Refractive Indices Of Liquid Crystals And Their Applications In
Display And Photonic Devices

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Refractive Indices of Liquid Crystals and Their Applications in Display and Photonic Devices

by

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ABSTRACT

Liquid crystals (LCs) are important materials for flat panel display and photonic devices. Most LC devices use electrical field-, magnetic field-, or temperature-induced refractive index change to modulate the incident light. Molecular constituents, wavelength, and temperature are the three primary factors determining the liquid crystal refractive indices: $n_e$ and $n_o$ for the extraordinary and ordinary rays, respectively. In this dissertation, we derive several physical models for describing the wavelength and temperature effects on liquid crystal refractive indices, average refractive index, and birefringence. Based on these models, we develop some high temperature gradient refractive index LC mixtures for photonic applications, such as thermal tunable liquid crystal photonic crystal fibers and thermal solitons.

Liquid crystal refractive indices decrease as the wavelength increase. Both $n_e$ and $n_o$ saturate in the infrared region. Wavelength effect on LC refractive indices is important for the design of direct-view displays. In Chapter 2, we derive the extended Cauchy models for describing the wavelength effect on liquid crystal refractive indices in the visible and infrared spectral regions based on the three-band model. The three-coefficient Cauchy model could be used for describing the refractive indices of liquid crystals with low, medium, and high birefringence, whereas the two-coefficient Cauchy model is more suitable for low birefringence liquid crystals. The critical value of the birefringence is $\Delta n \approx 0.12$. 
Temperature is another important factor affecting the LC refractive indices. The thermal effect originated from the lamp of projection display would affect the performance of the employed liquid crystal. In Chapter 3, we derive the four-parameter and three-parameter parabolic models for describing the temperature effect on the LC refractive indices based on Vuks model and Haller equation. We validate the empirical Haller equation quantitatively. We also validate that the average refractive index of liquid crystal \( <n> \) decreases linearly as the temperature increases. Liquid crystals exhibit a large thermal nonlinearity which is attractive for new photonic applications using photonic crystal fibers. We derive the physical models for describing the temperature gradient of the LC refractive indices, \( dn_e/dT \) and \( dn_o/dT \), based on the four-parameter model. We find that LC exhibits a crossover temperature \( T_o \) at which \( dn_o/dT \) is equal to zero. The physical models of the temperature gradient indicate that \( n_e \), the extraordinary refractive index, always decreases as the temperature increases since \( dn_e/dT \) is always negative, whereas \( n_o \), the ordinary refractive index, decreases as the temperature increases when the temperature is lower than the crossover temperature \( (dn_o/dT < 0 \) when the temperature is lower than \( T_o \)) and increases as the temperature increases when the temperature is higher than the crossover temperature \( (dn_o/dT > 0 \) when the temperature is higher than \( T_o \)).

Measurements of LC refractive indices play an important role for validating the physical models and the device design. Liquid crystal is anisotropic and the incident linearly polarized light encounters two different refractive indices when the polarization is parallel or perpendicular to the optic axis. The measurement is more complicated than
that for an isotropic medium. In Chapter 4, we use a multi-wavelength Abbe refractometer to measure the LC refractive indices in the visible light region. We measured the LC refractive indices at six wavelengths, $\lambda=450, 486, 546, 589, 633$ and 656 nm by changing the filters. We use a circulating constant temperature bath to control the temperature of the sample. The temperature range is from 10 to 55 °C. The refractive index data measured include five low-birefringence liquid crystals, MLC-9200-000, MLC-9200-100, MLC-6608 ($\Delta\varepsilon=-4.2$), MLC-6241-000, and UCF-280 ($\Delta\varepsilon=-4$); four middle-birefringence liquid crystals, 5CB, 5PCH, E7, E48 and BL003; four high-birefringence liquid crystals, BL006, BL038, E44 and UCF-35, and two liquid crystals with high $dn/dT$ at room temperature, UCF-1 and UCF-2. The refractive indices of E7 at two infrared wavelengths $\lambda=1.55$ and 10.6 $\mu$m are measured by the wedged-cell refractometer method. The UV absorption spectra of several liquid crystals, MLC-9200-000, MLC-9200-100, MLC-6608 and TL-216 are measured, too. In section 6.5, we also measure the refractive index of cured optical films of NOA65 and NOA 81 using the multi-wavelength Abbe refractometer.

In Chapter 5, we use the experimental data measured in Chapter 4 to validate the physical models we derived, the extended three-coefficient and two-coefficient Cauchy models, the four-parameter and three-parameter parabolic models. For the first time, we validate the Vuks model using the experimental data of liquid crystals directly. We also validate the empirical Haller equation for the LC birefringence $\Delta n$ and the linear equation for the LC average refractive index $\langle n \rangle$.

The study of the LC refractive indices explores several new photonic applications for liquid crystals such as high temperature gradient liquid crystals, high thermal tunable
liquid crystal photonic crystal fibers, the laser induced 2D+1 thermal solitons in nematic crystals, determination for the infrared refractive indices of liquid crystals, comparative study for refractive index between liquid crystals and photopolymers for polymer dispersed liquid crystal (PDLC) applications, and so on. In Chapter 6, we introduce these applications one by one. First, we formulate two novel liquid crystals, UCF-1 and UCF-2, with high $dn_s/dT$ at room temperature. The $dn_s/dT$ of UCF-1 is about 4X higher than that of 5CB at room temperature. Second, we infiltrate UCF-1 into the micro holes around the silica core of a section of three-rod core PCF and set up a highly thermal tunable liquid crystal photonic crystal fiber. The guided mode has an effective area of 440 $\mu$m$^2$ with an insertion loss of less than 0.5dB. The loss is mainly attributed to coupling losses between the index-guided section and the bandgap-guided section. The thermal tuning sensitivity of the spectral position of the bandgap was measured to be 27 nm/°C around room temperature, which is 4.6 times higher than that using the commercial E7 LC mixture operated at a temperature above 50 °C. Third, the novel liquid crystals UCF-1 and UCF-2 are preferred to trigger the laser-induced thermal solitons in nematic liquid crystal confined in a capillary because of the high positive temperature gradient at room temperature. Fourth, we extrapolate the refractive index data measured at the visible light region to the near and far infrared region basing on the extended Cauchy model and four-parameter model. The extrapolation method is validated by the experimental data measured at the visible light and infrared light regions. Knowing the LC refractive indices at the infrared region is important for some photonic devices operated in this light region. Finally, we make a completely comparative study for refractive index between two photocurable polymers (NOA65 and NOA81) and two
series of Merck liquid crystals, E-series (E44, E48, and E7) and BL-series (BL038, BL003 and BL006) in order to optimize the performance of polymer dispersed liquid crystals (PDLC). Among the LC materials we studied, BL038 and E48 are good candidates for making PDLC system incorporating NOA65. The BL038 PDLC cell shows a higher contrast ratio than the E48 cell because BL038 has a better matched ordinary refractive index, higher birefringence, and similar miscibility as compared to E48. Liquid crystals having a good miscibility with polymer, matched ordinary refractive index, and higher birefringence help to improve the PDLC contrast ratio for display applications.

In Chapter 7, we give a general summary for the dissertation.
To my beloved parents and sister
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<td>LC</td>
<td>liquid crystal</td>
</tr>
<tr>
<td>$n_e$</td>
<td>extraordinary refractive index</td>
</tr>
<tr>
<td>$n_o$</td>
<td>ordinary refractive index</td>
</tr>
<tr>
<td>RGB</td>
<td>red, green and blue</td>
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<tr>
<td>LCPBGs</td>
<td>liquid crystal photonic bandgap fibers</td>
</tr>
<tr>
<td>PDA</td>
<td>personal digital assistant</td>
</tr>
<tr>
<td>LCoS</td>
<td>liquid crystal on silicon</td>
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<tr>
<td>PCFs</td>
<td>photonic crystal fibers</td>
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<tr>
<td>LCPCF</td>
<td>liquid crystal filled photonic crystal fiber</td>
</tr>
<tr>
<td>M-TIR</td>
<td>modified total internal refraction</td>
</tr>
<tr>
<td>PBG</td>
<td>photonic bandgap</td>
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<tr>
<td>PDLC</td>
<td>polymer dispersed liquid crystal</td>
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<tr>
<td>ITO</td>
<td>thin indium-tin-oxide</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>IR</td>
<td>infrared</td>
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<td>HDTV</td>
<td>high definition television</td>
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<tr>
<td>VOA</td>
<td>variable optical attenuator</td>
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<tr>
<td>CRT</td>
<td>cathode-ray tube</td>
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**CONFERENCE AND PRESENTATIONS**


3. C. H. Wen, S. Gauza, Jun Li, H. Wang, S. T. Wu and X. Liang, “High contrast


CHAPTER 1: INTRODUCTION

1.1 Motivation

Liquid crystals are widely used in display and photonics industries due to their unique electro-optic properties. In display areas, LC has been widely used in desktop monitors, laptop computer, cell phones, personal digital assistant (PDA), digital watches, front and rear projection displays, microdisplay, and so on. Recently, much more attentions are paid to the study of high definition televisions (HDTVs). Penetrating into the television market is so called the third wave of liquid crystal display (LCD). In photonic devices, LC could be used in phase modulators, optical phased array (OPA), variable optical attenuator (VOA), optical switching, optical interconnections, tunable photonic crystal fibers (PCF), and so on.

A liquid crystal display consists of an array of tiny segments (called pixels) that can be manipulated to present information. This basic idea is common to all displays, ranging from simple calculators to a full color LCD television. An LCD consists primarily of two glass plates separated by a thin (~5 μm) gap. The first glass plate is deposited with arrays of thin-film transistors (TFTs), and the second plate is with color filters. The LC sandwiched between the glass substrates functions as a light modulator. There is no bulky picture tube. This makes LCDs practical for applications where size (as
well as weight) is important. In general, LCDs consume much less power than their cathode-ray tube (CRT) counterparts.

Nematic liquid crystal materials generally have several common characteristics, rod-like molecular structure, and rigidness of the long axis. The unique characteristic of nematic liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. Liquid crystal is a kind of anisotropic medium due to the rod-like molecular shape and the alignment along the director. The polarized light encounters different refractive index due to the different polarization of the incident light. The polarized light encounters the extraordinary refractive index $n_e$ when the light polarization is along the director, while it encounters the ordinary refractive index $n_o$ when the light polarization is perpendicular to the director. Birefringence $\Delta n$ is defined as the difference between $n_e$ and $n_o$, i.e., $\Delta n = n_e - n_o$. Liquid crystal molecules can be reoriented by the electric field or magnetic field and their effective birefringence changes accordingly. Thus, the incident light experiences different phase retardation as the electric field or magnetic field changes. 21-24

In order to realize a full color display, three main colors RGB (red, green blue) are required. Both the extraordinary and ordinary refractive indices decrease as the wavelength increases. As a result, birefringence decreases with wavelength in the visible spectral region. For isotropic media, the wavelength dependent refractive index can be described by Cauchy equation, i.e., the refractive index of an isotropic medium decreases as the wavelength increases. To optimize the cell design of LCD panel, we must know the refractive indices of the LC employed. We can measure the refractive indices of an LC at discrete wavelengths, but it is difficult to measure them continuously in the whole
visible light spectrum. It is necessary to find a physical model to understand the origins of LC refractive indices and their dependency on the wavelength. Based on Vuks equation or the three-band model, we derived the extended Cauchy model for describing the wavelength dependent refractive indices of liquid crystals. According to the extended Cauchy model, both $n_e$ and $n_o$ decrease as wavelength increases and saturate in the infrared region. The extended Cauchy model was validated by the experimental data measured using a multi-wavelength Abbe refractometer (Atago: DR-M4) in our lab. Some liquid crystals still hold a large birefringence in the infrared spectrum. Thus, LCs are also useful in some photonic devices such as optical switch, variable optical attenuator for optical communication application, IR dynamic scene projector, and so on. However, refractive indices measurement at an infrared wavelength is less convenient than that in the visible region. The absorption strengths in the infrared region are about two orders of magnitude weaker than that in the UV light region. Thus, the resonant enhancement of these bands to the LC refractive indices and birefringence is small and localized.$^{21, 25}$ We can extrapolate the experimental data obtained from the visible spectral region to a specific IR wavelength. This extrapolation method was validated based on the refractive indices measured at two IR laser wavelengths using the so called wedged-cell refractometer.

Temperature effect on liquid crystal refractive indices also plays an important role in display applications, especially for projection displays, and liquid crystal on silicon (LCoS) for microdisplay. Due to the thermal effect of the lamp, liquid crystal panel of projection display could reach 50~60 °C. It is important and necessary to know the LC properties at the anticipated operation temperature beforehand. To measure the refractive
indices at one temperature point is easy, however, to measure the refractive indices in the whole nematic range is not easy, especially, when the temperature exceeds the instrument’s limit. For instance, the commercial Abbe refractometer has a temperature range from 5 to 55 °C. Finding a physical model to describe the temperature effect on liquid crystal refractive indices becomes necessary. Based on Vuks equation, Haller equation and density function of liquid crystals, we derive the four-parameter model for describing the temperature effect on liquid crystal refractive indices.\textsuperscript{26-34} We further simplify the four-parameter model to the three-parameter parabolic model when an LC with high melting point and low birefringence is considered. By connecting a circulating constant temperature bath (Atago: 60-C3) to the Abbe refractometer, we can measure the LC refractive indices at different temperature points in the range from 10 to 55 °C. The measured experimental data are used to validate the two models. Experiments agree well with the models.

Liquid crystals exhibit a large optical nonlinearity arising from the optically induced reorientation of the LC director. On the other hand, liquid crystals naturally possess a large temperature nonlinearity. In chapter 3, we derive the physical models for temperature gradient, $dn_o/dT$ and $dn_e/dT$, based on the four-parameter model. Liquid crystals with high temperature gradient are useful for the laser-induced thermal grating in nematic liquid crystal films.\textsuperscript{35} Recently, novel photonic applications, tunable photonic crystal fiber, and laser induced thermal solitons in the nematic liquid crystals require a kind of liquid crystal with high temperature gradient at room temperature for the ordinary refractive index, $dn_o/dT$. The factors which determine the $dn_o/dT$ value are analyzed based on the physical model we derived. Guidelines are found to formulate new liquid
crystals to meet the demands. Two liquid crystal mixtures, named UCF-1 and UCF-2 which have a large \( \frac{dn_o}{dT} \) value at room temperature, are formulated in our lab.

Photonic crystal fibers (PCFs) have attracted significant attention these years and much research has been devoted to design fibers for various applications, such as supercontinuum generation, high power double-clad fiber lasers, air core fibers for high power laser delivery, and so on. However, these applications all depend on the static properties of the fiber. It is desirable to dynamically change the transmission properties of the fiber and, thereby, tune or trim them. Photonic Crystal Fibers (PCFs) have a specific arrangement of air holes running along the length of the fiber. The microstructure gives a high degree of design flexibility and many interesting designs have been demonstrated. By infiltrating the high-index liquid, oil, or liquid crystals into the microscope holes, the fiber devices with tunable transmission properties are fabricated. The photonic bandgaps in the LC filled section could be electrically tuned by placing the LCPCF (liquid crystal photonic crystal fiber) between electrodes. Recently, LC infiltrated photonic crystal fibers with thermal tunable and switchable bandgaps were demonstrated. To acquire a highly thermal tunable bandgaps for LCPCF, special liquid crystals with high \( \frac{dn_o}{dT} \) values at room temperature are needed. By infiltrating UCF-1, an LC mixture with a large \( \frac{dn_o}{dT} \) at room temperature, into a three-rod core PCF, a bandgap tuning sensitivity of 27 nm/°C is achieved in the vicinity of the room temperature.

The study of solitons in liquid crystals is an important branch in the science of nonlinear optics and materials science. Solitons are localized waves that travel without much change in shape. In the mathematic literature the word “soliton” refers to solitary traveling waves which preserve their identities after a pairwise collision. In 2001,
Warenghem reported the first “thermal soliton” observed in dye-doped nematic liquid crystals confined in a capillary.\textsuperscript{36-38} The nonlinear mechanism responsible for the thermal soliton is the thermal indexing. To trigger the so called “thermal” soliton, liquid crystals with a large $dn_a/dT$ value at room temperature are highly preferred.

### 1.2 Liquid crystals

Liquid crystals are beautiful and mysterious materials which are widely used in display and photonics industry. Liquid crystal phase were firstly discovered by an Austrian botanist named Friedrich Reinitzer. As is commonly known to all, matter exists in three states, solid, liquid and gas. However, this is not quite correct and there exhibits the fourth state which is called liquid crystal or mesophase. Liquid crystals exhibit intermediate thermodynamic phases between the crystalline solid and the isotropic liquid state. A liquid crystal can flow like an ordinary liquid, while keeps some properties of a crystalline phase, for example the birefringence. The distinguished characteristic of liquid crystals is that the molecules tend to align along a common axis, called the director. The molecules in the liquid phase have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and isotropic liquid phases. Figure 1 shows the average alignment of the molecules for each phase.\textsuperscript{21-24}
Three types of liquid crystals have been discovered so far, thermotropic, lyotropic and polymeric. Among these three, the thermotropic liquid crystals have been studied extensively and their applications have reached a mature stage. The mesophase is formed by heating a solid or cooling an isotropic liquid; it exists in certain temperature range. Lyotropic liquid crystals are receiving increasing scientific and technological attention because of the way they reflect the unique properties of their constituent molecules. This kind of mesophase is formed by dissolving an amphiphilic mesogen in a suitable solvent, under appropriate conditions of concentration, temperature, and pressure. Molecular aggregates or micelles are often formed. Polymeric liquid crystals are potential candidates for electronic devices and ultra-high-strength materials. Some polymers exist as an LC mesophase under suitable conditions of temperature, pressure, and concentration.

Thermotropic liquid crystals go through a series of phase transitions, from solid to liquid crystal, from liquid crystal to isotropic liquid and finally change to gas phase, as

Figure 1: The average alignment of the molecules for solid, anisotropic liquid crystal and isotropic liquid phases.
the temperature increases. Thermotropic liquid crystal can exist in three phases, nematic, smectic, and cholesteric, which are shown in figure 2.

![Figure 2: Three thermotropic liquid crystals: nematic, smectic and cholesteric.](image)

In Greek, the word nematic means thread. The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction, i.e., along the director. The liquid crystal molecules can be reoriented by an electric field or a magnetic field when the field strength exceeds the Freedericksz transition threshold. The orientation of the director is also imposed by the boundary conditions. There is no long-range correlation between the centers of mass of the molecules, which can translate freely. This property determines the fluid character of the
nematic phase. The axis of uniaxial symmetry has no polarity. Although the constituent molecules may be polar, it does not lead to a macoscopic effect.\textsuperscript{22}

Cholesteric liquid crystal is equivalent to a nematic except for the chiral-induced twist in the directors. Similar to the nematic phase, however, in the cholesteric phase, molecules in the different layers orient at a slight angle relative to each other (rather than parallel as in the nematic). Each consecutive molecule is rotated slightly relative to the one before it. Therefore, instead of the constant director of the nematic, the cholesteric director rotates helically throughout the sample. Many cholesterol esters exhibit this phase, hence name of cholesteric is used. An important feature of the cholesteric mesophase is the pitch. The pitch, $p$, is defined as the distance it takes for the director to rotate one full turn in the helix. The helical structure results in selective reflection in wavelength and circular polarization. The polarization state of the reflected and transmitted waves depend on the pitch length of the cholesteric. Firstly, if the helical pitch is much larger than the incident wavelength, both reflected and transmitted waves are plane-polarized and periodically modulated by the pitch of the liquid crystal structure. Secondly, if the helical pitch is much smaller than the wavelength, there are two circularly polarized waves in the medium. Thirdly, if the incident wavelength is comparable to the helical pitch, the reflected light is strongly circularly polarized. One circular component is almost totally reflected while the other passes through practically unchanged. The reflected wave preserves its sense of circular polarization.\textsuperscript{21}

There are at least nine distinct smectic phase bearing the designations: Smectic A, B, C, ……, I, with the phase being labeled not according to any microscopic properties, but rather by the chronological order of their discovery. X-ray diffraction studies showed
that in the smectic A phase, the long molecular axes are arranged perpendicular to the planes of the layers. However, the lateral distribution of the molecules within each layer is nearly random. The molecules in the smectic A layers can rotate freely along their long axes. Molecules in smectic B phase are arranged in layers with the molecular centers positioned in a hexagonally close-packed array. The molecular long axes are orthogonal to the layer planes. No interdigitation or tilting within the layers occurs as for the smectic A. The layer spacing of the smectic B is found to be approximately equal to the molecular length according to the X-ray analysis. The molecules in each layer are tilted at an angle to the layer normal for the smectic C. This tilt varies with temperature and often increases with decreasing temperature. The smectic C phase has a higher entropy than that of the smectic B, but lower than the smectic A. Thus, the phase transition temperature of the smectic B is often the lowest, followed by the smectic C and smectic A. Chiral smectic C, or Sm-C*, is an interesting class of liquid crystal materials. The structure of Sm-C* is similar to that of smectic C except for a helical tilt distributions from layer to layer. The helical pitch is dependent on the temperature. The tilt angle decreases resulting in an increasing helical pitch length as temperature increases. Therefore, the optical properties of the Sm-C* are sensitive to temperature and can be used as temperature sensor. Another exciting feature of the Sm-C* phase is the ferroelectricity.\textsuperscript{21} Ferroelectric LCs have been found useful for display and light switches because of their fast response time and bistability.
1.3 Refractive indices of liquid crystals

Refractive indices of a liquid crystal (LC) are fundamentally interesting and practically useful parameters. Liquid crystal is uniaxial and anisotropic. It has two principle refractive indices, \( n_e \) and \( n_o \). The extraordinary refractive index, \( n_e \), is observed for an extraordinary wave associated with a light wave where the electric vector vibrates parallel to the optical axis. The ordinary refractive index, \( n_o \), is observed for a linearly polarized light wave where the electric vector is perpendicular to the optical axis. The values of \( n_e \) are usually larger than those of \( n_o \). The birefringence is defined by the difference between \( n_e \) and \( n_o \). Most liquid crystals have a positive birefringence, i.e. \( \Delta n > 0 \).

Most liquid crystal light modulators, e.g., flat panel display devices, utilize the electric-field-induced refractive index change to modulate light.\(^1\) In addition to the molecular constituents, wavelength and temperature are the two most important factors affecting the LC refractive indices. For instance, to achieve a full-color display three primary colors [red, green, and blue (RGB)] are used. It is essential to know the wavelength-dependent refractive indices of the LC mixture employed in order to optimize the cell design. As the operating temperature changes, the refractive indices change accordingly. The temperature effect is particularly important for projection displays and liquid crystal on silicon (LCoS) for microdisplay applications.\(^2-6\) Due to the thermal effect of the lamp, the temperature of the display panel could reach 50-60 °C. It is important to know the LC properties at the anticipated operating temperature beforehand. Furthermore, the thermal nonlinearity of liquid crystal refractive indices is also very
important for some new photonic applications, such as the tunable liquid crystal photonic bandgap fibers (LCPBGs) and thermal soliton in nematic liquid crystals confined in capillaries. Both prefer a liquid crystal with a large temperature gradient of ordinary refractive index \( \frac{dn_o}{dT} \) at room temperature. For liquid crystal photonic bandgap fibers, the tuning sensitivity of the photonic bandgaps could be greatly increased by infiltrating this kind of liquid crystals into the periodically arranged microscopic air holes around the core in photonic crystal fibers. To successfully trigger the thermal solitons in liquid crystal confined in a capillary with a lower power laser, it also requires this kind of liquid crystals with high \( \frac{dn_o}{dT} \) values at room temperature. Thus, there is a need to find a physical model to describe the temperature gradient of liquid crystals. Further, the developed guidelines could be useful for designing the desired liquid crystals.

In an isotropic fluid or gas, the refractive index is described by the well-known Lorentz-Lorenz equation. It relates the macroscopic refractive index to microscopic molecular polarizability. The wavelength effect on the refractive index of an isotropic media could be described by the famous Cauchy dispersion. However, liquid crystal is a media and a complex molecular system involving short and long range molecular interactions. It gives contrary results if directly applying the Lorentz-Lorenz equation to liquid crystals. Several models have attempted to address the wavelength and temperature dependencies of the LC refractive indices. Each approach has its own merits and demerits. In 1966, Vuks made a bold assumption that the internal field in a crystal is isotropic in all directions and brought forward a model for describing the refractive indices of anisotropic media. The Vuks model is analogous to the classical Clausius-Mossotti and Lorentz-Lorenz equation for correlating the microscopic LC molecular
polarizabilities to the macroscopic refractive indices. The differences between the Vuks model and the Lorentz-Lorenz equation are in two folds: 1) $n^2$ is replaced by $<n^2>$ in the denominator and 2) $\alpha$ is replaced by $\alpha_e$ or $\alpha_o$. Vuks validated his model based on the experimental data of several crystals. However, the wavelength and temperature effects are not described explicitly in Vuks model. Wu brought forward the three-band model and single-band model for describing the wavelength effect on liquid crystal refractive indices based on the LC’s electronic absorption bands in the UV spectrum. The single-band model\textsuperscript{21,27} gives an explicit expression on the wavelength and temperature dependence for birefringence, but not for the individual refractive indices. On the other hand, the three-band model\textsuperscript{21,28,30} describes the origins of the LC refractive indices for single LC compounds. Unfortunately, the three-band model needs three fitting parameters for each LC compound. In order to calculate the refractive indices at a given wavelength, we must measure the three absorption wavelengths ($\lambda_i$, $i=0,1,2$) corresponding to the three bands. If a LC mixture consists of 5-10 distinct molecular structures, it would be too complicated for the three-band model to quantitatively describe the LC refractive indices of the mixture.

Haller brought forward an empirical equation for describing the temperature dependent order parameter $S$ when the temperature is not too close to the clearing point. Further, he gave an empirical equation for describing the temperature effect on the birefringence of liquid crystals when the temperature is not near the clearing point. However, the relationship between the individual liquid crystal refractive index and temperature are still not disclosed. De Jeu, Blinov, Warenghem, Abdulhalim and so on all made some contributions to the development of liquid crystal refractive indices in
literature.\textsuperscript{22-24,29} However, the more complete, accurate and practical physical models for describing the wavelength and temperature effects on the liquid crystal refractive indices are still needed for display and photonic applications.

Although the original Cauchy equation\textsuperscript{40} was intended for the \textit{isotropic} gases and liquids, it has been attempted to fit the wavelength-dependent refractive indices of some \textit{anisotropic} liquid crystals.\textsuperscript{43,44} The fitting results are reasonably good except that the physical origins of the Cauchy coefficients are not clear. Recently, we derived the extended Cauchy equations\textsuperscript{45-47} based on the three-band model\textsuperscript{28,30} or Vuks equation, respectively, for describing the wavelength effect on the refractive indices of \textit{anisotropic} liquid crystals. The extended Cauchy equations are applicable not only to single compounds but also to LC mixtures. Good fittings are found in the off-resonance region. If the LC birefringence is low, then the three coefficients in the extended Cauchy model can be reduced to two and the fitting process becomes simpler.

Since a LC is a complex molecular system involving short and long range molecular interactions, its refractive indices are quite different from an isotropic liquid. In Vuks model, the internal field was assumed to be isotropic. Vuks validated the model by using the experimental data of several anisotropic crystals such as naphthalene, diphenyl, anthracene, and phenanthrene.\textsuperscript{26} Since Vuks model has been used widely to describe the LC refractive indices, it is necessary to validate the model directly by using the experimental data of liquid crystal materials. To validate Vuks equations for the LC molecular system is a challenging task because the LC molecular polarizabilities involve short range and long range interactions. We derive the Vuks equations in different forms
so that their validity can be easily examined by measuring the wavelength and temperature dependent refractive indices. We find the Vuks equation is self-consistent.48

Based on the Vuks equation, we derive two novel equations for liquid crystal refractive indices, $n_e$ and $n_o$, which correspond to the extraordinary and ordinary light, respectively.45-47 The equations relate average microscopic polarizability $<\alpha>$, pack density $N$, differential molecular polarizability $\gamma_e - \gamma_o$ and order parameter $S$ of LC molecules to the refractive indices $n_e$ and $n_o$, respectively. The two equations decouple $n_e$ from $n_o$ which are coupled together by $<n^2>$ in Vuks equation. Then, we derive a four-parameter model for describing the temperature effect on the LC refractive indices. The four-parameter model is further simplified to the three-parameter parabolic model for low birefringence LCs with a high clearing temperature.47,49

Further, we derive the expressions for the temperature gradient, $dn_e/dT$ and $dn_o/dT$, based on the four-parameter model.50 Afterwards, we discuss and analyze the factors affecting the temperature gradient of the LC refractive indices. We propose a new physical concept, the crossover temperature, based on the physical model of $dn_o/dT$. The crossover temperature is defined as the temperature at which $dn_o/dT = 0$. The $dn_o/dT$ values are smaller than zero when the temperature is lower than the crossover temperature and $n_o$ decreases as the temperature increases. On the contrary, the $dn_o/dT$ value is larger than zero when the temperature is higher than the crossover temperature and $n_o$ increases as the temperature increases. The $dn_e/dT$ values are equal to the sum of two negative terms, i.e. $dn_e/dT$ value is always negative throughout the nematic
range. Thus, we can explain why $n_e$ always decreases as temperature increases and $n_o$ decreases at the beginning then increase as temperature increases in the nematic range.

The guidelines are found useful for designing LC mixtures with a large positive $dn_o/dT$. Two new LC mixtures, UCF-1 and UCF-2, were formulated based on these guidelines. The $dn_o/dT$ of UCF-1 is ~ 4X higher than that of 5CB compound at the room temperature.

### 1.4 Photonic crystal fibers

Photonic crystal fibers (PCFs) were first demonstrated in 1996 and have generated much attention since then. PCFs are optical fibers that employ a microstructured arrangement of low-index material in a background material of higher refractive index. The background material is often undoped silica and the low index region is typically provided by air voids running along the length of the fiber.

PCFs may be divided into two categories, high index guiding fibers and low index guiding fibers. Similar to conventional fibers, high index guiding fibers are guiding light in a solid core by the modified total internal reflection (M-TIR) principle. The total internal reflection is caused by the lower effective index in the microstructured air-filled region. Low index guiding fibers guide light by the photonic bandgap (PBG) effect. The light is confined to the low index core as the PBG effect makes propagation in the microstructured cladding region impossible.
The strong wavelength dependency of the effective refractive index and the inherently large design flexibility of the PCFs allows for a whole new range of novel properties. Such properties include endlessly single-moded fibers, extremely nonlinear fibers and fibers with anomalous dispersion in the visible wavelength region.

M-TIR is analogous to the total internal reflection known from standard optical fibers. It relies on a high index core region, typically pure silica, surrounded by a lower effective index provided by the microstructured region. Figure 3 shows a section of photonic crystal fiber and we can see clearly the periodic microstructure from the cross section.

![Photonic Crystal Fiber Diagram](image)

**Figure 3:** The structure of a high-index photonic crystal fiber.

The effective index of such a fiber can be approximated by a standard step index fiber with a high index core and a low index cladding. However, the refractive index of
the microstructured cladding in PCFs exhibits a wavelength dependency very differently from that of pure silica, an effect which allows PCFs to be designed with a complete new set of properties not possible with standard technology. For example, the strong wavelength dependence of the refractive index allows design of endlessly single-moded fibers where only a single mode is supported regardless of optical wavelength. Furthermore, it is possible to alter the dispersion properties of the fibers, thereby making it possible to design fibers with an anomalous dispersion at visible wavelengths. More complex index structure can also be constructed by utilizing arrangements of holes of different size in various periodic or nonperiodic structures.

Photonic crystal fibers (PCFs) belong to the category of devices as they exhibit a microstructured refractive index profile in the fiber cross section. Many devices have been demonstrated, ranging from dispersion controllers to fiber lasers and nonlinear devices. The optical properties of PCFs could be modified by filling the air holes with liquids, oils, fluids, polymers, or liquid crystals and the tunability of PCFs could be achieved using the properties of these materials. This was achieved by taking advantage of the thermo-optic effect in the infused materials to induce index changes either using an external heater or the absorption of a guided pump beam in dye-doped LCs. The exploitation of the thermo-optic effect allows thermally actuated devices to be continuously tuned, except at phase transition in the LC devices, which can yield threshold-like response. Electrical control of a LC-filled PCF (LCPCF) has also been proposed and demonstrated. The fiber was transformed from an M-TIR to a PBG fiber type by infiltrating the high-index liquid crystal into the microscopic holes. Then, the LCPCF was placed between two electrodes. The LC molecules are reoriented accordingly
to the field which induced a change in the refractive index of the LC when an electrical field was applied. This device could be used as an optical switch.\textsuperscript{16-18}

To achieve a highly thermal tunable photonic crystal fiber, we infiltrated a kind of novel liquid crystal with a high temperature gradient at temperature, i.e. high $dn_a/dT$ at room temperature, into the microscopic holes around the core of a three-rod core PCF. The bandgaps of the LCPCF shift toward the red light side as the temperature increases. The thermal tuning sensitivity of the spectral position of the bandgap is about 27 nm/°C, which is 4.6X higher than that of a commercial available LC (E7). This type of device could be used to switch the laser beam from the pump laser to the probe laser and further modulate the amplitude of the probe laser by setting the probing laser wavelength on the red side edge of the bandgap while heating the LCPCF.\textsuperscript{19,20}
CHAPTER 2: WAVELENGTH EFFECT ON LIQUID CRYSTAL REFRACTIVE INDICES

2.1 Introduction

Liquid crystal refractive indices are fundamentally important and practically useful parameters. Most LC-based devices use the electric, magnetic and thermal-induced refractive index change to modulate the light for information display, light switching, laser beam steering, etc.

Several models have been developed for describing the wavelength effects on liquid crystal refractive indices.\textsuperscript{21-34} The three-coefficient Cauchy equation is found to fit well the wavelength dependent refractive index of isotropic media. Although it also fits well with the anisotropic LCs, the physical meaning is vague.\textsuperscript{40} Vuks model was proposed and validated based on the isotropic field in crystals and the experimental data of several crystals such as naphthalene, diphenyl, anthracene and phenanthrene.\textsuperscript{26} However, it only correlates the relationship between the refractive indices and the microscopic polarizabilities, but shows no detailed relationship between the wavelength and the refractive index. The major absorption bands of a LC compound occurs in two spectral regions: ultraviolet (UV) and infrared (IR). For a conjugated LC molecule, three electronic absorption bands ($\lambda_i, i=1-3$) exist in the UV region. There are three kinds of electronic transitions in the UV spectrum. In the near IR region, some overtone molecular
vibration bands begin to appear. In the mid (3-5 µm) and long IR (7-14 µm) regions, there are many fundamental molecular vibration bands. However, the oscillator strength of vibrational absorption is typically two orders weaker than the electronic transitions. In the visible region, the absorption is usually quite small. The major optical loss originates from light scattering due to the LC director fluctuations, rather than absorption. The resonant enhancement of the vibrational bands to the refractive indices or birefringence is localized to the vicinities of the bands. So the resonant enhancement of the electronic absorption bands makes much more contributions to the LC refractive indices or birefringence than that from the vibration bands. Wu brought forward the three-band model and single-band model for describing the wavelength effect on the LC refractive indices and birefringence, respectively, based on these absorption bands in the UV spectrum. The three-band model shows clearly the origin of LC refractive indices. However, it is more suitable for describing the refractive indices of a LC compound.

Liquid crystals used in practice are the eutectic mixtures that consist of a dozen LC compounds. Each of the LC compounds may have different absorption bands and it would be too complicated for the three-band model to quantitatively describe the LC refractive indices of the mixture.

In this work, we derived the extended Cauchy equation for describing the wavelength effect on liquid crystal refractive indices based on the three-band model. In fact, we could also derive the extended Cauchy equation based on the Vuks equation. The refractive indices of dozens of liquid crystals are measured using a multi-wavelength Abbe refractometer or a wedged-cell refractometer. The experimental data are used to
validate the extended Cauchy model. The validation will be presented in Chapter 5. Excellent agreement between theory and experiment is achieved.

2.2 Three-band Model

The major absorption of a LC compound occurs in two spectral regions: ultraviolet (UV) and infrared (IR). The $\sigma \rightarrow \sigma^*$ electronic transitions (the $\lambda_0$ band) take place in the vacuum UV (100-180 nm) region whereas the $\pi \rightarrow \pi^*$ electronic transitions (the $\lambda_1$ and $\lambda_2$ bands) occur in the UV (180-400 nm) region. It should be mentioned that the $\lambda_0$ band appears in the vacuum region (its actual wavelength has not been measured, but we know the central wavelength is somewhere around 120-150 nm). The transition intensity of the $\lambda_0$ band is very strong since there are many $\sigma$-electrons available in a liquid crystal molecule. The $\lambda_1$ band of several conjugated LC molecules occurs at about 200 nm; it consists of two closely overlapping bands ($\lambda_{1a}$ and $\lambda_{1b}$ with $\lambda_{1b} > \lambda_{1a}$). The $\lambda_{1a}$ band exhibits a strong transition intensity and a large absorption anisotropy and its wavelength is not too sensitive to the molecular conjugation length. However, the $\lambda_{1b}$ band shifts toward the longer wavelength for a more conjugated LC molecules. Its transition intensity and absorption anisotropy may be much lower than the $\lambda_{1a}$ band’s, depending on the conjugation length. For simplicity, we could use the average value of the $\lambda_1$ band. The wavelength, the transition intensity and absorption anisotropy increase as the conjugation increase. If a LC molecule has a longer conjugation, its electronic transition wavelength would extend to a longer UV wavelength.
In the near IR region, some overtone molecular vibration bands appear.\textsuperscript{21,25} The fundamental molecular vibration bands, such as CH, CN, and C=C, occur in the mid and long IR regions. Typically, the oscillator strength of these vibration bands is about two orders of magnitude weaker than that of the electronic transitions. Thus, the resonant enhancement of these bands to the LC refractive indices and birefringence is localized.\textsuperscript{21,28,30}

\begin{align}
    n_e & \approx 1 + g_{0e} \frac{\lambda^2 \lambda_0^2}{\lambda^2 - \lambda_0^2} + g_{1e} \frac{\lambda^2 \lambda_1^2}{\lambda^2 - \lambda_1^2} + g_{2e} \frac{\lambda^2 \lambda_2^2}{\lambda^2 - \lambda_2^2}, \quad (2-1) \\
    n_o & \approx 1 + g_{0o} \frac{\lambda^2 \lambda_0^2}{\lambda^2 - \lambda_0^2} + g_{1o} \frac{\lambda^2 \lambda_1^2}{\lambda^2 - \lambda_1^2} + g_{2o} \frac{\lambda^2 \lambda_2^2}{\lambda^2 - \lambda_2^2}. \quad (2-2)
\end{align}

where \( g_i \sim NZ_i f_i \) are proportionality constants, \( Z_0 \) is the number of responsible \( \sigma \) electrons and \( Z_1 = Z_2 \) is the number of \( \pi \) electrons in a LC compound. These \( g_i \)'s determine the temperature effect of the refractive indices. The three-band model describes the origins of refractive indices of LC compounds. However, a commercial mixture usually consists of several compounds with different molecular structures in order to obtain a wide nematic range. The individual \( \lambda_i \)'s are therefore different so that Eqs. (2-1) and (2-2) would have too many unknowns to describe the refractive indices of a LC mixture.

The \( \lambda_0 \)-band makes a greater contribution to \( n_e \) and \( n_o \) than the sum of the \( \lambda_1 \)-band and \( \lambda_2 \)-band since there are so many \( \sigma \) electrons. The contribution of the \( \lambda_1 \)-band to both \( n_e \) and \( n_o \) remains more or less a constant. However, the \( \lambda_2 \)-band makes a greater contribution to \( n_e \) than \( n_o \). This is because the oscillator strength of the \( \lambda_2 \)-band is larger for the e-ray than the o-ray. The oscillator strength of the e-ray for the
\( \lambda_1 - band \) is about the same as the \( \lambda_2 - band \). However, owing to the longer wavelength of the \( \lambda_2 - band \), its contribution to \( n_e \) is greater than that of the \( \lambda_1 - band \). For the contributions of each band to the birefringence, the \( \lambda_2 - band \) makes the primary contribution, followed by the \( \lambda_1 \) and then the \( \lambda_0 \) bands. This is because the \( \lambda_2 - band \) has the largest absorption anisotropy and longest wavelength. The total contribution of the two \( \pi \rightarrow \pi^* \) transitions accounts for about 80\% and the \( \sigma - \sigma^* \) transition for 20\% to overall birefringence at off-resonance region.

Generally, the \( \sigma - \sigma^* \) transitions have very high optical density, but their absorption is nearly isotropic. So these transitions make the primary contribution to refractive indices and a secondary contribution to birefringence in the visible region. The \( \pi \rightarrow \pi^* \) transition occur at long wavelength and exhibit relatively large anisotropy. These delocalized \( \pi \) electrons greatly enhance the differential molecular polarizability. As a result, their contribution to birefringence is dominant. However, due to the limited number of \( \pi \) electrons in a LC, the \( \pi \rightarrow \pi^* \) transition intensities are about one order of magnitude lower than those of \( \sigma - \sigma^* \) transition, resulting in a lower contribution to the refractive indices.

### 2.3 Extended Cauchy Model

Based on the three-band model, we derived the extended Cauchy model for describing the wavelength effect on the refractive indices of liquid crystals. Originally, Cauchy equation was used to describe the wavelength effect on the refractive index of
isotropic media. Here, we extend the Cauchy equation to describing the refractive indices of anisotropic liquid crystals. In the following paragraphs, I show the theoretical derivations for the extended Cauchy model.

The three-band model, Equations (2-1) and (2-2), can be rewritten as follows:

$$n_e \approx 1 + g_{0e} \frac{\lambda_0^2}{1 - \left(\frac{\lambda_0}{\lambda}\right)^2} + g_{1e} \frac{\lambda_1^2}{1 - \left(\frac{\lambda_1}{\lambda}\right)^2} + g_{2e} \frac{\lambda_2^2}{1 - \left(\frac{\lambda_2}{\lambda}\right)^2}, \quad \text{(2-3)}$$

$$n_o \approx 1 + g_{0o} \frac{\lambda_0^2}{1 - \left(\frac{\lambda_0}{\lambda}\right)^2} + g_{1o} \frac{\lambda_1^2}{1 - \left(\frac{\lambda_1}{\lambda}\right)^2} + g_{2o} \frac{\lambda_2^2}{1 - \left(\frac{\lambda_2}{\lambda}\right)^2}. \quad \text{(2-4)}$$

Here, $\lambda_0$, $\lambda_1$ and $\lambda_2$ (with $\lambda_2 > \lambda_1$) denote the resonance wavelengths of the $\sigma - \sigma^*$ and two $\pi \rightarrow \pi^*$ transitions, and $g_0$, $g_1$ and $g_2$ are the corresponding proportionality constants which depend on the oscillator strength and temperature. For a conjugated LC molecule, its $\lambda_0$ band is located in the vacuum UV region ($\lambda_0 \sim 120$ nm), $\lambda_1$ is around 190-210 nm; not too sensitive to the LC structure, and $\lambda_2$ increases substantially as the molecular conjugation increases. For example, for the 4-cyano-4-n-pentyle-cyclohexane-phenyl (5PCH) LC compound, its $\lambda_1 \sim 200$ nm and $\lambda_2 \sim 235$ nm while for the 4-cyano-4-n-pentylbiphenyl (5CB) its $\lambda_1$ shifts to 210 nm and $\lambda_2$ shifts to 282 nm.

In the off-resonance region, $\lambda > \lambda_i$, $i=0$, 1, 2, the terms $\lambda_i^2 / \lambda^2$ ($i=0$, 1, 2) in the denominator are much smaller than 1 and Eqs. (2-3) and (2-4) can be expanded into power series. Keeping the first three terms, we obtain
\[ n_e \equiv 1 + g_{0e} \lambda_0^2 \left(1 + \frac{\lambda_0^2}{\lambda^2} + \frac{\lambda_0^4}{\lambda^4}\right) + g_{1e} \lambda_1^2 \left(1 + \frac{\lambda_1^2}{\lambda^2} + \frac{\lambda_1^4}{\lambda^4}\right) + g_{2e} \lambda_2^2 \left(1 + \frac{\lambda_2^2}{\lambda^2} + \frac{\lambda_2^4}{\lambda^4}\right), \quad (2-5) \]

\[ n_o \equiv 1 + g_{0o} \lambda_0^2 \left(1 + \frac{\lambda_0^2}{\lambda^2} + \frac{\lambda_0^4}{\lambda^4}\right) + g_{1o} \lambda_1^2 \left(1 + \frac{\lambda_1^2}{\lambda^2} + \frac{\lambda_1^4}{\lambda^4}\right) + g_{2o} \lambda_2^2 \left(1 + \frac{\lambda_2^2}{\lambda^2} + \frac{\lambda_2^4}{\lambda^4}\right). \quad (2-6) \]

Grouping the similar terms together, we obtain the extended Cauchy equations

\[ n_e \equiv A_e + \frac{B_e}{\lambda^2} + \frac{C_e}{\lambda^4}, \quad (2-7) \]

\[ n_o \equiv A_o + \frac{B_o}{\lambda^2} + \frac{C_o}{\lambda^4}, \quad (2-8) \]

where

\[ A_e = 1 + g_{0e} \lambda_0^2 + g_{1e} \lambda_1^2 + g_{2e} \lambda_2^2, \quad (2-9) \]

\[ B_e = g_{0e} \lambda_0^4 + g_{1e} \lambda_1^4 + g_{2e} \lambda_2^4, \quad (2-10) \]

\[ C_e = g_{0e} \lambda_0^6 + g_{1e} \lambda_1^6 + g_{2e} \lambda_2^6, \quad (2-11) \]

And

\[ A_o = 1 + g_{0o} \lambda_0^2 + g_{1o} \lambda_1^2 + g_{2o} \lambda_2^2, \quad (2-12) \]

\[ B_o = g_{0o} \lambda_0^4 + g_{1o} \lambda_1^4 + g_{2o} \lambda_2^4, \quad (2-13) \]

\[ C_o = g_{0o} \lambda_0^6 + g_{1o} \lambda_1^6 + g_{2o} \lambda_2^6. \quad (2-14) \]

Therefore, the 3-coefficient Cauchy equations are derived from the three-band model and are applicable to the anisotropic media. Each Cauchy coefficient is related to the resonance wavelengths \( \lambda_i \) and transition intensity \( g_i \) as shown from Eq. (2-9) to (2-14). For instance, if a LC compound contains only \( \sigma \) electrons (e.g., cyclohexane rings), then \( \lambda_1 \) and \( \lambda_2 \) do not exist. The \( n_e \) and \( n_o \) are determined solely by the \( \lambda_0 \) terms.
As a result, the ABC coefficients would be small and the refractive indices in the visible region would be relatively small and insensitive to the wavelength. On the other hand, a linearly conjugated LC would exhibit a longer $\lambda_2$ and larger $g_2$ so that its refractive indices, especially birefringence ($\Delta n = n_e - n_o$), would be greatly enhanced. From Eqs. (2-7) and (2-8), both $n_e$ and $n_o$ decrease as the wavelength increases. In the long wavelength regime where $\lambda \gg \lambda_2$, $n_e$ and $n_o$ are reduced to $A_e$ and $A_o$, respectively, and are insensitive to the wavelength. Hence, birefringence ($\Delta n = A_e - A_o$) is also insensitive to the wavelength. This result is consistent with the prediction of the single band model.27

A LC mixture usually consists of several single compounds in order to widen the nematic range. Let us assume there are $m$ compounds in the LC mixture and each compound contributes a molar fraction $X_i$ ($i=1, 2, \ldots m$) to the refractive indices of the mixture. The refractive indices ($n_{ei}$ and $n_{oi}$) of the $i^{th}$ component are expressed by Eq. (4). The refractive index of the mixture is a superposition of the individual components:46

\[
\begin{align*}
    n_e &\cong \sum_{i=1}^{m} X_i (A_{ei} + \frac{B_{ei}}{\lambda^2} + \frac{C_{ei}}{\lambda^4}), \\
    n_o &\cong \sum_{i=1}^{m} X_i (A_{oi} + \frac{B_{oi}}{\lambda^2} + \frac{C_{oi}}{\lambda^4}), \\
    X_1 + X_2 + \ldots + X_m &= 1.
\end{align*}
\]

Let $A'_{e,o} = \sum_{i=1}^{m} X_i (A_{e,o})_i$, $B'_{e,o} = \sum_{i=1}^{m} X_i (B_{e,o})_i$, and $C'_{e,o} = \sum_{i=1}^{m} X_i (C_{e,o})_i$, Eqs. (2-15) and (2-16) are reduced to:

\[
\begin{align*}
    n_e &\cong A_e + \frac{B_e}{\lambda^2} + \frac{C_e}{\lambda^4}, \\
    n_o &\cong A_o + \frac{B_o}{\lambda^2} + \frac{C_o}{\lambda^4}.
\end{align*}
\]
Eqs. (2-18) and (2-19) represents the refractive indices of a LC mixture and has the same form as Eqs. (2-7) and (2-8) which is for LC compounds, except for different Cauchy coefficients.

The three-coefficient Cauchy equations have been used to fit experimental results of LC mixtures. Good agreement is found in the off-resonance region.46 An undesirable feature is that it involves three fitting parameters. To reduce the fitting parameters to two, we need to prove that the third terms, i.e. the $\lambda^{-4}$ terms, in Eqs. (2-18) and (2-19) can be ignored under certain conditions.

Once the ABC coefficients are determined, the refractive indices of the LC at any wavelength can be extrapolated. Knowing the refractive index data as a continuous function of wavelength spanning from visible to infrared region is very important for the simulation study of display and photonic device design.

### 2.4 Two-coefficient Cauchy Model

The fluorinated liquid crystals60,61 exhibit a high resistivity, low viscosity, and excellent material stability, and have become the mainstream for direct-view and projection displays. For a 90° twisted nematic cell, to satisfy the Gooch-Tarry first minimum condition30 the required $d\Delta n/\lambda$ is equal to $\sqrt{3}/2$. A cell gap $d\approx 4-5$ µm is commonly chosen in order to achieve high manufacturing yield. For the green band centered at $\lambda=550$ nm, the LC birefringence should around 0.1. The fluorinated cyclohexane phenyl has $\Delta n$ in this range. The $\lambda_{2}$-band of such a LC structure occurs at
~210 nm which is far from the visible (i.e. $\lambda_2 << \lambda$) and, moreover, its transition oscillator strength is weak, which means the $g_{2e,o}$ coefficients are small.

From Eqs. (2-7) and (2-11), the $C_e / \lambda^4$ term of the single LC compound can be rewritten as:

$$
\frac{C_e}{\lambda^4} = g_{0e} \lambda_0^2 \left( \frac{\lambda_0}{\lambda} \right)^4 + g_{1e} \lambda_1^2 \left( \frac{\lambda_1}{\lambda} \right)^4 + g_{2e} \lambda_2^2 \left( \frac{\lambda_2}{\lambda} \right)^4 .
$$

(2-20)

For a low birefringence LC compound in the off-resonance region, all the $(\lambda_i / \lambda)^4$ terms (where $i=0$, 1 and 2) in Eq. (2-20) are relatively small so that the $C_e / \lambda^4$ term is much smaller than the first two terms in Eq. (2-7) and can be ignored. Similarly, the third term for $n_o$ as shown in Eq. (2-8) can be neglected, too. As a consequence, the refractive indices of a low birefringence LC compound are reduced to

$$
n_e \approx A_e + \frac{B_e}{\lambda^2},
$$

(2-21)

$$
n_o \approx A_o + \frac{B_o}{\lambda^2}.
$$

(2-22)

Based on the same arguments shown from Eq. (2-15) to Eq. (2-19), Eqs. (2-21) and (2-22) hold equally well for low birefringence LC mixtures. From equation (2-21) and (2-22), there are only two Cauchy coefficients for each refractive index. If we measure the refractive index at two wavelengths, then the two Cauchy coefficients (A and B) can be obtained and the refractive indices at any wavelength can then be calculated. The A and B coefficients are related to each band through equations derived before. Their physical meanings are clear.
2.5 Conclusion

In this chapter, we have reviewed the physical models for describing the wavelength effect on liquid crystal refractive indices. Each model has its own merits and shortcomings. Vuks model relates the macroscopic refractive indices to the microscopic molecular polarizabilities. Three-band model shows the origin of the LC refractive indices, but it is more suitable for a LC compound. Single band model gives the LC birefringence as a function of the wavelength, however, it does not correlate the individual refractive index changes to the wavelength. We derived the extended Cauchy model for describing the wavelength effect on the LC refractive indices in the visible and infrared regions based on the three-band model. For a low-birefringence TFT liquid crystal, the extended Cauchy model could be further simplified to the two-coefficient Cauchy model by neglecting the third terms. The derived models are validated by the refractive index data measured in our lab. The detailed validations will be shown in Chapter 5.
CHAPTER 3: TEMPERATURE EFFECT ON LIQUID CRYSTAL REFRACTIVE INDICES

3.1 Introduction

Thermal effect on liquid crystals is very important for projection displays. The display panels could reach 50 to 60 °C due to thermal effect of the lamp. The birefringence decreases as temperature increases, leading to a smaller phase retardation. However, the viscosities of liquid crystals decrease greatly as temperature increases, leading to a faster response time. It is necessary and very important to know the LC properties at the operation temperature beforehand in order to make accurate designs.

Most LC based devices use thermotropic liquid crystals. The electro-optic properties of thermotropic liquid crystals depend on the temperature. The refractive indices are also sensitive to the temperature, especially the extraordinary refractive index, $n_e$. There are few physical models describing the temperature effect on LC refractive indices in the literature. Haller’s equation discloses the relationship between the birefringence and temperature, but not for the individual refractive indices. At a given wavelength, the refractive index of isotropic media decreases linearly as the temperature increases. Thus, it is reasonable to predict that the LC refractive index in the isotropic phase decreases linearly as the temperature increases. This prediction was validated by the experimental data. Next question is: will the individual refractive indices in the
nematic phase also decrease linearly as the temperature increases too? Apparently, the answer is no. There are no linearly relationship between \( n_e \) and the temperature, or between \( n_o \) and the temperature. We defined the average refractive index \( <n> \) as \( <n> = (n_e + 2n_o)/3 \) and found there is a linearly relationship between \( <n> \) and the temperature. Same as the refractive index of isotropic medium, \( <n> \) decreases linearly as temperature increases in the nematic phase. However, the decreasing slope in the nematic phase is a little larger than that in the isotropic phase.\textsuperscript{33,49} It is due to the abrupt drop of LC density at the clearing point.\textsuperscript{62,63}

We derived the four-parameter model for describing the temperature effect on the LC refractive indices based on the Haller’s equation, Vuks equation and the linear relationship between \( <n> \) and the temperature.\textsuperscript{49} The four-parameter model discloses clearly how the temperature affects the LC refractive indices. We further simplified the four-parameter model to the three-parameter parabolic model when the temperature is far from the clearing point. The three-parameter parabolic model indicates that there is a parabolic relationship between the LC refractive indices and the temperature when the temperature under consideration is far from the clearing point. The three-parameter parabolic model is more suitable for liquid crystals with a low birefringence. We will validate the four-parameter model and the three-parameter parabolic model in Chapter 5.

The thermal nonlinearity of liquid crystals is very important for some photonic applications, such as the thermal grating in nematic liquid crystal films, tunable liquid crystal photonic crystal fibers, thermal solitons in nematic liquid crystal confined in a capillary, and so on. We built the physical models for the thermal gradient, \( dn_o/dT \) and \( dn_e/dT \), of liquid crystals basing on the four-parameter model. By analyzing the
physical models of $dn_o/dT$ and $dn_e/dT$, we identified the parameters that affect the $dn_o/dT$ and $dn_e/dT$ values. Thus, guidelines are found to formulate novel liquid crystals with high $dn_o/dT$ values at room temperature. Two new liquid crystals, UCF-1 and UCF-2, with high $dn_o/dT$ value at room temperature are formulated.\(^{50}\)

By analyzing the physical models of $dn_o/dT$ and $dn_e/dT$, we found the value of $dn_e/dT$ is always negative, however, the value of $dn_o/dT$ could be negative or positive and depending on the sum of two terms with contrary signs. We first brought forward the conception, the crossover temperature, for nematic liquid crystals. The cross-over temperature is defined as the temperature at which $dn_o/dT$ equal to zero. The physical models of $dn_o/dT$ and $dn_e/dT$ could also be used to explain the varying tendency of $n_e$ and $n_o$ following with the temperature. The extraordinary refractive index, $n_e$, always decreases as the temperature increases since the $dn_e/dT$ is always negative. However, the ordinary refractive index, $n_o$, decreases first and then increases as the temperature goes beyond the cross-over temperature. It is because the $dn_o/dT$ is smaller than zero when the temperature is lower than the crossover temperature, whereas it is larger than zero when the temperature is beyond the crossover temperature. Both $dn_e/dT$ and $dn_o/dT$ increase dramatically as the temperature is approaching the clearing point. As a result, both $n_e$ and $n_o$ change very fast. $n_e$ is equal to $n_o$ and anisotropy disappears when the temperature reaches the clearing point.
3.2 Vuks Equation and the Expansions

In the literature, there are several models attempting to describe the temperature effect of LC refractive index. The classical Clausius-Mossotti equation correlates the dielectric constant $\varepsilon$ at low frequencies of an isotropic media with molecular polarizability ($\alpha$) as follows:\(^{41}\):

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha. \quad (3-1)$$

In Eq. (3-1), $N$ is the molecular packing density, or number of molecules per unit volume. In the optical frequency regime, we substitute $\varepsilon = n^2$ and obtain the Lorentz-Lorenz equation\(^{41}\):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha. \quad (3-2)$$

For an anisotropic LC, there are two principal refractive indices, $n_e$ and $n_o$, where $n_e$ and $n_o$ are refractive indices for the extraordinary ray and ordinary ray, respectively. In principle, each refractive index should be related to the corresponding molecular polarizabilities, $\alpha_e$ and $\alpha_o$. An early approach replaces both $n^2$ in Eq. (3-2) by $n_{e,o}^2$ and $\alpha$ by $\alpha_{e,o}$\(^{64,65}\). However, this model does not fit the experimental results well. Vuks made a bold assumption that the internal field in a crystal is the same in all directions:\(^{26}\)

$$E_i = \frac{<n^2> + 2}{3} E, \quad (3-3)$$
where $E_i$ is the internal field, the average field that acts on a molecule, and $E$ is the macroscopic electric field. This assumption is later validated experimentally. With this assumption, Vuks derived the following equation for anisotropic media:\(^{24}\)

$$\frac{n_{e,o}^2 - 1}{<n^2> + 2} = \frac{4\pi}{3} N\alpha_{e,o}. \quad (3-4)$$

where

$$\left\langle n^2 \right\rangle = \frac{(n_e^2 + 2n_o^2)}{3}, \quad (3-5)$$

$$N = \frac{\rho N_A}{M}, \quad (3-6)$$

where $\rho$ is the LC density, $M$ is the molecular weight, and $N_A$ is the Avogadro’s number.

Equation (3-4) is different from Eq. (3-2) in two aspects: 1) the $n^2$ term in the denominator of Eq. (3-2) is replaced by $\left\langle n^2 \right\rangle = \frac{(n_e^2 + 2n_o^2)}{3}$ while the $n^2$ term in the numerator is replaced by $n_{e,o}^2$, and 2) the $\alpha$ is replaced by $\alpha_{e,o}$.

In Eq. (3-4), $n_e$ and $n_o$ are coupled together so that the relationship between the refractive indices and the corresponding molecular polarizabilities is not clear. To reveal this relationship, we should decouple $n_e$ from $n_o$ by solving Eq. (3-4). Substituting Eq. (3-5) to Eq. (3-4) and separating $n_e$ and $n_o$, we obtain\(^{45}\)

$$n_e = \left[ 1 + \frac{4\pi N\alpha_e}{1 - \frac{4}{3} \pi N <\alpha>} \right]^{\frac{1}{2}}, \quad (3-7)$$
\[ n_o = \left[ 1 + \frac{4\pi N\alpha_o}{1 - \frac{4}{3}\pi N \langle \alpha \rangle} \right]^{\frac{1}{2}}, \tag{3-8} \]

Where \( \langle \alpha \rangle \) is the average polarizability of the LC molecule and is defined as:

\[ \langle \alpha \rangle = \frac{\alpha_o + 2\alpha_i}{3}. \tag{3-9} \]

When \( \alpha_{e,o} \) is small, the term \( 4\pi N\alpha_{e,o}/(1 - \frac{4}{3}\pi N \langle \alpha \rangle) \) is small and Eqs. (3-7) and (3-8) can be expanded into power series:

\[ n_{e,o} \approx 1 + \frac{2\pi N\alpha_{e,o}}{1 - \frac{4}{3}\pi N \langle \alpha \rangle}. \tag{3-10} \]

In the extreme case that \( N\alpha_i \to 0 \), the original Vuks equation [Eq. (3-4)] leads to \( n_e = n_o \sim 1 \). These results are consistent with Eq. (3-10). However, for most liquid crystals developed so far, their refractive indices are around 1.45-1.75. Therefore, the second terms in the square root of Eqs. (3-7) and (3-8) is larger than 1, but less than 2.1; the middle point is \( \sim 1.5 \). Under such a circumstance, Eqs. (3-7) and (3-8) cannot be expanded into power series directly. In order to make a series expansion, we rewrite Eqs. (3-7) and (3-8) as:

\[ n_e = \sqrt{2.5} \left[ 1 + \frac{(x_e - 1.5)}{2.5} \right]^{rac{1}{2}}, \tag{3-11} \]

\[ n_o = \sqrt{2.5} \left[ 1 + \frac{(x_o - 1.5)}{2.5} \right]^{rac{1}{3}}, \tag{3-12} \]
\[
\chi_{e,o} = \frac{4\pi N\alpha_{e,o}}{1 - \frac{4}{3}\pi N <\alpha>}. \tag{3-13}
\]

The absolute value of \((\chi_{e,o} - 1.5)/2.5\) in Eqs. (3-11) and (3-12) is smaller than \(\sim 0.2\). By expanding Eqs. (3-11) and (3-12) into power series and keeping the first two terms, we obtain\(^4^8\)

\[
n_e \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5\pi N\alpha_e} \left(1 - \frac{4}{3}\pi N<\alpha>\right), \tag{3-14}
\]

\[
n_o \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5\pi N\alpha_o} \left(1 - \frac{4}{3}\pi N<\alpha>\right). \tag{3-15}
\]

During the series expansion, the second order terms \(\sqrt{2.5} \left(\frac{\chi_{e,o} - 1.5}{2.5}\right)^2\) in Eqs. (3-14) and (3-15) are neglected because they contribute less than 0.57% to the entire refractive index values. The expressions (3-14) and (3-15) presented here are more accurate than those we derived earlier.\(^4^5\)

From above equations, the wavelength and temperature dependent refractive indices of liquid crystals are determined by \(\alpha_e, \alpha_o, <\alpha>\) and \(N\). We need to find how \(\alpha_e\) and \(\alpha_o\) vary with wavelength and temperature. Liquid crystal is a state of matter with physical properties lying between an isotropic liquid and a perfect crystal. Thus, its molecular differential polarizability \(\alpha_e - \alpha_o\) is related to the crystalline state \(\gamma_e - \gamma_o\) by the order parameter \(S\) as: \(^4^2\)

\[
\alpha_e - \alpha_o = S(\gamma_e - \gamma_o). \tag{3-16}
\]
The average molecular polarizability \(<\alpha>\) and \(<\gamma>\) are related to their individual molecular polarizability as:\(^{42}\)

\[
\langle \alpha \rangle = \frac{1}{3}(2\alpha_o + \alpha_e), \quad \text{(3-17)}
\]

\[
\langle \gamma \rangle = \frac{1}{3}(2\gamma_o + \gamma_e). \quad \text{(3-18)}
\]

Based on Eqs. (3-16), (3-17) and (3-18), the individual molecular polarizability can be expressed as:\(^{45}\)

\[
\gamma_e = \langle \alpha \rangle + \frac{2(\alpha_e - \alpha_o)}{3S}, \quad \text{(3-19)}
\]

\[
\gamma_o = \langle \alpha \rangle - \frac{\alpha_e - \alpha_o}{3S}, \quad \text{(3-20)}
\]

\[
\alpha_o = \langle \gamma \rangle - \frac{S}{3}(\gamma_e - \gamma_o), \quad \text{(3-21)}
\]

\[
\alpha_e = \langle \gamma \rangle + \frac{2S}{3}(\gamma_e - \gamma_o), \quad \text{(3-22)}
\]

Substituting Eqs. (3-21) and (3-22) back to (3-17), we prove that:\(^{42,45}\)

\[
\langle \gamma \rangle = \langle \alpha \rangle. \quad \text{(3-23)}
\]

That means the average molecular polarizability in the liquid crystal state and crystalline state is essentially equal. Plug Eqs. (3-21)-(3-23) back to Eqs. (3-14) and (3-15), we obtain:\(^{48}\)

\[
n_e \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \frac{\pi N \langle \alpha \rangle}{1 - \frac{4}{3} \pi N \langle \alpha \rangle} + \frac{4\sqrt{10}}{15} \frac{\pi N S \langle \gamma_e - \gamma_o \rangle}{1 - \frac{4}{3} \pi N \langle \alpha \rangle}, \quad \text{(3-24)}
\]
Here, $\gamma_e - \gamma_o$ is the differential molecular polarizability in the crystalline state,\textsuperscript{42,66} and $S$ is the order parameter. In a temperature not too close to the clearing temperature, $T_c$, the order parameter can be approximated as follows:\textsuperscript{32}

\begin{equation}
S = (1 - T / T_c)^{\beta}.
\end{equation}

In Eq. (3-26), the exponent $\beta$ is a material constant. For many LC compounds, $\beta \approx 0.2$ is not too sensitive to the LC molecular structures.

Based on Eqs. (3-24) and (3-25), we can calculate the average refractive index, which is defined as $< n > = (n_e + 2n_o)/3$, and obtain the following equation:\textsuperscript{48}

\begin{equation}
<n> \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \frac{\pi N\langle \alpha \rangle}{1 - \frac{4}{3} \pi N\langle \alpha \rangle}.
\end{equation}

Birefringence, which is defined as the difference between $n_e$ and $n_o$, can be expressed as following equation:

\begin{equation}
\Delta n = \frac{2\sqrt{10}}{5} \frac{\pi S(\gamma_e - \gamma_o)}{1 - \frac{4}{3} \pi N\langle \alpha \rangle}.
\end{equation}

By plugging Eqs. (3-27) and (3-28) into Eqs. (3-24) and (3-25), we can derive $n_e$ and $n_o$ into the following simple forms:\textsuperscript{49,50}

\begin{equation}
n_e = < n > + \frac{2}{3} \Delta n,
\end{equation}
\[ n_o = \langle n \rangle - \frac{1}{3} \Delta n. \]  

Eq. (3-27) indicates the average refractive index \( \langle n \rangle \) is decided by the average polarizability \( \langle \alpha \rangle \) and packing density \( N \). From Eq. (3-28), we can see that the LC birefringence is decided by the order parameter \( S \), packing density \( N \), the average polarizability \( \langle \alpha \rangle \) and the differential molecular polarizability in the crystalline state, \( \gamma_c - \gamma_o \). However, Eq. (3-27) does not disclose clearly the relationship between \( \langle n \rangle \) and temperature and Eq. (3-28) does not disclose clearly the relationship between \( \Delta n \) and temperature, too. Here, \( N \) is the molecular pack density, or number of molecular per unit volume which is equal to \( \frac{\rho N_A}{M} \). The term \( 4\pi N \langle \alpha \rangle / 3 \) in the denominator of Eqs. (3-27) and (3-28) is much smaller than one and the average polarizability \( \langle \alpha \rangle \) is not sensitive to temperature.\(^{42,48,67}\) Thus, the average refractive index \( \langle n \rangle \) is mainly determined by the density of liquid crystals and the birefringence \( \Delta n \) is mainly determined by order parameter \( S \) and density at a given wavelength.

Eq. (3-27) could be simplified as

\[ \langle n \rangle \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \pi N \langle \alpha \rangle + \frac{3}{\sqrt{10}} \left( \frac{4}{3} \pi N \langle \alpha \rangle \right)^2 \]  

(3-31)

Eq. (3-31) could be further simplified by neglecting the third term since term

\[ \frac{4}{3} \pi N \langle \alpha \rangle \]  

is much smaller than one. Then, we get

\[ \langle n \rangle \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \pi N \langle \alpha \rangle. \]  

(3-32)

By plugging Eq. (3-6) into Eq. (3-32), we get
\[ <n> \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \frac{N_A \pi \langle \alpha \rangle}{M} \rho. \]  

(3-33)

The density of liquid crystals has a quasi linear relationship with temperature which could be expressed as

\[ \rho = A' - B'T. \]  

(3-34)

where \( A' \) and \( B' \) are constant for a given liquid crystal.

Plugging Eq. (3-34) into (3-33), we derived

\[ <n> \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \frac{N_A \pi \langle \alpha \rangle A'}{M} - \frac{2\sqrt{10}}{5} \frac{N_A \pi \langle \alpha \rangle B'}{M} T. \]  

(3-35)

In Eq. (3-35), \( M \) is the molecular weight which is constant for a given LC, \( N_A \) is the Avogadro’s number, and \( \langle \alpha \rangle \) is not sensitive to temperature at a given wavelength. So Eq. (3-35) can be expressed as

\[ <n> = A - BT, \]  

(3-36)

where \( A \) and \( B \) are constant and have the form below:

\[ A = \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \frac{N_A \pi \langle \alpha \rangle A'}{M}, \]  

(3-37)

\[ B = \frac{2\sqrt{10}}{5} \frac{N_A \pi \langle \alpha \rangle B'}{M}. \]  

(3-38)

From Eq. (3-36), we can see the average refractive index of liquid crystals has a quasi linear relationship with temperature. The theory agrees well with the experimental result.

We can also understand it as following analysis. An isotropic medium has only one refractive index which has a linear relationship with temperature at a certain
wavelength. The anisotropy disappears ($S = 0$) when the temperature is beyond the clearing point. Eqs. (3-24) and (3-25) are reduced to the same form shown as below:

$$n_{iso} \approx \frac{7}{2\sqrt{10}} + \frac{2\sqrt{10}}{5} \frac{\pi N\langle\alpha\rangle}{1 - \frac{4}{3} \pi N\langle\alpha\rangle}.$$  

(3-39)

where $n_{iso}$ represents the LC refractive index at the isotropic state. Comparing Eq. (3-39) and (3-27), we find $\langle n \rangle$ and $n_{iso}$ have the same form except that term $N\langle\alpha\rangle$ in the two equations represents the value at different phase states, nematic and isotropic, respectively. So we have reason to believe the average refractive index also has a linear relationship with temperature since $\langle n \rangle$ and $n_{iso}$ have the same form.

The average polarizability $\langle \alpha \rangle$ and the differential molecular polarizability in the crystalline state, $\gamma_e - \gamma_o$, are insensitive to temperature given a wavelength. The order parameter $S$ is much more sensitive to the temperature than the packing density $N$. So Eq. (3-28) can be further simplified as

$$\Delta n = (\Delta n)_o S,$$  

(3-40)

$$\langle \Delta n \rangle_o = \frac{2\sqrt{10}}{5} \frac{\pi N(\gamma_e - \gamma_o)}{1 - \frac{4}{3} \pi N\langle\alpha\rangle}.$$  

(3-41)

The order parameter $S$ can be expressed as

$$S = (1 - \frac{T}{T_c})^\beta.$$  

(3-42)

Plugging Eq. (3-42) into (3-40), we get

$$\Delta n = (\Delta n)_o (1 - \frac{T}{T_c})^\beta.$$  

(3-43)
Eq. (3-43) has the same form as the Haller equation, but is derived in another way. Eqs. (3-36) and (3-43) will be validated by the experiment discussed in Chapter 5.

3.3 Validation of Vuks Equation

Vuks equation correlates the refractive indices of anisotropic media to their molecular polarizabilities and assumes that the internal field in crystals is isotropic in all directions. It has validated by the experimental data of several crystals such as naphthalene, diphenyl, anthracene and phenanthrene. In this chapter, we validate the Vuks equation using the refractive index data of liquid crystals directly. In the following paragraphs, we expand the Vuks model into different forms which make the experimental validation easier.

In Eq. (3-4), the macroscopic LC refractive indices $n_e$ and $n_o$ can be measured easily, however, the microscopic molecular polarizabilities $\alpha_e$ and $\alpha_o$ are difficult to determine directly. To validate Vuks equations, we rewrite Eq. (3-4) as follows:

$$\frac{n_e^2 - 1}{<n^2> + 2} = \frac{4\pi}{3} N\alpha_e, \quad (3-44)$$

$$\frac{n_o^2 - 1}{<n^2> + 2} = \frac{4\pi}{3} N\alpha_o. \quad (3-45)$$

Multiplying both sides of Eq. (3-45) by 2 and then add the corresponding terms with Eq. (3-44), we obtain the following equation\footnote{48}

$$\frac{(n_e^2 + 2n_o^2) - 3}{<n^2> + 2} = \frac{4\pi}{3} N(\alpha_e + 2\alpha_o). \quad (3-46)$$

Equation (3-46) can be rewritten as
\[
\frac{<n^2>-1}{<n^2>+2} = \frac{4\pi}{3} N <\alpha> ,
\]

(3-47)

where the average molecular polarizability is defined as \( <\alpha> = (\alpha_e + 2\alpha_o)/3 \). To evaluate Eq. (3-47) experimentally, we need to correlate \( N <\alpha> \) with another measurable macroscopic parameter, such as the average refractive index.

In order to realize the goal, we rewrite Eq. (3-27) as follows:

\[
1 - \frac{3}{\sqrt{10} <n> - 0.5} \approx \frac{4}{3} \pi N \langle \alpha \rangle .
\]

(3-48)

Equation (3-48) correlates \( N \langle \alpha \rangle \) to the average refractive index \( <n> \). This is an important step as the microscopic quantity \( N \langle \alpha \rangle \) can be determined experimentally by measuring the LC refractive indices. In order to compare with Eq. (3-48), we rewrite Eq. (3-47) as

\[
1 - \frac{3}{<n^2>+2} = \frac{4}{3} \pi N \langle \alpha \rangle .
\]

(3-49)

By comparing Eq. (3-48) with Eq. (3-49), we find

\[
<n^2> + 2 \approx \sqrt{10} <n> - 0.5 .
\]

(3-50)

The significance of Eq. (3-50) is that the sophisticated microscopic Vuks equation can now be validated by two simple macroscopic parameters \( <n^2> \) and \( <n> \). These two parameters can be obtained by measuring the individual refractive indices \( n_e \) and \( n_o \) of the liquid crystal. In Chapter 5, we will use the experimental data of five LC materials with birefringence ranging from 0.08 to 0.35 to validate Eq. (3-50).
3.4 Four-parameter Model

In Eqs. (3-29) and (3-30), \( <n> \) is the average refractive index and \( \Delta n \) is the birefringence. Meanwhile, birefringence is dependent on the order parameter \( S \). Based on Haller’s equation and our derivations above, the temperature-dependent birefringence has the form shown in Eq. (3-43).32

In Eq. (3-43), \( (\Delta n)_\circ \) is the LC birefringence in the crystalline state (or \( T=0 \) K), the exponent \( \beta \) is a material constant, and \( T_c \) is the clearing temperature of the LC material under investigation. The average refractive index decreases linearly with increasing temperature as shown in Eq. (3-36).49

Substituting Eqs. (3-43) and (3-36) back to Eqs. (3-29) and (3-30), we derive the four-parameter model for describing the temperature dependence of the LC refractive indices:49

\[
\begin{align*}
n_e(T) &= A - BT + \frac{2(\Delta n)_\circ}{3}(1 - \frac{T}{T_c})^\beta, \\
n_o(T) &= A - BT - \frac{(\Delta n)_\circ}{3}(1 - \frac{T}{T_c})^\beta.
\end{align*}
\]

(3-51)  

(3-52)

At the first glance, Eqs. (3-51) and (3-52) seem to have four fitting parameters. As a matter of fact, parameters \( A \) and \( B \) can be obtained from fitting the temperature-dependent \( <n(T)> \) data at a given wavelength, and parameters \( (\Delta n)_\circ \) and \( \beta \) can be obtained by fitting the temperature-dependent \( \Delta n \) data. Thus, once we have measured the temperature-dependent \( n_e \) and \( n_o \), we rearrange the data into \( <n(T)> \) and \( \Delta n(T) \) so that the parameters \([A, B]\) and \([ (\Delta n)_\circ, \beta ]\) can be obtained fairly straightforwardly.
The four-parameter model clearly describes the detailed relationship between the refractive indices and temperature in the whole nematic range.

### 3.5 Three-parameter Parabolic Model

For direct-view and projection liquid crystal displays, the LC mixture employed usually exhibits a low birefringence and high clearing temperature ($T_c > 90\, ^\circ\text{C}$). Under the condition that $T << T_c$, the $(1 - T / T_c)^\beta$ term in Eqs. (3-51) and (3-52) can be expanded into power series. Keeping the first three terms, we obtain:\(^49\)

\[
\begin{align*}
n_e(T) &= A_e - B_e T - C_e T^2, \\
n_o(T) &= A_o - B_o T + C_o T^2,
\end{align*}
\]

where \( A_e = A + \frac{2(\Delta n)_o}{3} \), \( B_e = B + \frac{2(\Delta n)_o \beta}{3T_c} \), \( C_e = \frac{(\Delta n)_o \beta(1 - \beta)}{3T_c^2} \), \( A_o = A - \frac{(\Delta n)_o}{3} \), \( B_o = B - \frac{(\Delta n)_o \beta}{3T_c} \), and \( C_o = \frac{(\Delta n)_o \beta(1 - \beta)}{6T_c^2} \). Equations (3-53) and (3-54) indicate that the LC refractive indices have a parabolic relationship with temperature for the low birefringence and high clearing point LC material when the operating temperature is not very close to the clearing point. For \( n_e \), the placket of the parabola is downward and, however, for \( n_o \) the placket is upward.

### 3.6 Temperature Gradient \( dn_e/dT \) and \( dn_o/dT \)

Based on Eqs. (3-51) and (3-52), we derive the \( dn_e/dT \) and \( dn_o/dT \) as follows:\(^50\)
\[ \frac{dn_e}{dT} = \frac{d < n >}{dT} + 2 \frac{d \Delta n}{3 \frac{dT}{dT}}, \quad (3-55) \]

\[ \frac{dn_o}{dT} = \frac{d < n >}{dT} - \frac{1}{3} \frac{d \Delta n}{dT}. \quad (3-56) \]

Furthermore, we derive the \( \frac{dn_e}{dT} \) and \( \frac{dn_o}{dT} \) as follows based on the Eqs. (3-55) and (3-56):

\[ \frac{dn_e}{dT} = -B - \frac{2 \beta (\Delta n)_o}{3T_c (1 - \frac{T}{T_c})^{1-\beta}}, \quad (3-57) \]

\[ \frac{dn_o}{dT} = -B + \frac{\beta (\Delta n)_o}{3T_c (1 - \frac{T}{T_c})^{1-\beta}}. \quad (3-58) \]

In Eq. (3-57), both terms in the right-hand side are negative, independent of temperature. This implies that \( n_e \) decreases as the temperature increases throughout the entire nematic range. However, Eq. (3-58) consists of a negative term \((-B)\) and a positive term which depends on the temperature. In the low temperature regime \( (T \ll T_c) \), the positive term could be smaller than the negative term resulting in a negative \( \frac{dn_o}{dT} \). As the temperature increases, the positive term also increases. As \( T \) approaches \( T_c \), \( \frac{dn_o}{dT} \) jumps to a large positive number. In the intermediate, there exists a transition temperature where \( \frac{dn_o}{dT} = 0 \). We define this temperature as the cross-over temperature \( T_o \) for \( n_o \). To find \( T_o \), we simply solve \( \frac{dn_o}{dT} = 0 \) from Eq. (3-58). \(^{50}\)

From Eq. (3-58), \( \frac{dn_o}{dT} \) is determined by five parameters \( (B, \beta, (\Delta n)_o, T \text{ and } T_c) \). Among these five, \( \beta \) and \( T \) can be treated as constants: \( \beta \sim 0.2 \) and \( T \sim 295K \) (room
temperature). Therefore, we only need to consider the remaining three parameters. A smaller \( B \) helps to boost the \( \frac{dn_o}{dT} \) value. Among the LC materials investigated, we found that the compounds containing isothiocyanato (NCS) polar group possess a slightly smaller \( B \) coefficient and higher birefringence than the cyano (CN) compounds. Therefore, the remaining two parameters, high birefringence and low clearing temperature, play crucial roles in determining the \( \frac{dn_o}{dT} \) and cross-over temperature. However, these two requirements are often contradicting to each other. Most of the high birefringence LC compounds are associated with high melting and clearing temperatures due to their long molecular conjugation. From Eq. (3-58), the \( T_e \) effect is particularly significant. If the \( T_e \) of a LC material is much higher than room temperature, then its cross-over temperature would be relatively high and \( \frac{dn_o}{dT} < 0 \) at room temperature. Mixture E7 is such an example; its \( T_e \) is \(-60^\circ C\) and its \( \frac{dn_o}{dT} \) is negative at room temperature.\(^{68}\)

Although a large positive \( \frac{dn_o}{dT} \) can always be obtained by raising the operating temperature to clearing point, in practice this is undesirable for two reasons. First, in this regime a small temperature fluctuation would cause a large \( \frac{dn_o}{dT} \) change. Second, light scattering due to LC director fluctuations is strong near the phase transition\(^{35}\). Many devices are preferred to operate at room temperature. Thus, it is highly desirable to design a LC mixture exhibiting a large \( \frac{dn_o}{dT} \) at room temperature.
3.7 Conclusion

In this chapter, we have reviewed the physical models for describing the temperature effect on liquid crystal refractive indices. Each model has its merits and shortcomings. Vuks model does not give an explicit relationship between the temperature and the LC refractive indices. Haller equation is an empirical equation which discloses the detailed relationship between the LC birefringence and the temperature. The average LC refractive index has a linear relationship with temperature. Based on Vuks model, we derived the expressions for the average refractive index \( <n> \) and birefringence \( \Delta n \), respectively, by making some reasonable approximations. The four-parameter model was obtained for describing the temperature effect on the liquid crystal refractive indices. The temperature gradients of the extraordinary refractive index \( (dn_e/dT) \) and the ordinary refractive index \( (dn_o/dT) \) were derived based on the four-parameter model. The concept of the crossover temperature \( T_o \) was proposed for the first time. Guidelines for formulating liquid crystal mixtures with a high \( dn_o/dT \) value at room temperature are established. High birefringence, lower clearing point and smaller \( B \) coefficient help to boost \( dn_o/dT \) at room temperature. Based on these simple guidelines, we formulated two exemplary liquid crystal mixtures, designated as UCF-1 and UCF-2, and compared their physical properties with a commonly used commercial liquid crystal compound 5CB. The \( dn_o/dT \) of UCF-1 is \(~4X\) higher than that of 5CB at room temperature.
CHAPTER 4: MEASUREMENTS

4.1 Introduction

In this chapter, we will describe our experimental methods for measuring the refractive indices of liquid crystals. Both wavelength and temperature effects are investigated. Several measurement methods have been reported for measuring the LC refractive indices and birefringence, e.g., Abbe refractometer,\textsuperscript{45-50} wedged-cell refractometer method,\textsuperscript{58,59} phase retardation method,\textsuperscript{21,69,70,71} Talbot-Rayleigh refractometer\textsuperscript{34}, extension of phase modulation Ellipsometry method,\textsuperscript{72} Jelley-Leitz Refractometer method,\textsuperscript{73} and spectroscopic ellipsometer method.\textsuperscript{74} Each measurement method has its own merit and shortcomings.

Originally, Abbe refractometer was designed for measuring the refractive index of isotropic media. To measure the anisotropic LC refractive indices, we must coat a surfactant layer onto the surfaces of the two prisms in order to align the liquid crystals. The surfactant could be lecithin or 0.294\%wt HMAB + methanol solution. The LC molecules are aligned perpendicular to the prism surfaces. Thus, we can measure both the ordinary refractive index and extraordinary refractive index using a polarizing eyepiece. However, the current Abbe refractometer could not be used to measure the LC refractive indices at the infrared light spectrum since it is too faint to see the boundary line even we
install a infrared viewer. The wedged-cell refractometer method was used to measure the index in the infrared region. By measuring the distance between the LC cell and the screen, and the distance between the intersection points of refracted light beam with the screen, we could get the refractive index data after some simple arithmetic calculations. The phase retardation method can be used to measure the LC birefringence, but not for the individual refractive indices. At this time, the spectroscopic ellipsometer method can only be used to measure the index at room temperature. Though the Talbot-Rayleigh refractometer can measure the index quickly, the measurement are not as accurate as the Abbe refratometer.

In our lab, we use a multi-wavelength Abbe refractometer to measure the LC refractive indices. We have six interference color filters with $\lambda = 450, 486, 546, 589, 633,$ and 656 nm. By changing the color filters, we can measure the LC refractive indices at six different wavelengths. We use a circulating constant temperature bath to control the temperature of the sample. The temperature range is from 10 to 55 °C. We use the 0.294% HMAB+methanol solution to align the LC molecules. The LC molecules are aligned perpendicular to the surfaces of the prisms. The refractive index data are measured by the wedged-cell refractometer method at $\lambda = 1.55$ and 10.6 $\mu m$, respectively. The measured data at the visible and infrared regions are used to validate the physical models we derived. The UV absorption spectra affect the material’s photostability and birefringence. The UV absorption spectra of several liquid crystals are also measured and analyzed.
4.2 Measurement of liquid crystal refractive indices at visible light spectrum

We measured the refractive indices of dozens of liquid crystals using a Multi-wavelength Abbe refractometer (Atago DR-M4) at $\lambda=450, 486, 546, 589, 633, \text{and} 656$ nm. The light source employed in the experiment is a unpolarized halogen lamp. The accuracy of the Abbe refractometer is up to the fourth decimal. For a given wavelength, we measured the refractive indices from 15 to 55 °C at 5 °C intervals. The temperature of the Abbe refractometer is controlled by a circulating constant temperature bath (Atago Model 60-C3). The temperature accuracy is $\pm 0.2$ °C. The LC molecules are aligned perpendicular to the main and secondary prism surfaces of the Abbe refractometer by coating these two surfaces with a surfactant comprising of 0.294 wt% hexadecyletrimethyle-ammonium bromide (HMAB) in methanol solution. Both $n_e$ and $n_o$ are obtained through a polarizing eyepiece. Figure 4 shows the multiwavelength Abbe refractometer with a circulating temperature bath in our lab.
Figure 4: The multiwavelength Abbe refractometer (Atago: DR-M4) including a circulating constant bath and six interference color filters.

The measured refractive index data of liquid crystals at the visible light spectrum are listed in the tables below:

Table 1: The measured refractive indices ($n_e$ and $n_o$) of MLC-9200-000 at λ=450, 486, 546, 589, 633, and 656 nm at different temperatures. The data with an asterisk are fitting values using the extended Cauchy equation, Eqs. (2-18) and (2-19) because these values are too small to measure from our Abbe refractometer.
Table 2: The measured refractive indices \( (n_e\text{ and } n_o) \) of MLC-9200-100 at \( \lambda = 450, 486, 546, 589, 633, \) and 656 nm at different temperatures. The data with an asterisk are fitting values using the extended Cauchy equation, Eqs. (2-18) and (2-19) because these values are too small to measure from our Abbe refractometer.

<table>
<thead>
<tr>
<th>T (°C)</th>
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<th>546</th>
<th>589</th>
<th>633</th>
<th>656</th>
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<td>( n_o )</td>
<td>( n_e )</td>
<td>( n_o )</td>
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<td>( n_o )</td>
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Table 3: The measured refractive indices \( (n_e\text{ and } n_o) \) of MLC-6608 at \( \lambda = 450, 486, 546, 589, 633, \) and 656 nm at different temperatures. The data with an asterisk are fitting values using the extended Cauchy equation, Eqs. (2-18) and (2-19) because these values are too small to measure from our Abbe refractometer.

<table>
<thead>
<tr>
<th>T (°C)</th>
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<th>546</th>
<th>589</th>
<th>633</th>
<th>656</th>
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Table 4: The measured refractive indices \((n_e\text{ and } n_o)\) of TL-216 at \(\lambda=450, 486, 546, 589, 633,\) and 656 nm at different temperature.

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<th>(n_o)</th>
<th>(n_e)</th>
<th>(n_o)</th>
<th>(n_e)</th>
<th>(n_o)</th>
<th>(n_e)</th>
<th>(n_o)</th>
<th>(n_e)</th>
<th>(n_o)</th>
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Table 5: The measured refractive indices \((n_e\text{ and } n_o)\) of E44 at \(\lambda=450, 486, 546, 589, 633,\) and 656 nm at different temperatures.

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<th>(n_o)</th>
<th>(n_e)</th>
<th>(n_o)</th>
<th>(n_e)</th>
<th>(n_o)</th>
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<th>(n_o)</th>
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Table 6: The measured refractive indices \((n_e \text{ and } n_o)\) of E7 at \(\lambda=450, 486, 546, 589, 633,\) and 656 nm at different temperature.

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<th>546</th>
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<th>633</th>
<th>656</th>
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<td></td>
<td></td>
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Table 7: Measured refractive indices ($n_e$ and $n_o$) of 5CB at $\lambda$=546, 589, and 633 nm, and at different temperatures.

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Table 8: Measured refractive indices \( n_e \) and \( n_o \) of 5PCH at \( \lambda\)=546, 589, and 633 nm, and at different temperatures.

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Table 9: Measured refractive indices ($n_e$ and $n_o$) of MLC-6241-000 at $\lambda=$589, 633 and 656 nm, and at different temperatures.

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4.3 Measurement of liquid crystal refractive indices at infrared light spectrum

We use the wedged-cell refractometer method to measure the LC refractive indices at wavelength equal to 1.55 and 10.6 $\mu$m.\textsuperscript{58,59} Figure 5 depicts the experimental apparatus for measuring the refractive indices of E7 at $\lambda=1.55$ and 10.6 $\mu$m. A laser diode operating at the fundamental Gaussian mode was used as the light source. The laser was especially designed to be injected into an optical fiber. In order to obtain a free propagating laser beam, a collimator was connected to the output side of the optical fiber. The laser beam was linearly polarized by means of a polarizer and the polarization axis was 45° with respect to the LC directors. The beam diameter was condensed to $\sim$1 mm by two con-focal lenses ($L_1$ and $L_2$) shown in Fig. 1. To form a wedged LC cell, two ITO (indium-tin-oxide) glass substrates were separated by two spacers having different thicknesses. The wedge angle was measured by an optical method to be $\theta = 0.04017$ radians with a precision of $6\times10^{-5}$ radians.
The alignment of the LC inside the cell is planar which was obtained by buffing the spin-coated poly-vinyl alcohol layer. The assembled LC cell exhibited a good molecular alignment, as inspected from a polarizing optical microscope. During experiments, the front substrate was arranged to be normal to the incoming infrared laser beam. The wedged cell was enclosed inside a thermostat and the sample temperature was controlled within 0.1 °C accuracy. A point-like detector designed for operation at $\lambda=1.55$ or 10.6 $\mu$m was mounted on a micrometric track. Under such condition, the detector can be moved up and down with a very precise control of its position. The position of the refracted laser beam is easily detected by moving the detector on the track. The detector signal is displayed on a LeCroy digital oscilloscope. The measurement principle consists of the evaluation of the deviation angle experienced by the laser beam due to the
refraction of the beams by the LC material. In fact, when the laser beam passes through
the wedged LC cell it undergoes a splitting process, and two beams (ordinary and
extraordinary) emerge from the cell. The refractive indices are then retrieved by using the
Snell law and simple geometrical calculations. The little shifts due to the presence of the
glass substrates are also taken into account. The accuracy on the measurement of the
refractive indices is estimated to be ~0.7 %.

The experimental apparatus used for the measurement at 10.6 µm wavelength is
analogous to the aforementioned one. The laser source is a CW CO2 laser that operates on
the fundamental Gaussian mode at \( \lambda = 10.6 \) µm (line P20). The detector used is the
infrared pyroelectric video camera (Spiricon Pyrocam III, model PY-III-C-A). The two
glass substrates of the wedged cell are now replaced by two ZnSe plates that allow the
transmission of the CO2 laser beam. In this case, the estimated accuracy on the refractive
indices is 0.5 %.\(^{36}\)

The refractive index data of E7 measured at wavelength equal to 1.55 and 10.6
µm are listed in Table 10.
Table 10: Measured refractive indices ($n_e$ and $n_o$) of E7 at $\lambda$=1.55 and 10.6 µm, at different temperatures.

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4.4 Measurement of UV absorption spectra

The UV absorption spectra of MLC-9200-000, MLC-9200-100, MLC-6608, and TL-216 were measured at $T = 23 \, ^\circ\text{C}$ by dissolving each LC mixture into a UV transparent LC host MLC-6815. To avoid detector saturation, the guest LC mixture was controlled at 1 wt %. We used the dual channel Cary 500 UV spectrophotometer and quartz cells for the UV measurements. The quartz substrates were sputtered with SiO$_2$ alignment layers for achieving homogeneous alignment, but no indium-tin-oxide conductive electrode was deposited. The cell gap was controlled at $d=6 \, \mu\text{m}$.

Figure 6 depicts the UV absorption spectra of 1 wt % MLC-9200-000, MLC-9200-100, MLC-6608, and TL-216 dissolved in MLC-6815. The dashed, dashed-dot, black solid line, and grey solid line represent their UV absorption spectra, respectively. In Fig. 1, MLC-9200-100 has a longer resonance absorption wavelength than MLC-9200-000. This explains why MLC-9200-100 ($\Delta n \approx 0.114$) exhibits a higher birefringence than MLC-9200-000 ($\Delta n \approx 0.085$). MLC-9200-000 and MLC-6608 ($\Delta n \approx 0.083$) have similar resonance absorption peaks so that the two LC mixtures have a comparable birefringence, but their dielectric anisotropy has opposite signs. Among the four mixtures studied, TL-216 has the longest absorption wavelengths. Thus, TL-216 has the highest birefringence among these LC mixtures investigated. However, its UV stability is the worst among these four. UV stability is especially important to LCoS projection display where the ultra-high-pressure lamp emits harmful UV contents. Although UV and blue cutoff wavelength filters are used to remove the harmful UV contents, any residual transmitted UV light could degrade the long-term stability of the LC materials or alignment layers.$^{75}$
Whichever fails first will deteriorate the LC panel’s overall performance and limit the projector’s lifetime.

Figure 6: UV absorption spectrum of 1 wt % MLC-9200-000, MLC-9200-000, MLC-6608, and TL-216 dissolved in a UV transparent MLC-6815 mixture. Measurement was made at T=23 °C. The dashed, dashed-dot, black solid, and grey solid lines are UV absorption spectra of MLC-9200-000, MLC-9200-100, MLC-6608, and TL-216, respectively. Cell gap d=6 µm.
4.5 Summary

We have measured the liquid crystal refractive indices using a multi-wavelength Abbe refractometer in the visible spectral region and a wedged cell refractometer method in the IR region. In the visible region, six interference color filters with \( \lambda = 450, 486, 546, 589, 633 \) and 656 nm are used. To investigate temperature effect, we use a circulating constant temperature bath to control the sample temperature. The temperature range is from 10 to 55 °C. The LC refractive indices at \( \lambda = 1.55 \) and 10.6 \( \mu \text{m} \) are measured by the wedged-cell refractometer method. The UV absorption spectra of several liquid crystals are measured, too. In Chapter 5, these experimental data are used to validate the physical models we derived.
CHAPTER 5: EXPERIMENTAL VALIDATIONS OF THE DERIVED THEORETICAL MODEL

In this Chapter, the measured $n_e$ and $n_o$ data are used to validate the derived theoretical models: extended Cauchy model, two-coefficient Cauchy model, four-parameter model, and three-parameter parabolic model. We also show how to validate the Vuks equation by using the experimental data of liquid crystals.

5.1 Extended and two-coefficient Cauchy models

The classical Cauchy model is used to describes the wavelength-dependent refractive index of isotropic media. Here, we extend the Cauchy model to describing the wavelength effect on the refractive indices of anisotropic liquid crystals, including low, moderate, and high birefringence liquid crystals. The two-coefficient Cauchy model is simplified from the extended Cauchy model to describe the wavelength dispersion of the low birefringence liquid crystals. In this section, we will use several liquid crystals with low, moderate, and high birefringence to validate the extended Cauchy model and the simplified two-coefficient Cauchy model.

We have selected seven LC mixtures, MLC-9200-000, MLC-9200-100, MLC-6241-000, MLC-6608, TL-216, E44, E7 and two LC compounds (5CB and 5PCH) as examples to validate the physical models we derived. The first five LC mixtures are commonly employed for TFT-LCD applications. MLC-9200-000 and MLC-9200-100 are Merck two-bottle mixtures. These two mixtures have very similar physical properties except for different birefringence. MLC-9200-000 has $\Delta n \sim 0.085$ and MLC-9200-100 has $\Delta n \sim 0.114$. By mixing these two bottles in a proper fraction, birefringence in the 0.085-
0.114 range can be formulated. The mixture MLC-6608 (Δn~0.083) has a negative
dielectric anisotropy, Δε=−4. It is a representative mixture for vertical alignment. Lastly,
TL-216 is a high birefringence (Δn~0.213) LC mixture used in a color-sequential liquid-
crystal-on-silicon (LCoS) projection display. Excellent agreement between theory and
experiment is obtained.

Figure 7: Wavelength-dependent refractive indices of MLC-9200-000 and MLC-9200-
100 at T= 25 °C. Open and filled circles and triangles, respectively, represent the
experimental data for n_e and n_o of MLC-9200-000 and MLC-9200-100. Solid and dashed
lines are fittings by using the three-coefficient, Eqs. (2-7) and (2-8) and the
two-coefficient, Eqs. (2-21) and (2-22) Cauchy models, respectively. The fitting
parameters are listed in Table 1.

Figure 7 depicts the wavelength-dependent refractive indices of MLC-9200-000
and MLC-9200-100 at T = 25 °C. The open and filled circles represent the experimental
data of n_e and n_o for MLC-9200-000, and the open and filled triangles are the
corresponding $n_c$ and $n_o$ for MLC-9200-100, respectively. The solid and dashed lines are fittings using the three-coefficient, Eqs. (2-18) and (2-19) and two-coefficient Cauchy model Eqs. (2-21) and (2-22), respectively. Table 11 lists the fitting parameters. In figure 7, all the solid and dashed lines fit the experimental data very well and the dashed lines almost completely overlap with the solid lines. It means the three- and two-coefficient Cauchy models fit the experimental data of MLC-9200-000 and MLC-9200-100 equally well. From Table 11, we find the fitting Cauchy coefficients $C_e$ and $C_o$ are considerably smaller than the $B_e$ and $B_o$ for both MLC-9200-000 and MLC-9200-100. This indicates that the magnitude of the $\lambda^{-4}$ term is much smaller than that of the $\lambda^{-2}$ term and can be ignored. For low birefringence LC materials, the two-coefficient Cauchy model works equally well as the three-coefficient one.
Table 11: The fitting parameters of MLC-9200-000, MLC-9200-100, MLC-6608, TL-216, E44, E7, 5CB, 5PCH, and MLC-6241-000 for the three- and two-coefficient Cauchy models. $T=25^\circ C$. The Cauchy coefficients $B$ and $C$ are in units of $\mu m^2$ and $\mu m^4$, respectively.

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<td>0.0281</td>
</tr>
<tr>
<td>5CB</td>
<td>Three-coefficient</td>
<td>1.6708</td>
<td>0.0081</td>
</tr>
<tr>
<td></td>
<td>Two-coefficient</td>
<td>1.6423</td>
<td>0.0251</td>
</tr>
<tr>
<td>5PCH</td>
<td>Three-coefficient</td>
<td>1.5801</td>
<td>0.0073</td>
</tr>
<tr>
<td></td>
<td>Two-coefficient</td>
<td>1.5766</td>
<td>0.0094</td>
</tr>
<tr>
<td>MLC-6241-000</td>
<td>Three-coefficient</td>
<td>1.5397</td>
<td>0.0075</td>
</tr>
<tr>
<td></td>
<td>Two-coefficient</td>
<td>1.5395</td>
<td>0.0076</td>
</tr>
</tbody>
</table>

Figure 8 depicts the wavelength-dependent refractive indices of MLC-6608 and TL-216 at $T=25^\circ C$. MLC-6608 is a negative LC mixture; its dielectric anisotropy is $\Delta\varepsilon = -4.2$. The open and filled circles and triangles represent the experimental data of $n_e$ and $n_o$ for MLC-6608 and TL-216, respectively. The solid and dashed lines are fittings using the three-coefficient Eqs. (2-18) and (2-19) and two-coefficient Cauchy models Eqs. (2-21) and (2-22). The fitting parameters are listed in Table 2. In figure 8, the dashed lines almost completely overlap with the solid lines; both models fit the experimental data of MLC-6608 very well. However, there are some differences between the fitting curves using the three- and two-coefficient models for TL-216. The fitting
error of the three-coefficient Cauchy model ($\chi^2 \sim 10^{-7}$) is one order smaller than that of the two-coefficient Cauchy model ($\chi^2 \sim 10^{-6}$). Here, the $\chi^2$ deviation is defined as the sum of the squares of observed values minus expected values and then divided by the expected values. In Table 11, the Cauchy coefficients $C_e$ and $C_o$ are considerably smaller than $B_e$ and $B_o$ for MLC-6608, however, the coefficient $C_e$ is comparable to $B_e$ for TL-216. This indicates that both the three- and two-coefficient Cauchy models fit the experimental data of MLC-6608 well, but the three-coefficient Cauchy model fits the $n_e$ data better than the two-coefficient Cauchy model for TL-216. Thus, for TL-216 the $\lambda^{-4}$ term is comparable to the $\lambda^{-2}$ term and cannot be ignored.

Figure 8: Wavelength-dependent refractive indices of MLC-9200-000 and MLC-9200-100 at $T= 25$ °C. Open and filled circles and triangles, respectively, represent the experimental data for $n_e$ and $n_o$ of MLC-9200-000 and MLC-9200-100. Solid and dashed lines are fittings by using the three-coefficient, Eqs. (2-7) and (2-8) and the two-coefficient, Eqs. (2-21) and (2-22) Cauchy models, respectively. The fitting parameters are listed in Table 11.
In Figure 9, we show the wavelength-dependent refractive indices of E44, E7, 5CB, 5PCH and MLC-6241-000 at \( T = 25{^\circ}C \). The birefringence of E44, E7, 5CB, 5PCH and MLC-6241-000 is \( \sim 0.258, 0.217, 0.177, 0.116 \) and 0.086, respectively, at \( \lambda = 589 \text{ nm} \) and \( T = 25{^\circ}C \). The open and filled pentagons, circles, squares, upward- and downward-triangles are the \( n_e \) and \( n_o \) of E44, E7, 5CB, 5PCH and MLC-6241-000, respectively. The solid and dashed lines are fittings using the three-coefficient, Eqs. (2-18) and (2-19), and two-coefficient Eqs. (2-21) and (2-22) Cauchy models. The fitting parameters are listed in Table 2. From figure 9, the three-coefficient Cauchy model fits the experimental \( n_e \) and \( n_o \) data for all the four liquid crystals well. However, the two-coefficient Cauchy model does not fit the experimental results of E44, E7, and 5CB so nicely as the three-coefficient Cauchy model because these three LCs have a higher birefringence. For 5PCH (\( \Delta n \sim 0.1158 \)), the two-coefficient Cauchy model fits the experimental \( n_e \) and \( n_o \) data fairly well although the three-coefficient Cauchy model has slightly better fitting. For MLC-6241-000, the fittings by the three- and two-coefficient Cauchy models overlap each other, similar to the other low birefringence liquid crystals. From Figures 7, 8, and 9, we found a boundary value of birefringence (\( \Delta n = 0.12 \)) below which the three- and two-coefficient Cauchy models fit the LC refractive indices \( n_e \) and \( n_o \) equally well. However, for a high birefringence (\( \Delta n > 0.12 \)) liquid crystal the three-coefficient Cauchy model must be used.
Figure 9: Wavelength-dependent refractive indices of E44, E7, 5CB, 5PCH and MLC-6241-000 at T=25 °C. The open and filled pentagons, circles, triangles, upward- and downward-triangles represent the experimental data of $n_e$ and $n_o$ for E44, E7, 5CB, 5PCH, and MLC-6241-000, respectively. While solid and dashed lines are fittings using the three-coefficient Eqs. (2-18) and (2-19) and two-coefficient Eqs. (2-21) and (2-22) Cauchy models, respectively. The fitting parameters are listed in Table 11.

In summary, the two-coefficient Cauchy model can be used for describing the wavelength effect of low birefringence ($\Delta n < 0.12$) LC mixtures, no matter they are positive or negative $\Delta \varepsilon$ materials. Since the two-coefficient model has only two parameters, it is more convenient to fit with experimental data. However, for a LC mixture with high birefringence ($\Delta n > 0.12$), the three-coefficient Cauchy model should be used because the $\lambda^{-4}$ term is comparable to the $\lambda^{-2}$ term and cannot be neglected. Based on our experimental results of a dozen LC compounds and mixtures, $\Delta n \sim 0.12$ can
be treated as the division between the 2-coefficient and 3-coefficient Cauchy models. In addition, using the extended Cauchy model we can extrapolate the infrared refractive indices based on the data measured in the visible spectral region. The extrapolated results agree well with those measured directly.$^{59}$
5.2 Validation of Vuks Model

Lorentz-Lorenz formula relates the refractive index with the polarizability of isotropic media. It is widely used for the determination of the average polarizability of anisotropic molecules. In 1964, Vuks made a drastic assumption that the internal field in a crystal is the same in all directions and derived the Vuks equation based on the Lorentz-Lorenz equation. Vuks equation correlates the individual component of refractive index with the individual component of the polarizability. He used the experimental data of several crystals, naphthalene, diphenyl, anthracene and phenanthrene, to validate the equation and good agreement between theory and experiment was achieved. After four decades, Vuks equation has been widely used to correlate the refractive indices with the polarizabilities of liquid crystals. Moreover, several physical models are derived based on the Vuks equation. Thus, it is necessary to validate the Vuks equation using the experimental data of liquid crystals directly. The idea on how to validate Vuks equation was shown in Sec. 3.3. We use low, moderate, and high-birefringence liquid crystals to validate Vuks model.21

Figure 10 depicts the temperature-dependent birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000 and UCF-280 measured at $\lambda=589$ nm. The filled circles, squares, open circles, filled downward-triangles, and open upward-triangles are the measured birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000 and UCF-280, respectively, at different temperatures. The temperature range for the experiment is from 10 to 55 °C. At room temperature and $\lambda=589$ nm, the birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000 and UCF-280 is 0.35, 0.2, 0.12, 0.086 and 0.085, respectively. The solid lines represent fittings using the Haller equation, Eq. (3-43). The clearing point for UCF-35,
5CB, 5PCH, MLC-6241-000, and UCF-280 is 95.3, 33.4, 52.9, 100 and 66.2 °C, respectively. From these fittings, we find \(((\Delta n)_o, \beta)\) = [0.5727, 0.2719], [0.3505, 0.1889], [0.1706, 0.1512], [0.1221, 0.2209] and [0.1426, 0.2513] for UCF-35, 5CB, 5PCH, MLC-6241-000 and UCF-280, respectively. Although UCF-280 has a larger \((\Delta n)_o\) than MLC-6241-000, its clearing temperature is much lower. As a result, its birefringence at room temperature is lower than that of MLC-6241-000 due to the order parameter effect.

![Figure 10: Temperature-dependent birefringence \((\Delta n)\) of UCF-35 (filled circles), 5CB (open squares), 5PCH (open circles), MLC-6241-000 (filled downward-triangles) and UCF-280 (open upward-triangles) at \(\lambda=589\) nm. The five solid lines are fitting curves using \(\Delta n = (\Delta n)_o (1 - T / T_c)^\beta\), where \(T_c\) is the clearing point.](image-url)
In Figure 11, we plot the values of \((<n^2>+2)\) and \((\sqrt{10} < n > -0.5)\) of 5CB and 5PCH in the same figure in order to validate Eq. (3-50) which is a close approximation of Vuks equation. The filled and open squares, circles, and upward-triangles are the measured values of \(<n^2>+2\) and \(\sqrt{10} < n > -0.5\) at \(\lambda=546, 589\) and 633 nm, respectively. From Fig. 5, we find that these data almost overlap each other. The difference is as small as \(\sim 0.2\%\) for 5CB and \(\sim 0.1\%\) for 5PCH. From Eq. (3-36), the right side of Eq. (3-50) can be written as

\[
\sqrt{10}\langle n \rangle - 0.5 = \sqrt{10}(A - BT) - 0.5. \tag{5-1}
\]
Figure 11: Validation of Eq. (3-50) using the experimental data of 5CB and 5PCH. Filled squares, circles and upward-triangles are the calculated values of $<n^2> + 2$ at $\lambda = 546$, 589 and 633 nm, respectively. Open squares, circles and upward-triangles are the corresponding values of $\sqrt{10} <n> - 0.5$. Solid lines are fitting results using Eq. (5-1).

The solid lines shown in Figure 11 are fitting results using Eq. (5-1). The fitting parameters are: 

$[A, B] = [1.7751, 5.81 \times 10^{-4}], [1.7674, 5.79 \times 10^{-4}]$, and $[1.7601, 5.75 \times 10^{-4}]$ for 5CB at $\lambda = 546$, 589 and 633 nm, respectively. The corresponding $[A, B]$ values for 5PCH are $[1.6837, 5.09 \times 10^{-4}], [1.6795, 5.06 \times 10^{-4}]$, and $[1.6684, 4.82 \times 10^{-4}]$. From Figure 11, the agreement between experiment and fitting results is excellent for 5CB and 5PCH. The experimental data measured at different wavelengths and temperatures of 5CB and 5PCH all satisfy Eq. (3-50) very well. Therefore, Vuks equation is proven to be...
self-consistent for describing the refractive indices of LC compounds (5CB and 5PCH) although the isotropic local field is assumed.

Figure 12: Validation of Eq. (3-50) using the experimental data of UCF-35, UCF-280, and MLC-6241-000. Filled squares, circles and upward-triangles are the calculated values of $<n^2> + 2$ at $\lambda=656$ nm for UCF-35, MLC-6241-000 and UCF-280, respectively. Open squares, circles, and upward-triangles are the calculated values of the corresponding values of $\sqrt{10} <n> - 0.5$. Solid lines are fitting results using Eq. (5-1).

Figure 12 shows a similar plot for UCF-35, MLC-6241-000 and UCF-280. The filled squares, circles and upward-triangles are the measured values for $<n^2> + 2$ at $\lambda=656$ nm for UCF-35, MLC-6241-000 and UCF-280, respectively. The open squares, circles, and upward-triangles are the corresponding values for $\sqrt{10}\langle n\rangle - 0.5$ at $\lambda=656$ nm. In Fig. 6, we plot the data at $\lambda=656$ nm because UCF-35 has more complete experimental
data at this wavelength. The refractive indices of these three LC mixtures vary from ~1.46 to ~1.86. Despite such variation, Eq. (3-50) still holds very well.

In Figure 12, all the experimental data of the left and right terms of Eq. (3-50) overlap quite well for UCF-35, MLC-6241-000 and UCF-280 although UCF-35 has 4X higher birefringence than the other two mixtures. The difference between the right- and left-hand terms of Eq. (3-50) is as small as ~0.5% for UCF-35 and ~0.1% for MLC-6241-000 and UCF-280. Solid lines are the fitting results using Eq. (5-1). The fitting parameters are: \([A, B] = [1.8003, 5.12 \times 10^{-4}], [1.6216, 4.05 \times 10^{-4}], \) and \([1.6511, 4.79 \times 10^{-4}]\) for UCF-35, MLC-6241-000 and UCF-280, respectively. The fitting results agree very well with the experimental data. Therefore, Vuks equation is proven to be self-consistent for both high and low birefringence LC mixtures.

As shown in Figs. 11 and 12, the \(n^2\) term is slightly larger than the \(\sqrt{10} n\) term. This is because we have omitted the higher order terms while deriving Eqs. (3-11) and (3-12) which, in turn, lead to Eqs. (3-48) and (3-50). The five LC materials we selected have refractive index spanning from ~1.46 to ~1.86. All the experimental data satisfy Eq. (3-50) quite well. It implies that the Vuks equation is valid for describing LC refractive indices independent of their molecular structures and electron conjugation length.

Since Vuks equation correlates the macroscopic refractive index to the microscopic molecular polarizability, if we know refractive index, then we can calculate the molecular polarizability, or vise versa. For instance, if we plug the measured \(n_e\) and
\( n_o \) data back to Eq. (3-4), we can calculate the \( \alpha_e \) and \( \alpha_o \) values of the five LC compounds and mixtures at different temperatures and wavelengths.

In Eq. (3-4), there is still an unknown parameter \( N; \) the number of molecules per unit volume. However, \( N \) is equal to \( \frac{\rho N_A}{M} \), where \( \rho \) is the LC density, \( M \) is the molecular weight, and \( N_A \) is the Avogadro’s number. Rearranging Eq. (3-4), we find

\[
\alpha_e = \frac{3M}{4\pi\rho N_A} \cdot \frac{n_e^2 - 1}{\langle n^2 \rangle + 2}, \quad (5-2)
\]

\[
\alpha_o = \frac{3M}{4\pi\rho N_A} \cdot \frac{n_o^2 - 1}{\langle n^2 \rangle + 2}. \quad (5-3)
\]

Let us use 5CB as an example to calculate the molecular polarizabilities, \( \alpha_e \) and \( \alpha_o \). For 5CB, the molecular weight is \( M=249.3 \) g/mol and the density \( \rho(T) \) is taken from that measured by Zeller.\(^{62}\) Using our measured refractive indices at \( \lambda=589 \) nm, we can calculate the \( \alpha_e \) and \( \alpha_o \) of 5CB from Eqs. (5-2) and (5-3).

Figure 13 plots the temperature-dependent \( \alpha_e, \alpha_o \) and \( \langle \alpha \rangle \) of 5CB at \( \lambda=589 \) nm. The open and filled circles represent the calculated values for \( \alpha_e \) and \( \alpha_o \), respectively. In the isotropic state, \( \alpha_e \) and \( \alpha_o \) are equal. The open triangles represent the calculated average polarizability \( \langle \alpha \rangle \) in the nematic phase. From Fig. 13, \( \alpha_e \) decreases while \( \alpha_o \) increases as the temperature increases. However, the average polarizability \( \langle \alpha \rangle \) is quite insensitive to the temperature. The average polarizability for 5CB at \( \lambda=589 \) nm is found to be \( \langle \alpha \rangle \sim 3.3 \times 10^{-23} \text{ cm}^{-3} \), which agrees very well with the calculated value \( \langle \alpha \rangle \sim 3.25 \times 10^{-23} \text{ cm}^{-3} \) published by Sarkar et al.\(^{67}\)
Figure 13: Temperature-dependent molecular polarizabilities, $\alpha_e$ and $\alpha_o$, of 5CB at $\lambda=589$ nm. Open and filled circles are the results for $\alpha_e$ and $\alpha_o$, respectively. Triangles represent the average polarizability $<\alpha>$. In the isotropic phase, $\alpha_e = \alpha_o$. 
5.3 Validation of Four-parameter Model and Three-parameter Parabolic Model

Temperature effect plays a key role for projection displays since the display panel could reach 50 ~ 60 °C due to the thermal effect of the lamp. In chapter 3, we derived the four-parameter model and three-parameter parabolic model for describing the temperature effect on the LC refractive indices based on the Vuks equation. The four-parameter model describes the temperature effect on the low, moderate, and high-birefringence liquid crystals very well. The three-parameter parabolic model is mainly used for describing the temperature effect of the low birefringence liquid crystals with a high clearing temperature when the temperature is not close to the clearing temperature. To validate the four-parameter model, we use the model to fit the experimental data of 5CB, 5PCH, MLC-6241-000, and UCF-35 measured at λ=546, 589, and 633 nm. Excellent agreement between the four-parameter model and the experimental data is obtained. To validate the three-parameter parabolic model, we fit the model with the experimental data of MLC-6241-000. The agreement is also excellent.

5.3.1 Validation of the Four-parameter Model

Although the four-parameter model has four unknowns: $A$, $B$, $(\Delta n)_o$ and $\beta$, they can be obtained by the two-step fittings. In experiment, we measured the refractive indices ($n_e$ and $n_o$) using Abbe Refractometer at six wavelengths in the temperature range from 10 to 55 °C. Once the refractive indices are measured, birefringence and
average refractive index can be calculated. The first step is to use Eq. (3-36) to fit the average refractive index data and obtain parameters A and B. The second step is to use Eq. (3-43) to fit the birefringence data and extract \((\Delta n)_o\) and \(\beta\). Finally, we plug these two sets of parameters into Eqs. (3-51) and (3-52) to calculate the refractive indices and compare the calculated results with the measured ones. We use four different materials: 5CB, 5PCH, MLC-6241-000 and UCF-35 to validate the four-parameter model. At room temperature, the birefringence of UCF-35, 5CB, 5PCH and MLC-6241-000 is 0.35, 0.2, 0.12 and 0.085, respectively, at \(\lambda=589\) nm. And their clearing temperature is 368.3, 306.6, 325.9 and 373.7 K, respectively. Excellent agreement is obtained between the calculated results and experimental data of these four different materials.

Figure 14 depicts the temperature-dependent average refractive index of 5CB, 5PCH, UCF-35 and MLC-6241-000 at \(\lambda=589\) nm. Circles, upward-triangles, squares and downward-triangles represent experimental data for 5CB, 5PCH, MLC-6241-000 and UCF-35, respectively, while solid lines are fitting results using Eq. (3-36). The fitting parameters for these four materials are listed in Table 12. The average refractive index decreases linearly as the temperature increases. In the isotropic phase, the refractive index also decreases linearly with the increased temperature. Near the isotropic temperature, there is a sudden decrease in refractive index because of the second order phase transition which results in a density fluctuation. The filled circles and triangles in Figure 14 are the isotropic refractive index for 5CB and 5PCH, respectively. They also decrease linearly with increasing temperature in the isotropic state, but the slope is slightly different from that of the nematic state.
Figure 14: Temperature-dependent average refractive index \(<n>\) of 5CB, 5PCH, MLC-6241-000 and UCF-35 at \(\lambda = 589\) nm. Open circles, upward-triangles, squares and downward-triangles are average refractive index \(<n>\) of 5CB, 5PCH, MLC-6241-000 and UCF-35, respectively. Solid lines are fittings by using Eq. (3-36). The fitting parameters are listed in Table 12. The filled circles and triangles are isotropic refractive index for 5CB and 5PCH, respectively.

Figure 10 depicts the temperature-dependent birefringence of 5CB, 5PCH, MLC-6241-000 and UCF-35 at \(\lambda = 589\) nm. The filled circles, squares, open circles, filled downward-triangles, and open upward-triangles are the measured birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000 and UCF-280, respectively, at different temperatures. The solid lines are fitting results using Eq. (3-43). The fitting parameters for these four
materials at $\lambda = 589$ nm are also listed in Table 12. Through fittings, we obtain parameters $(\Delta n)_o$ and $\beta$.

Table 12: Fitting parameters for the average refractive index $<n>$ and birefringence $(\Delta n)$ of four LCs at $\lambda = 589$ nm.

<table>
<thead>
<tr>
<th>LC</th>
<th>$&lt;n&gt;$</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B (K$^{-1}$)</td>
</tr>
<tr>
<td>5CB</td>
<td>1.7674</td>
<td>5.79x10$^{-4}$</td>
</tr>
<tr>
<td>5PCH</td>
<td>1.6795</td>
<td>5.07x10$^{-4}$</td>
</tr>
<tr>
<td>MLC-6241-000</td>
<td>1.6233</td>
<td>4.00x10$^{-4}$</td>
</tr>
<tr>
<td>UCF-35</td>
<td>1.8187</td>
<td>5.32x10$^{-4}$</td>
</tr>
</tbody>
</table>

For a full color display, we need to know the refractive indices at the three primary colors. Figure 15 depicts the temperature-dependent refractive indices of 5CB at $\lambda = 546$, 589 and 633 nm. Squares, circles and triangles are experimental data measured at $\lambda = 546$, 589, and 633 nm, respectively, and solid lines are fitting results using the four-parameter model. The agreement is excellent. In an isotropic phase, the optical anisotropy disappears, i.e. $n_e = n_o$, regardless of wavelength. The fitting parameters for the four-parameter model are listed in Table 13. As shown in Figure 15, the agreement between the four-parameter model and experimental data is excellent.

Due to the shorter molecular conjugation, 5PCH has a lower birefringence than 5CB, however, its clearing temperature is higher. Thus, similar to 5CB, 5PCH has been
widely used in many commercial LC mixtures. Figure 16 depicts the temperature-dependent refractive indices of 5PCH at \( \lambda = 546, 589 \) and 633 nm. Squares, circles and triangles are the experimental data measured at \( \lambda = 546, 589, \) and 633 nm, respectively, and solid lines are fitting results using the four-parameter model. Above clearing point (\( T_c = 325.9 \) K), the optical anisotropy vanishes so that \( n_e = n_o \). The fitting parameters for the four-parameter model are listed in Table 14. Excellent agreement between the four-parameter model and experimental data is achieved.

Figure 15: Temperature-dependent refractive indices of 5CB at \( \lambda = 546, 589 \) and 633 nm. Squares, circles and triangles are experimental data for refractive indices measured at \( \lambda = 546, 589, \) and 633 nm, respectively. Solid lines are fittings using the 4-parameter model Eqs., (3-51) and (3-52). The fitting parameters are listed in Table 13.
Table 13: Fitting parameters for the average refractive index \(<n>\) and birefringence \((\Delta n)\) of 5CB at \(\lambda=546, 589\) and 633 nm.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>(&lt;n&gt;)</th>
<th>(A)</th>
<th>(B) (K(^{-1}))</th>
<th>((\Delta n)_o)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>546</td>
<td>1.7751</td>
<td>5.81\times10^{-4}</td>
<td>0.3594</td>
<td>0.1862</td>
<td></td>
</tr>
<tr>
<td>589</td>
<td>1.7674</td>
<td>5.79\times10^{-4}</td>
<td>0.3505</td>
<td>0.1889</td>
<td></td>
</tr>
<tr>
<td>633</td>
<td>1.7601</td>
<td>5.75\times10^{-4}</td>
<td>0.3389</td>
<td>0.1855</td>
<td></td>
</tr>
</tbody>
</table>

Figure 16: Temperature-dependent refractive indices of 5PCH at \(\lambda=546, 589\) and 633 nm. Squares, circles and triangles are experimental data for refractive indices measured at \(\lambda=546, 589\) and 633 nm, respectively. Solid lines are fittings using the 4-parameter model, Eqs. (3-51) and (3-52). The fitting parameters are listed in Table 14.
Table 14: Fitting parameters for the average refractive index $<n>$ and birefringence ($\Delta n$) of 5PCH at $\lambda$=546, 589 and 633 nm.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$&lt;n&gt;$</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B (K$^{-1}$)</td>
</tr>
<tr>
<td>546</td>
<td>1.6837</td>
<td>5.09x10$^{-4}$</td>
</tr>
<tr>
<td>589</td>
<td>1.6795</td>
<td>5.06x10$^{-4}$</td>
</tr>
<tr>
<td>633</td>
<td>1.6684</td>
<td>4.82x10$^{-4}$</td>
</tr>
</tbody>
</table>

Figure 17 depicts the temperature-dependent refractive indices of MLC-6241-000 and UCF-35 at $\lambda$ = 589 nm. Circles and squares are measured refractive indices of MLC-6241-000 and UCF-35, respectively. Solid lines are fitting results using the four-parameter model. The fitting parameters for the four-parameter model are listed in Table 12. Excellent agreements are achieved between the four-parameter model and experimental data.

Therefore, the four-parameter model fits very well with all the four LC materials we studied although their birefringence values span a wide range. It is an accurate model to describe the temperature effect on the refractive indices of liquid crystals.
Figure 17: Temperature-dependent refractive indices of UCF-35 and MLC-6241-000 at λ= 589 nm. Squares and circles are experimental data for refractive indices of UCF-35 and MLC-6241-000, respectively. Solid lines are fittings using the four-parameter model, Eqs. (3-51) and (3-52). Dashed lines are fittings using the three-parameter parabolic model, Eqs. (3-53) and (3-54). The fitting parameters for the two models are listed in Tables 12 and 15, respectively.
5.3.2 Validation of the Three-parameter parabolic Model

For a low $\Delta n$, high $T_c$ LC compound or mixture, the four-parameter model can be reduced to a three-parameter parabolic model. To validate the parabolic model, we chose two LC mixtures: MLC-6241-000 ($\Delta n \sim 0.085$) and UCF-35 ($\Delta n \sim 0.35$); their clearing temperatures are 100 and 95.3 °C, respectively. Figure 17 depicts the temperature-dependent refractive indices of MLC-6241-000 and UCF-35 at $\lambda = 589$ nm. Circles and squares are measured refractive indices of MLC-6241-000 and UCF-35, respectively. Solid lines are fitting results using the four-parameter model and dashed lines are fitting results using the three-parameter parabolic model. The fitting parameters for the three-parameter parabolic model are listed in Table 15. For MLC-6241-000, the fitting parameters ($A_e$, $B_e$, $C_e$) for $n_e$ are (1.6495, 2.00x10$^{-5}$, 9.25x10$^{-7}$) and ($A_o$, $B_o$, $C_o$) for $n_o$ are (1.6343, 7.50x10$^{-4}$, 7.21x10$^{-7}$), respectively. For UCF-35, the fitting parameters ($A_e$, $B_e$, $C_e$) for $n_e$ are (1.0367, -0.0069, 1.00x10$^{-5}$) and ($A_o$, $B_o$, $C_o$) for $n_o$ are (1.8276, 0.0019, 3.24x10$^{-6}$), respectively.

At room temperature, the birefringence of MLC-6241-000 and UCF-35 are around 0.085 and 0.35 at $\lambda = 589$ nm, respectively. In Fig. 17, the three-parameter parabolic model (dashed lines) fits the experimental data of the two materials very well and almost overlaps each other with the four-parameter model when the temperature is far from the clearing point. In the three-parameter model, we predict all the $A_{e,o}$, $B_{e,o}$ and
coefficients should be positive. From this viewpoint, the three-parameter parabolic model fits the experimental data of MLC-6241-000 better than that of UCF-35 because one of the fitting parameters $B_e$ for UCF-35 is negative although its value is relatively small. To explain this discrepancy, we need to review the assumption made during the derivation of Eqs. (3-53) and (3-54). The two assumptions made there are: 1) the LC birefringence is low, and 2) $T \ll T_c$. Under these conditions, the four-parameter model can be expanded into power series which leads to the four-parameter parabolic model. However, the birefringence of UCF-35 is quite high so that the power expansion is less accurate. Consequently, the fitting results for UCF-35 are less satisfactory. Thus, the three-parameter parabolic model is more suitable for the low birefringence LC materials while the operating temperature is far from the clearing temperature.

Table 15: Fitting parameters for the 3-parameter parabolic model, Eqs.(3-53) and (3-54). $\lambda=589$ nm. The LC mixtures studied are MLC-6241-000 and UCF-35.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$n_e$</th>
<th>$n_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_e$</td>
<td>$B_e(K^{-1})$</td>
</tr>
<tr>
<td>MLC-6241-000</td>
<td>1.6495</td>
<td>2.00x10^{-5}</td>
</tr>
<tr>
<td>UCF-35</td>
<td>1.0367</td>
<td>-0.0069</td>
</tr>
</tbody>
</table>
5.4 Summary

In chapter 5, the experimental data of liquid crystal refractive indices are used to validate the extended three-coefficient and two-coefficient Cauchy models, the four-parameter model, the three-parameter parabolic model, and the Vuks model. Liquid crystals with low birefringence (MLC-9200-000, MLC-9200-100, MLC-6241-000, MLC-6608, UCF-280), middle birefringence (5PCH, 5CB, E7, TL-216), and high birefringence (E44, UCF-35) are used to validate these physical models. The three-coefficient Cauchy model describes the wavelength effect on liquid crystal refractive indices very well, whereas the two-coefficient Cauchy model is only suitable for the low birefringence (\( \Delta n < 0.12 \)) liquid crystals. The four-parameter model describes the temperature effect on liquid crystal refractive indices very well, whereas the three-parameter parabolic model is only suitable for low birefringence liquid crystals with a high clearing point and the temperature considered is far below the clearing point at the same time. Vuks model which is very similar to Lorentz-Lorenz equation is proven to be self-consistent using our experimental data for the first time. Experiment agrees very well with theory.
CHAPTER 6: APPLICATIONS IN DISPLAY AND PHOTONIC DEVICES

Liquid crystals are widely used in display and photonic devices. Our work not only explains the essence of the physical phenomena for liquid crystals but also explores new display and photonic applications. The derived physical models show how the LC refractive indices change as a function of wavelength and temperature. It is important for optimizing the device designs of direct-view and projection displays. The temperature gradient models clearly the factors affecting the values of $dn_e/dT$ and $dn_o/dT$. The models tell us how to design a liquid crystal with high $dn_e/dT$ at room temperature. These high liquid crystals are useful for the thermally tunable liquid crystal photonic crystal fibers (LCPCFs) and the thermal soliton in nematic liquid crystals. We could extrapolate the LC refractive index data measured in the visible region to any infrared wavelength using the extended Cauchy model and the four-parameter model. Thus, the complete LC refractive index data in the infrared region could be achieved. It is important to know the LC property in the infrared region in which liquid crystals are also widely used. These models are also useful for finding the index-matched liquid crystals and photopolymers for polymer dispersed liquid crystal (PDLC) applications.

This chapter describes the following topics: high temperature-gradient refractive index liquid crystals, highly thermally tunable liquid crystal photonic crystal fibers, the
6.1 High Temperature-gradient Refractive Index Liquid Crystals

Based on the guidelines discussed in Section 3.6, we find that high birefringence, low clearing point and small $B$ coefficient help to enhance $dn_o/dT$ value at room temperature. We formulated two LC mixtures, UCF-1 and UCF-2, which exhibit a high temperature-gradient refractive index.

In order to obtain high $dn_o/dT$ at room temperature, we need to select liquid crystals with high birefringence, lower clearing temperature and a small $B$ coefficient. To formulate such specific mixtures, we used some laterally substituted isothiocyanato (NCS) tolanes. Due to the lateral fluoro or methyl substitution, these NCS tolanes exhibit a relatively low clearing temperature. The compounds containing the NCS polar group possesses a smaller B coefficient than the cyano (CN) compounds. The molecular structures and their corresponding phase transition temperatures (PTT) are listed in Table 16.

The phase transition temperatures of these LC compounds were measured by using a high sensitivity differential scanning calorimeter (DSC, TA Instrument Model Q-100) at 2 °C/min scanning rate. By changing the ratio of these single compounds, we prepared two mixtures, designated as UCF-1 and UCF-2. Their clearing temperatures are 29.7 °C and 32.3 °C, respectively, and melting point below -20 °C. The physical
properties of UCF-1 and UCF-2 were measured at room temperature (23°C) and results are listed in Table 17.

Table 16: Molecular structures and phase transition temperatures (PTT) of the compounds used for formulating mixtures. Here, Cr, N, S and I stand for crystalline, nematic, smectic, and isotropic phase, respectively.

<table>
<thead>
<tr>
<th>LC compounds</th>
<th>Structures</th>
<th>PTT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP3NCS</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;-NCS</td>
<td>Cr 3.0 N 41.3 I</td>
</tr>
<tr>
<td>PTP4NCS</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;-NCS</td>
<td>Cr 44.0 S&lt;sub&gt;K&lt;/sub&gt; 70.5 S&lt;sub&gt;E&lt;/sub&gt; 86.9 I</td>
</tr>
<tr>
<td>PTP(3F)4NCS</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;-NCS</td>
<td>Cr 38.6 I</td>
</tr>
<tr>
<td>PTP(3Me)4NCS</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;-NCS</td>
<td>Cr 42.3 I</td>
</tr>
</tbody>
</table>

Table 17: Physical properties of UCF-1 and UCF-2. Δn was measured at λ = 589 nm and T=23 °C.

<table>
<thead>
<tr>
<th>LC Materials</th>
<th>V&lt;sub&gt;th&lt;/sub&gt; (V&lt;sub&gt;rms&lt;/sub&gt;)</th>
<th>ε∥</th>
<th>ε⊥</th>
<th>Δε</th>
<th>K&lt;sub&gt;11&lt;/sub&gt; (pN)</th>
<th>K&lt;sub&gt;33&lt;/sub&gt; (pN)</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCF-1</td>
<td>1.01</td>
<td>13.6</td>
<td>5.2</td>
<td>8.4</td>
<td>4.66</td>
<td>11.4</td>
<td>0.2545</td>
</tr>
<tr>
<td>UCF-2</td>
<td>1.15</td>
<td>13.6</td>
<td>4.9</td>
<td>8.7</td>
<td>5.90</td>
<td>11.0</td>
<td>0.2755</td>
</tr>
</tbody>
</table>

We measured the refractive indices of our new mixtures using the Multi-wavelength Abbe refractometer and compared results with three commercial single
compounds: 5CB, 6CB, and 5PCH (cyano-chclohexane-phenyl). These LC mixtures are nematic at room temperature (T~22°C).

To demonstrate the high $\Delta n$ advantage, we intentionally designed the UCF-1 and UCF-2 to have similar clearing temperatures as 6CB and 5CB, respectively. Figure 18 depicts the temperature-dependent refractive indices of UCF-1 and 6CB at $\lambda=589$ nm. Red circles and black triangles represent experimental data for UCF-1 and 6CB, respectively, while solid lines are the fitting results using Eqs. (3-51) and (3-52). The fitting parameters $[A, B]$ and $[(\Delta n)_0, \beta]$ are listed in Table 18. The agreement between experiment and theory is pretty good.
Table 18: Fitting parameters for the average refractive index $<n>$ and birefringence ($\Delta n$) of the five LCs studied: UCF-1, 6CB, UCF-2, 5CB and 5PCH at $\lambda$=589 nm.

<table>
<thead>
<tr>
<th>LC Materials</th>
<th>$&lt;n&gt;$</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B (K$^{-1}$)</td>
</tr>
<tr>
<td>UCF-1</td>
<td>1.8112</td>
<td>5.08x10$^{-4}$</td>
</tr>
<tr>
<td>6CB</td>
<td>1.7491</td>
<td>5.47x10$^{-4}$</td>
</tr>
<tr>
<td>UCF-2</td>
<td>1.8100</td>
<td>4.90x10$^{-4}$</td>
</tr>
<tr>
<td>5CB</td>
<td>1.7674</td>
<td>5.79x10$^{-4}$</td>
</tr>
<tr>
<td>5PCH</td>
<td>1.6795</td>
<td>5.07x10$^{-4}$</td>
</tr>
</tbody>
</table>

From Figure 18, UCF-1 has a higher $n_e$, $n_o$ and $\Delta n$ than 6CB. At room temperature (T~295K), the birefringence of UCF-1 is $\Delta n$~0.25, as compared to ~0.15 for 6CB. As temperature increases, $n_e$ decreases while $n_o$ increases for both UCF-1 and 6CB except at a different rate. The clearing point for UCF-1 and 6CB is 302.7K and 301.1K, respectively. In the isotropic state, the refractive index of UCF-1 and 6CB decreases linearly with increasing temperature. From Figure 18, we find UCF-1 has a much larger $dn_o/dT$ than 6CB in the nematic range. We will compare the $dn_o/dT$ quantitatively for all the LC studied later.

Similarly, we prepared UCF-2 to match the clearing temperature of 5CB. The clearing point for UCF-2 and 5CB is 305.3K and 306.4 K, respectively. Figure 19 depicts the temperature-dependent refractive indices of UCF-2 and 5CB at $\lambda$=589 nm. Magenta circles and blue triangles represent experimental data for UCF-2 and 5CB, respectively, while solid lines are fitting results using Eqs. (3-51) and (3-52). The fitting parameters
$A$, $B$, $(\Delta n)_0$ and $\beta$ are also listed in Table 18. From Figure 19, UCF-2 has a higher $n_e$, $n_o$ and $\Delta n$ than 5CB.

Figure 19: Temperature-dependent refractive indices of UCF-2 and 5CB at $\lambda=589$ nm. Magenta circles and blue triangles are refractive indices of UCF-2 and 5CB, respectively, and solid lines are fitting results using Eqs. (3-51) and (3-52). The fitting parameters are listed in Table 18.

Figure 20 depicts the temperature-dependent average refractive index $\langle n \rangle$ for UCF-1, UCF-2, 6CB and 5CB at $\lambda=589$ nm. The circles represent the experimental data and solid lines are fitting results using Eq. (3-36). Indeed, $\langle n \rangle$ decreases linearly as the temperature increases. The fitting parameters $A$ and $B$ for these four materials are listed in Table 18.
Figure 20: Temperature-dependent average refractive index of UCF-1, UCF-2, 6CB and 5CB at \( \lambda = 589 \) nm. Circles represent experimental data and solid lines are fitting results using Eq. (3-36). The fitting parameters \( A \) and \( B \) for these four materials are listed in Table 18.

Figure 21 depicts the temperature-dependent \( \Delta n \) of UCF-1, UCF-2, 6CB and 5CB at \( \lambda = 589 \) nm. The circles are experimental data while solid lines are fitting results using Eq. (3-43). The fitting parameters \( (\Delta n)_0 \) and \( \beta \) are listed in Table 18.
Figure 21: Temperature-dependent birefringence of UCF-1, UCF-2, 6CB and 5CB at $\lambda = 589$ nm. Red, Magenta, black and blue circles represent experimental data while solid lines are fitting results using Eq. (3-43). The fitting parameters $(\Delta n)_0$ and $\beta$ are listed in Table 18.

Using the parameters listed in Table 18, we are able to calculate the $dn_e / dT$ and $dn_o / dT$ for UCF-1, UCF-2, 6CB, 5CB and 5PCH using Eqs. (3-57) and (3-58). Because $dn_e / dT$ is always negative, we plot $-dn_e / dT$ instead. Results are shown in Figure 22 where solid and dashed lines represent the calculated $dn_o / dT$ and $-dn_e / dT$ by using Eqs. (3-58) and (3-57) for these five LCs, respectively.
Figure 22: Temperature-dependent $dn_e/dT$ of UCF-1, UCF-2, 6CB, 5CB, and 5PCH at $\lambda=589$ nm. Red, magenta, black, blue and green solid lines represent the calculated $dn_e/dT$ curves for UCF-1, UCF-2, 6CB, 5CB, and 5PCH, respectively, while the dashed lines represent the calculated $-dn_o/dT$ curves. The parameters $B$, $(\Delta n)_0$ and $\beta$ used in the calculations are listed in Table 18.

From Figure 22, we find the $dn_e/dT$ (dashed lines) for both LCs remains negative throughout their nematic range. That means the extraordinary refractive index decreases as the temperature increases in the entire nematic range. However, $dn_o/dT$ changes sign at the cross-over temperature $T_o$. For practical applications, it is desirable to operate the LC device at room temperature (RT). Therefore, we should design a LC with cross-over temperature lower than 295K to assure a positive $dn_o/dT$ at RT. From Figure 14, the cross-over temperature ($T_o$) of UCF-1, UCF-2, 6CB, 5CB and 5PCH is $\sim$254K (or -19 °C), $\sim$255K (or -18 °C), $\sim$280.8K (or 7.8 °C), $\sim$282.9K (or 9.9 °C) and $\sim$315.9K (or...
42.9°C), respectively. Based on Eq. (3-58), low $T_c$ and high birefringence are two important factors for achieving a large $dn_o/dT$ at RT. The clearing point for UCF-1, UCF-2, 6CB, 5CB and 5PCH is 302.7K, 305.3K, 301.1K, 306.4K, and 326K, respectively. Thus, the $n_o$ of UCF-1, UCF-2, 6CB, and 5CB increases with increasing temperature when $T$ is greater than RT but less than $T_c$. For 5PCH, its cross-over temperature is higher than RT so that its $dn_o/dT$ remains negative when $T < T_o$. The cross-over temperature we obtained for 5PCH agrees very well with the experimental data reported by the Merck group. As the temperature approaches $T_c$, both $dn_c/dT$ and $dn_o/dT$ change dramatically as shown clearly in Figure 22.

From Fig. 14, the $dn_o/dT$ (in unit of K$^{-1}$) of UCF-1, UCF-2, 6CB, and 5CB at RT is 1.73x10$^{-3}$, 1.27x10$^{-3}$, 9.24x10$^{-4}$, and 4.60x10$^{-4}$, respectively. Due to the higher birefringence and a slightly lower clearing temperature, the $dn_o/dT$ of UCF-1 is ~4X higher than that of 5CB at RT. As $T$ approaches $T_c$, the $dn_o/dT$ of each LC increases by more than one order of magnitude than that in the nematic phase. However, in the vicinity of phase transition temperature, a small temperature fluctuation would cause a big change in $dn_o/dT$. Moreover, light scattering is present in the vicinity of phase transition temperature.

In summary, We have analyzed the factors affecting the $dn_o/dT$ of a LC material. High birefringence and low clearing temperature are the two most critical parameters. Based on these simple guidelines, we formulated two exemplary high birefringence and low clearing temperature LC mixtures, UCF-1 and UCF-2, using the laterally substituted isothiocyanato tolane compounds. The $dn_o/dT$ of UCF-1 is about
4X higher than that of 5CB at room temperature. Moreover, the melting temperature of UCF-1 and UCF-2 is below $-20 \, ^\circ C$, which is much lower than that of 5CB and 6CB. The novel liquid crystals explores the new photonic applications such as highly thermal tunable liquid crystal photonic crystal fibers, the thermal solitons in nematic liquid crystals, and so on.

### 6.2 Highly Thermal Tunable Liquid Crystal Photonic Crystal Fibers

Photonic crystal fibers (PCFs), also referred to as microstructured optical fibers, have a microstructured cross section of air holes running along the length of the fiber, which is usually made from silica. In recent years much attention has been focused on developing and designing photonic crystal fibers for various applications such as super-continuum generation, nonlinear signal processing in high-speed optical time domain multiplexing communication systems, high-power double-clad fiber lasers, air core fibers for high power laser delivery, etc.

However, these applications are all relying on fibers with static properties. For certain applications, it is desirable to dynamically alter the transmission properties of the fiber and, thereby, tune/trim them. For example, in applications involving dispersion, polarization or attenuation, the transmission properties can be changed while keeping the signal within the fiber. For this purpose, photonic crystal fibers are an interesting candidate, since the air holes give close access to the guiding light in the core and opens up for using liquids or liquid crystals infiltrated into the capillaries instead of air.$^{41}$ The optical properties of the liquids or liquid crystals are usually easier to modify than the
silica, and this, therefore, opens up a new application, e.g., tunable photonic crystal fiber based components.

Photonic crystal fibers can guide light using two very different principles. The first is modified total-internal reflection (MTIR), which relies on guiding in a high-index core surrounded by a low-index cladding materials. The second is guiding in a low-index core surrounded by a cladding arrangement of high-index rods. Light coupled into the core can be guided through anti-resonant reflection from the rods, which forms a sort of 2D Fabry-Perot activities surrounding the core. This is also referred to as the photonic bandgap effect if the rods are periodic, because when calculating the allowed optical modes in the periodic structure, gaps appear between bands of allowed modes. Within these gaps, a guided mode can exist when a low-index defect is created in the periodic structure.

The photonic bandgaps of a LC-filled PCF can be thermally tuned using nematic, smectic A, and cholesteric mesophases, and these phases yields different functionalities such as threshold switching or linear shifting of the bandgaps. In the latter case, thermal shifting the bandgaps can for example be achieved by utilizing the temperature dependence of the ordinary refractive index, $dn_0/dT$, of nematic LCs by resistive or optically induced heating. In this case, it is desirable to have a high tuning sensitivity around room temperature in order to decrease the power consumption and ease the device handling. Further, for applications involving for example dispersion trimming of short laser pulses with high peak power it is desirable to use single-mode PCFs having a very large mode area in order to have a low fraction of the field propagating in the LC.
In collaborating with a group from Denmark, we have demonstrated a highly tunable large-core single-mode photonic bandgap fiber, which has a core diameter of 25 \( \mu \)m, an effective mode area of 440 \( \mu \)m\(^2\) and a high tuning sensitivity near room temperature.\(^{20}\) This is achieved using UCF-1 and a three-rod core PCF.\(^{20}\)

In this experiment we used two meters of a so-called LMA25 PCF, where the core is surrounded by six rings of air holes arranged in a triangular lattice (Figure 23, inset). The hole diameter (d), inter hole distance (\( \Lambda \)), core size and outer diameter was 2.9\( \mu \)m, 11.2\( \mu \)m, 25\( \mu \)m and 470\( \mu \)m, respectively. The large mode-area is obtained using a three-rod core design\(^9\). The endlessly single mode property for index-guiding is retained by scaling the relative hole diameter to \( d/\Lambda = 0.26 \), which is slightly larger than the theoretical limit of 0.25. High leakage and bend loss was observed for \( \lambda < 1 \mu m \) due to the relatively small air holes.

First, the air holes were filled with the commercial available nematic LC E7 (Merck, Darmstadt, Germany) for 10mm of the length using capillary forces. The LC was heated to isotropic phase and cooled down again slowly to achieve a homogenous alignment. Polarized microscopy observations on a single silica capillary tube, with an inner diameter of 6\( \mu \)m, indicated that the LC was planar aligned, i.e., with the LC director aligned along the fiber axis, and, therefore, with the ordinary index (\( n_o \)) predominantly determining the spectral features of the fibre.

Figure 23 shows the transmission spectrum at temperatures between \( T = 40^\circ \)C and 55\( ^\circ \)C in steps of 5\( ^\circ \)C. The transmission spectrum was obtained by butt-coupling an endlessly single mode PCF with 10\( \mu \)m core diameter to both ends of the LMA25. White light from a halogen-tungsten white light source was coupled into one end and the
transmission spectrum were recorded by an optical spectrum analyser (ANDO AQ6317B) and normalized to the spectrum of an un-filled fibre.\textsuperscript{20}

Figure 23: Transmission spectrum for the three-rod core PCF, where the air holes has been filled for 10mm of the length with the nematic liquid crystal E7 (Merck, Darmstadt, Germany). Inset shows an optical micrograph of the PCF end facet. Hole diameter and inter hole distance is 2.9\textmu{}m and 11.2\textmu{}m, respectively.

The bandgap centered around \(\lambda=1300\text{nm}\) has a bandwidth of 345-410\text{nm}, which depends on temperature. As the temperature is increased, the center wavelength of the bandgap shifts toward longer wavelength due to a positive \(dn_e/dT\), which increases as the clearing temperature of E7 is approached (\(T_c=58^\circ\text{C}\)). At the same time, the bandwidth of the bandgap increases, which implies that the shorter and longer bandgap edge to experience a different shift, i.e., the long wavelength edge experiences a larger shift than the short wavelength edge. The tuning sensitivity at 52.5\textdegree{}C was measured at the long...
wavelength edge of the bandgap to 7nm/°C or 0.46% per °C when normalized to the center wavelength at the bandgap edge. The small transmission peak at 1650nm is a direct feature of the LC anisotropy, which causes a splitting in effective index of the TE$_{01}$ and the TM$_{01}$ cladding states supported by a LC infiltrated micro channel. The splitting is observed since the electric field of the TE$_{01}$ is solely in the transversal direction, while the TM$_{01}$ has a part of the electric field in the longitudinal direction. The TM$_{01}$ mode, therefore, experiences the extraordinary index of the LC and a gap in effective index is formed between the bands derived from the TE$_{01}$ and TM$_{01}$ cladding states.

Simulations using the refractive indices of E7 presented in a previous publication$^{19}$ confirmed the presence of a guided mode in this bandgap. The simulation were performed by solving the wave equation using a home-developed plane wave tool, expanding the vectorial magnetic field of the eigenmodes in plane waves and using a tensorial dielectric function as described by Meade$^{79,80}$ and Johnson$^{81}$. A supercell consisting of 8x8 elementary cells of the periodic cladding structure is used. Supercell convergence was enhanced by use of a coupling-reducing k-point$^{82}$

The insertion loss of the LC device is difficult to establish exactly due to Fabry-Perot effects between the two end-facets forming the butt coupling, which cause ripples in the transmission spectrum. We estimate the loss to be less than 0.5dB.

The tuning sensitivity at room temperature can be increased using an optimized LC mixture, which has high $dn_o/dT$ at room temperature. Therefore, another LCPCF sample was prepared using the same approach as with E7 but with the nematic LC mixture UCF-1.$^{50}$ Polarized microscopy observations on a single capillary tube with
UCF-1 also indicated a planar alignment of the LC director. Figure 24 shows the transmission spectrum for the filled PCF.

![Transmission Spectrum](image)

Figure 24: Temperature dependent transmission spectra for the three-rod core PCF, where the air holes have been filled for 10mm of the length with UCF-1.

The spectrum shows high transmission in two bandgaps, bandgap A centered around 1150 nm and bandgap B centered around 1700 nm. In between these two bandgaps, a weaker transmission peak appears. This feature is also a direct consequence of the LC anisotropy, which causes a splitting of the EH$_{11}$ mode of an LC-infiltrated microchannel from the HE$_{12}$ and HE$_{31}$ modes,\textsuperscript{83} so that a narrow bandgap opens up between the cladding states derived from these modes. As observed from figure 24, the width and transmission of the bandgap is reduced as the temperature of UCF-1 is increased, which is due to a decreasing anisotropy as the temperature approaches the...
clearing temperature of UCF-1 ($T_c=29.7^\circ$C), whereby the splitting of the EH$_{11}$, HE$_{12}$ and HE$_{31}$ cladding modes is diminished.

The refractive indices of UCF-1 are shown on figure 25 and were measured using a Multiwavelength Abbe Refractometer (Atago DR-M4), and fitted using the extended Cauchy equations. The extrapolated data at the infrared spectrum are used to do the simulations.

Figure 25: Wavelength- and temperature-dependent refractive indices $n_e$ and $n_o$ of UCF-1 at $T=25^\circ$C and $27.5^\circ$C. Circles and rectangles are measured refractive indices at $\lambda=450$, 486, 546, 589, 633, and 656 nm and at $T=25^\circ$C and $27.5^\circ$C, respectively. Solid and dashed curves are fitting curves using the extended Cauchy equation, Eqs. (2-7) and (2-8). The fitting curves are extrapolated to the infrared region based on the experimental data measured in the visible spectral region.
Figure 26 shows a comparison between the measured normalized transmission spectrum of bandgap B and simulation of two-times the coupling loss between the index-guided mode (unfilled PCF) and the bandgap-guided mode (LC filled PCF) evaluated using overlap integrals and the refractive indices of UCF-1 shown on figure 25. Insets show simulated mode fields of the index-guided mode in an unfilled PCF (TIR mode), a PBG guided mode at the center and at the short wavelength edge of the bandgap.

Figure 26: Transmission spectrum of the UCF-1 filled PCF (solid line) and simulated coupling loss (dotted line) from the index-guiding to the bandgap-guiding part of the PCF. Insets show an index-guided mode and PBG guided modes at the bandgap center and edge.
The simulated coupling loss agrees well with the shape of the PBG spectrum, and it is, therefore, concluded that coupling loss (<0.5dB) is the dominant loss mechanism, as was also found by Steinvurzel et al.\textsuperscript{84} The deviation at $\lambda>1.65\mu m$ is caused by intensity fluctuations of the halogen-tungsten white light source. In the center of Bandgap B, simulation showed that only 0.4-0.5% of the field energy was propagating in the LC, while simulation on a LC infiltrated single-rod core PCF with $d=3\mu m$ and $\Lambda=7\mu m$\textsuperscript{7} indicated that approximately 4-5% of the field was propagating in the LC. This indicates that the interaction of field and LC can be reduced one order of magnitude by using a three-rod core design and reducing the relative hole size, while retaining high spectral tuning sensitivity.

The spectral tuning sensitivity of the UCF-1 infiltrated PCF at 28°C was measured at the long wavelength edge of bandgap A to 27nm/°C or 2.1% when normalized. The tuning sensitivity at room temperature using UCF-1 is, therefore, approximately 4.6 times higher than when using E7 above 50°C, which is directly related to a higher temperature gradient of UCF-1 at room temperature compared to E7 as shown in figure 27. The temperature gradient at $\lambda=589$ nm was calculated using a four-parameter model\textsuperscript{17} for describing the temperature effect on the LC refractive indices. The four parameters were gained by fitting the temperature dependent LC refractive indices measured at temperature from 15 to 55 °C with a 5 °C interval and at $\lambda=589$ nm.
Figure 27: $dn_o/dT$ and $-dn_e/dT$ for E7 and UCF-1 calculated at $\lambda=589$nm.

In summary, a highly tunable single mode photonic bandgap fiber device has been demonstrated, which utilizes a three-rod core PCF and a specially prepared liquid crystal mixture (UCF-1) with high temperature gradient refractive index at room temperature in order to obtain a large mode area and high tuning sensitivity. The guided mode has an effective area of 440 $\mu$m$^2$ with an insertion loss of less than 0.5dB. The loss is mainly attributed to coupling losses between the index-guided section and the bandgap-guided section. The thermal tuning sensitivity of the spectral position of the bandgap was measured to be 27 nm/°C around room temperature, which is 4.6 times higher than that using the commercial E7 LC mixture operated at a temperature above 50 °C.
6.3 Thermal Solitons in Nematic Liquid Crystals

Soliton is a wave that is defined by some rules: 1) a travelling wave, 2) carrying an energy that is finite and localized, 3) stable, 4) display elastic behavior during collision, and 5) as the beam carries on more energy than the solitary wave should do, it splits into several solitons. The name soliton comes from this particle-like behavior. A spatial optical soliton is an electromagnetic wave with its energy localized in space. The 2D+1 notation refers to the symmetry; the energy is confined in a 2D transverse plane and propagates in the third direction. To excite a soliton would require a nonlinear response from the material.

In 2001, Warenghem reported the first “thermal soliton” observed in dye-doped nematic liquid crystals confined in a capillary. For a range of input power, the laser beam is no longer diverging nor focusing and it propagates straightly, over a long distance compared to the Rayleigh range of the initial beam. The transverse profile of these beams is studied and found to be constant. They also conducted the collision experiments and found that the behavior of the thermal soliton is consistent with the required elastic collision.

The nonlinear mechanism responsible for the thermal soliton is the thermal indexing. The 5CB LC used has a positive temperature gradient of ordinary refractive index. The role of the positive temperature gradient is to enhance the focusing property. In their experiment, they doped a few percent of dye molecules into 5CB to increase the temperature more quickly since the temperature gradient of 5CB in the room temperature
is not large enough to trigger the thermal soliton. Our high temperature-gradient LC mixtures UCF-1 and UCF-2 would be particularly desirable for enhancing the thermal soliton properties.

6.4 Infrared Refractive Indices of Liquid Crystals

Liquid crystals (LCs) possess a relatively large birefringence ($\Delta n = n_e - n_o$) in the infrared (IR) region $^{60-71}$ and have been used extensively for dynamic scene projectors, $^{93}$ laser beam steering, $^{94,95}$ tunable bandgap photonic crystal fibers, $^{16-20}$ and millimeter-wave electronic phase shifters. $^{96,97}$ Simple methods, such as voltage- or wavelength-dependent phase retardation methods have been developed for measuring the IR birefringence of LCs. $^{52}$ However, only few methods, e.g., the Talbot-Rayleigh refractometer and wedged cell refractometer, are available for measuring the individual extraordinary ($n_e$) and ordinary ($n_o$) refractive indices in the IR region. By contrast, in the visible spectral region, the LC refractive indices can be measured quite easily by the commercial Abbe refractometer. Its accuracy is up to the fourth decimal point ($\pm 0.0002$). However, the usable range of Abbe refractometer is limited to the visible and near IR spectra because of the faint refractive light from the main prism and the transparency of the prism.

The major absorption of a LC compound occurs in two spectral regions: ultraviolet (UV) and IR. $^{12}$ The $\sigma \rightarrow \sigma^*$ electronic transition take place in the vacuum UV (100-180 nm) region whereas the $\pi \rightarrow \pi^*$ electronic transition occur in the UV (180-400 nm)
nm) region. If a LC molecule has a longer conjugation, its electronic transition wavelength would extend to a longer UV wavelength. In the near IR region, some overtone molecular vibration bands appear. The fundamental molecular vibration bands, such as CH, CN, and C=C, occur in the mid and long IR regions. Typically, the oscillator strength of these vibration bands is about two orders of magnitude weaker than that of the electronic transitions. Thus, the resonant enhancement of these bands to the LC birefringence is localized. Thus, it is reasonable for us to extrapolate the data at the visible light region to the infrared region.21,25

Next, we will show how to link the visible and IR refractive indices by the extended Cauchy equations and validate the method. Then, we will show how to get the refractive indices in the whole nematic phase based on the four-parameter model by using the extrapolated $n_e$ and $n_o$. First, we measured the refractive indices of E7 LC mixture at six visible wavelengths using an Abbe refractometer and two IR wavelengths ($\lambda=1.55$ and 10.6 $\mu$m) using a wedged cell refractometer. We fit the visible refractive index data with the extended Cauchy equation. Once the three Cauchy coefficients are obtained, we use the extended Cauchy equations to extrapolate the refractive indices to the IR wavelengths. These extrapolated data almost strike through the experimental results.

The refractive indices of E7 were measured at $\lambda = 450, 486, 546, 589, 633,$ and 656 nm in the temperature range from 15 to 50 °C at 5 °C intervals and at $\lambda=1.55$ and 10.6 $\mu$m. The measured data are listed in Tables 6 and 10. Figure 28 depicts the temperature-dependent refractive indices of E7 at $\lambda=589$ nm. Open squares, circles, and upward-triangles represent $n_e$, $n_o$, and average refractive index $\langle n \rangle$ for E7, respectively. The solid curves are fitting results using Eqs. (3-51) and (3-52). The fitting parameters
\[ [A, B, (\Delta n)_o, \beta] \] are [1.7546, 5.36 \times 10^{-4}, 0.3768, 0.2391]. The solid straight lines are fitting results using Eq. (3-36). The fitting parameters \([A, B]\) are [1.7546, 5.36 \times 10^{-4}]. Clearly, the average refractive index decreases linearly as the temperature increases.

Figure 28: Temperature-dependent refractive indices of E7 at \(\lambda=589\) nm. The open squares and circles represent the \(n_e\) and \(n_o\) measured at \(\lambda=589\) nm using the multi-wavelength Abbe refractometer. The open upward triangles are average refractive index \langle n \rangle calculated by the experimental data. The solid curves are the fittings using the four-parameter model [Eqs. (3-51) and (3-52)]. The fitting parameters \([A, B, (\Delta n)_o, \beta]\) are [1.7546, 5.36 \times 10^{-4}, 0.3768, 0.2391]. The solid straight line is the fitting using Eq. (3-36). The fitting parameters \([A, B]\) are [1.7546, 5.36 \times 10^{-4}].

Next, we use the extended Cauchy model to fit the refractive indices \(n_e\) and \(n_o\), measured at the abovementioned visible wavelengths and temperature range. Then we get the six Cauchy coefficients \([A_e, B_e, C_e]\) and \([A_o, B_o, C_o]\) for \(n_e\) and \(n_o\), respectively.
In Table 19, we show the fitting parameters \([ A_e, B_e, C_e ]\) and \([ A_o, B_o, C_o ]\) for the extended Cauchy model [(Eqs. (2-7) and (2-8))] in the temperature range from 15 to 50 °C by using the experimental data measured in the visible spectrum.

Table 19: Fitting parameters for the extended Cauchy model [(Eqs. (2-7) and (2-8))] at different temperatures (in °C) by using the experimental data measured at visible wavelengths (in \(\mu m\)).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
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<th>(n_o)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A_e)</td>
<td>(B_e (\mu m^2))</td>
</tr>
<tr>
<td>15</td>
<td>1.7055</td>
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<td>45</td>
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<td>0.0083</td>
</tr>
<tr>
<td>50</td>
<td>1.6395</td>
<td>0.0095</td>
</tr>
</tbody>
</table>

Figure 29 depicts the wavelength-dependent refractive indices of E7 at \(T = 25\) °C. The open squares and circles represent the \(n_e\) and \(n_o\) of E7 in the visible region while the downward and upward triangles stand for the measured data at \(\lambda = 1.55\) and 10.6 \(\mu m\), respectively. The solid curves are the fittings to the experimental \(n_e\) and \(n_o\) data in the
visible spectrum by using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 19. In figure 29, we extrapolate the extended Cauchy model to the near and far infrared spectra. The extrapolated lines almost strike through the center of the experimental data measured at $\lambda=1.55$ and 10.6 $\mu$m. The largest difference between the extrapolated and experimental data is only 0.4%. Considering the experimental error in the wedged cell refractometer method, the agreement between experiment and theory is very good. Figure 21 also indicates that the refractive indices will saturate in the far infrared region. The extended Cauchy model predicts that $n_e$ and $n_o$ would saturate to $A_e$ and $A_o$ in the long IR wavelength, respectively. For E7, the measured $(n_e, n_o)$ at $\lambda=10.6$ $\mu$m are (1.6914, 1.4936) while the fitting parameters $(A_e, A_o)$ are (1.6933, 1.4994). The difference is less than 0.38%.59

Temperature-dependent refractive indices are important for practical applications, such as projection displays and thermal-induced photonic band-gap tuning. It is highly desirable to predict the refractive indices at the designated operating temperature of a LC device, especially in the IR region. Here, we extrapolate the IR refractive indices using the extended Cauchy model and compare with those measured directly at $\lambda=1.55$ and 10.6 $\mu$m at T=15, 20, 25, 30, 35, 40, 45, and 50 °C. Then by using the four-parameter model [Eqs. (3-51) and (3-52)] to fit the extrapolated data at $\lambda=1.55$ and 10.6 $\mu$m, we obtain the refractive indices $n_e$ and $n_o$ in the whole nematic phase range at these two wavelengths.
Figure 29: Wavelength-dependent refractive indices of E7 at $T = 25 \, ^\circ C$. The open squares and circles are the $n_e$ and $n_o$ of E7 measured in the visible spectrum. The solid curves are the fittings to the experimental data using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 19. The downward and upward triangles are $n_e$ and $n_o$ of E7 measured at $T = 25 \, ^\circ C$ and $\lambda = 1.55$ and 10.6 $\mu$m, respectively.

Figure 30 depicts the temperature-dependent refractive indices of E7 at $\lambda = 1.55$ $\mu$m. The open circles are the $n_e$ and $n_o$ extrapolated from the extended Cauchy model. The open triangles are the average refractive index $\langle n \rangle$ calculated from the extrapolated $n_e$ and $n_o$. The solid curves are the fittings using the four-parameter model [Eqs. (3-51) and (3-52)]. The solid straight line is the fitting using Eq. (3-36). The fitting parameters are listed in Table 20. The filled circles are the refractive indices measured by the wedged LC cell refractometric method. The filled triangles are the average refractive index $\langle n \rangle$. 

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calculated from the experimental data. In Figure 30, excellent agreement among the extended Cauchy model, four-parameter model, and measured experimental data is found. The difference between the predicted values and the experimental data is less than 0.38%. The difference may be caused partly by the measurement error and by the local molecular overtone vibration bands. In Figure 30, the average refractive index $\langle n \rangle$ decreases linearly as the temperature increases. In the isotropic phase range, $n_e$ equals to $n_o$ and the anisotropy vanishes. The refractive index in the isotropic phase also decreases linearly as the temperature increases.
Figure 30: Temperature-dependent refractive indices of E7 at $\lambda=1.55$ $\mu$m. The filled circles are the refractive indices $n_e$ and $n_o$ measured by the wedged LC cell method. The filled-triangles are the average refractive index $<n>$ calculated by the experimental data. The open circles are the $n_e$ and $n_o$ extrapolated from the experimental data measured at visible spectrum using the extended Cauchy model. The open triangles are average refractive index $<n>$ calculated by the extrapolated $n_e$ and $n_o$. The solid curves are the fittings using Eqs. (3-51) and (3-52). The solid straight line is the fitting using Eq. (3-36). The fitting parameters are listed in Table 20.
Table 20: Fitting parameters for the average refractive index \( \langle n \rangle \) and birefringence \( (\Delta n) \) of E7 at \( \lambda = 1.55 \) and 10.6 \( \mu \)m calculated by the extrapolated refractive indices from the visible spectrum.

<table>
<thead>
<tr>
<th>( \lambda ) (( \mu )m)</th>
<th>( \langle n \rangle )</th>
<th>( \Delta n )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B (K(^{-1}))</td>
</tr>
<tr>
<td>1.55</td>
<td>1.7230</td>
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</tr>
<tr>
<td>10.6</td>
<td>1.7201</td>
<td>5.25x10(^{-4})</td>
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</tbody>
</table>

Figure 31 depicts the temperature-dependent refractive indices of E7 at \( \lambda = 10.6 \) \( \mu \)m. The open circles represent the extrapolated \( n_e \) and \( n_o \) from the experimental data measured at visible wavelengths using the extended Cauchy model. The open triangles are the average refractive index \( \langle n \rangle \) calculated by the extrapolated \( n_e \) and \( n_o \). The solid curves are the fittings using the four-parameter model [Eqs. (3-51) and (3-52)]. The solid straight line is the fitting using Eq. (3-36). The fitting parameters are listed in Table 20. The filled circles are the refractive indices \( n_e \) and \( n_o \) measured by the wedged cell refractometer method. The filled triangles are the average refractive index \( \langle n \rangle \) calculated by the experimental data. In figure 31, excellent agreement among the extended Cauchy model, four-parameter model, and experimental data is also found. The difference between the theoretical values and the experimental data is less than 0.4%. The difference may result from the local molecular vibrations. In the low IR region, several molecular vibration bands exist. Because of relatively weak oscillator strength, their contribution to
the refractive indices is localized. In figure 31, the average refractive index $\langle n \rangle$ decreases linearly as the temperature increases.

![Figure 31: Temperature-dependent refractive indices of E7 at $\lambda=10.6 \, \mu\text{m}$. The filled circles are the refractive indices $n_e$ and $n_o$ measured by the wedged LC cell refractometer method. The filled-triangles are the average refractive index $\langle n \rangle$ calculated by the experimental data. The open circles represent the $n_e$ and $n_o$ extrapolated from the experimental data measured at visible spectrum using the extended Cauchy model. The open triangles are the average refractive index $\langle n \rangle$ calculated by the extrapolated $n_e$ and $n_o$. The solid curves are the fittings using Eqs. (3-51) and (3-52). The solid straight line is the fitting using Eq. (3-36). The fitting parameters are listed in Table 20.](image)

Overall, the difference between the predicted model values and experimental data measured by the wedged cell refractometer method is less than 0.4%. Taking into account the measurement errors and the effects of local molecular vibration bands, such a small
difference is acceptable. That means the extrapolated IR refractive indices from those measured by the Abbe refractometer (visible wavelengths) and those measured directly from the wedged cell refractometer at discrete IR laser wavelengths are consistent. The advantages of using Abbe refractometer are twofold: it is easy to use and less time consuming. As we discussed before, the oscillator strength of these vibration bands is about two orders of magnitude weaker than that of the electronic transitions. The resonant enhancement of these bands to the LC refractive indices and birefringence are localized. Thus, we can extrapolate the visible spectral data to the refractive indices at the non-resonant IR wavelengths by the extended Cauchy equation. Further, basing on the extrapolated data, we can predict the refractive indices at these IR wavelengths in the whole LC nematic range by the four-parameter model.\textsuperscript{59}

In summary, we have measured the refractive indices of E7 in the visible, near and far IR spectral regions. In the visible region, a multi-wavelength Abbe refractometer was proven to be powerful and accurate. In the near IR (\(\lambda=1.55\ \mu\text{m}\)) and long IR (\(\lambda=10.6\ \mu\text{m}\)) regions, the LC refractive indices can be measured using a wedged cell refractometer method. These data can be fitted smoothly by the extended Cauchy model.
6.5 Refractive Index Matching between Liquid Crystal and Photopolymers for Polymer Dispersed Liquid Crystal (PDLC) Application

6.5.1 Introduction

Polymer-dispersed liquid crystal (PDLC) and polymer-stabilized liquid crystal (PSLC) are useful for displays\textsuperscript{1,98-100}, tunable wavelength filters\textsuperscript{101-103}, tunable liquid crystal lenses,\textsuperscript{104,105} and polarization independent phase modulators\textsuperscript{106}. In a PDLC, the refractive index difference between the LC droplets and polymer matrix plays an important role in determining the voltage-off and voltage-on state transmittance. In a normal-mode PDLC, the droplet size is controlled at \( \sim 1 \text{ \mu m} \), which is comparable with the visible light wavelength. In the voltage-off state, the droplets are randomly oriented. The index mismatch between the LC (whose average refractive index is given by: \( \langle n \rangle = (n_e + 2n_o) / 3 \)) and polymer matrix (\( n_p \)) affects the light scattering capability. For a given droplet size, the larger the index mismatch, the higher the light scattering. Conversely, in the voltage-on state the LC directors inside the droplets are reoriented along the electric field direction so that the refractive index becomes \( n_o \); the ordinary refractive index. If \( n_o \sim n_p \), then the PDLC becomes isotropic and will have an excellent transmittance. Therefore, the preferred LC material for PDLC is not only high birefringence (\( \Delta n = n_e - n_o \)) but also good index match between \( n_o \) and \( n_p \). In a PSLC system, polymer networks help to improve response time\textsuperscript{107}. A good index match would reduce light scattering.
In this chapter, we compare the refractive index of cured polymers with liquid crystals at different wavelengths and temperatures. The fabrication method of the thin cured polymer films is briefly described. The refractive index of the cured polymer films (NOA65 and NOA81) and six nematic liquid crystals (BL038, BL006, BL003, E48, E44, and E7) were measured using a multi-wavelength Abbe refractometer. We compare the refractive index between NOA 65 and these six commercial liquid crystals, and NOA81 with two UCF high birefringence mixtures: UCF-1 and UCF-2. Then, we fabricate some PDLC cells using the four selected index-matched LC mixtures in the NOA65 polymer system and characterize their electro-optic properties at $\lambda=633$ nm. Finally, we obtain good correlation between material and device performances.

6.5.2 Refractive Index Measurements for Photopolymers and Liquid Crystals

NOA65 (Norland Optical Adhesive) is a favorite photocurable polymer because its refractive index ($n_p \sim 1.52$) is close to the $n_o$ of many commercial LC mixtures. On the other hand, NOA81 has a higher refractive index ($n_p \sim 1.56$), which is close to the $n_o$ of our UCF high birefringence LC mixtures. In this study, we compare the refractive indices of NOA65 with six Merck LC mixtures, and NOA81 with two UCF high birefringence LC mixtures using a multiwavelength Abbe refractometer (Atago DR-M4). Before UV curing, NOA65 and NOA81 are clear and colorless liquids. The measurement of the monomers is fairly simple. However, in a practical device, such as a PDLC, all the
monomers are cured to form a polymer matrix. Therefore, it is more meaningful to measure the refractive index of the cured polymers than the monomers.

In order to fabricate a polymer film, we infiltrated the monomers into an empty cell with a 1-mm gap using capillary flow. The cells were placed on a hot plate with a constant temperature (T~50 °C). Then, we illuminated the cell with a uniform UV light (I =14 mW/cm²) for 40 minutes because of the large cell gap. We then peeled off the glass substrates and removed the thick polymer film under a high temperature (T~120 °C). The film was kept in a stove with a constant temperature of 50 °C for 12 hours to age completely. The cured polymer film of NOA65 is quite flexible, while the cured NOA81 is a little hard. In order to get an accurate measurement, we cut the films into rectangular parallelepipeds of the following dimensions: 15-mm long, 9-mm wide, and 1-mm thick. The bottom surface of the samples was polished so that it made contact with the main prism surface of the Abbe refractometer completely. First, we put a small drop of contact liquid (monobromonaphthalene) on the main prism, then put the sample on and ensured the contact liquid spread evenly between the sample and the main prism. It is important to get rid of any dusts and bubbles between the solid sample and the main prism. A lighting glass was used to compensate for the weak light because the samples are thin. Similarly, we spread a small amount of the contact liquid on the top surface of the sample and put the lighting glass on top of the contact liquid. The thin contact liquid should spread evenly between the sample and the lighting glass. Now the contact liquid is sandwiched as films between the main prism and the sample, and between the sample and the lighting glass. The incident light entered the sample slightly aslant from the upside.
Figure 32 shows the experimental setup for measuring the cured polymer films. By moving the lighting glass to the front and rear, pressing the lighting glass to the sample by fingers, and adjusting the height and angle of the light guide, we found a clear and correct boundary line. This is the sign for the accurate measurements using the Abbe refractometer. We measured the refractive indices of LCs and polymers at six wavelengths: 450, 486, 546, 589, 633, and 656 nm. By connecting a constant circulating temperature bath (Atago 60-C3) with the Abbe refractometer, we measured the temperature-dependent refractive index of the samples from 15 to 55 °C at 5 °C intervals.

Figure 32: The experimental setup for measuring the refractive index of cured polymer films: NOA65 and NOA81.
Figure 33 shows the wavelength- and temperature-dependent refractive index of the cured NOA65 polymer. The squares, circles, upward-triangles, downward-triangles, diamonds, and pentagons represent the measured refractive index of NOA65 at $\lambda=450, 486, 546, 589, 633, \text{ and } 656$ nm, respectively. The measured refractive index data of NOA65 are listed in Table 21. In Figure 33, we find the refractive index of NOA65 decreases linearly as temperature increases at a given wavelength. The solid lines are fittings using Eq. (3-36). The fitting values of $A$ and $B$ are listed in Table 22. This linear decrease with increasing temperature is due to the isotropic nature of NOA65. As the temperature increases, its density decreases linearly causing a decrease in the refractive index.
Figure 33: Wavelength- and temperature-dependent refractive index of cured NOA65. The squares, circles, upward-triangles, downward-triangles, diamonds, and pentagons represent the measured refractive index of NOA65 at $\lambda=450$, 486, 546, 589, 633 and 656 nm, respectively. Solid lines are fittings using Eq. (3-36) and the fitting parameters are listed in Table 22.
Table 21: The measured refractive index of cured NOA65 film at \(\lambda=450, 486, 546, 589, 633,\) and \(656\) nm at different temperatures.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(\lambda) (nm)</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tr>
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</table>

Table 22: The fitting parameters for the refractive index [Eq. (3-36)] of NOA65 and NOA81 at \(\lambda=450, 486, 546, 589, 633\) and \(656\)nm.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
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<th>NOA81</th>
<th></th>
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</thead>
<tbody>
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<td></td>
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<td>1.74\times10^{-4}</td>
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</tr>
</tbody>
</table>

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Figure 34 shows a similar plot for NOA81. The squares, circles, upward-triangles, downward-triangles, diamonds, and pentagons represent the measured refractive index of NOA81 at $\lambda=450, 486, 546, 589, 633,$ and 656 nm, respectively. The measured refractive index data of NOA81 are listed in Table 23. Similarly to NOA65, the refractive index of NOA81 decreases linearly as the temperature increases. The solid lines in Figure 34 are fittings using Eq. (3-36) and the fitting parameters are listed in Table 22. We also measured the wavelength- and temperature-dependent refractive index of NOA65 and NOA81 in the monomer state. After UV curing, the refractive index of the cured polymers increases 1.7% and 2.2% for NOA65 and NOA81, respectively. This slight refractive index increase originates from the increased density of the polymer after cross-linking.

Table 23: The measured refractive index of cured NOA81 film at $\lambda=450, 486, 546, 589, 633,$ and 656 nm at different temperatures.

<table>
<thead>
<tr>
<th>T (°C )</th>
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<th>546</th>
<th>589</th>
<th>633</th>
<th>656</th>
</tr>
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<tr>
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<td>1.5621</td>
</tr>
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<tr>
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</tr>
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<td>1.5583</td>
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</table>
Figure 34: Wavelength- and temperature-dependent refractive index of cured NOA81. The squares, circles, upward-triangles, downward-triangles, diamonds, and pentagons represent the measured refractive index of NOA81 at $\lambda$ = 450, 486, 546, 589, 633 and 656 nm, respectively. Solid lines are fittings using Eq. (3-36) and the fitting parameters are listed in Table 22.

For a normal-mode PDLC, the light scattering in the voltage-off state depends on the LC birefringence; the higher the birefringence, the higher the scattering efficiency. In the voltage-on state, the transmittance depends on the refractive index match between the LC ($n_o$) and the polymer matrix ($n_p$). If $n_o \sim n_p$, then the on-state will be highly transparent. After having measured the $n_p$ of NOA65, we selected two commercial high birefringence LC series with their $n_o$ close to $n_p$. The two LC series are BL-series (BL038, BL006, and BL003) and E-series (E48, E44, and E7). To measure the refractive indices, we aligned the LCs perpendicular to the main and secondary prism surfaces of...
the Abbe refractometer by coating these two surfaces with a surfactant comprising of 0.294 wt % hexadecyletri-methyle-ammonium bromide (HMAB) in methanol solution. The measured extraordinary \((n_e)\) and ordinary \((n_o)\) refractive indices of E44, E7, E48, BL038, BL006, and BL003 are listed in Tables 5, 6, 24, 25, 26 and 27 respectively. From these data, we find that \(n_e\) always decreases as temperature increases, whereas \(n_o\) declines modestly first and then increases after the temperature passes the crossover temperature\(^{50}\). The average refractive index \(\langle n \rangle\) (which is defined as \((n_e + 2n_o)/3\)) also decreases linearly as temperature increases\(^ {49}\).

Table 24: The measured refractive indices \((n_e\) and \(n_o)\) of E48 at \(\lambda = 450, 486, 546, 589, 633,\) and 656 nm at different temperatures.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>450</th>
<th>486</th>
<th>546</th>
<th>589</th>
<th>633</th>
<th>656</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T) (°C)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>15</td>
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<td>1.5399</td>
<td>1.7969</td>
<td>1.5366</td>
<td>1.7715</td>
<td>1.5282</td>
</tr>
<tr>
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<td>1.5391</td>
<td>1.7912</td>
<td>1.5360</td>
<td>1.7660</td>
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</tr>
<tr>
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<td>1.5384</td>
<td>1.7850</td>
<td>1.5353</td>
<td>1.7601</td>
<td>1.5268</td>
</tr>
<tr>
<td>30</td>
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<td>1.5403</td>
<td>1.7782</td>
<td>1.5342</td>
<td>1.7542</td>
<td>1.5261</td>
</tr>
<tr>
<td>35</td>
<td>1.7942</td>
<td>1.5403</td>
<td>1.7720</td>
<td>1.5345</td>
<td>1.7478</td>
<td>1.5255</td>
</tr>
<tr>
<td>40</td>
<td>1.7869</td>
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<td>1.7649</td>
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<td>1.7411</td>
<td>1.5252</td>
</tr>
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<td>45</td>
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<td>1.5339</td>
<td>1.7263</td>
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</tr>
<tr>
<td>55</td>
<td>1.7608</td>
<td>1.5392</td>
<td>1.7399</td>
<td>1.5343</td>
<td>1.7176</td>
<td>1.5252</td>
</tr>
</tbody>
</table>
Table 25: The measured refractive indices \((n_e \text{ and } n_o)\) of BL038 at \(\lambda=450, 486, 546, 589, 633,\) and 656 nm at different temperature.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>450</th>
<th>486</th>
<th>546</th>
<th>589</th>
<th>633</th>
<th>656</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T) (°C)</td>
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<td></td>
</tr>
<tr>
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<tr>
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<td>1.8142</td>
<td>1.5311</td>
</tr>
<tr>
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<td>1.5469</td>
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<td>1.5396</td>
<td>1.8086</td>
<td>1.5305</td>
</tr>
<tr>
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<td>1.8611</td>
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<td>1.5385</td>
<td>1.8029</td>
<td>1.5299</td>
</tr>
<tr>
<td>35</td>
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<td>1.8271</td>
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<td>1.7971</td>
<td>1.5291</td>
</tr>
<tr>
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<td>1.5447</td>
<td>1.8206</td>
<td>1.5375</td>
<td>1.7907</td>
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</tr>
<tr>
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<td>1.8066</td>
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<td>1.5363</td>
<td>1.7709</td>
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</tr>
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</table>

Table 26: The measured refractive indices \((n_e \text{ and } n_o)\) of BL006 at \(\lambda=450, 486, 546, 589, 633,\) and 656 nm at different temperature.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>450</th>
<th>486</th>
<th>546</th>
<th>589</th>
<th>633</th>
<th>656</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T) (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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</tr>
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Table 27: The measured refractive indices ($n_e$ and $n_o$) of BL003 at $\lambda$=450, 486, 546, 589, 633, and 656 nm at different temperature.

<table>
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<th>T (°C)</th>
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<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_o$</th>
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<th>$n_o$</th>
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<td>1.8374</td>
<td>1.5408</td>
<td>1.8082</td>
<td>1.5324</td>
<td>1.7943</td>
<td>1.5279</td>
<td>1.7838</td>
<td>1.5246</td>
<td>1.7793</td>
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</tr>
<tr>
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<td>1.5403</td>
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<td>1.5314</td>
<td>1.7891</td>
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<td>1.7790</td>
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<td>1.7742</td>
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<tr>
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<td>1.5306</td>
<td>1.7837</td>
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<td>1.7736</td>
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<td>1.5216</td>
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<td>1.8199</td>
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<td>1.7916</td>
<td>1.5302</td>
<td>1.7780</td>
<td>1.5254</td>
<td>1.7682</td>
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<td>1.7636</td>
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</tr>
<tr>
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<td>1.5379</td>
<td>1.7857</td>
<td>1.5293</td>
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<td>1.5246</td>
<td>1.7625</td>
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<tr>
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<td>1.7661</td>
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<td>1.7564</td>
<td>1.5203</td>
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<td>1.8001</td>
<td>1.5369</td>
<td>1.7728</td>
<td>1.5279</td>
<td>1.7598</td>
<td>1.5234</td>
<td>1.7501</td>
<td>1.5197</td>
<td>1.7458</td>
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<tr>
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<td>1.5444</td>
<td>1.7931</td>
<td>1.5366</td>
<td>1.7662</td>
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<td>1.7438</td>
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<td>1.5190</td>
<td>1.7327</td>
<td>1.5176</td>
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</table>

6.5.3 Refractive Index Comparison

The wavelength-dependent refractive index of the UV-cured polymers can be described by the extended Cauchy equation, Eqs. (2-7) and (2-8). NOA81 ($n_p \sim 1.56$) has a higher refractive index than NOA65 ($n_p \sim 1.52$). For a linearly conjugated LC, a high $n_o$ often leads to a high $\Delta n$. Most of the commercially available high birefringence ($\Delta n \sim 0.20-0.28$) liquid crystals have $n_o \sim 1.50-1.52$. These are the mixtures of cyanobiphenyls and cyanoterphenyls, e.g., Merck E-series and BL-series. Only some high
birefringence (\(\Delta n \geq 0.4\)) LCs have \(n_o > 1.55\). These are mainly isothiocyanato-tolane mixtures, e.g., UCF-series. Thus, we compare the index matching of some Merck E-series (E7, E48, and E44) and BL-series (BL003, BL006, and BL038) liquid crystals with NOA65, and some high birefringence UCF mixtures (UCF-1 and UCF-2) with NOA81.

Figure 35 shows the measured refractive index of the UV-cured NOA65 and the ordinary refractive index of E48, E44, and E7, as a function of wavelength at \(T=20^\circ C\). The filled circles, open squares, upward triangles, and downward triangles are the measured ordinary refractive index of NOA65, E48, E44, and E7, respectively. The respective solid lines represent the fittings of each material using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters \(A\), \(B\) and \(C\) are listed in Table 28. From figure 35, E48, E44, and E7 all have a good index matching with NOA65. More specifically, E44 has the best match in the red spectral region while E7 and E48 have the best match in the blue region. In the green region (\(\lambda=546\) nm), E44 has a slightly higher index, while E7 and E48 are slightly lower than NOA65, but the difference is in the third decimal.

Figure 36 shows the refractive index of the cured NOA65 and the ordinary refractive index of BL038, BL006, and BL003 as a function of wavelength at \(T=20^\circ C\). The filled circles, open squares, upward-triangles, and downward-triangles are the measured ordinary refractive index of NOA65, BL038, BL006, and BL003, respectively. The solid lines represent the fittings of each material using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 28. In Figure 36, BL038, BL006, and BL003 have a similar trend in \(n_o(\lambda)\). The index matching with NOA65 is
pretty good in the green and red spectral regions. A larger deviation is observed in the blue region, but the difference is still in the third decimal.

Figure 35: Wavelength dependent refractive index of NOA65 and the ordinary refractive index of E48, E44 and E7 at T=20 °C. The open squares, upward-triangles and filled circles, downward-triangles are the measured refractive index of E48, E44, NOA65 and E7, respectively. The solid lines represent the fittings using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 28.

Table 28: The fitting parameters for the refractive index [Eqs. (2-7) and (2-8)] of NOA65 and NOA81 and the ordinary refractive index of E48, E44, E7, BL038, BL006, BL003, UCF-1 and UCF-2 at T= 20 °C.

<table>
<thead>
<tr>
<th>Cauchy coefficients</th>
<th>NOA65</th>
<th>E48</th>
<th>E44</th>
<th>E7</th>
<th>BL038</th>
<th>BL006</th>
<th>BL003</th>
<th>NOA81</th>
<th>UCF-1</th>
<th>UCF-2</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>1.5130</td>
<td>1.5027</td>
<td>1.5018</td>
<td>1.4995</td>
<td>1.5042</td>
<td>1.5034</td>
<td>1.5056</td>
<td>1.5519</td>
<td>1.5439</td>
<td>1.5422</td>
</tr>
<tr>
<td>B (µm²)</td>
<td>0.0045</td>
<td>0.0055</td>
<td>0.0089</td>
<td>0.0068</td>
<td>0.0065</td>
<td>0.0085</td>
<td>0.0057</td>
<td>0.0036</td>
<td>0.0038</td>
<td>0.0043</td>
</tr>
<tr>
<td>C (µm³)</td>
<td>1.8×10⁻⁴</td>
<td>5.6×10⁻⁴</td>
<td>1.0×10⁻⁴</td>
<td>4.1×10⁻⁴</td>
<td>4.7×10⁻⁴</td>
<td>1.9×10⁻⁴</td>
<td>5.9×10⁻⁴</td>
<td>4.9×10⁻⁴</td>
<td>0.0019</td>
<td>0.0018</td>
</tr>
</tbody>
</table>
The ordinary refractive index of NOA81 is larger than NOA65. The measured value of NOA81 at $\lambda=589$ nm and $T=20$ °C is 1.5662. No commercially available LC mixtures have such a high $n_o$. We have formulated two new LC mixtures designated as UCF-1 and UCF-2 whose ordinary refractive index matches with NOA81. Figure 37 shows the refractive index of the cured NOA81 and the ordinary refractive index of UCF-1 and UCF-2 as a function of wavelength at $T=20$ °C. The filled circles, open squares, and upward-triangles are the measured ordinary refractive index of NOA81, UCF-1, and
UCF-2, respectively. The solid lines represent the fittings of each material using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 28. In Figure 37, the $n_o$ of UCF-1 and UCF-2 match well with that of NOA81 in the red region. As the wavelength gets shorter, the deviation increases gradually. This is because the longest electronic absorption band ($\lambda_2$) of the high birefringence LCs usually extends to ~350 nm region. The resonance-enhanced refractive index is large as the wavelength approaches $\lambda_2$.

![Figure 37: Wavelength dependent refractive index of NOA81 and the ordinary refractive index of UCF-1 and UCF-2 at T=20 °C. The filled circles, open squares and upward-triangles are the measured refractive index of NOA81, UCF-1 and UCF-2, respectively. The solid lines represent the fittings using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 28.]
In a PDLC system, good index matching ($n_o \sim n_p$) between the employed polymer and liquid crystal helps to improve the transmittance in the voltage-on state. On the other hand, a larger index mismatch ($\langle n \rangle > n_p$), i.e., a higher birefringence LC enhances the light scattering efficiency in the voltage-off state. However, refractive index match or mismatch is not the only factor deciding the PDLC performance. UV stability of liquid crystals and miscibility between polymers and liquid crystals also play important roles affecting the PDLC properties. As we discussed before, the E-series and BL-series liquid crystals all have a good index match with NOA65. All these six liquid crystals are good candidates for PDLC application when NOA65 is used. In the visible spectrum, E48 and E7 have very similar ordinary refractive index at $T=20$ °C, as do BL038 and BL003. However, E48 (BL038) has a higher birefringence than E7 (BL003). Thus, we choose to compare the NOA65 PDLC systems using BL038, E48, BL006, and E44.

### 6.5.4 PDLC Cell Fabrication and Measurements

To prepare PDLC samples, we mixed NOA65 with E48, E44, BL038, and BL006; each at 30:70 wt% ratio. To ensure a uniform mixing, we stirred the LC/monomer mixtures using magnetic stirrers for half an hour at $T=120$ °C (put the bottles with the LC/monomer on a hot plate). Each LC/monomer mixture was then injected to an empty glass cell (cell gap ~ 8 μm) in the isotropic state. The inner surfaces of the glass substrates were coated with a thin indium-tin-oxide (ITO) layer, but no polyimide layer.
To cure the samples, the cells were exposed to UV light (I=65 mW/cm$^2$) for 15 minutes at T=20 °C.

The voltage-dependent transmittance (VT) curves were measured and used to compare the contrast ratio of the PDLC cells. The experimental setup is shown in Figure 38. An unpolarized He-Ne laser ($\lambda$=633 nm) beam was normally incident on the PDLC cell. A photodiode detector was placed at 25 cm behind the cell. The corresponding collection angle is ~2°. A LabVIEW data acquisition system was used to control the applied voltage and record the measured VT curves.

Figure 38: The experimental setup for measuring the transmittance of the PDLC cells.
6.5.5 Results and Discussions

From the measured VT curves, we find that BL038 is better than BL006, and E48 is better than E44 in the NOA65 PDLC systems, although these four LC mixtures all have a good index match with NOA65. The BL038 (E48) PDLC cell exhibits a lower transmittance in the voltage-off state and a higher transmittance in the voltage-on state than that of BL006 (E44). It implies that the refractive index match is not the only factor affecting the contrast ratio of a PDLC; the LC/polymer miscibility also plays an important role. It is likely that BL038 and E48 have a better miscibility in NOA65 than BL006 and E44.

In Figure 39, we compare the normalized VT curves of the BL038 and E48 PDLC cells at \( \lambda = 633 \text{ nm} \). For both cells, the polymer (NOA65) and LC ratio is 30:70 and cell gap is 8 \( \mu \text{m} \). To calibrate the substrate reflection losses, the transmittance of the PDLC cell is normalized to that of a homogeneous cell filled with the corresponding liquid crystal. The red line represents the transmittance of the BL038 PDLC cell and the blue line represents the transmittance of the E48 PDLC cell. In Figure 39, the BL038 PDLC cell has a lower transmittance at \( V=0 \) and a higher transmittance in the on-state than E48. The saturation voltage of both cells happens at \( \sim 20 \text{ V}_{\text{rms}} \), thus, we define the contrast ratio as: \( \text{CR} = \frac{T(V=20 \text{ V}_{\text{rms}})}{T(V=0)} \). The measured contrast ratio is 13:1 and 10:1 for the BL038 and E48 PDLC cells, respectively. We could enhance contrast ratio by using a thicker cell gap. The tradeoff is the increased operating voltage.
Figure 39: Voltage-dependent normalized transmittance of the BL038 and E48 PDLC cells at $\lambda=633$ nm. For both cells, the LC:NOA65 ratio is 70:30. The two cells have same thickness ($d=8\mu m$) and have no polyimide layer on the glass substrates.

Two factors contributing to the higher contrast ratio of the BL038 PDLC cell over E48 are higher birefringence and better index matching with NOA65. In Figure 40, we compare the wavelength-dependent refractive index of NOA65 and the ordinary refractive index of BL038 and E48 at $T=20$ °C. The filled circles, open squares, and upward-triangles are the measured refractive index of NOA65, BL038, and E48, respectively. The solid lines represent the fittings using the extended Cauchy model [Eq. (2-7) and (2-8)]. The fitting parameters are listed in Table 28. From Figure 40, we find that BL038 has a better index match than E48 at $\lambda=633$ nm. Thus, the BL038 PDLC cell has a higher transmittance in the voltage-on state than the E48 cell when the He-Ne laser...
(λ=633 nm) is used. However, this explanation is only qualitative. In the voltage-on state, the LC directors near the inner boundaries of the droplets are hardly reoriented by the electric field because of the strong surface anchoring. These anchored LC directors have some $n_c$ components. As a result, the effective refractive index in the voltage-on state is slightly larger than $n_o$. It is difficult to estimate how much these boundary layers contribute to the effective refractive index.

![Wavelength dependent refractive index of NOA65 (circles) and the ordinary refractive index of BL038 (squares) and E48 (triangles) at T=20 °C. The solid lines represent the fittings using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 28.](image)

Figure 40: Wavelength dependent refractive index of NOA65 (circles) and the ordinary refractive index of BL038 (squares) and E48 (triangles) at T=20 °C. The solid lines represent the fittings using the extended Cauchy model [Eqs. (2-7) and (2-8)]. The fitting parameters are listed in Table 28.
Figure 41 shows the wavelength-dependent birefringence of BL038 and E48 at T=20 °C. The squares and triangles represent the experimental data of BL038 and E48, respectively. The solid lines are fittings using the following single-band birefringence dispersion model27:

\[
\Delta n(\lambda) = G \frac{\lambda^2 \lambda^*}{\lambda^2 - \lambda^*^2},
\]

where \(G\) is a proportionality constant and \(\lambda^*\) is the mean resonant wavelength of the liquid crystal. The fitting parameters \([G (\mu m^{-2}), \lambda^* (\mu m)]\) for BL038 and E48 are \([3.509, 0.252]\) and \([3.210, 0.244]\), respectively. In Figure 41, BL038 exhibits a larger birefringence than E48 in the entire visible spectral region. Thus, the difference between the average refractive index of BL038 and the refractive index of NOA65 is larger than that between E48 and NOA65, i.e., the refractive index mismatch between BL038 and NOA65 is larger than that between E48 and NOA65. A larger index mismatch leads to a higher scattering efficiency. As a result, the BL038 PDLC cell has a lower transmittance at V=0 than the E48 cell.
Figure 41: Wavelength dependent birefringence of BL038 (squares) and E48 (triangles) at $T=20$ °C. The solid lines are fittings using the single-band model [Eq. (6-1)]. The fitting parameters $[G(\mu m^{-2}), \lambda^*(\mu m)]$ for BL038 and E48 are $[3.509, 0.252]$ and $[3.210, 0.244]$, respectively.
6.5.6 Conclusion

In this chapter, the refractive index of cured polymers, NOA65 and NOA81, were measured at six visible wavelengths and in the temperature range from 20 to 55 °C using a multi-wavelength Abbe refractometer. The refractive indices of Merck E-series (E48, E44, and E7) and BL-series (BL038, BL006, and BL003) LC mixtures were measured. Comparative study on the refractive index between these liquid crystals and cured polymers was made. Among the LC materials we studied, BL038 and E48 are good candidates for making PDLC system incorporating NOA65. Indeed, the BL038 PDLC cell shows a higher contrast ratio than the E48 cell because BL038 has a better matched ordinary refractive index, higher birefringence, and similar miscibility as compared to E48. Liquid crystals having a good miscibility with polymer, matched ordinary refractive index, and higher birefringence help to improve the PDLC contrast ratio for display applications.
CHAPTER 7: GENERAL SUMMARY

This dissertation has accomplished following three objectives: 1) development of physical models for LC refractive indices, 2) establishment of guidelines for formulating high \( \frac{dn_o}{dT} \) LC mixtures and 3) applications of these physical models in displays and photonic devices including optimum design for displays, high thermally tunable liquid crystal photonic crystal fibers, thermal solitons in nematic liquid crystals, infrared refractive indices of liquid crystals, and index-matched polymer-dispersed liquid crystals (PDLC).

7.1 Development of Physical Models for Explaining the Wavelength Effect on Liquid Crystal Refractive Indices

We have derived and compared the three- and two-coefficient Cauchy models for describing the wavelength effect on the refractive indices of liquid crystals based on the three-band model and Vuks model. If the LC birefringence is larger than \( \sim 0.12 \), the three-coefficient Cauchy model should be used. On the other hand, if the LC birefringence is smaller than \( \sim 0.12 \), the \( \lambda^d \) term can be ignored and the two-coefficient Cauchy model
works equally well as the three-coefficient Cauchy model. Most of TFT LC mixtures developed for direct-view and projection displays have a relatively low birefringence. Thus, the two-coefficient Cauchy model is adequate. The original Cauchy equation is aimed to describe the refractive index of isotropic media. However, we extend the Cauchy equation to describe the refractive indices of anisotropic media. The extended Cauchy model indicates both $n_e$ (extraordinary refractive index) and $n_o$ (ordinary refractive index) decrease as the wavelength increase in the visible and infrared regions. Due to the weak oscillator strength of the absorptions in the infrared region, the resonant enhancements of these absorptions to the LC refractive indices are localized. Generally, the LC refractive indices change a little in the near infrared region and saturate in the mid and far infrared regions.

7.2 Development of Physical Models for Explaining the Temperature Effect on Liquid Crystal Refractive Indices

We have also derived and compared the four-parameter and three-parameter parabolic models for describing the temperature effect on the refractive indices of LCs based on the Vuks equation and Haller equation. The four-parameter model fits the experimental data very well in the whole nematic range. These four parameters can be obtained by two-stage fittings. The four-parameter model can be further simplified to the three-parameter parabolic model if the birefringence is low and the operating temperature is not too close to the clearing temperature. Using the four-parameter model, we could
extrapolate the LC refractive indices in the whole nematic range. To know the LC properties at the operating temperature beforehand is very important for projection display and photonic applications.

7.3 Validation of Vuks Model

Vuks model is analogous to the classical Lorentz-Lorenz equation which describes the refractive index of isotropic media. Vuks assumes the internal field is isotropic in the crystals and relates the macroscopic refractive indices to the microscopic polarizabilities of the molecules. Vuks validated his model using the measured refractive indices and molecular polarizabilities of several crystals. Most physical models we derived for liquid crystals are based on the Vuks model. Thus, it is necessary to validate the Vuks model using the experimental data of liquid crystals directly. The Vuks equation is validated to be self-consistent, for the first time, by the measured refractive indices of liquid crystals.

7.4 Developments of Physical Models for the Temperature Gradient of LC refractive indices and Guidelines for Formulating High $dn_e/dT$ Liquid Crystals

The temperature gradients of LC refractive indices, $dn_e/dT$ and $dn_o/dT$ are derived based on the four-parameter model. We brought forward a new concept, the
crossover temperature $T_o$ at which $dn_o/dT$ is equal to zero. The $dn_e/dT$ remains negative throughout the nematic range. On the other hand, $dn_o/dT$ is negative when the temperature is below the crossover temperature ($T_o$) but becomes positive when the temperature is beyond $T_o$. This indicates that $n_e$, the extraordinary refractive index, decreases monotonously as temperature increases throughout the nematic range whereas $n_o$, the ordinary refractive index, could decrease or increase with temperature depending on where the crossover temperature is. Both $dn_e/dT$ and $dn_o/dT$ change sharply as the temperature approaches the clearing temperature. However, the light scattering is large when the temperature approaches the clearing point.

We have analyzed the physical origins of the temperature gradient of the ordinary refractive index ($dn_o/dT$) of liquid crystals. To achieve a large $dn_o/dT$, high birefringence and low clearing temperature play crucial roles. Based on these simple guidelines, we formulated two exemplary liquid crystal mixtures, designated as UCF-1 and UCF-2, and compared their physical properties with a commonly used commercial liquid crystal compound 5CB. The $dn_o/dT$ of UCF-1 is ~4X higher than that of 5CB at room temperature. Moreover, the melting temperature of UCF-1 and UCF-2 is below ~20°C, which is much lower than that of 5CB and 6CB. These high $dn_o/dT$ liquid crystals are useful for new photonic applications, such as the highly thermally tunable liquid crystal photonic crystal fibers, the laser-induced thermal solitons in nematic liquid crystals.
7.5 High Thermally Tunable Liquid Crystal Photonic Crystal Fibers and Thermal Solitons in Nematic Liquid Crystals

The new liquid crystals with high temperature gradient of ordinary refractive index are preferred for the liquid crystal infiltrated photonic bandgap fiber device and the thermal soliton in nematic liquid crystal confined in a capillary. For the liquid crystal-infiltrated photonic crystal bandgap fibers, the high $dn_o/dT$ liquid crystals greatly improve the tuning sensitivity of the spectral position of the bandgaps. Cooperating with a Danish group, we demonstrate a high thermally tunable single mode liquid crystal photonic bandgap fiber device, which utilizes a three-rod core PCF and infiltrated with UCF-1 in order to obtain a large mode area and high thermal tuning sensitivity. The guided mode has an effective area of 440 $\mu$m$^2$ with an insertion loss of less than 0.5dB. The thermal tuning sensitivity of the spectral position of the bandgap was measured to be 27 nm/°C around room temperature, which is 4.6X higher than that using a commercial Merck E7 at temperature above 50 °C. To trigger the thermal soliton in nematic liquid crystal confined in a capillary easily, a liquid crystal with high positive $dn_o/dT$ ordinary refractive index are preferred to reduce the laser power.
7.6 Infrared Refractive Indices of Liquid Crystal

Liquid crystals are widely used in the photonic devices operated in the infrared region since many liquid crystals still hold high birefringence in the infrared region. Thus, knowing the LC refractive indices at the designated infrared wavelength helps to optimize the device design. However, the measurement of the LC refractive indices in the infrared region is difficult and time consuming. Basing on the extended Cauchy model and the four-parameter model, we could successfully extrapolate the refractive indices measured in the visible light region to the infrared region. We show the validity to link the experimental data measured in the visible region to infrared by the extended Cauchy equation. The data measured at $\lambda = 1.55$ and 10.6 $\mu$m, respectively, by the wedged-cell refractometer method are used to validate the method. Good agreement among the extended Cauchy model, four-parameter model, and experimental data is achieved.

7.7 Index-matched Polymer-dispersed Liquid Crystals (PDLC)

Finally, the comparative study between liquid crystals and photopolymers was developed for polymer-dispersed liquid crystals (PDLC) applications. The extended Cauchy model and the four-parameter model are used to realize this goal. The refractive index of cured polymers, NOA65 and NOA81, were measured at six visible wavelengths
and in the temperature range from 20 to 55 °C using a multi-wavelength Abbe refractometer. The refractive indices of Merck E-series (E48, E44, and E7) and BL-series (BL038, BL006, and BL003) LC mixtures were measured. Comparative study on the refractive index between these liquid crystals and cured polymers was made. Among the LC materials we studied, BL038 and E48 are good candidates for making PDLCs system incorporating NOA65. Indeed, the BL038 PDLC cell shows a higher contrast ratio than the E48 PDLC cell because BL038 has a better matched ordinary refractive index, higher birefringence, and similar miscibility as compared to E48. Liquid crystals having a good miscibility with polymer, matched ordinary refractive index, and higher birefringence help to improve the PDLC contrast ratio and transmittance for display applications.
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