyungGuen et al. "Direct Observation of Diffuse Cone Behavior in de Vries Smectic-A and

    -C Phases of Organosiloxane Mesogens." *Physical Review Letters* 106.8 (2011): 087801.

    APS. Web. 4 June 2013.