Research into Order Parameters and Graphene Dispersions in Liquid Crystal Systems using Raman Spectroscopy

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

2014

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Research into Order Parameters and Graphene Dispersions in Liquid Crystal Systems using Raman Spectroscopy

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Thesis for the degree of Doctor of Philosophy
2014

Abstract

Polarized Raman Spectroscopy (PRS) is one of the experimental methods which can be employed to deduce orientational order parameters, e.g. \( \langle p_{200} \rangle \), \( \langle p_{400} \rangle \), in liquid crystals from the experimental depolarization ratio graph via fitting. However, it has long been known that the order parameters deduced from the different vibrational modes are found to be different within the same sample. As a result, only certain vibrational modes can be reliably selected for analysis, limiting the application of PRS. The possible explanations are discussed in this thesis. The first explanation is given by considering a dipole tilt \( \beta_0 \) which is defined as the tilt angle of the dipole vibrational direction and the molecular long axis. A second explanation comes from assuming different vibrational symmetries, i.e. cylindrical or elliptic cylindrical. Molecular biaxial order parameters are introduced in both explanations. A systematic check via calculation shows that a common set of order parameters (including molecular biaxial order parameters) can be obtained with different depolarization ratio graphs when the explanations are considered. Both depolarization ratio graphs can also agree well with that obtained from phenyl and cyano stretching modes experimentally. A supplementary discussion shows that by using the first explanation, \( \langle p_{400} \rangle \) which, in previous fitting, shown an excessive value by using cyano stretching mode is reduced (15% reduced at \( \beta_0 = 15^\circ \), \( \langle p_{402} \rangle = 0.0536 \)).

PRS is also employed to analyse the order parameters in a bent-core system using a molecular model with the bend angle \( \Omega \) and tilt angle \( \theta_0 \). The effects of each of the uniaxial and phase biaxial order parameters are considered. With a total Raman tensor generated by the sum of Raman tensor from each arm, reasonable uniaxial order parameters fitting values can be obtained from PRS without considering biaxial order parameters. These results agree well with those deduced from the refractive index measurements, which shows a new approach to the investigation of bent-core systems. However, it is also shown that introducing phase biaxial order parameters can’t provide robust fitting, leading inaccurate fitting values in the end.

Several different liquid crystals (5CB, E7, HAT-6 and SSY) have been examined on seeking graphene/graphene oxide dispersions in liquid crystal systems. Unfortunately, no stable dispersion was obtained by applying simple experimental techniques. However, a highlight comes from the test of a lyotropic liquid crystal formed by a discotic molecule in NMP suggesting a possible dispersion medium for graphene. Meanwhile, by using Raman spectroscopy, the interaction between liquid crystal molecules and graphene can be obtained from the peak shift of vibrational modes. The experimental results suggest a stronger interaction in E7 compared to 5CB. No shift in ZLI-1695 indicates the different effects from the rigid core. Further, the discotic liquid crystal (HAT-6) shows a strong interaction with graphene. These facts lead to a conclusion that the interaction still exists in the graphene/liquid crystal dispersion providing a guide on controlling and optimizing the dispersion quality for the future research.
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Acknowledgement

I first would like to show my sincerely thanks to my supervisor, Prof. Helen Gleeson on guiding me in this work. These thanks are not only because of her help, advice and support, but also, for the endless patience she has gifted me. Without her, I will never learn so much and finish the work. Thanks go to Prof. John Goodby, Dr. Verena Görtz and Dr. Stephen Cowling for the synthesis of the bent-core and discotic materials. I must also thank Dr. Rahul Raveendran-Nar, Dr. Thanasis Georgiou and Dr. I-ling Tsai for providing me the excellent graphene and graphene oxide materials. Thank you, Dr. Jichen Li for providing me the computer and Material Studio for simulations. I’m also very grateful to all the people in our group especially Prof. Cliff Jones, Dr. Sarabjot Kaur, Dr. Mamatha Nagaraj, Dr. Linan Tian and Harry Liu for your good suggestions and help on my work.

In a less academic sense, I must first thank my forever beloved father. Without you, I’ll not determine myself in physics research. Thanks to my mother, for your selfless love for on me. In the end, special thanks go to my wife Xin, who gives me love and power every day.
Chapter 1

Introduction

The primary aim of this project is to investigate the usage of Polarized Raman Spectroscopy in understanding liquid crystal orientational properties with a variety of liquid crystal system including both uniaxial and biaxial systems. Raman Spectroscopy is also applied to the investigation of the graphene dispersions in different liquid crystals such as calamitic, discotic and chromonic. In the initial part of this thesis, we are going to discuss what liquid crystals are and their properties, providing background knowledge to the materials studied. The definition and basic properties of liquid crystals will be discussed in Section 1.1. Then several different liquid crystals systems including calamitic, discotic and lyotropic systems will be discussed (Section 1.2). The optical properties of liquid crystal will be briefly discussed in Section 1.3 and finally, some basic techniques in liquid crystal research will be introduced in Section 1.4.

1.1. Liquid Crystals

Liquid crystals were first discovered by an Austrian scientist, Friedrich Reinitzer in 1888\textsuperscript{1,2}. The name, liquid crystal, describes a state which is an intermediate between the isotropic liquid state and the crystal state, and are thus less ordered compared with the crystal phase while more ordered than the liquid phase. The liquid crystal state is famous for its anisotropic properties. This state exhibits different results on the measurement of properties including elastic constants, dielectric constants and refractive index, depending on the measurement direction\textsuperscript{3}. As a consequence, complex responses to external
influence such as electric fields and mechanical distortions are found and we can change the effective properties of liquid crystals simply by changing these external stimuli.

Not every material exhibits a liquid crystal state. Typically, a large degree of molecular anisotropy of chemical groups is required in liquid crystal molecules. This fact leads to the result that in liquid crystals, either the shape of the molecule has one axis which is larger than the other two, or there are different solubility properties. In most liquid crystal materials, a dimensionless unit vector \( \mathbf{n} \) called the director, is introduced to represent the direction of molecular preferred orientation. Since there is no physical polarity along the director direction in most liquid crystal materials, \( \mathbf{n} \) and \(-\mathbf{n}\) are fully equivalent. Typically, liquid crystal materials are sorted into several different classes by their molecular shape, orientational order, the way they form liquid crystal state, and moreover, the material used to from liquid crystal. In the same liquid crystal material, different phases or mesophases are also observed. Different mesophases are classified according to the different positional order and orientational order, and whether this order is short-range or long-range. These mesophases in liquid crystals can transfer from one kind to another or to isotropic phase according to the temperature (thermotropic liquid crystals) or dissolution property (lyotrophic liquid crystals).

1.2. Categories of Liquid Crystals

1.2.1. Calamitic Liquid Crystals

The most studied and most typical category of liquid crystals is called calamitic, meaning rod-like. The basic molecular structure of a calamitic liquid crystal can be illustrated as in Fig. 1.1.

\[
\begin{array}{c}
R \quad \text{A} \quad \text{B} \quad \text{R'}
\end{array}
\]

Fig. 1.1 The basic structure of a molecule in a calamitic liquid crystal. Section A and B are the rigid core of the molecule while section \( R \) and \( R' \) are the terminal group.

The most important section of a calamitic liquid crystal molecule is the rigid core, as shown in section A and B in Fig. 1.1, to maintain the anisotropic molecular structure.
Usually, this part is a linearly linked ring structure that could be either phenyl ring (e.g. 5CB with a biphenyl as the core) or cyclohexyl ring (e.g. ZLI-1695 with a bicyclohexyl as the core). The ring structures can be linked directly or combined with linking groups such as -CO$_2$-, -CH$_2$CH$_2$- and -CHN-. The linking groups provide extra anisotropy and linearly to the molecules$^3$. It is not enough to form a liquid crystal phase only with the rigid core, some flexibility is necessary to stabilise the molecular alignment and changing the melting point. This flexibility is usually achieved by adding alkyl or alkoxy chains at section R or R’ like a “tail” in Fig.1.1. The length of this “tail” will affect the phase formed in the liquid crystal material. Also, some terminal group (e.g. CH$_3$, CN, F and CF$_3$) can be placed at R and R’ in Fig.1.$^3$. In some situations, a linking group may also appear between the rigid core and the terminal chains$^3$. Finally, some lateral substituents (e.g. F, Cl, CN, and CH$_3$) will also attached to the rigid core to manipulate the physical properties$^3$. There are several different phases in calamitic liquid crystals. Here we only consider two main kinds of phases which are the nematic and smectic phases of the calamitic liquid crystal.

**Calamitic Nematic Phases**

The calamitic nematic phase is the most commonly seen phase in the calamitic liquid crystals and is schematically shown in Fig.1.2. This phase usually appears immediately below the isotropic phase and is characterised by the molecular long-range orientational order of the molecular long axis roughly parallel to the director. Usually the molecular long axis is assumed to be along the molecular rigid core. Besides, the nematic phase has no molecular positional order$^6,^9$.

![Fig. 1.2 Brief illustration of the nematic phase in calamitic liquid crystal with the director direction $\hat{n}$.](image)
**Calamitic Smectic Phases**

The smectic phases of a calamitic liquid crystal exist at lower temperatures than the nematic phase due to the more ordered structure compared with the nematic phase. The molecules in the smectic phases not only maintain a level of orientational order, as in the nematic phase, but also have the positional ordering such that molecules align themselves in layers\(^\text{10}\). The molecules form layered structure with the translational movement between different layers is hindered, but the molecules can move around in one layer and moreover, the layers may entangle with each other. The smectic phases are more "solid-like" compared with the nematic phase because of the existence of the layered structure. The two most commonly seen smectic phases are the smectic A and C phased which are shown in Fig.1.3. In the smectic A (SmA) phase, the director \(\hat{n}\) coincides with the layer normal \(\hat{k}\) while for the smectic C (SmC) phase, the director is at an angle respect to the layer normal \(\hat{k}\). Smectic A and C have the simplest structure in smectic phases. Besides the smectic A and C phases, there are many of the smectic phases, characterized by different types and degrees of positional and orientational order\(^\text{10,11}\).

![Fig. 1.3 Brief illustration of the a) smectic A phase and b) smectic C phase. In the plots, \(\hat{k}\) is the layer normal vector and \(\hat{n}\) is the director](image)

**1.2.2. Discotic Liquid Crystals**

The existence of discotic liquid crystals systems in which the molecules are disc-like, was first proved to be true in 1977\(^\text{12}\). The study of discotic liquid crystals began with the investigation of the smallest possible core, benzene, in 1977 by Chandrasekhar\(^\text{12}\), and after that, a variety of polyaromatic cores such as triphenylene or phthalocyanine and even polycyclic aromatic hydrocarbons were discovered showing liquid crystal phases\(^\text{3}\).
Discotic liquid crystal molecules typically include a rigid aromatic core (within the dashed line circle in Fig. 1.4) and the flexible peripheral chains ($R_{1-6}$ in Fig. 1.4). Such systems have been attracting growing interest because of their fundamental importance as model systems for the study of charge and energy transport, and due to the possibilities of their application in organic electronic devices\textsuperscript{13}. A symmetrical rigid core exists to maintain the disc-like structure of the molecule and primarily generate the molecular anisotropic properties. The liquid crystal phase is easier to form in systems with relatively large core diameters\textsuperscript{3}. The discotic liquid crystal materials are usually in the crystal state at room temperature and the liquid crystal phase usually appears at high temperature. Varieties of flexible peripheral chains contribute to the maintenance of a disc-like structure as well as reducing the melting point\textsuperscript{6}.

Fig. 1.4 Brief illustration of a discotic liquid crystal molecule based on triphenylene core. The structures in the circle is the disc-like aromatic core and $R_{1-6}$ are the peripheral chains

Two basic types of discotic mesophase have been widely recognized, they are the nematic phase and the columnar phases.

**Discotic Nematic Phase**

The discotic liquid crystal can also form a nematic phase designated $N_D$ with molecular anisotropic direction aligned along the director direction. The only difference compared with a calamitic nematic phase is that the molecular anisotropic direction is perpendicular to the disc-like core and thus the director direction is perpendicular to the stack plane as shown in Fig. 1.5\textsuperscript{14}. The discotic nematic phase presents the same optical textures as that of the calamitic nematic phase when viewed between crossed polarizers under a microscope\textsuperscript{7}. Due to the very random structure, the discotic nematic phase is the least viscous liquid crystal discotic phase. A few disc-shaped materials also have been
discovered generating a columnar nematic (N_{Col}) phase\(^3\). Within this N_{Col} phase, a few discotic liquid crystal molecules form a short column and these short columns adopt a discotic nematic packing arrangement. With the additional order introduced by the column, this phase appears at lower temperatures than the N_D phase and has a higher viscosity.

Fig. 1.5 Molecular arrangements within a). the discotic nematic phase and b). the columnar nematic phase. The short arrows indicate the direction perpendicular to the disk plane in individual molecules.

**Discotic Columnar Phase**

In common with the smectic phases in calamitic liquid crystals, there are also a higher ordered liquid crystal mesophases in discotic liquid crystal systems, namely, the columnar phases.

Fig. 1.6 Molecular arrangements within a). the hexagonal columnar phase and b). the rectangular columnar phase.

The columnar phases are classified primarily according to the different symmetry class of the two dimensional lattice of columns. Fig.1.6 shows two kinds of columnar mesophases: the hexagonal columnar phase (D_h) and the rectangular columnar phase (D_l).
The hexagonal columnar phase $D_{h}$ has a hexagonal structure viewed along the director, formed by the column of the molecules. Hexagonal columnar phase is usually further classified into two categories according to whether the molecules within the columnar arrays are ordered ($D_{ho}$) or disordered ($D_{hd}$) as shown in Fig. 1.7. The difference between these two phases are reflected on the horizontal shift of the disc-like molecules and can be distinguished based on X-ray diffraction data\textsuperscript{15}. However, the transition between the two phases is not strictly defined\textsuperscript{16}. Two other higher ordered arrangements in the columnar array, which are named plastic, with the molecular position in column is strictly ordered but the disc-like molecules have a rotational disorder and helical that similar to plastic but the rotational disorder follows the helical arrangement were been reported\textsuperscript{17}.

![Different arrangements of disc-like molecules within the column in the columnar phases. The arrows indicate the variance of random change](image)

Fig. 1.7 Different arrangements of disc-like molecules within the column in the columnar phases. The arrows indicate the variance of random change

Viewed along the director, the rectangular columnar phase forms a rectangular lattice structure. Only one arrangement in the column array, disordered (as shown in Fig. 1.7), exists and is named as $D_{rd}$ in the rectangular columnar phase which is different from the hexagonal columnar phase\textsuperscript{3}. Compared with the case in smectic phase, two more categories of rectangular columnar phase appear depending on whether the director is tilt or not with respect to the column axis.

Generally speaking, the vast majority of discotic liquid crystals exhibit columnar phases (95%), some of them additionally show the nematic phase and only a few exhibit only nematic phase\textsuperscript{3,6}. Further, the discotic liquid crystals are more sensitive to the slight changes in molecular structure compared with calamitic liquid crystals. This fact makes the research on discotic liquid crystals much harder since even a small perturbation on the structure can destroy the liquid crystalline order\textsuperscript{3}.  

7
1.2.3. Lyotropic Liquid Crystals

A liquid crystalline material is called lyotropic if long-range orientational order is induced by the addition of a solvent. Thus the formation of lyotropic liquid crystal is related to the dissolution property. The molecules that generate lyotropic liquid crystal phase are amphiphilic with the structure example shown in Fig.1.8.

![Fig. 1.8 A schematic molecular structure for a lyotropic liquid crystal.](image)

The amphiphilic molecules comprise a hydrophilic head group which acts as the solubilizing group and a long hydrophobic attached chain. Examples of amphiphilic compounds are usually the phospholipids or salts of fatty acids, as shown in Fig.1.9. After being dissolved into a solvent (water for example), the hydrophilic end will turn to the interface with water while the hydrophobic end will leave far away from the interface, so the amphiphilic molecules will form spherical, cylindrical or ellipsoidal structures which are called micelles as shown in Fig.1.10. According to whether the solvent is polar or non-polar, micelles and reverse micelles are generated respectively. Under certain conditions of concentration and temperature, micelles can form ordered structures and thus the liquid crystal phase is generated.

![Fig. 1.9 Examples of the hydrophilic solubilizing group](image)

![Fig. 1.10 Cross section of a micelle and a reverse micelle](image)
Even through the lyotropic liquid crystal is formed primarily according to the dissolution properties of the system. Temperature also acts as a factor that affects the phases formation. A critical temperature exists in the lyotropic liquid crystals, below which the micelles will generate, thus lyotropic liquid crystal phase form. This critical temperature is called the Krafft point, and is often labelled as $T_K$. Since there are two factors that may affect the lyotropic liquid crystal phase, it is easier to illustrate the behaviour by using the phase diagram with the horizontal axis for concentration of amphiphilic molecules and the vertical axis stands for temperature. Lyotropic liquid crystals can form a variety of different phases according to the different arrangement of the amphiphilic molecules. Some of them have extremely complex structure and here only several basic phases are shown below.

**Lamella Phase**

The structure of the lamella lyotropic crystal (L$_{a}$) is shown in Fig.1.11. Instead of forming micelles, the amphiphilic molecules form a bilayer membrane and stack together in the solvent as in a calamitic smectic phase. This phase has the highest concentration among lyotropic liquid crystal phases. However, even though there is less water in this phase, it has a lower viscosity compared with other phases because the different layers could slide over each other.

![Fig. 1.11 Cross section of the lamella lyotropic liquid crystal phase.](image)

**Hexagonal Phase**

Lyotropic liquid crystals can also form a hexagonal phase similar to the thermotropic liquid crystals as shown in Fig.1.12. Instead of generating a spherical
micelles structure, the micelle here is a cylindrical tube packed in a hexagonal arrangement. The hexagonal lyotropic liquid crystal phase contains more water than lamella phase. However, even though it has more water in it, it is viscous because the cylindrical tubes are not easily to moving around. There are two types of hexagonal lyotropic phase, the hexagonal phase \( \text{H}^1 \) in which the molecules form a micelle and the reversed hexagonal phase \( \text{H}^2 \) with reversed micelles in it. The \( \text{H}^1 \) phase is the most commonly seen hexagonal phase while the \( \text{H}^2 \) phase has a higher viscosity and is rarely seen.

![Fig. 1.12 Cross section of hexagonal lyotropic liquid crystal](image)

**Cubic Phase**

In the cubic lyotropic liquid crystals, the micelles construct a cubic lattice and thus the name cubic comes from (as shown in Fig.1.13). Similar to the hexagonal phase, the cubic lyotropic phase also has two basic phases, \( \text{I}^1 \) phase with micelle in it or, named water continuous, and the \( \text{I}^2 \) phase with reversed micelles in it which also called non-polar chain continuous. In addition to the phase formed by micelles, cubic lyotropic phases also have two more possible phases which are devoted \( \text{V}^1 \) and \( \text{V}^2 \). These two phases are not made up with small micelle. Instead, there is a large continuous channelled network in these phases: \( \text{V}^1 \) for water continuous and \( \text{V}^2 \) for non-polar chain continuous. The cubic lyotropic phase is extremely viscous, even more viscous than the hexagonal phase due to the lack of shear plane.
In addition to the normal lyotropic phases mentioned above, there are a special phase in lyotropic liquid crystal named chromonic which can be considered to be the discotic phase of lyotropic liquid crystals. In the chromonic phases, the molecules are no longer amphiphilic molecules. Instead, the molecules have a rigid aromatic core which is board-like and solubilising groups around the core, as shown in Fig. 1.14. As within the discotic phase, the rigid aromatic cores stack face to face and form a columnar structure. Then these columns generate lattices and form liquid crystal phases.

Compared to the discotic liquid crystal, two basic mesophases can also appear in chromonic phase, which are the nematic phase (N) in low concentration and the more ordered M phase at higher concentration, which is similar to the hexagonal columnar discotic phase. Notice that there are no micelles in chromonic phase, thus the Krafft point does not exist in chromonic phase\textsuperscript{18}.
1.3. Liquid Crystal Optical Properties

The most important optical property of liquid crystal is birefringence which is caused by the intrinsic anisotropic properties. For a liquid crystal sample, due to birefringent property, light traveling through the liquid crystal will split to two different components: one is ordinary ray (O-ray) with a constant refractive index $n_o$, thus the velocity of O-ray is constant through the liquid crystal. Another one is extraordinary ray (E-ray) which, as its name, does not obey the Snell’s refraction law. More importantly, the E-ray experience different refractive index $n_e$ according to the different directions, thus the velocity is different according to the transparent direction. There is a special axis in liquid crystals which is called optical axis. Along this axis, E-ray have a refractive index value exactly same to the O-ray, then there is no difference between these two components along optical axis.

![Fig. 1.15](image)

As shown in Fig.1.15, we can express the liquid crystal in a Cartesian coordinate with the refractive indices along the three axes are $n_x$, $n_y$, and $n_z$. For the general case, $n_x \neq n_y \neq n_z$, there are two optical axes, thus this liquid crystal belongs to biaxial system. However, as biaxial system is usually hard to investigate, a special system is usually used for investigation. In this case, the refractive indices have the relation that $n_z \neq n_y = n_x$ which is known as uniaxial system and the number of optical axis becomes one as shown in Fig.1.15 (Details can be seen in optical textbook or refer to Appendix A.1).
We will now investigate the well aligned area in a uniaxial liquid crystal material. If the refractive index in this area are defined with \( n_x = n_y = n_\perp \) and \( n_z = n_\parallel \). The relationship between \( n_\perp \), \( n_\parallel \) and \( n_e \), \( n_o \) are shown in eq.1.1 and eq. 1.2 (the mathematic derived process is in optical textbook or referring to Appendix A.2) where \( \varphi \) is the angle between the incoming beam direction and the optical axis.

\[
n_o = n_\perp, \quad \text{(1.1)}
\]

\[
n_e = \frac{n_\parallel n_\perp}{\sqrt{n_\parallel^2 \cos^2 \varphi + n_\perp^2 \sin^2 \varphi}}, \quad \text{(1.2)}
\]

Notice that according to eq.1.1, the optical axis in the uniaxial liquid crystal phase is the director direction in nematic phase. After a polarized light beam goes into the aligned liquid crystal, due to the difference on the refractive index of O-ray and E-ray, the velocities of them have different and phase difference \( \delta \) of O-ray and E-ray will appears, thus the polarization properties of the beam will change after the beam comes out of the liquid crystal. The phase difference \( \delta \) is decided according to eq.1.3.

\[
\delta = \frac{2 \pi}{\lambda_0} (n_e - n_o) d, \quad \text{(1.3)}
\]

where \( \lambda_0 \) is the incoming beam wavelength in the vacuum and \( d \) is the thickness or length of the liquid crystal which the beam goes through. If the liquid crystal is placed between the crossed polarizers, two situations will appears. Firstly, if the polarized beam is along the optical axis (\( \varphi = 0 \) in eq.1.2), no phase difference \( \delta \) appears, leading to the result that no light can go through the crossed polarizer. Secondly, if the polarized beam is along the direction other than optical axis, (\( \varphi \neq 0 \) in eq.1.2), the phase difference appears. As a result, the polarization property of the incoming beam will change, leading to light transmission after the crossed polarizers. So different texture will be observed depend on the orientational properties of liquid crystal phase.

If an aligned nematic liquid crystal is placed between the crossed polarizers and the director direction is perpendicular to the incoming beam direction (\( \varphi = 90^\circ \)) as shown in Fig.1.16. Then according to eqs.1.1 and 1.2, \( n_o \) and \( n_e \) could be expressed simply by \( n_\perp \) and \( n_\parallel \) respectively. If a rotation angle \( \theta \) is defined as the angle between the polarized direction of the polarizer and the director direction then according to eq.1.3,
the polarized beam with phase difference $\delta$ equals to $2m\pi$ ($m$ is an integer) will maintain the original polarized direction and then is blocked by the analyzer. The polarized beam with phase difference $\delta$ equals to $2m\pi + \pi$ will have a $2\theta$ rotation on the polarized direction and becomes the mirror image about the director direction. Then the beam is not perfect by blocked and the light intensity after the crossed polarizers depends on the rotation angle $\theta$. A special situation will appears where the rotation angle $\theta$ equals to $45^\circ$, the light after the liquid crystal material polarized along the analyzer direction, thus the intensity reaches the maximum. In addition, the beam with polarization direction parallel to director direction ($\theta = 0^\circ$) and parallel to $n_e$ direction ($\theta = 90^\circ$) will not change polarize direction, thus, has no contribute to the outcome beam. The beam with other phase difference $\delta$ will transform to ellipse polarized beam and contribute a little to the outcome beam. According to the discussion, only the beam with phase different of $2m\pi + \pi$ contribute to the outcome intensity. So the relationship between the wavelength and liquid crystal refractive index of this nematic liquid crystal is as shown in eq.1.4,

$$\left( m + \frac{1}{2} \right) \lambda_0 = (n_\perp - n_\parallel) d = \Delta n d$$

(1.4)

So certain birefringence colour ($\lambda_0$) is decided by nematic liquid crystal sample property $d$ and liquid crystal property $\Delta n$. Since temperature change will affect the structure of liquid crystal which will further affect $\Delta n$. Thus, a colour change can also be identified by changing liquid crystal temperature.

Fig. 1.16 A well aligned uniaxial nematic liquid crystal sample with thickness $d$ is placed between a crossed polarizer. The director direction is tilt from the incoming beam direction with a tilt angle $\theta$. 

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1.4. Basic Techniques in Liquid Crystal Research

1.4.1. Liquid Crystal Samples

As shown in Fig.1.17, a normal liquid crystal sample consists of two pieces of substrate which are usually made of glass with indium tin oxide (ITO) layer attached on it to generate electric field.

In order to investigate the anisotropic property of liquid crystals, a uniformly aligned sample is needed instead of many domains with random direction. The alignment layer is used to provide a single aligned direction in the liquid crystal sample. There are two basic sample structures in liquid crystal research, homogenous (or planar) alignment and homeotropic alignment layers in which the director is parallel and perpendicular to the substrate surface respectively. Both the ITO layers and alignment layer are attached to the glass firmly so we can assume them as the substrate. Homogenous alignment is achieved by drying a long chain polymer like polyvinyl alcohol (PVA) on the ITO glass surface and then rubbing the surface to orient the polymer. The liquid crystal molecules are confined along the rubbing direction and parallel to the substrate surface as shown in Fig.1.17a). The homeotropic alignment is achieved by drying 15wt% cetrimonium bromide (CTAB) (an amphiphilic molecule) water solvent on the ITO glass. Then the CTAB molecules are aligned perpendicular to the substrate surfaces which are then used to align the molecules as shown in the Fig.1.17b.
Polymer spacers with certain thickness are placed between the substrates to generate a defined thickness. Usually, 5 µm, 10 µm, 20 µm and up to 50 µm are the scale of commercial cells. The liquid crystals are filled into the cells with the desired thickness and sealed with UV glue.

1.4.2. Optical Polarizing Microscopy

As the most widely used technique in liquid crystal research, optical polarizing microscopy is a simple and efficient way of characterizing and identifying most liquid crystal phases. This technique depends on the observation of the birefringent texture between the crossed polarizers which is usually sensitive to the structure change. The microscope structure is shown in Fig.1.19. Two light path setups could be used in optical polarizing microscopy: reflection and transmission as shown in Fig.1.19 with green and yellow lines separately for the light path. Both of these two setups could be used according to the experiment. Despite of the birefringent colour which can be seen with optical polarizing microscopy, optical polarizing microscopy is more widely used on identifying the liquid crystal phases as discussed in Section 1.3.7.
Fig. 1.19 Brief structure of the optical polarizing microscope. The green light path indicates the reflection measurement and the yellow light path indicates the transmission measurement.

### 1.5. Summary

In this chapter, the basic background relating to the liquid crystals have been reviewed, especially the three important liquid crystal categories: calamitic, discotic and lyotropic, which we’ll investigate in this thesis. Details about the basic phases that each type of liquid crystal can generate were discussed. Then the background of birefringence in the liquid crystals was discussed with the important conclusion that by observing the birefringent texture of the liquid crystal, we can get information about the liquid crystal structure. This fact leads to optical polarizing microscopy, as the very basic technique used in birefringence observation, and this technique was discussed at the end of this introducing chapter.
References

1. F. Reinitzer, Monatshefte für Chemie und verwandte Teile anderer Wissenschaften 9, 421 (1888).
Outline of the thesis

--------------Order Parameter Research using Polarized Raman Spectroscopy--------------

Chapter 2: Introduction of the Raman Scattering and Polarized Raman Spectroscopy

In this chapter, details of the Raman scattering are provided and the basic theory of Polarized Raman Spectroscopy (PRS) is discussed. Also some background on the Orientational Distribution Function (ODF) in liquid crystals and the most important concept, order parameters, are presented. Two previous approaches (Jen et al.’s and Jones et al. ’s methods) to obtain order parameters using PRS are also described in the end.

Chapter 3: Experimental Procedure and a Discussion of the Failings of Jones et al.’s Method

In this chapter, the experimental procedure of Jones et al. ’s method is discussed with the advantages. However, there is a long existing problem for Jones et al. ’s method that for a given sample, the order parameters deduced from different vibrational modes along the molecular long axis are different. An example to this discrepancy is given and one possible reason is briefly checked.

Chapter 4: Discussion of the Discrepancy of Order Parameter Values Deduced from Different Vibrational modes and a New Fitting Approach

In this chapter, two possible explanations for the discrepancy are discussed. Biaxial molecular order parameters are introduced in these explanations. Systematic checks are shown referring to the effects of each explanation and molecular biaxial order parameter on the final results. Evidences to support these explanations are discussed.

Chapter 5: Investigation of Bent-core Liquid Crystal System Order Parameter Fitting using PRS

In this chapter, a modified analysis method evolved from Southern et al.’s method has been carried out for a bent-core liquid crystal system. The phase biaxial order parameters are introduced in the discussion. The effects of each parameter on the result are discussed.
In the end some experimental attempts to investigate a bent-core smectic liquid crystal are shown.

------------Graphene and Graphene Oxide Liquid Crystal Dispersion Research---------

**Chapter 6: Introduction to Graphene and Graphene Oxide**

In this chapter, a brief background review of graphene and graphene oxide is given. The graphene and graphene oxide sample used in this project are also introduced.

**Chapter 7: Investigation of Graphene and Graphene Oxide Dispersions in Liquid Crystal Environments**

In this chapter, a variety tests are carried out on the graphene dispersions in different liquid crystal systems including calamitic (5CB, E7 and ZLI1695), discotic (HAT-6) and chromonic (Sunset Yellow). Experimental results are summarized.

**Chapter 8: Observing the Interaction between Liquid Crystal Molecules and Graphene using Raman Spectroscopy**

In this chapter, experimental results of the interaction between liquid crystal molecules and graphene are discussed. Two categories of liquid crystals: calamitic (5CB, E7 and ZLI-1695) and discotic (HAT-6) have been used in the research.

**Chapter 9: Conclusions and Future Work**

In this chapter, the conclusions and highlights from the thesis are summarized. Several future works about the alignment of liquid crystals on anisotropic surface and non-ionic chromonic liquid crystal phase formed by discotic molecules are discussed.
Chapter 2

Introduction of the Raman Scattering and Polarized Raman Spectroscopy

Raman scattering is the inelastic scattering of photons and was first discovered and named after Chandrasekhar Venkata Raman in 1928\textsuperscript{1}. Since a Raman spectrum is related to certain chemical species in the material\textsuperscript{2}, Raman scattering is widely used in identifying the components or structure of the materials. In research of the anisotropic materials like liquid crystals, in addition to the usage in identifying the structure, Raman scattering is also applied to quantify the orientational order in the material. This is important for liquid crystal research since it is the combination of order and fluidity that makes liquid crystals important technological materials. The order is described quantitatively through the order parameters, which requires the knowledge of the orientational distribution function (ODF). The ODF in nematic liquid crystals is described in terms of the Legendre polynomials $\langle P_{l,m,n} \rangle$, where the indices $L$, $m$ and $n$ take integer values. There are many approaches to measuring the order parameters in liquid crystals including optical techniques\textsuperscript{3}, analysis of infrared spectra\textsuperscript{4-6}, x-ray\textsuperscript{7-10} or neutron scattering\textsuperscript{11, 12}, ESR spectroscopy\textsuperscript{13} and nuclear magnetic resonance\textsuperscript{14}. However, Polarized Raman Spectroscopy (PRS), which depends on the Raman spectroscopy technique, is a powerful experimental method for the investigation of the order parameters since it can be used to obtain not only second order terms as can other experimental techniques, but also the next higher order term with $L=4$ which can be obtained by few other experimental methods. Further, Raman spectroscopy requires no special sample preparation and is a readily accessible laboratory-based technique,
advantages over the other possible approaches to determining the higher ordered order parameters. There are a variety of papers discussing the measurement methods used to obtain the order parameter from the PRS data\textsuperscript{15-20}.

In this chapter, we’ll go through the basic background about the origin of Raman scattering in Section 2.1. Then the theoretical definition of depolarization ratio will be shown in Section 2.2. Finally, the analysis method by Jen \textit{et al}. and Jones \textit{et al} using PRS to obtain the order parameters will be reviewed in the final section (Section 2.3).

### 2.1. Raman Scattering

When a beam of light is incident on a material, several different scattering situations will occur. The predominant part of the light scattering is elastic scattering, named Rayleigh scattering, in which the material absorbs the radiation energy and re-emitted at the same frequency as the incident light. Since there is no energy exchange, Rayleigh scattering only depends on the incident beam. Different from the Rayleigh scattering, the Raman scattering is one of the inelastic scattering phenomenon in which the scattered light has a wavelength shift (energy shift) compared with the original light. The shift in Raman Scattering comes from the energy exchange between the incident photons and the vibrational or rotational movement of molecular groups. Thus the shift in wavelength can be associated with the chemical groups in the material\textsuperscript{2}. The spectral range of the Raman shift for different chemical species generally lies between 200 cm\textsuperscript{-1} and 3000 cm\textsuperscript{-1}, with organic structures concentrated at around 1600 cm\textsuperscript{-1} (e.g. the phenyl stretching mode has a Raman shift around 1606 cm\textsuperscript{-1})\textsuperscript{21}.

The details of the theory of Raman scattering will be discussed now. The incident electromagnetic wave can induce polarization in a material. If the electric field of the incoming beam is written as $E$ and the induced polarization is written as $P$ the relation can be expressed as,

$$ P = \alpha E = \alpha E_0 \cos(2\pi \nu_0 t), \quad (2.1) $$

where $\nu_0$ is the frequency of the incoming beam, $\alpha$ is the polarizability. Notice that the
Raman scattering is related to a certain vibrational mode in the molecule, the polarizability is related to the atom displacement $Q$. If we assume the atoms of the vibrational mode are moving in simple harmonic motion, then the displacement could be expressed as,

$$Q = Q_0 \cos(2\pi v_{\text{vib}}t).$$  \hspace{1cm} (2.2)

Here the $v_{\text{vib}}$ is the atom vibration frequency which depends on the specific vibration. $Q_0$ is the maximum displacement around the equilibrium position of the atom. Since the polarizability $\alpha$ is a function of $Q$, applying a Taylor expansion to $\alpha$ in terms of $Q$ around the equilibrium position, the equation below is obtained,

$$\alpha(Q) = \alpha_0 + \frac{\partial \alpha}{\partial Q} Q + \cdots.$$ \hspace{1cm} (2.3)

Here, $\alpha_0$ is the polarizability at the equilibrium position which is induced by the incoming beam. Keeping the first two terms and ignoring the higher order terms in eq.2.3 and then substituting eqs.2.2 and 2.3 into eq.2.1, eq.2.4 can be obtained.

$$P = \alpha E(v) = \alpha E_0 \cos(2\pi v_0 t) = \left[\alpha_0 + \frac{\partial \alpha}{\partial Q} Q_0 \cos(2\pi v_{\text{vib}} t)\right] E_0 \cos(2\pi v_0 t)$$

$$= \alpha_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial Q} Q_0\right) E_0 \cos(2\pi v_{\text{vib}} t) \cos(2\pi v_0 t)$$

$$= \alpha_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial Q} Q_0\right) E_0 \left[\cos[2\pi t(v_0 - v_{\text{vib}})] + \cos[2\pi t(v_0 + v_{\text{vib}})]\right] \hspace{1cm} (2.4)$$

Three scattering beam frequencies, $v_0$, $v_0 - v_{\text{vib}}$ and $v_0 + v_{\text{vib}}$ are obtained in eq.2.4. The first frequency is exactly same as the incident beam which is the Rayleigh scattering. The other two frequencies are shifted compared with the incident beam frequency and they represent the frequencies of Raman scattering. It is worthy of note that the shift in the frequency is directly related to the vibration frequency according to eq.2.4. The lower frequency represents the Stokes Raman scattering while the higher frequency represent the anti-Stokes Raman scattering. The scattered intensity of light from a material is dependent on the square of the induced polarization. So according to eq.2.4, the relation between the Raman scattering intensity and Raman tensor is shown in eq.2.5,
Definitely, the electric field of the incoming beam (given by $E_0$) and the maximum displacement around the equilibrium position for certain vibration (given by $Q_0$) also contributes to the intensity according to eq.2.4, and the amount of sample material will also affect the intensity. However, these values ($E_0$ and $Q_0$) are constant for certain incoming beam and certain vibration. So concentrated on certain vibration with same light source, $\alpha'$ is assumed as the only parameter that affects Raman intensity in the thesis.

\[
I \propto P^2 \Rightarrow I_{\text{Raman}} \propto \left( \frac{\partial \alpha}{\partial Q} \right)^2 \Rightarrow I_{\text{Raman}} \propto (\alpha')^2.
\]  \hspace{1cm} (2.5)

Fig. 2.1 The comparison of the Rayleigh scattering and Raman scattering.

The above discussion depends on classical mechanics, Fig.2.1, however, shows a comparison between these three components according to the quantum mechanics. After the molecule absorbs an incoming beam with a frequency of $\nu_0$, it is excited to a virtual energy state from the molecular ground state. The energy gap between the base state and the excited state is $h\nu_0$ which is decided by the phonon of the incoming beam ($h$ is the Planck constant). Since the molecule will most probably return to its original base state directly, thus the Rayleigh scattering is predominant part of the scattering. For Stokes scattering, the molecules do not return the ground state, instead, they return to a higher energy state with the energy gap of $h\nu_{\text{vib}}$, which is decided by the molecular vibrational mode, thus the frequency is lower than the original frequency. For anti-Stokes scattering, the molecules are excited from the higher energy state which has an energy gap of $h\nu_{\text{vib}}$ to the base state and return to base state, as the consequence the frequency is higher than original.
Strictly speaking, the polarization $P$ and electric field $E$ should be vectors in eq.2.1., thus the polarizability must be a tensor $\alpha$, then a Raman tensor $\alpha'$ can be defined by eq.2.6 as below:

$$\alpha' = \frac{\partial \alpha}{\partial Q} = \begin{pmatrix} \alpha'_{xx} & \alpha'_{xy} & \alpha'_{xz} \\ \alpha'_{yx} & \alpha'_{yy} & \alpha'_{yz} \\ \alpha'_{zx} & \alpha'_{zy} & \alpha'_{zz} \end{pmatrix}.$$  \hspace{1cm} (2.6)

Notice that according to the symmetry, polarizability tensor $\alpha$ should be symmetric$^{22}$, thus the Raman tensor $\alpha'$ must be a symmetric matrix in Raman scattering.

### 2.2. Depolarization Ratio

If a plane-polarized light (e.g. laser) is incident on the material, the Raman scattered light from the sample will be polarized in a direction depending on the molecular arrangement in the material. The Raman scattered light is called depolarized light since the polarized direction of the original light is usually changed$^{23}$. If we check the depolarized light intensity after an analyzer, then the depolarization ratio $R$ is defined as the ratio between the intensities where the analyzer is perpendicular (perpendicular component $I_\perp$) and parallel (parallel component $I_\parallel$) to the incoming beam polarization direction as shown in Fig.2.2. The expression for depolarization ratio $R$, is given in eq.2.7

$$R = \frac{I_\perp}{I_\parallel}.$$  \hspace{1cm} (2.7)

![Fig. 2.2 Illustration of the depolarization ratio.](image-url)
The theoretical expression of depolarization ratio in the isotropic materials can be expressed with respect to the Raman tensor of certain vibration as shown in eq.2.8\(^{24}\).

\[
R = \frac{3(A_1 + B_1)}{10C_1 + 4(A_1 + B_1)},
\]

(2.8)

where,

\[
A_1 = \frac{1}{3} \left[ (\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + (\alpha'_{zz} - \alpha'_{xx})^2 \right],
\]

(2.9)

\[
B_1 = 2 \left[ (\alpha'_{xy})^2 + (\alpha'_{xz})^2 + (\alpha'_{yz})^2 \right],
\]

(2.10)

\[
C_1 = \frac{1}{3} (\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz})^2.
\]

(2.11)

According to eq.2.8, the depolarization ratio is a constant in isotropic materials. However, in liquid crystals, as anisotropic materials, the depolarization ratio is no longer constant and is modified by parameters called order parameters which represent the liquid crystal ordering property. Thus by measuring the depolarization ratios, information about the liquid crystal ordering can be obtained. In the next section, the order parameters and relevant theory will be reviewed.

### 2.3. Order Parameter Analysis

#### 2.3.1. Orientational Distribution Function (ODF) and Order Parameters

The anisotropic properties come from the arrangement of the anisotropic molecules in a liquid crystal. Thus knowing the arrangement of the molecules is an important step in liquid crystal research. The position of one molecule can be characterised by three independent angles which are known as the Euler angles \(\Omega(\alpha, \beta, \gamma)\) as shown in Fig.2.3.
Fig. 2.3 Illustration of the Euler angles $\Omega(\alpha, \beta, \gamma)$. The $x_d y_d z_d$ frame is the director frame in which the director direction lies on the $z_d$ axis. The $x_m y_m z_m$ frame is the molecular frame with the molecular long axis lying along the $z_m$ axis.

However, in a many-body system like liquid crystal, it is impossible to describe every molecular position due to the complex interactions in the system. To solve this, mean field theory (MFT) is widely used to simplify the interaction between many-bodies in a system to a single molecule in a potential field. After this simplification, the molecular arrangement can be described via an orientational distribution function (ODF) $f(\alpha, \beta, \gamma)$ by applying statistical methods. The ODF indicates the possibility of a molecule locating at a certain orientation $\Omega(\alpha, \beta, \gamma)$. Among the discussions of ODF and its further usage, Maier-Saupe (MS) theory is widely accepted in the uniaxial nematic phase\textsuperscript{25,26} and is further developed by Humphries, James and Luckhurst which is known as the HJL theory\textsuperscript{27}. In this section, the theory was reviewed according to Ref.\textsuperscript{27}.

As with the basic method of mean field theory, the interaction between liquid crystal molecules is simplified to a potential field which is called pseudo-potential defined as in eq.2.12,

$$U = \sum_{L,n} \langle u_{LL:n} \rangle \langle P_L(\cos \beta) \rangle P_L(\cos \beta),$$

(2.12)

where $\langle u_{LL:n} \rangle$ is the statistical average of the expansion coefficient, $P_L(\cos \beta)$ is the $L$th Legendre polynomial and $\langle P_L(\cos \beta) \rangle$ is the statistical average of the Legendre
polynomials which are further defined as the order parameters. The order parameters are the most important parameters in the investigation of liquid crystal order properties and can be used to identify the phase transitions in liquid crystals. A higher order parameter value represents a better ordered liquid crystal structure while the lowest value, 0, indicates the system is in the isotropic phase. Notice that the index $L$ only takes even values in a uniaxial system of rod-like molecules which is considered to lack polarity.

With the definition of the pseudo-potential, the ODF can be written as eq.2.13 using the Boltzmann distribution,

$$f(\beta) = \frac{-\frac{U}{kT}}{\int e^{-\frac{U}{kT}} \sin \beta \, d\beta}, \quad (2.13)$$

where $k$ is the Boltzmann constant and $T$ is the temperature. Notice that the system is a uniaxial system with rod-like molecules, so the distribution is only related to the angle from the director direction $\beta$. So the statistical average can be expressed with the Legendre polynomials as in eq.2.14,

$$\langle P_L(\cos \beta) \rangle = \int P_L(\cos \beta) f(\beta) \sin \beta \, d\beta = \int P_L(\cos \beta) \frac{-\frac{U}{kT}}{\int e^{-\frac{U}{kT}} \sin \beta \, d\beta} \sin \beta \, d\beta. \quad (2.14)$$

Usually, the pseudo-potential expression (eq.2.12) is expanded to the fourth rank ($L = 4$) which is,

$$U = \langle u_2 \rangle \langle P_2(\cos \beta) \rangle P_2(\cos \beta) + \langle u_4 \rangle \langle P_4(\cos \beta) \rangle P_4(\cos \beta)$$

$$= \langle u_2 \rangle \left( \langle P_2(\cos \beta) \rangle P_2(\cos \beta) + \lambda \langle P_4(\cos \beta) \rangle P_4(\cos \beta) \right), \quad (2.15)$$

where

$$\langle u_L \rangle = \sum_n \langle u_{L,n} \rangle, \quad (2.16)$$

$$P_2(\cos \beta) = \frac{1}{2} (3 \cos^2 \beta - 1), \quad (2.17)$$

$$P_4(\cos \beta) = \frac{1}{8} (35 \cos^4 \beta - 30 \cos^2 \beta + 3). \quad (2.18)$$
Notice that $\lambda$ is the ratio $\langle u_4 \rangle / \langle u_2 \rangle$ and it is an experimental fitting parameter$^3$, $\langle u_2 \rangle$ can be determined via eq.2.19 where the $\langle u_2 \rangle^{(0)}$ is a temperature independent constant$^{20}$, $V$ is the molar volume and $\gamma$ is an arbitrary parameter$^{27}$, the value of which is determined from the experimental data.

$$\langle u_2 \rangle = \frac{\langle u_2 \rangle^{(0)}}{V\gamma} \quad (2.19)$$

Substituting eqs.2.15-2.18 into eq.2.14, two equations can be obtained with parameters $\langle P_2(\cos \beta) \rangle$ and $\langle P_4(\cos \beta) \rangle$. By solving these two equations, the theoretical values of $\langle P_2(\cos \beta) \rangle$ and $\langle P_4(\cos \beta) \rangle$ can be obtained. This theoretical discussion gives a good reference with which to compare the experimental results.

In addition to such theoretical method that can be used to estimate the order parameters, ODF can be also expressed with Wigner D-matrices as seen in eq.2.20$^{16,28}$,

$$f(\alpha, \beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m,m'=-L}^{L} \frac{2L + 1}{8\pi^2} \langle D_m^{L*} \rangle \langle D_m^{L'} \rangle (\alpha, \beta, \gamma) \ D_{m'm}^{L}(\alpha, \beta, \gamma), \quad (2.20)$$

where $m$, $m'$ and $L$ are integers and $m$ and $m'$ take the value between $-L$ to $L$. The superscript * denotes the complex conjugate and the Wigner D-matrices is defined as,

$$D_{m'm}^{L}(\alpha, \beta, \gamma) = e^{-im'\alpha} d_{m'm}^{L}(\beta) e^{-im\gamma}. \quad (2.21)$$

If we use uniaxial system as the example, the molecular orientational distribution must be symmetrical with respect to the director axis. Thus the distribution function is independent of $\alpha$, so that the ODF should not have an $\alpha$ term and $m'$ must equals to zero$^{16}$, according to the definition of the Wigner D-matrix in eq.2.21. Also, if we assume the molecule is rod-like with cylindrical symmetry, and then the rotational distribution around the molecular long axis should not appear, thus $m$ should also equal zero. With these constraints, the ODF can be expressed as,

$$f(\beta) = \sum_{L=0}^{\infty} \frac{2L + 1}{8\pi^2} \langle D_{00}^{L*} \rangle D_{00}^{L}(\beta). \quad (2.22)$$
Expanding eq. 2.22 to the fourth rank, after simplification (see Appendix A.3), the ODF can be rewrite as, eq. 2.23.

\[
f(\beta) = \left( \frac{1}{8\pi^2} \right) \left[ 1 + \frac{5}{2} \langle P_{200} \rangle (3\cos^2\beta - 1) + \frac{9}{8} \langle P_{400} \rangle (35\cos^4\beta - 30\cos^2\beta + 3) \right].
\] (2.23)

Eq. 2.23 is the typical ODF that is used in the PRS analysis method. Notice that we use the form \( \langle P_{lm\cdot\cdot} \rangle \) from now on to represent the order parameter (e.g. \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) for \( \langle P_2(\cos\beta) \rangle \) and \( \langle P_4(\cos\beta) \rangle \) respectively).

### 2.3.2 Order Parameter Analysis from Polarized Raman Spectroscopy (PRS)

According to eq. 2.5, the Raman scattering intensity is proportional to the square of differential polarizability which is represented by the Raman tensor. Theoretically speaking, the Raman tensor should be a property of the bulk material in laboratory frame or director frame which will be expressed as \( \alpha'_L \) and \( \alpha'_D \) respectively. However, it will be very hard to deal with in liquid crystal system due to the extra time dependence from the rotational motion of the molecules\(^{16}\). In practice, the Raman tensor is assumed to be a microscopic property of the molecule as labeled \( \alpha'_{M} \). Combining \( \alpha'_{M} \) with the ODF, it is possible to express the macroscopic property \( \alpha'_L \) and \( \alpha'_D \). Local field corrections are assumed not to be important during this process, which is supported by the empirical evidence\(^{16, 29, 30}\). Further, Jen \emph{et al.} also made a hypothesis in their method that \( \alpha'_{M} \) is unchanged in the molecular frame when the liquid crystal phases change\(^{16}\). Based on these preconditions, Jen \emph{et al.} developed an analysis method in 1970s\(^{15, 16}\) which was modified and improved by Jones \emph{et al.} 2004\(^{17}\). These two methods will be reviewed in this section.

**Jen \emph{et al.} ’s Method**

Jen and coworkers published a measurement method for order parameters in a uniaxial nematic phase using PRS in 1977\(^{16}\). In their method three scattered intensities (\( I_{xx} \) etc.) are collected as shown in Fig. 2.4. A homogenous aligned liquid crystal sample
is used with the director along the Z axis of the laboratory frame. By using different combinations of the directions of the polarizer and analyzer with respect to the director, three intensities are obtained, and then two depolarization ratio values can be found as shown in eqs.2.24 and 2.25.

Fig. 2.4 Three intensities, $I_{xx}$, $I_{xz}$ and $I_{zz}$ collected in Jen et al.'s method\textsuperscript{16}. The different intensities depend on the different orientations of the polarizer direction and analyzer direction. The $z$ direction is the director direction.

\[ R_1 = \frac{I_{xz}}{I_{zz}}, \]  
(2.24)

\[ R_2 = \frac{I_{xx}}{I_{zz}}. \]  
(2.25)

Taking refractive indices into consideration, according to Lax and Nelson\textsuperscript{31}, correction terms must be used and the corrected equation are shown in eqs.2.26 and 2.27. The effect of alignment layer was not discussed. However, considering the very thin thickness of alignment layer, the correction should be sufficient.

\[ R_1 = C_n r_1, \]  
(2.26)

\[ R_2 = \frac{r_2}{C_n}, \]  
(2.27)

where,
In eq.2.28, \( n_{\text{glass}} \) represents the refractive index of the cover glass, \( n_{xx} \) and \( n_{zz} \) are the refractive indices along the \( z \) and \( x \) axes. \( r_1 \) and \( r_2 \) are the theoretical depolarization ratios which can be expressed in terms of differential polarizability\(^\text{16} \).

\[
C_n = \left( \frac{n_{\text{glass}} + n_{zz}}{n_{\text{glass}} + n_{xx}} \right)^2. \tag{2.28}
\]

\[
r_1 = \frac{\langle \alpha'_{L_{xx}} \rangle^2}{\langle \alpha'_{L_{zz}} \rangle^2}, \tag{2.29}
\]

\[
r_2 = \frac{\langle \alpha'_{L_{xx}} \rangle^2}{\langle \alpha'_{L_{xx}} \rangle^2} = \frac{\langle \alpha'_{L_{xx}} \rangle^2}{\langle \alpha'_{L_{xx}} \rangle^2}, \tag{2.30}
\]

With the assumptions that the molecule is rod-like and has uniaxial symmetry, the relationship between the order parameter and differential polarizability are shown below.

\[
A_2^{-2} \langle \alpha'_{L_{xx}} \rangle^2 = \frac{1}{9} + \frac{3}{16} B_2 + \frac{1}{4} C_2 + \frac{1}{18} D_2 + \frac{11}{288} D_2^2 + \left( \frac{1}{8} B_2 + \frac{1}{2} C_2 - \frac{1}{6} D_2 - \frac{5}{48} D_2^2 \right) \langle \cos^2 \beta \rangle \\
+ \left( \frac{3}{16} B_2 - \frac{3}{4} C_2 + \frac{3}{32} D_2^2 \right) \langle \cos^4 \beta \rangle, \tag{2.31}
\]

\[
A_2^{-2} \langle \alpha'_{L_{xz}} \rangle^2 = \frac{1}{4} B_2 + \frac{1}{4} C_2 - \left( \frac{3}{4} C_2 - \frac{1}{8} D_2^2 \right) \langle \cos^2 \beta \rangle - \left( \frac{1}{4} B_2 - C_2 + \frac{1}{8} D_2^2 \right) \langle \cos^4 \beta \rangle, \tag{2.32}
\]

\[
A_2^{-2} \langle \alpha'_{L_{zz}} \rangle^2 = \frac{1}{9} + \frac{1}{2} B_2 - \frac{1}{9} D_2 + \frac{1}{36} D_2^2 - \left( B_2 + 2 C_2 - \frac{1}{3} D_2 + \frac{1}{6} D_2^2 \right) \langle \cos^2 \beta \rangle \\
+ \left( \frac{1}{2} B_2 - 2 C_2 + \frac{1}{4} D_2^2 \right) \langle \cos^4 \beta \rangle. \tag{2.33}
\]

Where in this case,

\[
A_2 = \alpha'_{M_{xx}} + \alpha'_{M_{yy}} + \alpha'_{M_{zz}}, \tag{2.34}
\]

\[
B_2 = \left( \frac{1}{A_2^2} \right) \left[ \frac{1}{4} \left( \alpha'_{M_{xx}} - \alpha'_{M_{yy}} \right)^2 + \alpha'_{xy}^2 \right], \tag{2.35}
\]

\[
C_2 = \left( \frac{1}{A_2} \right) \left( \alpha'_{M_{xz}}^2 + \alpha'_{M_{yz}}^2 \right), \tag{2.36}
\]

\[
D_2 = \left( \frac{1}{A_2^2} \right) \left( 2 \alpha'_{M_{zz}} - \alpha'_{M_{xx}} - \alpha'_{M_{yy}} \right). \tag{2.37}
\]

In these equations, the Raman tensor components with index \( L \) are in the
laboratory frame and refer to the macroscopic property of the liquid crystal (notice that the laboratory frame is coincident with the director frame in Jen et al.’s method), while the Raman tensor component with index $M$ are the in the molecular frame which represents the microscopic properties of the molecule. Further, the terms in $\langle \cos^2 \beta \rangle$ and $\langle \cos^4 \beta \rangle$ are used to express the order parameters.

$$\langle P_{200} \rangle = \frac{1}{2} (3 \langle \cos^2 \beta \rangle - 1), \quad (2.38)$$

$$\langle P_{400} \rangle = \frac{1}{8} (35 \langle \cos^4 \beta \rangle - 30 \langle \cos^2 \beta \rangle + 3). \quad (2.39)$$

With the equations mentioned above, the depolarization ratio in isotropic phase can be obtained using eq.2.40. In addition, combined with the fact that order parameters are zero in isotropic phase, the depolarization ratio measured in isotropic phase $R_{\text{iso}}$ is not related to the order parameter and a relationship is obtained which is equivalent to eq.2.8 after simplification.

$$R_{\text{iso}} = \frac{3}{45} \frac{12B_2 + 12C_2 + D_2^2}{12B_2 + 12C_2 + D_2^2}. \quad (2.40)$$

However, the Raman tensor is still complex with many unknown Raman tensor terms and that increases the difficulty of analysis. Thus further transformations are needed. For certain vibrational modes, there is a special axis (the vibrational symmetry axis according to Jen et al.\textsuperscript{16}) that, along this axis, the Raman tensor can be expressed in a diagonal form,

$$\alpha'_S = \begin{pmatrix} \alpha'_{sxx} & 0 & 0 \\ 0 & \alpha'_{syy} & 0 \\ 0 & 0 & \alpha'_{szz} \end{pmatrix} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha'_{szz}. \quad (2.41)$$

Here the index $S$ represents the symmetry centre frame. Usually the symmetry centre axis is tilted from the molecular long axis with a tilt angle $\beta_0$ according to Jen et al.\textsuperscript{16}, with the tensor frame transformation, it is possible to express the Raman tensor components in the molecular frame and re-express the parameters $A_2$, $B_2$, $C_2$ and $D_2$ as shown below,

$$A_2 = 1 + a + b, \quad (2.42)$$
\[ B_2 = \left( \frac{1}{4A_2^2} \right) [a - b + (1 - a)\sin^2\beta_0]^2, \]  
\[ C_2 = \left( \frac{1}{A_2^2} \right) (1 - a)^2 \sin^2\beta_0 \cos^2\beta_0, \]  
\[ D_2 = \left( \frac{1}{A_2^2} \right) [2 - (a + b) - 3(1 - a)\sin^2\beta_0]. \]  

In this situation, the depolarization ratio in the isotropic phase can be written as

\[ R_{iso} = \frac{3(a^2 + b^2 + 1 - a - b - ab)}{5(a + b + 1)^2 + 4(a^2 + b^2 + 1 - a - b - ab)}. \]  

After this process, there are still many parameters left which still makes it hard to determine the order parameters values. So further assumptions were made, i.e. that the vibration is uniaxial symmetric, which means \( a=b=r \). Then the parameters \( A_2, B_2, C_2 \) and \( D_2 \) can be expressed as,

\[ A_2 = 1 + 2r, \]  
\[ B_2 = \left( \frac{1}{4A_2^2} \right) (1 - r)^2 \sin^4\beta_0, \]  
\[ C_2 = \left( \frac{1}{A_2^2} \right) (1 - r)^2 \sin^2\beta_0 \cos^2\beta_0, \]  
\[ D_2 = \left( \frac{1}{A_2} \right) (1 - r)(3 \cos^2\beta_0 - 1). \]

In this situation, the depolarization ratio in the isotropic phase can be written as,

\[ R_{iso} = \frac{(1 - r)^2}{3 + 4r + 8r^2}. \]

Usually, the vibrational mode is chosen with the condition that the symmetry axis is along the molecular long axis, thus \( \beta_0 \) is zero in most measurement and eqs.2.47-2.50 are further simplified. Further, within Jen et al.’s method, he made an assumption that the value of \( r \) is constant even in different liquid crystal phases. Under this assumption, the value of \( r \) can be calculated from the depolarization ratio in the isotropic phase. With the value of \( r \) determined, the parameters \( A_2, B_2, C_2 \) and \( D_2 \) can be found and finally combined with the depolarization ratios in the liquid crystal phase obtained from the Raman experiment, allowing the order parameters to be solved from the depolarization.
Jen et al. ’s method works well for the $\langle P_{200} \rangle$ value when compared with the theory and with the results from experiment. However, the values of $\langle P_{400} \rangle$ determined in this way are much lower than the theoretical prediction and can even become a negative value, which is unphysical. The main issue is whether the value of $r$ is constant as considered in Jen et al. ’s assumptions.

**Jones et al. ’s Method**

Later, Jones et al. published a paper in 2004, reporting a new analysing method using fitting procedure which gives much better estimate value. Jones et al. ’s method uses the same theoretical background as Jen et al. ’s method. However instead of fixing the liquid crystal sample in the experiment, depolarization ratio was determined as a function of rotation angle $\theta$, by rotating the liquid crystal sample as shown in Fig.2.5. Then the order parameters are obtained by fitting the theoretical curve with the experimental depolarization ratio graph.

Fig. 2.5 Brief illustration of Jones et al. ’s method. The sample is rotated in the $x_L, o z_L$ plane with the rotational angle $\theta$ defined as the angle between $z_L$ and the director direction of the planar aligned nematic liquid crystal.

With the assumptions that 1) the vibrational symmetry direction is parallel to the molecular long axis, 2) the vibration bond has a uniaxial cylindrical symmetry so the Raman tensor is diagonal form, then the equations for the intensities are shown in eqs.2.52 and 2.53 (details in Appendix A.4).

$$I_{\|}(\theta) = k(\alpha_3'_{sxz})^2 (A_3 + B_3\langle P_{200} \rangle + 3C_3\langle P_{400} \rangle - 3B_3\langle P_{200} \rangle \cos^2 \theta - 30C_3\langle P_{400} \rangle \cos^2 \theta$$
\[ I_\perp(\theta) = k \left( a'_{zzz} \right)^2 (D_3 - E_3 \langle P_{200} \rangle - 4C_3 \langle P_{400} \rangle + 35C_3 \langle P_{400} \rangle \cos^2 \theta \sin^2 \theta), \]

where,

\begin{align*}
A_3 &= \frac{8r^2 + 4r + 3}{15}; \\
B_3 &= \frac{(8r^2 - 2r - 6)}{21}; \\
C_3 &= \frac{(r - 1)^2}{35}; \\
D_3 &= \frac{(r - 1)^2}{15}; \\
E_3 &= -\frac{(r - 1)^2}{21};
\end{align*}

\( k \) is a constant which will not affect the depolarization ratio. Introducing the refractive index correction, \( k \) is replaced by \( k/(n_{glass} + n_{xx})^2 \) which is still a constant that will not affect the depolarization ratio and \( r \) is replaced by \( rC_n \) where \( C_n \) is a constant as defined in eq. 2.28\(^{17}\). With these equations and the experimental depolarization ratio graph, it is possible to fit the theoretical curve for specific values of \( \langle P_{200} \rangle, \langle P_{400} \rangle \) and \( r \). Not surprisingly, by choosing specific rotational angle values, we can obtain the same result as in Jen et al.’s method.

\begin{align*}
I_\parallel(\theta = 0^\circ) &= I_{zz} = k a'_{zzz} (A_3 - 2B_3 \langle P_{200} \rangle + 8C_3 \langle P_{400} \rangle), \\
I_\parallel(\theta = 90^\circ) &= I_{xx} = k a'_{zzz} (A_3 + \langle P_{200} \rangle + 3C_3 \langle P_{400} \rangle), \\
I_\perp(\theta = 90^\circ - 0^\circ) &= I_{xz} = k a'_{zzz} (D_3 - E_3 \langle P_{200} \rangle - 4C_3 \langle P_{400} \rangle). 
\end{align*}

2.4. Summary

In this chapter, the origin of Raman scattering alongside the theoretical background of Raman scattering were reviewed. According to the discussion, the Raman scattering intensity is proportional to the square of the differential polarizability and one can use this information to obtain the order parameters of anisotropic systems like liquid
crystals via observing the depolarization ratio. This leads to an important experimental method called Polarized Raman Spectroscopy (PRS), for measuring the order parameters. Two previous analysis methods, Jen et al.’s and Jones et al.’s methods, which analyse PRS data to obtain order parameters were discussed in this chapter. The general approach of these methods is to assume the macroscopic Raman tensor is the statistical average of all the microscopic molecular Raman tensors, determined with the help of certain orientational distribution function (ODF). Jen et al.’s method is straightforward, but gives an unphysical value on one of the order parameters (\(P_{400}\)). Jones et al. developed a method that gives a better fitting value on \(P_{400}\) than obtained from Jen et al.’s method. So our research will base on Jones et al.’s method. In next chapter, the experimental setups for PRS measurement will be discussed with a carefully comparison will be given regarding to the difference between Jen et al.’s and Jones et al.’s method. We will also introduce an important failing of Jones et al.’s method in the next chapter.
References


M. F. Vuks, Optics and Spectroscopy-Ussr 20, 361 (1966).


Chapter 3

Experimental Procedure and a Discussion of the Failings of Jones et al.’s Method

A review of the basic backgrounds of PRS and the theoretical background of Jen et al.’s and Jones et al.’s methods on order parameter analysis were given in Chapter 2. Since the assumption in Jen et al.’s method that the differential polarizability ratio \( r \) to be a constant, is demonstrated to be incorrect, Jones et al.’s method is preferred in obtaining order parameters. In this chapter, the details of the experimental setup of Jones et al.’s method will be discussed (Section 3.1). Details about the experimental process will be shown and more evidence will be provided showing why Jones et al.’s method gives a more reliable fitting value of \( \langle P_{400} \rangle \) compared to Jen et al.’s method in Section 3.2. However, despite the advantages of Jones et al.’s method, it is found that for a given sample, the order parameters deduced from different vibrational modes along the molecular long axis are different. An example of this discrepancy will be given and the possible reasons will be discussed briefly in Section 3.3.

3.1. Experimental Setup of Jones et al.’s Method

The experimental setup used to deduce order parameters in liquid crystals via Jones et al.’s method is shown in Fig.3.1. A Renishaw RM1000 Raman spectrometer was used in the experiment. A 515.32 nm solid state laser (Spectra-Physics) with a maximum output power of 50 mW was used as the light source. It is worthy of note that some of the
data obtained before 2011 were done with a 514 nm Argon ion laser with a maximum output power of 20 mW. The newer solid state laser has a higher divergence compared with the Argon ion laser. This means that the telescope beam expander system in the Raman spectrometer had to be adjusted for use with the solid state laser. Raman spectra were obtained from the scattered light of the liquid crystal, and were detected by a charge coupled detector (CCD). An Olympus ultra-long working distance 50× objective lens was used both to focus the laser beam to a diameter of 5µm on the sample and to collect the reflected Raman scattered light. A hot stage (Linkam HFS91) connected to a temperature controller (Linkam TMS93) was used to maintain the sample temperature with a relative accuracy of ±0.1 K(°C). A 1800 lines/mm grating was used in the Raman system to provide a wide measurement range of the frequency shift from 0 cm\(^{-1}\) to 3000 cm\(^{-1}\) with a resolution of 0.5 cm\(^{-1}\), covering all the main Raman peaks in liquid crystal materials.

![Diagram of experimental setup](image)

Fig. 3.1 A basic illustration of the experimental setup. The green line indicates the laser light path. The analyzer is parallel to the incoming beam polarization direction and the half wave plate is used to rotate the polarization direction by 90° to obtain the perpendicular measurement.

### 3.2. Experimental Procedure of Jones et al. ’s Method

In this section, a well-known calamitic nematic liquid crystal material, 4-cyano-4’-pentylbiphenyl, which is commonly known as 5CB, will be used to describe the experimental procedure of Jones et al.’s method. The molecular structure of 5CB is
shown in Fig.3.2 together with a Raman spectrum. 5CB forms a nematic liquid crystal phase at room temperature (273.2 K) with the clearing point, $T_{NI}$, at 308.3 K (35.1 °C).

Fig. 3.2 The Raman spectrum of 5CB (4-Cyano-4’-pentylibiphenyl) together with its molecular structure and N-I transition temperature. There are two important Raman peaks: the phenyl stretching peak and the cyano stretching peak appearing at 1606 cm$^{-1}$ and 2220 cm$^{-1}$ respectively.

A homogenously-aligned 5CB sample contained in a 5 µm thick cell was placed within the temperature controlled hot stage to maintain constant temperature. The hot stage was placed on the rotating sample stage. By rotating the sample stage, Raman spectra were collected at certain rotation angles from 0° to 360° at 5° intervals for both the parallel ($\lambda/2$ wave plate taken out) and perpendicular ($\lambda/2$ wave plate added in) configurations (detail discussions of the experiment method can be found in Appendix A.6.) The intensity of the Raman peak for each configuration, $I_\parallel$ and $I_\perp$, was deduced by fitting the Raman peaks of the chosen vibrational mode with a Lorentz function. The experimental depolarization ratio calculated from these two intensities was thus deduced as a function of rotation angle $\theta$. Eqs.2.52 and 2.53 describe the parallel and perpendicular intensities theoretically as a function of rotation angle $\theta$ and the differential polarizability ratio, $r$ with order parameters $\langle P_{000} \rangle$ and $\langle P_{400} \rangle$. Fitting the experimentally determined depolarization ratio to equations Eqs.2.52 and 2.53 allows the order parameters $\langle P_{000} \rangle$ and $\langle P_{400} \rangle$ to be deduced. The phenyl stretching mode (1606 cm$^{-1}$ in Fig.3.2) has been selected for analysis by most authors$^{1,2}$ to deduce the order parameters. As shown in Fig.3.3, the order parameters determined from the phenyl stretching mode are in good agreement with the theory predication.
Fig. 3.3 Plot of \( \langle P_{200} \rangle \) (black squares) and \( \langle P_{400} \rangle \) (red circles) as a function of temperature for 5CB compared with the theoretical prediction deduced from two different parameter sets (dashed line and solid line) according to the Humphries-James-Luckhurst theory. Dashed line: \( \lambda = 0.15; \gamma = 2 \) and solid line: \( \lambda = 0.15; \gamma = 0 \) (Theoretical plots from Southern’s work).

The advantage of Jones et al.’s method is that the assumption made by Jen et al. that the differential polarizability ratio, \( r \), is a constant can be ignored. By using Jones et al.’s method, the fact is revealed that \( r \) is approximately -0.14 in nematic phase compared with around -0.04 in isotropic phase as shown in Fig. 3.4. This proves that the differential polarizability ratio \( r \) in different phases is actually different.

Fig. 3.4 Plot of differential polarizability ratio, \( r \), as a function of temperature for 5CB. The transition between the nematic phase and the isotropic phase is included to show the significantly different \( r \) values determined in different phases.

Recalling that Jen et al.’s method gives low values for \( \langle P_{400} \rangle \), the reason for this can now be discussed. As shown in Fig. 3.5, The blue depolarization ratio graph is calculated via equations using Jones et al.’s method in which the order parameters \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) and the differential polarizability ratio \( r \) are taken to be 0.50, 0.20 and -0.20.
respectively to show a depolarization ratio graph similar to 5CB. On the other hands, the \( r \) value at the isotropic phase (-0.04) from Fig.3.4 is used as the reference \( r \) value. Then by adjusting values of \( \langle P_{200} \rangle, \langle P_{400} \rangle \) and \( r \), keeping the \( r \) value close to the reference value (-0.04), the red depolarization ratio graph can be generated which gives exactly same depolarization ratio value at \( R_1 \) and \( R_2 \) position. It is to be noted that \( R_1 \) and \( R_2 \) positions are the only two depolarization ratios used in Jen et al.’s method\(^5\). Thus by using Jen et al.’s method, there should be more than one sets of \( \langle P_{200} \rangle, \langle P_{400} \rangle \) and \( r \) generating certain depolarization ratio values at \( R_1 \) and \( R_2 \) position. However, in Jen et al.’s method, as discussed in Chapter 2, the \( r \) value is derived from the isotropic phase. Thus the set of order parameters and \( r \) value from the red depolarization ratio graph is the final results obtained by Jen et al.’s method. As shown in Fig.3.5, the \( \langle P_{200} \rangle \) value shows a small change (~6%) in the value but the value of \( \langle P_{400} \rangle \) from the red graph is 0.026 which is almost 10 times lower than the value from the blue graph. This much lower value is commonly seen from Jen et al.’s method\(^5\). So in conclusion, Jen et al.’s method only shows one possible solution with certain \( R_1 \) and \( R_2 \). But due to the fixed \( r \) value, the result from Jen et al.’s method does not reflect the correct depolarization graph, thus the \( \langle P_{400} \rangle \) value from Jen et al.’s method is not reliable.

Fig. 3.5 Depolarization graph according to eqs.2.52 and 2.53. The blue line shows the depolarization graph with \( \langle P_{200} \rangle = 0.5, \langle P_{400} \rangle = 0.2 \) and \( r = -0.2 \); The red line shows the depolarization graph with \( \langle P_{200} \rangle = 0.47, \langle P_{400} \rangle = 0.03 \) and \( r = -0.03 \). The two depolarization ratios \( R_1 \) and \( R_2 \) used in Jen et al.’s method is shown.

The discussion by Southern et al. also draws the same conclusion from 8CB experiment\(^2\). With the discussion in Ref. 2, Jones et al.’s method was modified and has become a robust analysis method for obtaining liquid crystal order parameters using PRS.
3.3. The Failing of Jones et al.’s method

As discussed in section 3.2, fitting to the full depolarization ratio obtained from Raman scattering experiments works well where the phenyl stretching mode is analysed, giving much more reasonable values for $\langle P_{400} \rangle$ than were deduced with the ‘two-point’ measurements used by Jen et al. However, a further discrepancy remains in Jones et al.’s method: it is reported that the order parameter values obtained from other vibrational modes such as the cyano stretching mode, are quite different from those obtained from the phenyl stretching mode. This issue will be discussed in this section, in which the cyano stretching mode is used as a direct comparison to the phenyl stretching mode, to show the discrepancy quantitatively.

Fig. 3.6 Experimental depolarization ratio data and the fitting curve with eqs.2.52 and 2.53. The data in a) and c) are the depolarization ratio as a function of rotation angle, deduced for the phenyl stretching mode at 1606 cm$^{-1}$, for a) a 5CB sample at 304 K (31°C) and c) the mixture E63 at 346 K (73°C). The data in b) and d) are for the cyano stretching mode at 2226 cm$^{-1}$ again for 5CB at 304 K(31°C) and E63 at 346 K (73°C) respectively. These data come from previous work using the Argon ion laser.

The cyano group is sited at the end of the 5CB molecule and, as shown in Fig.3.2, it shows a strong Raman peak at 2226 cm$^{-1}$. Following the same experimental procedure
as described in section 3.1, the depolarization graphs for both phenyl and cyano stretching modes can be obtained from 5CB as shown in Fig. 3.6a) and b). It is clear that the depolarization ratio graphs of these two vibrational modes have a huge difference. In particular, the peak in depolarization graph associated with the phenyl stretching mode between $\theta \sim 60^\circ$ and $240^\circ$ is fairly flat, while there is a deep trough in the data for the cyano stretching mode. Clearly, a detailed consideration of the reasons behind this issue is needed.

Extensive researches on 5CB show a well-known property that 5CB suffers from strong antiparallel ordering as a result of the strong dipolar interactions in the pure 5CB materials$^{7-9}$. Thus E63 which is a eutectic mixture designed to hinder the antiparallel ordering was used as a comparison$^{10}$. E63 has a clearing point of 358.8 K (85.8 $^\circ$C)$^{10}$ and major constituents are cyano-biphenyls as 5CB. Thus the Raman spectrum of E63 is very similar to 5CB. Considering both of these materials offers an opportunity to test whether the antiparallel order could have an impact on the Raman scattering of the system. Referring to Fig. 3.6c) and d), it is clear that the depolarization ratio plot of cyano stretching mode (Fig. 3.6c)) is also different from the one obtained from phenyl stretching mode (Fig. 3.6d)). Thus the effect of the antiparallel ordering can be ruled out since the same overall behaviour in E63 was observed as occurs in 5CB.

Fig. 3.7 Plot of $\langle P_{200} \rangle$ (black squares) and $\langle P_{400} \rangle$ (red circle) values versus temperature compared with the theoretical prediction in two sets of different parameter values (dashed line and solid line), according to the Humphries-James-Luckhurst theory$^3$ (Dashed line: $\lambda = 0.15$; $\gamma = 2$ and solid line $\lambda = 0.15$; $\gamma = 0$, plots from Southern’s thesis$^4$) Solid symbols are fitting results from phenyl stretching mode and empty with cross symbols are fitting results from cyano stretching mode. All data are for the 5CB sample. (Theoretical plots from Southern’s work$^4$)
The uniaxial order parameters, \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \), can be obtained by analysing the 5CB data using Jones et al.’s method. Figure 3.7 shows the order parameters obtained from the two vibrational modes. While the fitting values of \( \langle P_{200} \rangle \) are the same within experimental uncertainty, the fitting values of \( \langle P_{400} \rangle \) are very different, with the \( \langle P_{400} \rangle \) fitting values deduced from the data associated with the cyano stretching mode are significantly higher from the fitting values from the phenyl stretching mode and from the theoretical prediction. This illustrates that PRS works well if the order parameters are deduced from certain vibrational modes but not others using Jones et al.’s method.

After reviewing Jones et al.’s method, many assumptions were made to deduce the equations used. These assumptions will be the key to solve the discrepancy on the fitting values of the order parameters. So in next chapter, it will be checked whether relaxing some of the fundamental assumptions can explain the differences or, even better, allow self-consistent order parameters to be deduced.

3.4. Summary

In this chapter, a detailed experimental setup and procedure that allows liquid crystal order parameters to be deduced from the depolarization ratios following a modified Jones et al.’s method has been reviewed. The reason why Jones et al.’s method gives a much more robust evaluation of the \( \langle P_{400} \rangle \) value than Jen et al.’s method has been shown. However, it has been demonstrated that even though the modified Jones et al.’s method works well on the phenyl stretching mode, a different set of order parameters are obtained if the cyano stretching mode is studied in 5CB and E63. The observation shows that similar behaviour of the depolarization ratio graph can be obtained from the data referring to the same vibrational mode in 5CB and E63. This fact rules out the possibility that the antiparallel ordering in 5CB causes this discrepancy. Reviewing the Jones et al.’s method reveal quiet a lot assumptions. By giving some reasonable modification on the assumptions, the discrepancy may probably be explained. Thus this topic will be discussed in the next chapter.
References

Chapter 4

Discussion of the Discrepancy of Order Parameter Values Deduced from Different Vibrational Modes and a New Fitting Approach

The experimental method and advantages of the modified Jones et al.’s method for deriving order parameters with PRS have been reviewed in the previous chapter. The depolarization ratio equations are more generalized and reflect the change of depolarization ratio more precisely than Jen et al.’s method. Thus the low $\langle P_{400} \rangle$ obtained from Jen et al.’s method can be corrected and the order parameters obtained are more accurate. However, we also highlighted the existence of a discrepancy in the order parameter values derived from different vibrational modes\textsuperscript{1}. In this chapter, we will provide an explanation for the origin of this discrepancy by introducing a dipole tilt into consideration. The basic theory of the new analysis method will be described in Section 4.1. The effect of introducing the dipole tilt will be discussed in Section 4.2. The discussion of the fitting using the new method will be shown in Section 4.3. Following this approach, a modification is made to the analysis method to make it compatible for different vibrational modes. Then the simulation results will be presented in section 4.4. In the end of this chapter, a supplementary discussion will be described about another possible explanation on the discrepancy by considering the different vibrational symmetries of different vibrational modes. The main content of this chapter will be published in European Physical Journal E and is reproduced almost exactly as parts of this chapter with some supplementary information and work.
4.1. Details of a Modified Theoretical Approach

In order to understand the discrepancies that result from applying the standard analysis techniques of the depolarization ratios to deducing order parameters from vibrational modes other than the phenyl stretch, we now consider a new approach for fitting PRS data that combines Jen et al.’s frame transformation method\textsuperscript{2,3} and Jones et al.’s concept of a macroscopic rotation parameter $\theta$, as shown in Fig.4.1\textsuperscript{4}.

4.1.1. Basic Assumptions and Frame Setup

The most important concept in this modified theoretical approach is that the vibration centre direction is tilted from the molecular long axis. The vibration centre direction will be later assumed as the dipole symmetry direction. It is worthy of note that the term “dipole” here does not indicate the permanent dipole moment, it describes the bond that is excited by the incident photons. To make the discussion consistent, we call this vibration centre the dipole symmetry direction and the tilt is the dipole tilt, $\beta_0$ is the symbol used to describe this parameter. This concept was mentioned in PRS analysis by Jen et al. in 1977\textsuperscript{3}. However, this tilt is usually ignored since the vibrational modes used for investigation, such as the phenyl stretching mode, is assumed to align along the molecular long axis.

As in Jen et al.’s and Jones et al.’s methods, the first thing is to put forward the basic assumptions. The initial assumption will be made firstly that short range molecular interactions are ignored, thus the local field correction factor is not considered (i.e. $g=1$). Then the further assumptions are shown below.

1. The liquid crystal system is a uniaxial system.

2. The liquid crystal molecule is board-like as shown in Fig.4.1. $z_M$ of the molecular frame is along the molecular long axis. The board plane is the plane formed by the molecular long axis and the dipole tilt direction. $x_M$ is defined by the molecular secondary long axis of the board as shown in Fig.4.1.

3. The dipole itself has uniaxial symmetry (cylindrical symmetry).
Fig. 4.1 Four frames exist in our analysis: the laboratory frame \((x_L, y_L, z_L)\); the director frame \((x_D, y_D, z_D)\); the molecular frame \((x_M, y_M, z_M)\) and the dipole frame \((x_S, y_S, z_S)\). The dipole is tilted from the molecular long axis with a dipole tilt \(\beta_0\). The liquid crystal sample is rotating in \(x_LO''z_L\) plane with the laser incident along the \(y_L\) axis.

In Fig. 4.1, there are four relevant frames, the vibrational symmetry frame \(S\) with a component \(z_S\) along the dipole vibration direction; the molecular frame \(M\) which uses the molecular long axis as its \(z_M\) axis; the director frame \(D\) in which the component \(z_D\) is along the director direction; and the laboratory frame \(L\) with the \(x_LO''z_L\) plane as the liquid crystal sample’s rotation plane and \(y_L\) is the laser incidence direction with the polarization direction along the \(z_L\) axis.

### 4.1.2. Raman Tensor

As mentioned in Chapter 2, PRS generates a spectrum with Raman peaks for each Raman-active vibrational mode in which the intensity is proportional to the statistical average of square of Raman tensor which is as defined in eq. 4.1\(^5\).

\[
I_{ij} \propto \langle \alpha'_{Lij} \rangle^2 = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma \alpha'_{Lij} f(\alpha, \beta, \gamma). \quad (i, j = x, y, z) \quad (4.1)
\]

where the \(\alpha'_{Lij}\) is the Raman tensor components in the laboratory frame. \(f(\alpha, \beta, \gamma)\) is the orientational distribution function (ODF). Referring to Jen et al.’s method, the first step is to obtain the \(\alpha'_{S}\) in the diagonal form of the Raman tensor \(\alpha'_{S}\). The additional
condition of $\alpha'_S$, is that $\alpha'_{Sxx} = \alpha'_{Syy} \ll \alpha'_{Szz}$, which comes from the assumption that the dipole itself has uniaxial symmetry. Thus it is obtained as eq.4.2,

$$\alpha'_S = \begin{pmatrix} \alpha'_{Sxx} & 0 & 0 \\ 0 & \alpha'_{Syy} & 0 \\ 0 & 0 & \alpha'_{Szz} \end{pmatrix} = \alpha'_{Szz} \begin{pmatrix} r & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

(4.2)

where,

$$r = \frac{\alpha'_{Sxx}}{\alpha'_{Szz}} \tag{4.3}$$

Fig. 4.2 Illustration of the transition from the dipole frame to the molecular frame. On the right, from top to bottom are plots viewing from the $z_M$ and $z_S$ direction and along the $AOB$ direction.

As shown in Fig.4.1, the molecule is board-like instead of cylindrical rod-like as has been considered in past analyses. The dipole symmetry axis, $z_S$, and the molecular long axis, $z_M$, define the board plane, while $x_S$ and $x_M$ are parallel to the board plane. $\alpha'_S$ can be transformed to different frames using specific Euler angles for each transformation. The foremost transformation is from the dipole frame to the molecular frame, where the Euler angles of the transformation are $(\alpha_0, \beta_0, \gamma_0)$ as shown in Fig.4.2. Since the dipole was cylindrical symmetry, the dipole has rotational freedom along $z_S$. Thus $\gamma_0$ is set to zero. As shown in Fig.4.1, $x_m$ located in the molecular board plane defined by the molecular long axis $z_m$ and dipole direction $z_S$, thus $\alpha_0$ is zero.
Following these setups, the ambiguity in choosing $\alpha_0$ and $\gamma_0$ is removed. Thus the Euler angles for this transition can be written as $(0, \beta_0, 0)$.

Fig. 4.3 Illustration of the transition from the dipole frame to the molecular frame. On the right, from top to bottom are plots viewing from top to down along $z_D$ and $z_M$ direction and along the $A'O'B'$ direction.

The second transformation is from the molecular frame to the director frame. Since the molecules are no longer assumed to be cylindrically symmetric, all axes in the molecular frame are fixed as shown in Fig.4.1 and as a consequence, the Euler angles are also fixed and thus must be $(\alpha, \beta, \gamma)$ as shown in Fig.4.3. The Raman tensor can be rewritten as,

$$
\alpha_D' = \begin{pmatrix}
\alpha_D'_{xx} & \alpha_D'_{xy} & \alpha_D'_{xz} \\
\alpha_D'_{yx} & \alpha_D'_{yy} & \alpha_D'_{yz} \\
\alpha_D'_{zx} & \alpha_D'_{zy} & \alpha_D'_{zz}
\end{pmatrix}.
$$

Finally, the last transformation from the director frame to the laboratory frame is needed, as in Jones et al.’s method\textsuperscript{4}. The Euler angles should be $(\delta, \theta, \epsilon)$ as shown in Fig.4.4. As the director only rotates in the $x_L O'' z_L$ plane as mentioned in section 4.1, $\delta$ is zero. Besides, the liquid crystal is a uniaxial system which means the director frame is rotation free. Thus $\epsilon$ could be zero. The Euler angles are $(0, \theta, 0)$, where $\theta$ is the macroscopic rotation parameter, describing the rotation angle of the sample in laboratory frame. After this transformation, the tensor becomes:
Fig. 4.4 Illustration of the transition from the dipole frame to the molecular frame. On the right, from top to bottom are plots viewing from top to down along $z_L$ and $z_D$ direction and along the $A''O''B''$ direction.

The experimental data comes from the laboratory frame. As mentioned in the previous chapter about Jones et al.’s method, two configurations are used: parallel configuration relates to $\alpha'_{L,xx}$ and $\alpha'_{L,xz}$; perpendicular configuration relates to $\alpha'_{L,xx}$ and $\alpha'_{L,zx}$. Thus all tensor components with $y$ can be ignored. Using the condition that $\alpha'_{L,xx}(\theta) = \alpha'_{L,xx}(\theta + 90^\circ)$ and $\alpha'_{L,xx}(\theta) = \alpha'_{L,zx}(\theta)$, only two independent tensor components are left. Thus $\alpha''_\parallel(\theta)$ is used to express $\alpha'_{L,xx}$ and $\alpha'_{L,zx}$, and $\alpha''_\perp(\theta)$ is used to express $\alpha'_{L,xx}$ and $\alpha'_{L,zx}$, with $\alpha''_\parallel(\theta)$ and $\alpha''_\perp(\theta)$ deciding the intensities for the parallel and perpendicular measurement.

### 4.1.3. Intensity Expressions

The expression for the Raman peak intensity at certain rotation angle $\theta$ can then be written as,

$$l_\parallel(\theta) \propto \langle \alpha''_\parallel(\theta)^2 \rangle = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma \alpha''_\parallel^2 f(\alpha, \beta, \gamma), \quad (4.6)$$
\[
I_{\perp}(\theta) \propto (\alpha'_{\perp}(\theta)^2) = \int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \int_0^{2\pi} dy \alpha'_{\perp}^2 f(\alpha, \beta, \gamma). \quad (4.7)
\]

Combining the expression for the ODF in a uniaxial system with non-uniaxial molecules (for more details refer to Appendix A.3), we can integrate over the whole area to get the intensity (this process is done using Mathematica 7) as expressed in eqs.4.8 and 4.9.

\[
I_{\parallel} \propto \frac{1}{5} + \frac{4r^2}{15} + \frac{8r^2}{15} + \langle P_{200} \rangle \left[ \frac{1}{84} (3 + r - 4r^2)(1 + 3 \cos 2\beta_0)(1 + 3 \cos 2\theta) \right] \\
+ \langle P_{400} \rangle \left[ \frac{1}{17920} (-1 + r)^2 (9 + 20 \cos 2\beta_0 + 35 \cos 4\beta_0)(9 + 20 \cos 2\theta + 35 \cos 4\theta) \right] \\
+ \langle P_{202} \rangle \left[ \frac{1}{7} (3 + r - 4r^2)(1 + 3 \cos 2\theta)(\sin \beta_0)^2 \right] \\
+ \langle P_{402} \rangle \left[ \frac{3}{224} (-1 + r)^2 (5 + 7 \cos 2\beta_0)(9 + 20 \cos 2\theta + 35 \cos 4\theta)(\sin \beta_0)^2 \right] \\
+ \langle P_{404} \rangle \left[ \frac{132}{32} (-1 + r)^2 (9 + 20 \cos 2\theta + 35 \cos 4\theta)(\sin \beta_0)^4 \right], \quad (4.8)
\]

\[
I_{\perp} \propto \frac{1}{15} (-1 + r)^2 + \langle P_{200} \rangle \left[ \frac{1}{84} (-1 + r)^2 (1 + 3 \cos 2\beta_0) \right] \\
+ \langle P_{400} \rangle \left[ -\frac{1}{17920} (-1 + r)^2 (9 + 20 \cos 2\beta_0 + 35 \cos 4\beta_0)(-3 + 35 \cos 4\theta) \right] \\
+ \langle P_{202} \rangle \left[ \frac{1}{7} (-1 + r)^2 (\sin \beta_0)^2 \right] \\
+ \langle P_{402} \rangle \left[ -\frac{3}{224} (-1 + r)^2 (5 + 7 \cos 2\beta_0)(-3 + 35 \cos 4\theta)(\sin \beta_0)^2 \right] \\
+ \langle P_{404} \rangle \left[ -\frac{132}{32} (-1 + r)^2 (-3 + 35 \cos 4\theta)(\sin \beta_0)^4 \right]. \quad (4.9)
\]

Eqs.4.8 and 4.9 depend on the parameters \( r, \beta_0, \theta, \langle P_{200} \rangle, \langle P_{202} \rangle, \langle P_{400} \rangle, \langle P_{402} \rangle \) and \( \langle P_{404} \rangle \). In eqs.4.8 and 4.9, \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) are uniaxial order parameters. Moreover, since the molecules are assumed to be board-like, there will be a distribution according to the molecular rotation position, thus the molecular biaxial order parameters \( \langle P_{202} \rangle, \langle P_{402} \rangle \) and \( \langle P_{404} \rangle \) also appear. Finally, the depolarization ratio \( R \) can be obtained by taking the ratio of eqs.4.8 and 4.9 to give,

\[
R = \frac{I_{\perp}}{I_{\parallel}}. \quad (4.10)
\]
It is worthy of note that the refractive index correction is not considered since it is a constant and it only affects the \( r \) value\(^4\). Thus here we merge the effect of refractive index correction to the differential polarizability \( r \) value. It is interesting to point out that if \( \beta_0 = 0 \), all \( \sin \beta_0 \) terms turns to zero, thus eqs.4.8 and 4.9 reduce exactly to Jones et al.’s equations in eqs.2.52 and 2.53 with only three parameters \( (P_{200}) \), \( (P_{400}) \) and \( r^4 \). This is as expected since if no dipole tilt exists, our board-like molecular model will degenerate to uniaxial rod-like molecular model.

4.2. Theoretical Discussion of the New Approach

4.2.1. Discussion of the Effect on the Depolarization Ratio Graph

The effect of \( (P_{200}) \) and \( (P_{400}) \) on the form of the depolarization ratio graph has been discussed previously\(^4\), and the influence of the higher order terms has been considered briefly\(^6\), where the original assumptions were maintained. Here we mainly concentrate on the influence of the molecular biaxial order parameters \( (P_{202}) \), \( (P_{402}) \) and \( (P_{404}) \) in the form of the depolarization ratio after changing the assumptions, using eqs.4.8 and 4.9.

Fig.4.5 indicates the effect of each order parameter on the depolarization ratio with the dipole tilt \( \beta_0 \) set to be 10°. Fig.4.5a) shows the effect on the depolarization ratio when introducing a different \( (P_{202}) \) value. It is clear that by increasing the \( (P_{202}) \) value, the depolarization ratio value around the positions \( \theta=90^\circ \) and \( \theta=270^\circ \) increase while other parts have changed very little. This effect is similar to the effect of increasing the \( (P_{200}) \) value in Jones et al.’s method.

The most interesting effect comes from \( (P_{402}) \) as shown in Fig.4.5b). By increasing its value, the depolarization ratio is lowered at \( \theta=90^\circ \) and \( \theta=270^\circ \), while the depolarization ratio is increased around this point. The depolarization ratio around \( \theta=0^\circ \) and \( \theta=180^\circ \) is also decreased slightly, thus making the curve fluctuate more. Comparing the calculated graphs with the really different depolarization ratio graphs measured from
the phenyl stretching mode and the cyano stretching mode, shown before in Fig.3.6, it is obvious that the depolarization ratio graph with a high \( \langle P_{402} \rangle \) values shows a similar tendency to those of the cyano stretching mode. Remarkably, the effect of \( \langle P_{402} \rangle \) on the depolarization ratio graph is similar to the effect caused by \( \langle P_{400} \rangle \) in Jones et al.’s method which means that by increasing the \( \langle P_{402} \rangle \) value, the value of \( \langle P_{400} \rangle \) can be reduced. This fact indicates that \( \langle P_{402} \rangle \) may be the key point of solving the discrepancy. More careful discussions of the explanation on solving the discrepancy will be given in the following sections.

From Fig.4.5(c), there is clear evidence that \( \langle P_{404} \rangle \) does not have a strong effect on the depolarization ratio graph. Thus, \( \langle P_{404} \rangle \) is ignored and is set to be zero in the fitting process, which will be discussed in Section 4.3.

Fig. 4.5 Effects of the different order parameters on the form of the depolarization ratio graph are shown. In these calculations, \( \langle P_{200} \rangle =0.4; \langle P_{400} \rangle =0.2; \ r = -0.2; \beta = 10^\circ \). a) dependence on \( \langle P_{202} \rangle = 0 \) (solid), 0.1 (dash) and 0.2 (dot); b) dependence on \( \langle P_{402} \rangle = 0 \) (solid), 0.025 (dash) and 0.050 (dot); and c) dependence on \( \langle P_{404} \rangle = 0 \) (solid), 0.03 (dash) and 0.06 (dot).
In addition to the discussions above for each molecular biaxial order parameter, it is also worth discussing the effect of the dipole tilt $\beta_0$ on the depolarisation ratio plot. Fig.4.6 ignores all molecular biaxial order parameters by setting them to zero and only allows $\beta_0$ changing. It is clear that $\beta_0$ causes the opposite effect comparing to $\langle P_{402} \rangle$, however, only considering $\beta_0$ will not generate the difference appearing in the cyano stretching mode, unless the phenyl stretching mode has a huge dipole tilt which is not reasonable.

![Depolarization ratio plot](image)

Fig. 4.6 Effect of different dipole tilt parameter on the form of the dependence of the depolarization ratio on angle using eqs.4.8 and 4.9. $\langle P_{200} \rangle=0.4; \langle P_{400} \rangle=0.2; r=-0.2$ and $\beta_0 = 0^\circ$ (solid), $10^\circ$ (dash) and $20^\circ$ (dot).

4.2.2. Discussion of the Effect on the Fitting Result using Eqs.4.8 and 4.9

So far, some indications have been given that the molecular biaxial order parameters introduced by the dipole tilt $\beta_0$ may be the key on solving the discrepancy on order parameters when applying Jones et al.’s method on different vibrational modes. It is important to have a systematic check of the influence of each parameter in the fitting process. However, the existence of the seven fitting parameters makes the fitting a complex task. The fitting process is simplified by systematically keeping each molecular biaxial order parameter constant and considering the dipole tilt $\beta_0$ influence individually. The flow chart of the analysis method is shown in Fig.4.7. In this process, $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ are obtained using the eqs.4.8 and 4.9 with different values of dipole
tilt and constant molecular biaxial order parameter values. Following this process ensures that the fitting equation is similar to that Jones et al.’s method and modified to include the dipole tilt $\beta_0$. Hence, the uncertainty of the fitting is dramatically reduced with the reduction of fitting parameters. Fig.4.8 shows the results of fitting $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ from 5CB data at 300 K (27 °C), while systematically keeping biaxial order parameter constant as the dipole tilt $\beta_0$ is varied.

According to Fig.4.8, the $\langle P_{200} \rangle$ fitting value increases by 10% and the $\langle P_{400} \rangle$ fitting value increases about 40% at $\beta_0=15^\circ$ when no molecular biaxial order parameters are considered. So the order parameters fitting value will increase if only introducing the dipole tilt $\beta_0$ but ignoring the molecular biaxial order parameters. The increment becomes much obvious when $\beta_0$ is large (higher than 5° according to Fig.4.8).

Fig.4.8a) shows the effect of $\langle P_{402} \rangle$ on the fitting values of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ with different dipole tilt parameters. The $\langle P_{400} \rangle$ fitting value decreases after introducing $\langle P_{402} \rangle$. Also the $\langle P_{400} \rangle$ fitting value decreases 15% at $\beta_0=15^\circ$ when comparing with the case that both dipole tilt $\beta_0$ and $\langle P_{402} \rangle$ are ignored ($\beta_0 = 0^\circ$). Two conclusions can be gained from Fig.4.8a). Firstly, the increment of $\langle P_{400} \rangle$ fitting value introduced by dipole tilt $\beta_0$ can be reduced by introducing $\langle P_{402} \rangle$, especially when $\langle P_{402} \rangle$ is large. This reduction becomes obvious when $\beta_0$ is higher than 5° according to Fig.4.8a. Moreover, the $\langle P_{400} \rangle$ fitting value can even lower than the initial value when no
dipole tilt and molecular biaxial order parameter introduced. Secondly, the $\langle P_{200} \rangle$ fitting value is independent of the change on the $\langle P_{402} \rangle$ value, while it has a slightly change depending on the dipole tilt $\beta_0$. It is noted that $\langle P_{400} \rangle$ has remarkably high fitting value in the cyano stretching fitting results when applying Jones et al.’s method as shown in Fig. 3.7. So the effect that $\langle P_{402} \rangle$ decreases the fitting values of $\langle P_{400} \rangle$ acts as a positive modification on the analysis method. After combining the discussion above with the fact that $\langle P_{402} \rangle$ can lead the depolarization ratio graph to change in a similar way as in the cyano stretching mode as discussed in section 4.2.1, it is again strongly evidenced that $\langle P_{402} \rangle$ is one of the important factors in solving the discrepancy on order parameter values obtained from different vibrational modes.

Fig. 4.8 Effect of the dipole tilt parameter on uniaxial order parameters obtained from fitting 5CB data at 300K. In these plots, $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ are represented with squares and circles respectively. a) $\langle P_{202} \rangle = 0$ (solid symbols) and 0.25 (empty symbols); b) $\langle P_{402} \rangle = 0$ (solid symbols) and 0.0536 (empty symbols); c) $\langle P_{404} \rangle = 0$ (solid symbols) and 0.0625 (empty symbols).
Fig.4.8b) shows the effect of $\langle P_{202} \rangle$ on the fitting values of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ with different dipole tilt parameters. It again shows the relationship between $\langle P_{202} \rangle$ and $\langle P_{200} \rangle$ that the $\langle P_{200} \rangle$ value reducing about 10% at $\beta_0=15^\circ$ by introducing $\langle P_{202} \rangle$. Another thing is that the $\langle P_{200} \rangle$ fitting value almost keeps constant after introducing both dipole tilt $\beta_0$ and $\langle P_{202} \rangle = 0.25$. The conclusion from Fig.4.8b) is that firstly, $\langle P_{202} \rangle$ reduces the fitting value of $\langle P_{200} \rangle$. Moreover, by increasing $\langle P_{202} \rangle$, the increasing tendency on the fitting value of $\langle P_{200} \rangle$ caused by the dipole tilt $\beta_0$ is reduced which makes the $\langle P_{200} \rangle$ fitting value almost constant. Secondly, $\langle P_{202} \rangle$ changes will not affect the $\langle P_{400} \rangle$ fitting value. It can be seen from Fig. 4.8c) that $\langle P_{404} \rangle$ does not have strong effect on $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ as expected and shown previously in Fig.4.5c).

After reviewing the discussions above, a possible explanation for the discrepancy on order parameters by introducing the dipole tilt can be given. Firstly, the phenyl stretching mode has no or small dipole tilt. Then the $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ fitting values will not change a lot whether or not the dipole tilt and the molecular biaxial order parameters are introduced according to Fig.4.8. Thus Jones et al.’s method gives a good fitting value on the order parameters even though it doesn’t consider the dipole tilt and the molecular biaxial order parameters. Secondly, the cyano stretching mode, on the contrary, has a dipole tilt $\beta_0$ which is large enough (higher than $5^\circ$) to affect the order parameter fitting values. As discussed above, the $\langle P_{200} \rangle$ fitting value will only have small change due the reciprocal effect of $\beta_0$ and $\langle P_{202} \rangle$. But the $\langle P_{400} \rangle$ fitting value will have an obvious change depending on whether or not the dipole tilt and molecular biaxial order parameters are introduced. Thus the $\langle P_{400} \rangle$ fitting value will be larger than the theoretical predication due to the lack of the modification from the dipole tilt and this is what has seen from Fig.3.7 when the Jones et al.’s method was applied to the cyano stretching mode.

4.3. Discussion of the Modified Fitting Process

So far the modified theory approach has been discussed, based on some of the previous fitting methods described by Jones et al.\textsuperscript{4}. As an important section of an order parameters analysis, some fitting results based on the new approach (eqs.4.8 and 4.9) are
shown. First, it is worthy of note that some of the parameters are limited by definition, and in particular, the values for the various components of the order parameter must satisfy the conditions below.

\[ 0 \leq \langle P_{200} \rangle \leq 1; \quad 0 \leq \langle P_{400} \rangle \leq 1; \]  \hspace{1cm} (4.11)

\[ 0 \leq \langle P_{202} \rangle \leq 0.25; \quad 0 \leq \langle P_{402} \rangle \leq 0.0536; \quad 0 \leq \langle P_{404} \rangle \leq 0.0625 \]  \hspace{1cm} (4.12)

As a result of the discussion in the previous section, even though \( \langle P_{404} \rangle \) is set to zero in the fitting process, there are too many parameters (seven parameters from original from eqs.4.8 and 4.9 and one more to describes depolarisation ratio graph shift) to allow robust fitting to typical experimental data and obtaining values for each parameters. However, it is still possible to use this fitting to prove the effect of the newly introduced parameters and give further understanding why the order parameters obtained from different vibrational modes are different.

![Flow chart of the fitting method](image)

**Fig. 4.9** Flow chart of the fitting method
The flow chart of this fitting process is shown in Fig. 4.9. Data relating to the cyanogen and phenyl stretching modes of 5CB are used to illustrate the arguments. \( P_{200} \) and \( P_{400} \) are first obtained by using Jones et al.’s method with eqs. 2.52 and 2.53. By this process a cursory estimation of the two order parameters is obtained. The \( P_{200} \) fitting value after the first fitting is assumed to be a constant in the next fitting procedure since previous results indicate that \( P_{200} \) obtained from both the cyanogen and phenyl stretching modes are not very different (see Fig. 3.7). The data are then fitted using eqs. 4.8 and 4.9 with \( P_{400} \) initially set to the same value as obtained from the phenyl stretching mode and initial values obtained for \( \beta_0 \), \( P_{202} \) and \( P_{402} \) are 10°, 0.25 and 0.0536 respectively.

Fig. 4.10 shows a comparison of the fitting result obtained using the modified fitting method and Jones et al.’s method from both cyanogen and phenyl stretching mode when compared with the Maier-Saupe theory\(^7\). It is shown as before that the order parameter values obtained from the cyano stretching mode using Jones et al.’s method are far from the theoretical prediction. Moreover, when Jones et al.’s method is employed, the order parameter values obtained from the different vibrational modes are also quite far from each other. On the contrary, the order parameter values obtained from the modified method are closer to the theoretical prediction and also closer to the results from phenyl stretching mode using Jones et al.’s method.

Fig. 4.10 Comparison of the fitting results. The dashed line is the theoretical curve from Maier-Saupe mean-field theory, coming from Miyano’s paper\(^7,8\). The solid symbols are the fitting results from Jones et al.’s method and the empty symbols are from the new fitting method. The data related to phenyl and cyano stretching mode are labeled with square and triangle respectively.
The variation in the dipole tilts parameter as a function of $T/T_{NI}$ where $T_{NI}$ is the transition temperature from the nematic phase to the isotropic phase. The square and the triangle data indicate phenyl and cyano stretching modes respectively.

Fig. 4.11 shows that the fitting values of the dipole tilt $\beta_0$ against temperature. It is noticed that the value of $\beta_0$ is almost constant with respect to the temperature change, which are $\beta_0=19.7\pm 0.3^\circ$ for the cyano stretching mode and $7.9\pm 0.4^\circ$ for the phenyl stretching mode. This result agrees with our expectation that the dipole tilt parameter will be independent of temperature. The dipole tilt $\beta_0$ also has an obvious difference for cyano stretching mode and phenyl stretching mode. However, we previously thought the phenyl stretching mode would have a small dipole tilt, but the fitting result indicates that the dipole tilts of both the phenyl and cyano stretching mode are much larger than we expect.

The variation of the order parameter as a function of $T/T_{NI}$ where $T_{NI}$ is the nematic phase to isotropic phase transition temperature. The solid symbols are deduced from fitting to phenyl-stretching mode, while the open symbols relate to the cyano-stretching mode. The data with same label shape represent values for $\langle P_{200}\rangle$, $\langle P_{202}\rangle$, (inverted triangle), $\langle P_{400}\rangle$, (circle) and $\langle P_{402}\rangle$, (triangle) respectively from top to bottom (square, reversed triangle). Theoretical predication of $\langle P_{200}\rangle$ (black line) and $\langle P_{400}\rangle$ (red line) are based on: dashed line: $\lambda = 0.15$; $\gamma = 2$ and solid line $\lambda = 0.15$; $\gamma = 0$ according to the HJL theory.9
In Fig.4.12, the fitting values of $P_{200}$, $P_{202}$, $P_{400}$ and $P_{402}$ at different temperatures are shown. It can be observed that the order parameter fitting values deduced from the phenyl and cyano stretching modes are in good agreement. It is interesting to note that the fitting value of $P_{202}$ shows a similar, decreasing tendency when the temperature is increased, which also occurs for the fitting values of $P_{200}$ and $P_{400}$. This decreasing tendency agrees our expectation since by increasing the temperature to the transition temperature, the liquid crystal ordering should decay. However, the decreasing behaviour is not clear in the fitting value of $P_{402}$.

After the discussion including the theory and fitting in this section, there are strong evidences to conclude that the introduction of the dipole tilt $\beta_0$ helps to removes the discrepancy previously observed between the order parameter values deduced from different vibrational modes. The fitting method also gives a possible approach to obtain similar fitting values of $P_{200}$ and $P_{400}$ from the different vibrational modes.

However, some problems still exist. Firstly, we have not discussed the uncertainties that are inherent in the fitting process, even though it is important to recognize that there are uncertainties on the values of order parameter deduced from the fitting which would normally be included as error bars on the order parameters in Figs 4.10, 4.11 and 4.12. Due to the complexity of the equations, the uncertainties are hard to analyse systematically. So the fitting in this section is a supplementary to the explanation, and are perhaps best understood by systematically checking the influence of each parameter in the fitting process as shown in section 4.2.2. In order to make the fitting process more precise, a mathematical optimization on the fitting method is still needed. Secondly, the high fitting values of the dipole tilt $\beta_0$ and molecular biaxial order parameters $P_{202}$ and $P_{402}$ as shown in Fig.4.12 are problematic. Certainly, the uncertainty of the fitting method is one possible explanation. But as we discussed the larger dipole tilt and molecular biaxial order parameters can provide a better reduction on the fitting value of $P_{400}$. From this point of view, there may be more factors that can reduce the fitting value of $P_{400}$. Details will be given in Section 4.5.
4.4. Computer Simulation Discussion

It can be seen from the discussion in above sections that the inclusion of dipole tilt both modifies the equations that must be used in the analysis of the depolarization ratio deduced from PRS, and consequently allows the $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ order parameters deduced from different vibrational modes to be self-consistent. However, it is important to give a physical justification to including such a dipole tilt, as it is unreasonable to simply include additional fitting parameters.

The dipole tilt, $\beta_0$, was described by Jen as the tilt angle between the molecular long axis and vibrational symmetry axis. This can be investigated by using molecular simulation software. The program is Material Studio and the simulation is based on the DMol$^3$ package. DMol$^3$ package can be used to investigate of the properties of the chemical, electronic, optical and structural properties of a system in gas, solution, and solid environments without need for any experimental input. This simulation package is an ab-initio method which is based on Density Functional Theory (DFT). DFT is a quantum mechanical modelling method to investigate the electron structure of many-body system. Similar to the MFT theory, DFT treat the system as an electron moving in an effective potential field generated by the material. Also, to monitor the effective potential, an approximation is needed. In our simulation, a generalized gradient approximation (GGA) functional was used. Under this approximation, several different forms of functional are provided by DMol3 which including Perdew Wang at 1991 (PW91), Perdew Burke Eenzerhof (PBE), Reversed Perdew Wang (RPBE), PBE with Wu-Cohen exchange (WC). Even though this simulation is usually used for crystal simulation, we can still use the program since only the vibrational information of the molecules is needed. Moreover, as the basic assumption that the interaction between molecules is ignored, the simulation can be achieved by setting one molecule in each basic cell of this “crystal” with a huge crystal lattice scale.

The simulation results give information on all vibrational modes that are present in the chosen molecule, together with their phonon vibrational frequency. The phenyl and cyano stretching modes are of particular relevance to this study. The molecular long axis is defined to be the phenyl stretching direction, which assumes that the contributions from the alky chain average to same axis, along the rigid molecular core. Fig.4.13 shows the...
results of the simulation on the phenyl and cyano stretching vibrations. Both vibrations occur in the same direction, i.e. both vibrational symmetry axes are along the molecular long axis. This implies that the explanation that the two vibrational modes have different vibrational symmetry axes is problematic.

![Vibrational directions](image)

Fig. 4.13 Vibrational directions for: a) and b), the phenyl stretching mode; c) and d), the cyano stretching mode determined from the \textit{ab-initio} simulations.

If the simulation is correct and our explanation is maintained, then this result seems to imply that the definition of $\beta_0$ needs some modification. Importantly, we realise that the definition of $\beta_0$ must be the angle between the dipole and the molecular long axis in the theory. Then the question is whether the dipole direction is the vibrational symmetry direction. A suggestion has been given that the dipole direction has slightly different from the vibrational symmetry direction. Thus, a redefinition of $\beta_0$ is suggested as the tilt angle between the dipole direction and the molecular long axis. However, there is no robust evidence to support this redefinition thus further investigation in needed.

### 4.5. Another Explanation for the Discrepancy in Order Parameters

By introducing the dipole tilt $\beta_0$, it is possible to give an explanation to the discrepancy on the order parameters fitting values from the different vibrational modes. However, as discussed in section 4.4, the computational simulation can’t provide a robust evidence for the existence of a dipole tilt. Thus the dipole tilt will be ignored in this
section and another possible explanation will be given for solving the discrepancy in the order parameter values obtained from different vibrational modes.

### 4.5.1. Intensity Expression Discussion

After reviewing the previous analysis by Jen et al.\(^2\)\(^-\)\(^3\), another possibility is found for explaining the discrepancy which comes from a modification to the commonly used assumption that the dipole (vibration) is cylindrical symmetric. This assumption can reduce the fitting parameters and makes the fitting process reliable. Under this assumption, the Raman tensor for a certain vibration in the dipole frame is shown in eq.4.11,

\[
\alpha'_s = \begin{pmatrix}
\alpha'_{s_{xx}} & 0 & 0 \\
0 & \alpha'_{s_{yy}} & 0 \\
0 & 0 & \alpha'_{s_{zz}}
\end{pmatrix}
= \begin{pmatrix}
r\alpha'_{s_{zz}} & 0 & 0 \\
0 & r\alpha'_{s_{zz}} & 0 \\
0 & 0 & \alpha'_{s_{zz}}
\end{pmatrix}
= \begin{pmatrix}
r & 0 & 0 \\
0 & r & 0 \\
0 & 0 & 1
\end{pmatrix} \alpha'_{s_{zz}} \quad (4.11)
\]

It is clear that in order to support this assumption, a condition such that \(\alpha'_{s_{xx}} = \alpha'_{s_{yy}}\) is needed. It is worthwhile questioning whether this condition is valid for all vibrational modes. In order to check this assumption, we ignore the cylindrical symmetric assumption and use a generalized elliptic cylindrical symmetry. Actually, this situation is initially discussed in Jen et al.'s paper in 1977\(^3\). However, he turned to the cylindrical model in his subsequent analysis. If the dipole is elliptic cylindrical, \(\alpha'_{s_{xx}} \neq \alpha'_{s_{yy}}\) and the Raman tensor can be expressed as in equation 4.12.

\[
\alpha'_s = \begin{pmatrix}
\alpha'_{s_{xx}} & 0 & 0 \\
0 & \alpha'_{s_{yy}} & 0 \\
0 & 0 & \alpha'_{s_{zz}}
\end{pmatrix}
= \begin{pmatrix}
a\alpha'_{s_{zz}} & 0 & 0 \\
0 & b\alpha'_{s_{zz}} & 0 \\
0 & 0 & \alpha'_{s_{zz}}
\end{pmatrix}
= \begin{pmatrix}
a & 0 & 0 \\
0 & b & 0 \\
0 & 0 & 1
\end{pmatrix} \alpha'_{s_{zz}} \quad (4.12)
\]

In eq.4.12, two new differential polarizability ratios \(a\) and \(b\) are defined as eqs.4.13 and 4.14. Notice that the elliptic cylindrical symmetry will reduce to the cylindrical symmetry when \(a = b\).

\[
a = \frac{\alpha'_{s_{xx}}}{\alpha'_{s_{zz}}} \quad (4.13)
\]
The theoretical analysis process is easier than the one discussed in section 4.1. Since we are no longer considering the dipole tilt in this analysis, so the dipole tilt is set to be zero, thus the molecular frame is overlapping with the dipole frame in Fig.4.1, and only two coordinate transformations are needed. The first transformation is from the molecular frame to the director frame and the second transformation is from the director frame to the laboratory frame. Then the intensity expression can be easily obtained:

\[
I_\parallel \propto \frac{1}{15} (3 + 3a^2 + 2b + 3b^2 + 2a(1 + b)) \\
- \frac{1}{42} (P_{200})(-6 + 3a^2 - b + 3b^2 + a(-1 + 2b))(1 + 3 \cos 2\theta) \\
+ \frac{1}{2240} (P_{400})(8 + 3a^2 + 2a(-4 + b) - 8b + 3b^2)(9 + 20 \cos 2\theta + 35 \cos 4\theta) \\
+ \frac{1}{7} (P_{202})(a - b)(1 + 3a + 3b)(1 + 3 \cos 2\theta) \\
- \frac{3}{112} (P_{402})(a - b)(-2 + a + b)(9 + 20 \cos 2\theta + 35 \cos 4\theta) \\
+ \frac{1}{32} (P_{404})(a - b)^2(9 + 20 \cos 2\theta + 35 \cos 4\theta)
\] (4.15)

\[
I_\perp \propto \frac{1}{15} (1 + a^2 - b + a^2 - a(1 + b)) \\
- \frac{1}{42} (P_{200})(-2 + a^2 + a(2 - 4b) + 2b + b^2) \\
- \frac{1}{2240} (P_{400})(8 + 3a^2 + 2a(-4 + b) - 8b + 3b^2)(-3 + 35 \cos 4\theta) \\
+ \frac{1}{7} (P_{202})(a - b)(-2 + a + b) \\
+ \frac{3}{112} (P_{402})(a - b)(-2 + a + b)(-3 + 35 \cos 4\theta) \\
- \frac{1}{32} (P_{404})(a - b)^2(-3 + 35 \cos 4\theta)
\] (4.16)

It is worthy of note that the molecular biaxial order parameters appear in eqs.4.15 and 4.16 due to the elliptic cylindrical symmetry. With this model the molecule is no longer rotationally free, which means the molecular biaxial order parameters have effect on the Raman intensity. Moreover, every molecular biaxial order parameter terms in
eqs. 4.15 and 4.16 has \((a - b)\) term. Thus the molecular biaxial order parameters have effect on the Raman intensity only when the dipole satisfies the condition that \(a \neq b\).

### 4.5.2. Discussion of the Two Differential Polarizability Ratios

In this section, the effect of the two differential polarizability ratios will be firstly discussed without considering the molecular biaxial order parameters. Then the molecular biaxial order parameters will be introduced and discussed with the effect of each biaxial order parameter individually.

It is worthy of note that both \(a\) and \(b\) have an effect on the depolarization ratio. Thus we will discuss the effect of each of them on the depolarization ratio at the same time with the help of contour plots. However, it is hard to show the depolarization ratio \(R\) at different rotation angles \(\theta\) with the discussion of \(a\) and \(b\) at the same time. Thus only two symbolic rotation angles are used for the discussion. Since the differential polarizability ratio \(r\) is negative as discussed in previous chapter, the discussion of \(a\) and \(b\) will be discussed with negative value. Fig. 4.14 indicates the contour plots of the calculated depolarization ratio value at \(\theta = 0^\circ\) and \(\theta = 90^\circ\) depending on eq. 4.15 and 4.16. In this calculation, \(\langle P_{200} \rangle\) and \(\langle P_{400} \rangle\) are set to be 0.5 and 0.2 respectively, and all molecular biaxial order parameters are ignored by setting them to zero. According to these plots, the depolarization ratio values, \(R\), are symmetric to the line where \(a = b\). This indicates the exact same effect of \(a\) and \(b\) on the depolarization ratio. The \(R\) value at \(\theta = 0^\circ\) always increase if either \(a\) or \(b\) decreases according to Fig. 4.14a). The \(R\) value change is complex at \(\theta = 90^\circ\) such that the \(R\) value reaches a maximum at around \(a = b = -0.2\) and then decreases with any change of \(a\) and \(b\), according to Fig. 4.14b).
The contour plot of the depolarization ratio $R$ at: a) $\theta = 0^\circ$ and b) $\theta = 90^\circ$ with $\langle P_{200} \rangle = 0.5$, $\langle P_{400} \rangle = 0.2$, $\langle P_{202} \rangle = 0$, $\langle P_{402} \rangle = 0$ and $\langle P_{404} \rangle = 0$. The x axis and y axis are differential polarizability ratio $b$ and $a$ respectively.

The molecular biaxial order parameters will be introduced into consideration. As in the discussion of the molecular biaxial order parameters on depolarization ratio in Section 4.2.1, only one molecular biaxial order parameter is allowed to change at a time and the value for the molecular biaxial order parameters are as large as possible to present obvious difference. Then by comparing to Fig.4.14 we can check the effect of the molecular biaxial order parameters. Fig.4.15 indicates the contour plots when $\langle P_{202} \rangle = 0.25$ for the same $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ values as in Fig.4.14. The contour plots are rotated and shifted in Fig.4.15 compared with Fig.4.14 due to the existence of $\langle P_{202} \rangle$. After comparing Fig.4.14 and Fig.4.15, it can be concluded that an increase of $\langle P_{202} \rangle$ will raise the $R$ value at $\theta = 0^\circ$ and $\theta = 90^\circ$ when $a < b$ but reduce the $R$ value at $\theta = 0^\circ$ and $\theta = 90^\circ$ when $a > b$. The asymmetrical contour plots also mean that the effect of the two differential polarizability ratios is no longer same. According to Fig.4.15a), the $R$ value at $\theta = 0^\circ$ is not sensitive to the value change of $b$ when $a > -0.5$. However, the $R$ value increases by approximately 100% by decreasing $a$ from 0 to -0.5. The $R$ value at $\theta = 90^\circ$ has a huge (~100%) change according to the value of $a$ and $b$ when $-0.3 \leq b \leq 0$ and $-0.5 \leq a \leq -0.2$ respectively as shown in Fig.4.15b).
Fig. 4.15 The contour plot of the depolarization ratio $R$ at: a) $\theta = 0^\circ$ and b) $\theta = 90^\circ$ with $\langle P_{200} \rangle = 0.5$, $\langle P_{400} \rangle = 0.2$, $\langle P_{202} \rangle = 0.25$, $\langle P_{402} \rangle = 0$ and $\langle P_{404} \rangle = 0$. The $x$ axis and $y$ axis are differential polarizability ratio $b$ and $a$ respectively.

Fig. 4.16 The contour plot of the depolarization ratio $R$ at: a) $\theta = 0^\circ$ and b) $\theta = 90^\circ$ with $\langle P_{200} \rangle = 0.5$, $\langle P_{400} \rangle = 0.2$, $\langle P_{202} \rangle = 0$, $\langle P_{402} \rangle = 0.536$ and $\langle P_{404} \rangle = 0$. The $x$ axis and $y$ axis are differential polarizability ratio $b$ and $a$ respectively.

In Fig. 4.16, $\langle P_{402} \rangle$ is set to be 0.536 while other molecular biaxial order parameters are set to be zero. The $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ values are same as in Fig. 4.14. The effect of introducing $\langle P_{402} \rangle$ can be obtained according to Fig. 4.16. The contour plots are also not symmetrical, which is similar to the contour plots in Fig. 4.15. So the effect of $\langle P_{402} \rangle$ on the depolarization ratio is similar to $\langle P_{202} \rangle$. Increasing of $\langle P_{402} \rangle$ will rise $R$. 

value at $\theta = 0^\circ$ and $\theta = 90^\circ$ when $a < b$ but have opposite effect when $a > b$. However, The most obvious difference between Fig.4.15a) and Fig.4.16a) is the curvature direction. Thus the $R$ value increases in Fig.4.15a) while decreases in Fig.4.16a) when $\alpha$ is fixed and decreases $b$. Besides, the changing amounts of $R$ value are different. The $R$ values increase 4 times to the minimum value in Fig.4.16 for $\theta = 0$ and $\theta = 90^\circ$. The increase of $R$ values in Fig.4.15 is around 2 or 3 times for $\theta = 0$ and $\theta = 90^\circ$ respectively.

Finally, the contour plots found after introducing $\langle P_{404} \rangle$ is shown in Fig.4.17. In these contour plots, $\langle P_{404} \rangle$ is set to be 0.625 while other molecular order parameters are still zero. The $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ values are same as in Fig.4.14. Obviously the plots in Fig.4.17 are similar to the contour plots in Fig.4.14. The symmetrical contour plots indicate exactly the same effect of the two differential polarizability ratios $\alpha$ and $b$. However, there is an important difference between Fig.4.17a) and Fig.4.14a), which is the curvature direction. This difference indicates a decrease in the $R$ value at $\theta = 0^\circ$ when $a \neq b$ due to the existence of $\langle P_{404} \rangle$. On the other hand, the $R$ value also decreases due to $\langle P_{404} \rangle$ after comparing Fig.4.17b) and Fig.4.14b)

![Contour plots](image)

Fig. 4.17 The contour plot of the depolarization ratio $R$ at: a) $\theta = 0^\circ$ and b) $\theta = 90^\circ$ with $\langle P_{200} \rangle = 0.5$, $\langle P_{400} \rangle = 0.2$, $\langle P_{202} \rangle = 0$, $\langle P_{402} \rangle = 0$ and $\langle P_{404} \rangle = 0.0625$. The $x$ axis and $y$ axis are differential polarizability ratio $b$ and $a$ respectively.

According to the discussion above, the effect of the three molecular biaxial order parameters can be summarised. Firstly, the effect of the molecular biaxial order parameters is only seen on the depolarization ratio $R$ value when $a \neq b$. Secondly,
\( \langle P_{202} \rangle \) and \( \langle P_{402} \rangle \) cause an increase in the \( R \) value at \( \theta = 0^\circ \) and \( \theta = 90^\circ \) when \( a < b \) but cause the opposite effect when \( a > b \). The effect of \( \langle P_{402} \rangle \) is stronger than \( \langle P_{202} \rangle \). Thirdly, the \( R \) values at \( \theta = 0^\circ \) and \( \theta = 90^\circ \) are decreased due to \( \langle P_{404} \rangle \).

After this discussion, it can be concluded that the two differential polarizability ratios \( a \) and \( b \) have a strong effect on the depolarization ratio graph. However, the two differential polarizability ratios \( a \) and \( b \) must be discussed at the same time when considering their effect on depolarization ratio. \( a \) and \( b \) have a strong dependence on each other, which will introduce a huge uncertainty to the fitting process. Moreover, the molecular biaxial order parameters introduced when \( a \neq b \) also introduce strong degeneracy in the fitting process. Combining these two factors, the fitting will give us any random value depending on the initial parameter setting and an accurate fitting result is almost impossible to achieve. Thus as shown in Fig.4.18, instead of showing the fitting results, a set of order parameters will be presented which show the depolarization ratio graph similar to what was observed in considering the cyano and phenyl stretching modes as seen in Fig.3.6 in Chapter 3. The two depolarization ratio graphs share exactly same order parameters but the two graphs are completely different. The solid line in Fig.4.16 is similar to the phenyl stretching mode and \( a \) and \( b \) share the same value while the dashed line is similar to the cyano stretching mode with two different differential polarizability ratios \( a \) and \( b \).

![Fig. 4.18 Two calculated depolarization ratio graphs from eqs.4.15 and 4.16 with same set of order parameters: \( \langle P_{200} \rangle = 0.45 \), \( \langle P_{400} \rangle = 0.2 \), \( \langle P_{202} \rangle = 0.2 \), \( \langle P_{402} \rangle = 0.06 \) and \( \langle P_{404} \rangle = 0.04 \). Two different sets of polarizability ratios are used. The solid line has \( a = -0.13 \) and \( b = -0.13 \) while the dashed line has \( a = -0.05 \) and \( b = -0.20 \)](image)
Combining with the result shown in Fig.4.18, we can put forward a new explanation on why different order parameter values can be obtained from different vibrational modes using the analysis method of Jones et al.\textsuperscript{4}, especially why there are good results from the phenyl stretching mode but bad results from the cyano stretching mode\textsuperscript{1}. In this explanation, the phenyl stretching mode and the cyano stretching mode have different symmetry shapes. For the phenyl stretching mode, the vibration has cylindrical symmetry which satisfies the cylindrical symmetric assumption in Jones et al. ’s method. There is no difference between the two differential polarizability ratios and thus the molecular biaxial order parameters do not have effect on the depolarization graph. As a consequence, Jones et al. ’s method works very well for this stretching mode. On the contrary, the vibrational symmetry for the cyano stretching mode has elliptic cylindrical symmetry which breaks the cylindrical symmetric assumption. Then the difference between the two differential polarizability ratios cannot be ignored and the molecular biaxial order parameters generate a strong modification on the depolarization graph. Thus the cyano stretching mode has a quite different depolarization ratio graph and the Jones et al. ’s method cannot provide a good fitting to this stretching mode.

4.6. Summary

In this chapter, we have introduced a new approach that allows liquid crystal order parameters to be deduced from PRS measurements. The analysis is based on the basic assumptions that: firstly, the liquid crystal system is a uniaxial system; secondly, the liquid crystal molecule is biaxial or board like and the dipole itself has uniaxial symmetry. Then the addition of a dipole tilt $\beta_0$ to Jones et al.’s method offers an explanation of the long-standing problem that the order parameter values obtained from different vibrational mode are different. In our explanation, the phenyl stretching mode has a small or zero dipole tilt which can be ignored. Thus this stretching mode satisfies Jones et al.’s method well and good result can be obtained from Jones et al.’s method. But the cyano stretching mode, on the contrary, has a relatively large dipole tilt than the phenyl stretching mode. This dipole tilt can’t be ignored and it introduces molecular biaxiality in to consideration. Thus different order parameter fitting values are obtained with Jones et al.’s method. Systematic discussion has been conducted and robust evidence has been given to support
the explanation, with the fitting result showing a unified set of order parameters for different vibrational modes. However, the simulations do not indicate the existence of vibration tilt from the molecular long axis. So such an explanation is doubtful in the case of cyano biphenyl. So a redefinition of $\beta_0$ is suggested as the tilt angle between the molecular long axis and the dipole vibration direction. However, there is no robust evidence to support this redefinition. Consequently, at the end of this chapter, we ignore the dipole tilt and discuss another possible explanation, introducing different vibration symmetries into the model. In this explanation, the phenyl stretching mode has a cylindrical symmetry while the cyano stretching mode has an elliptic cylindrical symmetry. This leads to a difference in the depolarization ratio graph shown in the previous chapter. In both explanations, the introduction of more parameters into the theory makes it impossible to provide robust fitting to experimental data. However, calculations show that each of the possibilities considered gives a reasonable explanation for the long-observed discrepancy between the data associated with cyano and phenyl Raman modes, even though it is unlikely that these can be taken according to experiment.
References

Chapter 5

Investigation of Bent-core Liquid Crystal System Order Parameter Fitting using PRS

In Chapter 4, both a dipole tilt and an elliptic cylindrical dipole model were introduced to investigate the discrepancy between the order parameters obtained from different vibrational modes in a uniaxial system by PRS. These modifications introduced molecular biaxiality into the analysis method. After a careful consideration, it was concluded that the dipole tilt and the vibrational symmetry varies for different vibrational modes, thus the discrepancy in order parameter fitting values appears. In this chapter, a different system which is a bent-core liquid crystalline system (bent-core system for short) will be discussed. The name, “bent-core”, describes the bent molecular structure formed instead of the rod-like uniaxial molecular structure. Details of the structure of a bent-core system will be shown in Section 5.1 and 5.2. These materials attract our attention since some of these materials can possibly form a biaxial liquid crystal phase. Thus the bent-core system is unique and different from what was discussed in Chapters 3 and 4. Details of the difference will be discussed in Section 5.3. There are a lot of discussions on the experimental methods used on these materials. Among all the techniques, polarizing microscopy is the most efficient way to identify different liquid crystal phases, of which details can be found from Takezoe’s review\(^1\) and Southern’s PhD thesis\(^2\). X-ray diffraction is also widely used to determine the phase structure of the bent-core materials\(^1\). As discussed in Chapters 3 and 4, it is clear that Polarized Raman Spectroscopy (PRS) is a powerful technique to investigate liquid crystals, especially the order parameter. Thus some attempts of applying PRS to a bent-core system have been published\(^3,4\) and they
will be reviewed in Section 5.3. The theory describing the analysis methods for applying PRS to the bent-core systems will be discussed and some modification will be applied on Southern’s method in this chapter. The modified bent-core system model with its ODF will be shown in Sections 5.4 and 5.5. In section 5.6, the fitting is done firstly under two different coupling methods without considering the phase biaxial order parameters, in order to compare these two methods. The phase biaxial order parameters are taken into consideration in Section 5.7. Finally, several experimental techniques including optical microscopy, dielectric permittivity measurements and PRS measurements were used to investigate the properties of a bent-core material in Section 5.8. Due to the possibility of a biaxial phase formed in the bent-core system, the phase biaxiality in this chapter will be discussed and the molecular biaxiality for which we gave extensive discussions in Chapter 4 will be ignored.

5.1. Introduction to Bent-core Systems

The basic structure of a bent-core molecule is shown in Fig.5.1. Two rigid cores which have either the same or different structure are combined with a linking group. It is known that the liquid crystalline state is widely formed in different materials. Not only uniaxial molecules can form a liquid crystalline state, but also the complicated bent-core molecules. It was originally thought that bent-core molecules are not a good choice for forming a liquid crystal phase due to the large excluded volume\(^1\). However, Vorländer demonstrated that bent-core molecules containing azo-compounds could form liquid crystal phases\(^5\). But it was not until 1991, when Kuboshita et al. developed a new synthesis method for bent-core compounds which opened a new area on bent-core liquid crystal research\(^6\). Distinct from the calamitic liquid crystals, the linking group has a certain bend angle \(\Omega\) that makes the molecule bend. This bend angle is often assumed as a constant, which is supported by X-ray diffraction experiments for some molecules\(^2,3,7,8\). Due to the bent structure in the molecule, the name bent-core, or banana shape is used and many phases are referred to as B (bent-core) phases. The reasons that bent-core systems are a hot topic in recent years are, firstly, the polar properties which can be used for electro-optical switching\(^9\) and secondly, the macroscopic chirality which can occur despite the molecules being achiral which no chiral centre exists in the molecule\(^10\). A
variety of phase designated as B1 to B8 have been found with a wide variety of phase transitions\textsuperscript{1,11}.

Fig. 5.1 The basic structure of the bent-core molecule that forms bent-core liquid crystals. The two rigid cores are connected by the linking group which has a bend angle $\Omega$.

5.2. Brief Introduction to VBG93

VBG93 (C5-Ph-ODBP-Ph-OC12) is one of the oxadiazole materials synthesised by Dr. V. Görtz and Prof. J.W. Goodby with molecular structure shown in Fig. 5.2. This material has a phase transition from isotropic to nematic phase at 215 °C, then to a phase at 160 °C and finally becomes a crystal at 91 °C\textsuperscript{12}. The bend angle of the molecules is widely accepted to be 140° based on the X-ray scattering and this value will be used in the further discussion\textsuperscript{2,3,7,8,13,14}. The nematic phase between 160 °C and 215 °C attracts our attention since according to Southern’s work on SAXS, VBG93 is uniaxial nematic phase down to 177 °C and then it shows a possible biaxial nematic phase below 177 °C\textsuperscript{2}. So it is an ideal material for the investigation of biaxiality in liquid crystal system. In this chapter, the VBG93 data from Southern’s work will be used for discussion\textsuperscript{2,3}. Notice that the Southern’s data comes from the 20 mW and 514 nm Argon ion laser.

Fig. 5.2 The molecular structure and transition temperatures of VBG93
5.3. Review of the Approach used by Southern

In general, there are two kinds of biaxialities in the liquid crystal systems which are the phase biaxiality and molecular biaxiality. Before the detailed discussion, it is worthwhile clarifying the difference between the uniaxial systems which were discussed in Chapter 3 and 4 and the bent-core system. The term “uniaxial” in the uniaxial system means the liquid crystal phase is uniaxial which indicates that the molecules have only one preferred direction to align. At the same time, the molecules in a uniaxial system could be either uniaxial (Chapter 3) or biaxial (Chapter 4). On the other hand, the liquid crystal phase is not necessarily uniaxial in a bent-core system. As mentioned before, a possible biaxial phase, which means there is an additional preferred direction of the molecules, can also exist in the bent-core system\textsuperscript{2,3}. The molecules in a bent-core system are definitely biaxial due to the bend molecular structure. It is worthy of note that the molecular model in Chapter 4 could also be assumed as a bend shape for the vibrational mode with dipole tilt (e.g. cyano stretching mode) as shown in Fig.4.1. However, there is only one dipole which appears along the certain direction as in Fig.4.1. This is different from the bent-core model which has two dipoles located on two directions as shown in 5.1. Thus, even though the molecular models are all biaxial, the bent-core system is still different from what was discussed in Chapter 4.

The early work about applying PRS on the bent-core systems for biaxial properties investigation was done by Southern\textsuperscript{2,3}. In his analysis method, the phenyl stretching mode was used for analysis since it is along the rigid core direction of each arm. Then the bent-core molecules can be separated into two dipoles of the phenyl stretching mode with a constant angle known as the bend angle between them. These two phenyl stretching dipoles contribute to the Raman scattering separately. In other words, the bent-core molecules can be assumed as two rod-like molecules with a constant bend angle between them as shown in Fig.5.3. Combined with the fact that the molecular rotation (presented by $\gamma$ and $\gamma'$ in Fig.5.3) does not affect the final intensity expression for rod-like molecules, the rotation of each arm can be ignored and thus the molecular biaxiality is avoided. The arm 1 in Fig.5.3 has the Euler angles ($\alpha, \beta, \gamma$) to the director frame. In order to express the Euler angle for the other arm, it was set that the two arms of the bent-core molecules share the same $\alpha$ angle as shown in Fig.5.3. By doing this, the Euler angle for the other arm is ($\alpha, \beta + \Omega, \gamma'$) where $\Omega$ is the bend angle of the bent-core
molecule. The final Raman scattering intensities can be described by summing up the contribution of each arm. Based on these setups, a fitting method was published\(^2,4\). The fitting results indicated a possible biaxial phase in some of the oxadiazole material such as VBG93. A similar fitting method was also carried out in 2011\(^15\). In this method, they ignore the effect of molecular bend angle\(^15\). This method was later proved to be incomplete since they ignore the molecular bend and it will give a lower (~10% on \(\langle P_{200} \rangle \)) estimation of the uniaxial order parameters\(^16\).

![Diagram](image)

Fig. 5.3 The bent-core system model of Southern’s method. The bent-core molecule is divided to two phenyl stretching modes which locate on two arms of the molecule with bend angle \(\Omega\) between them. The Euler angle of each arm to the director frame \((x_Dy_Dz_D)\) are \((\alpha, \beta, \gamma)\) and \((\alpha, \beta + \Omega, \gamma')\).

However, there are still some problems in Southern’s method. Since the two arms share the same \(\alpha\) angle, the flexibility of arm 2 is confined. As shown in Fig.5.3, if arm 1 is kept in the position and arm 2 rotated around \(z_{arm1}\) axes, the Euler angle of arm 2 is changed but it still satisfies the bent-core molecular structure. This situation is not considered in Southern’s method. Thus the analysis method is not complete. So it is necessary to do some modification on Southern’s method.

### 5.4. Bent-core Molecular Model

Inspired by the work carried out by Southern in 2008\(^2,4\), some modifications will be made to that method to make it more suitable for the order parameter measurements in
a bent-core system. Before a systematic investigation, a model for the bent-core systems is needed for theoretical analysis. It is worthy of note that the molecular biaxiality in the bent-core system was ignored even though the molecules are definitely biaxial since too many parameters will cause problems in the fitting process. Fig. 5.4 shows the basic model of a bent-core system. The molecule’s long axis, which lies in a certain direction in the molecular bend plane, has a set of Euler angle $(\alpha, \beta, \gamma)$ from the liquid crystal director direction $\mathbf{n}$. Two different Raman active arms (arm 1 and arm 2) are along the two rigid cores which have different tilt angles from the molecular long axis. The tilt angles of arm 1 and 2 are $B_0$ and $B_0 + \Omega$ respectively. With this setup, the bent-core molecule can be assumed as a combination of two dipoles with tilt angle $B_0$ and $B_0 + \Omega$ with respect to the molecular long axis. It is worthy of note that the molecular model is same as Southern’s when $B_0 = 0$. However, the new model will enable the molecule to rotate instead of occupying the fixed position in Southern’s method. The relationship between the tilt angle and the bend angle will be discussed later. With this new model, flexibility is enabled in the molecules allowing a more general description.

![Diagram](image)

Fig. 5.4 The brief model of the bent-core system. Frame $x_Ly_Lz_L$ is the laboratory frame. The $x_Dy_Dz_D$ frame is the director frame in which the director lies on the $z_D$ axis. $z_D$ rotates in the $x_LOz_L$ with a rotation angle $\theta$. The $x_My_Mz_M$ frame is the molecular frame with molecular long axis lying on the $z_M$ axis. $z_{Sa1}$ and $z_{Sa2}$ indicate the direction of the two rigid core units.

The basic assumptions of this bent-core system model include:

- The two arms have exactly the same vibrational modes.
- The dipoles for each arm are exactly same and exhibit cylindrical symmetry.
- The liquid crystal system has no ferroelectricity properties which means $\mathbf{n} = -\mathbf{n}$. 

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5.5. Orientational Distribution Function (ODF) and Raman Tensor

Recall the discussion of the ODF in Chapter 2, which can be expanded and expressed by using Wigner D-matrices as below.

\[
f(\alpha, \beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m,m'=-L}^{L} \frac{2L + 1}{8\pi^2} \langle D_{m'm}^{L}(\alpha, \beta, \gamma) \rangle \langle D_{m'm}^{L}(\alpha, \beta, \gamma) \rangle \]

Since the molecular biaxiality is ignored, the molecular biaxial order parameters are all set to be zero, thus the orientational distribution function is simplified to \( f(\alpha, \beta) \). The ODF can be expressed by eq.5.2 (For more details refer to Appendix A.3).

\[
f(\alpha, \beta) = \left( \frac{1}{8\pi^2} \right) \left( 1 + \frac{5}{2} \langle P_{200} \rangle (3\cos^2 \beta - 1) + \frac{5}{2} \langle P_{220} \rangle (1 - \cos^2 \beta) \cos 2\alpha + \frac{9}{8} \langle P_{400} \rangle (35\cos^4 \beta - 30\cos^2 \beta + 3) + \frac{9}{8} \langle P_{420} \rangle (7\cos^2 \beta - 1) (1 - \cos^2 \beta) \cos 2\alpha + \frac{9}{8} \langle P_{440} \rangle 70(1 - \cos^2 \beta)^2 \cos 4\alpha \right) \]

Eq.5.2 also contains the biaxial order parameters \( \langle P_{220} \rangle, \langle P_{420} \rangle \) and \( \langle P_{440} \rangle \). Notice that these biaxial order parameters are different from that discussed in Chapter 4. In Chapter 4, the biaxial order parameters are \( \langle P_{202} \rangle, \langle P_{402} \rangle \) and \( \langle P_{404} \rangle \) which describe the molecular biaxiality. But \( \langle P_{220} \rangle, \langle P_{420} \rangle \) and \( \langle P_{440} \rangle \) in eq.5.2 are used to describe the biaxiality of the biaxial liquid crystal phase. However the liquid crystal system is complex for analysis with these molecular biaxial order parameters. So as a first stage, we will concentrate on the uniaxial phase of the bent-core system and ignore the effect of the molecular biaxial order parameters. Thus the ODF is further simplified to the expression below:

\[
f(\beta) = \left( \frac{1}{8\pi^2} \right) \left( 1 + \frac{5}{2} \langle P_{200} \rangle (3\cos^2 \beta - 1) + \frac{9}{8} \langle P_{400} \rangle (35\cos^4 \beta - 30\cos^2 \beta + 3) \right) \]

As discussed in section 5.3, the molecule has been separated into two individual dipoles. Combining the assumptions that the dipole has cylindrical symmetry and the two dipoles are the same, the Raman tensor for each arm can be obtained. They can be expressed in the diagonal form as shown in eq.5.4.
\[ \alpha'_{sa1} = \alpha'_{sa2} = \begin{pmatrix} \alpha'_{axx} & 0 & 0 \\ 0 & \alpha'_{ayy} & 0 \\ 0 & 0 & \alpha'_{azz} \end{pmatrix} = \alpha'_{azz} \begin{pmatrix} r & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{5.4} \]

where \( r \) is the differential polarizability ratio. It is worthy of note that the two diagonal tensors are in different frames. The \( z \) axes for arm 1 and 2 are \( z_{sa1} \) and \( z_{sa2} \) respectively as shown in Fig.5.3. In order to calculate the intensities expression, the Raman tensor of each arm needs three coordinate transformations to the laboratory frame. This is different from Southern’s method where only two transformations are needed since the diagonal form Raman tensor is in the “molecular” frame (recalling that the bent-core molecular is divided to two individual rod-like molecules in Southern’s method).

According to the discussion in Chapter 2, it is known that the Raman intensity of certain vibrational mode is proportional to the square of the Raman tensor. However there are two arms with same vibrational mode in bent-core molecule, both of them will perform Raman scattering and contribute to the same Raman peak intensity. Thus, there are two possible coupling methods to discuss for the contribution of each arm in bent-core molecule.

- **Coupling Method 1**: The two arms are assumed as an entirety. Both of them contribute to the molecular Raman tensor. Then the total intensity can be expressed as below:

\[
I_{\text{Total}} \propto \int_0^\pi f(\beta) \alpha'_{\text{total}}^2 \sin \beta \, d\beta = \int_0^\pi f(\beta) (\alpha'_{Larm1} + \alpha'_{Larm2})^2 \sin \beta \, d\beta \tag{5.5}
\]

where \( \alpha'_{Larm1} \) and \( \alpha'_{Larm2} \) represent the Raman tensor of each arm in the laboratory frame.

- **Coupling Method 2**: Each arm generates Raman scattering individually and the total intensity is the sum of two intensities. The total intensity can be expressed as below:

\[
I_{\text{Total}} = I_{Larm1} + I_{Larm2} \propto \int_0^\pi f(\beta) \alpha'_{Larm1}^2 \sin \beta \, d\beta + \int_0^\pi f(\beta) \alpha'_{Larm2}^2 \sin \beta \, d\beta = \int_0^\pi f(\beta) (\alpha'_{Larm1}^2 + \alpha'_{Larm2}^2) \sin \beta \, d\beta \tag{5.6}
\]
In Southern’s analysis, the Coupling Method 1 was used. However, we will check both of these two coupling methods for a complete discussion. The following section will discuss both of these approaches in detail.

5.6. Coupling Methods Discussion

In this section, the two different coupling methods will be discussed. In each of the discussions, the theoretical intensities expressions will be given at the beginning, then the effect of the bend angle $\Omega$ and the tilt angle $B_0$ on the depolarization ratio graphs will be discussed. After this, we will apply fitting based on the intensities expressions to VBG93 data. Since the phase biaxiality was ignored in the first discussion, the data used for this discussion is within the uniaxial nematic phase, where the phase biaxial order parameters do not have obvious effect on the fitting. Notice the fitting results obtained with the uniaxial molecular model will also be shown to show the necessity of introducing the bend angle in the bent-core system. During this process, the effect of the bend angle $\Omega$ and the tilt angle $B_0$ on the fitting results will also be discussed. Finally we will apply the fitting to the whole VBG93 data including the data in the possible biaxial phase. The fitting results are compared with refractive index measurement results, Southern’s fitting result and theoretical discussion. We can evaluate the two coupling methods in this process as well as checking the effect of ignoring the phase biaxial order parameters in the possible biaxial phase.

5.6.1. Coupling Method 1

The fitting process in the Coupling Method 1 first calculates the Raman tensor and then calculates the intensity as discussed in this section. After the calculations based on eq.5.5, the final expressions of intensity are shown below in eqs.5.7 and 5.8.

$$I_\parallel = \frac{2}{15}(5(1 + 2r + 3r^3) + (-1 + r)^2 \cos 2\Omega)$$

$$- \frac{1}{42}(P_{200})(-1 + r)(5 + 9r - (-1 + r) \cos 2\Omega + 3(3 + 4r) \cos 2B_0$$

$$+ 3(3 + 4r) \cos 2(B_0 + \Omega))(1 + 3 \cos 2\theta)$$
With these two intensity expressions, the depolarisation ratio for the whole rotation angle $\theta$ can be obtained. The first step is to check the effect of each order parameter on the depolarization ratio graph. As carried out in chapter 4, all parameters were set to constant values while only allowing tilt angle $B_0$ or bend angle $\Omega$ to change, and then plot the depolarization ratio graphs according to eqs.5.7 and 5.8. Firstly, Fig. 5.5a) shows the effect of $B_0$ on the depolarization ratio. It is observed that an increase in the tilt angle $B_0$ increases the depolarization ratio around $\theta=90^\circ$ and $\theta=270^\circ$ while lowering it slightly around $\theta=0^\circ$ and $\theta=180^\circ$. Secondly, Fig.5.5b) indicates the effect of bend angle $\Omega$ on the depolarization ratio. The depolarization ratio decreases for the complete rotation via decreasing in $\Omega$. The reduction is strong at around $\theta=90^\circ$ and $\theta=270^\circ$ while less effective at other rotation angles. From these figures, it is clear that the tilt angle $B_0$ and bend angle $\Omega$ have strong effect on the depolarization ratio and therefore they will affect the fitting values of the order parameters.

\[
I_\perp = \frac{1}{30} (-1 + r)^2 (5 + 3 \cos 2\Omega) + \frac{1}{84} (\langle P_{200} \rangle (-1 + r)^2 (1 + 3 \cos 2\Omega + 6 \cos 2B_0 + 6 \cos 2(B_0 + \Omega) )
- \frac{1}{17920} (\langle P_{400} \rangle (-1 + r)^2 (6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) )
+ 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega))(9 + 20 \cos 2\theta + 35 \cos 4\theta)
\]

(5.7)

(5.8)

Fig. 5.5 Effect of the tilt angle $B_0$ and bend angle $\Omega$ on the depolarization ratio with Coupling Method 1. In these plots, $\langle P_{200} \rangle = 0.45$, $\langle P_{400} \rangle = 0.2$ and $r = -0.15$. In a), bend angle $\Omega$ is set to be $140^\circ$ and the tilt angle $B_0$ is $0^\circ$ (black); $10^\circ$ (red) and $20^\circ$ (blue). In b), tilt angle $B_0$ is set to be $20^\circ$ and the bend angle $\Omega$ is $160^\circ$ (black); $140^\circ$ (red) and $120^\circ$ (blue).
Some fitting results with VBG93 data will be shown in this section. The fitting is based on the depolarization ratio expression using eqs.5.7 and 5.8. It is to be noted that the depolarisation ratio expression has six parameters: uniaxial order parameters $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$, the differential polarizability ratio $r$ which describes the relationship between $\alpha'_{xx}$ and $\alpha'_{xz}$, the bend angle $\Omega$, the tilt angle $B_0$ of arm 1. In the fitting process, we can set the bend angle $\Omega$ and tilt angle $B_0$ parameter and assume them to be constant during the fitting process to present different shapes of the molecule. As a consequence, there are only three parameters left so the fitting is easy to achieve.

<table>
<thead>
<tr>
<th>Adj.R-Square</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle P_{200} \rangle$</td>
<td>0.50</td>
<td>0.01</td>
</tr>
<tr>
<td>$\langle P_{400} \rangle$</td>
<td>0.26</td>
<td>0.01</td>
</tr>
<tr>
<td>$r$</td>
<td>-0.19</td>
<td>0.01</td>
</tr>
<tr>
<td>Fixed</td>
<td>$B_0$</td>
<td>0</td>
</tr>
<tr>
<td>Fixed</td>
<td>$\Omega$</td>
<td>180</td>
</tr>
</tbody>
</table>

Fig. 5.6 Fitting result for VBG93 using Coupling Method 1 with different molecular arrangements.

a) The bent-core molecular model is set with $B_0 = 0^\circ$ and $\Omega = 180^\circ$ (this can be assumed as uniaxial molecular model).

b) The bent-core molecular model is set with $B_0 = 20^\circ$ and $\Omega = 140^\circ$.

The phenyl stretching mode at 1606cm$^{-1}$ has been used for the analysis. Fig. 5.6 shows the fitting results for VBG93 data at 210°C (T/T$_{NI}=0.983$) at which VBG93 shows the uniaxial nematic phase. As mentioned before, the necessity of considering the bend angle will be shown by using the uniaxial molecular model for comparison. This uniaxial molecular model can be achieved by setting the bend angle $\Omega$ to be $180^\circ$ and tilt angle $B_0$.
$B_0$ to be $0^\circ$ in the bent-core molecular model. This setting will be used in the following discussion to represent the uniaxial molecular model. The fitting results are shown in Fig.5.6a). On the other hand, the bent-core molecular model is achieved by setting the bend angle $\Omega$ to be $140^\circ$ for VBG93 as mentioned$^{7,13,14}$ and the tilt angle $B_0$ equals to $20^\circ$. The fitting result is shown in Fig.5.6b).

It can be seen that both the uniaxial and bent-core molecular model give reasonable fitting results according to Fig.5.6. There is not a huge difference on the fitting results of the uniaxial order parameters. But similar conclusion can still be obtained after comparing the fitting result from Fig.5.6 that the uniaxial molecular model will give a lower fitting result$^{16}$. On the other hand, the differential polarizability ratio $r$ shows a difference between the two molecular models as in Fig.5.6. The difference in $r$ is due to the coupling method used. Since we assumed that the Raman tensor of each arm contributes to the total Raman tensor, the bend angle cannot be neglected in the total Raman tensor. As the result, the $r$ value will be affected by the bend angle $\Omega$ during the fitting process. After this discussion above, it is clear that the effect of the existence of the tilt angle $B_0$ and bend angle $\Omega$ can’t be ignored. So now the effect of $B_0$ and $\Omega$ on the order parameter fitting values will be examined.

![Flow chart of the fitting method](image)

Fig. 5.7 The flow chart of the fitting method.

All the discussions above on the bent-core molecular model depend on a special combination of tilt angle $B_0$ and the bend angle $\Omega$ ($B_0 = 20^\circ$ and $\Omega = 140^\circ$). However,
several generalized situations can be achieved by setting different combinations of these two angles. Thus the effect of different tilt angle \( B_0 \) and bend angle \( \Omega \) on the fitting value of order parameters can be discussed. The flow chart of the fitting method is shown in Fig.5.7. The change in the \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) fitting values with different tilt angle at a constant bend angle of 140° are shown in Fig.5.8. According to Fig.5.8, it is found that the fitting values of \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) are symmetrical with respect to \( B_0 = 20° \) with the lowest fitting value at \( B_0 = 20° \). The fitting values of \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) increase dramatically by about 30% and 88% at \( B_0 = 0° \) respectively. Further, the fitting values with \( B_0 = 20° \) is close to the fitting result with uniaxial molecular model. So it can be conclude that firstly, the tilt angle \( B_0 \) has a very strong effect on the fitting values of the uniaxial order parameters. This also indicates the direction of the molecular long axis should be carefully chosen. Secondly, the uniaxial molecular model will always give a lower fitting result compared with the bent-core molecular model.

Fig. 5.8 \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) at different tilt angle \( B_0 \) with a bend angle of 140°. The dashed line indicates the fitting value of \( \langle P_{200} \rangle \) (black) and \( \langle P_{400} \rangle \) (red) with the uniaxial molecular model. The data comes from phenyl stretching mode in VBG93 at 210 °C (T/T_{NI}=0.983).

Fig.5.9 shows that \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) change with different bend angle \( \Omega \) at varying tilt angles. From Fig.5.9, the fitting value is no longer symmetric as seen in Fig.5.8. However there is still a minimum position in each graph where the fitting values of \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) are close to that from the uniaxial molecular model and the fitting values are increased by either an increase or decrease in the bend angle. These positions include \( \Omega = 160° \) and 140° and these positions satisfy the condition:

![Graph showing fitting values](image_url)
Fig. 5.9 $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ as a function of different bend angles $\Omega$ with tilt angle at a)0º, b)10º and c)20º. The dashed lines indicate the fitting value of $\langle P_{200} \rangle$ (black) and $\langle P_{400} \rangle$ (red) with uniaxial molecular model. The data comes from the phenyl stretching mode in VBG93 at 210°C ($T/T_{NI}=0.983$).

Now we will apply the fitting process to VBG93 data at different temperatures. In this discussion, the bend angle $\Omega$ is fixed to 140º. It can be concluded from Fig.5.8 that the fitting values of the order parameters have some difference due to the different tilt angle. Thus we use the fitting value with $B_0=0^\circ$ and $B_0=20^\circ$ as the upper and lower boundary respectively to illustrate the possible area for the fitting order parameter values. Fig.5.10a) shows the $\langle P_{200} \rangle$ fitting results compared with refractive index measurement and Southern’s fitting results. It is clear that when the $T/T_{NI}$ is higher than 0.922, both the refractive index measurement results and Southern’s fitting results are located in the possible area of the fitting value of $\langle P_{200} \rangle$. The upper boundary ($B_0=0^\circ$) and the lower boundary ($B_0=20^\circ$) both show a similar decreasing tendency compared with the refractive
index measurement results. Fig. 5.10b) shows the $\langle P_{400} \rangle$ fitting results compared with Southern’s fitting results \(^3\). Similar conclusions can be obtained that the Southern’s fitting result located in the possible region of the fitting value of $\langle P_{400} \rangle$. However, it is worthy of note that the $\langle P_{400} \rangle$ value is very high especially the upper boundary value. This reminds us the extraordinary high fitting value of $\langle P_{400} \rangle$ in Chapter 4 and it was concluded that the molecular biaxial order parameters will decrease the $\langle P_{400} \rangle$ fitting result. Since the molecular biaxiality is ignored in the discussion in this chapter, the high $\langle P_{400} \rangle$ fitting value is within our expectation.

Fig. 5.10 a) $\langle P_{200} \rangle$ and b) $\langle P_{400} \rangle$ as a function of $T/T_{NI}$. The fitting result with $B_0=0^\circ$ and $B_0=20^\circ$ are denoted by a solid circle and solid square respectively. Southern’s fitting results \(^3\) are shown with empty triangle. All the data are compared with the refractive index measurement data (cross) from the research done by Kaur \(^8\).

Fig. 5.11 Differential polarizability ratio $r$ changes as a function of $T/T_{NI}$. The fitting result with $B_0=0^\circ$ and $B_0=20^\circ$ are denoted by a solid circle and solid square respectively.
It is seen that the fitting values of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ are discontinuous around $T/T_{NI} = 0.922$. This may be due to the transition from a uniaxial phase to a possible biaxial phase as discussed by Southern. This difference is also seen in the differential polarizability ratio (Fig. 5.11). The fitting value of $r$ is discontinuous with the error bar also increasing dramatically when temperature is lower than $T/T_{NI} = 0.922$. Apparently, the fitting equations need to include phase biaxial order parameters in the biaxial phase thus the fitting value of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ are inaccurate in biaxial region. A discussion with the biaxiality taken into account will be shown later in Section 5.7. Fig. 5.12 shows $\langle P_{400} \rangle$ as a function of $\langle P_{200} \rangle$ along with the theoretical prediction. It is to be noted that the $\langle P_{400} \rangle$ is high since the molecular biaxiality is ignored. Thus all the results are shifted up compared with the theoretical prediction. However, the curvature of the experimental data show a similar tendency compared with the theoretical prediction as shown in Fig. 5.12.

Fig. 5.12 $\langle P_{400} \rangle$ as a function of $\langle P_{200} \rangle$ compared with the theoretical curve from Maier-Saupe theory (solid line). Two set of fitting result with $B_0 = 0^\circ$ (square) and $B_0 = 20^\circ$ (circle) are shown. Southern’s fitting results (empty triangle) are shown as comparison.
5.6.2. Coupling Method 2

Following the same procedure as in Section 5.6.1, the fitting using the Coupling Method 2 which calculates the intensity first and then sums up the intensities will be shown in this section. The coupling equation is shown in eq.5.10:

\[ I_{\text{Total}} = I_{\text{arm1}} + I_{\text{arm2}} \propto \int_{0}^{\pi} f(\beta)\left( \alpha'_{L\text{arm1}}^2 + \alpha'_{L\text{arm2}}^2 \right) \sin \beta \, d\beta. \] (5.10)

The intensity expressions are:

\[ I_{\parallel} = \frac{2}{15}(3 + 4r + r^2) \]
\[ - \frac{1}{84}(P_{200})(-3 - 4r + r^2)(2 + 3 \cos 2B_0 + 3 \cos 2(\Omega + \Omega))(1 + 3 \cos 2\theta) \]
\[ + \frac{1}{17920}(P_{400})(-1 + r)^2(18 + 20 \cos 2B_0 + 35 \cos 4B_0 + 20 \cos 2(\Omega + \Omega)) \]
\[ + 35 \cos 4(B_0 + \Omega)(9 + 20 \cos 2\theta + 35 \cos 4\theta), \] (5.11)

\[ I_{\perp} = \frac{2}{15}(-1 + r)^2 \]
\[ + \frac{1}{84}(P_{200})(-1 + r)^2(2 + 3 \cos 2B_0 + 3 \cos 2(\Omega + \Omega)) \]
\[ - \frac{1}{17920}(P_{400})(-1 + r)^2(18 + 20 \cos 2B_0 + 35 \cos 4B_0 + 20 \cos 2(\Omega + \Omega)) \]
\[ + 35 \cos 4(B_0 + \Omega)(-3 + 35 \cos 4\theta). \] (5.12)

With these two intensity expressions, the depolarisation ratio for the whole rotation angle can be calculated. The effect of the tilt angle \( B_0 \) and the bend angle \( \Omega \) on the depolarization ratio are discussed with the same method as in Section 5.6.1. As shown in Fig. 5.13a), the effect of the tilt angle \( B_0 \) is similar to what was discussed with coupling Method 1 in Fig. 5.5a). With increasing the tilt angle, the depolarization ratio around \( \theta=90^\circ \) and \( \theta=270^\circ \) increases while the depolarization ratio decreases slightly around \( \theta=0^\circ \) and \( \theta=180^\circ \). Similar to the results in Fig.5.5b), the decreasing bend angle \( \Omega \) also decreases the depolarization ratio value around \( \theta=90^\circ \) and \( \theta=270^\circ \) as seen in Fig. 5.13b). However, by decreasing the bend angle \( \Omega \) value while the depolarization ratio around \( \theta=0^\circ \) and \( \theta=180^\circ \) increases dramatically.
Fig. 5.13 The effect of the tilt angle $B_0$ and bend angle $\Omega$ on the depolarization ratio using Coupling Method 2. In these plots, $\langle P_{200}\rangle=0.45$, $\langle P_{400}\rangle = 0.2$ and $r = -0.15$. In a), bend angle $\Omega$ is set to be 140° and the tilt angle $B_0$ is 0° (black); 10° (red) and 20° (blue). In a), tilt angle $B_0$ is set to be 20° and the bend angle $\Omega$ is 160° (black); 140° (red) and 120° (blue).

Fig. 5.14 Fitting result from VBG93 using Coupling Method 2 with different molecular arrangement. a) The bent-core molecular model is set with $B_0= 0^\circ$ and $\Omega= 180^\circ$ (this is equal to the uniaxial model). b) The bent-core molecular model is set with $B_0= 20^\circ$ and $\Omega= 140^\circ$. 
The fitting results from VBG93 at 210°C (T/T_{NI}=0.983) will be discussed. The phenyl stretching mode at 1606 cm\(^{-1}\) is used for the analysis. As the first step, the uniaxial molecular model was used for fitting. The fitting results are shown in Fig.5.14a). This fitting result from the uniaxial molecular model was used for comparison with the bent-core molecular model. The bent-core molecular model was achieved by setting the bend angle \(\Omega\) equals to 140° and tilt angle \(B_0\) equals to 20°. The fitting result is shown in Fig.5.14b). The fitting quality does not change in the two fittings in Fig.5.14. However, the fitting values have a dramatically difference between the uniaxial molecular model and bent-core molecular model. Both \(\langle P_{200} \rangle\) and \(\langle P_{400} \rangle\) are higher in the bent-core model than the uniaxial model. Especially \(\langle P_{400} \rangle\) is even doubled in the bent-core molecular model. On the other hand, the \(r\) value does not change which is different compared with Coupling Method 1.

The effect of tilt angle on the fitting values of \(\langle P_{200} \rangle\) and \(\langle P_{400} \rangle\) was discussed following the flow chart as shown in Fig.5.7 but using eqs.5.11 and 5.12. Fig.5.15 is the summary of fitting results. Similar to Fig.5.8, the symmetric fitting value around \(B_0=20^\circ\) appears again. But the fitting value of the order parameters is much higher than our expectation. The increment in \(\langle P_{400} \rangle\) and \(\langle P_{200} \rangle\) in Fig.5.15 is about 50% and 25% respectively. It is worthy of note that the fitting value is far from that from the uniaxial molecular model. This indicates that Coupling Method 2 is not a proper approach on obtaining order parameters.

Fig. 5.15 \(\langle P_{200} \rangle\) and \(\langle P_{400} \rangle\) at different tilt angle \(B_0\) with bend angle of 140°. The dashed line indicates the fitting value of \(\langle P_{200} \rangle\) (black) and \(\langle P_{400} \rangle\) (red) using the uniaxial molecular model. The data comes from Phenyl stretching mode in VBG93 at 210°C (T/T_{NI}=0.983).
Fig. 5.16 \( \langle P_{400} \rangle \) as a function of \( \langle P_{200} \rangle \) (solid scatter) compared with the theoretical curve from Maier-Saupe theory (dashed line). Two fitting values are picked out with \( \langle P_{400} \rangle \) fitting value shown in the plot. The theoretical \( \langle P_{400} \rangle_{\text{theory}} \) correspond to the \( \langle P_{200} \rangle \) fitting value of the two data point is also shown.

Fig.5.16 indicates the comparison of the fitting values from Fig.5.15 to the theoretical predication. It is clear that the fitting data is far from the theoretical predication. Two points (a and b in Fig.5.16) are picked out for illustration. The fitting values of \( \langle P_{400} \rangle \) are much larger (a: 116% and b: 95%) than the theoretical \( \langle P_{400} \rangle_{\text{theory}} \) at same \( \langle P_{200} \rangle \) value in Fig.5.16. Now it can concluded that the second approach cannot provide a reliable fitting value of order parameters, this coupling method will be abandoned in the following discussion.

5.7. Introducing Phase Biaxial Order Parameters in the Analysis Method

5.7.1. Theoretical Discussion of the Phase Biaxial Order Parameters

As mention in the introduction, the most important property of the bent-core liquid crystal system that attracts our attention is the possibility of phase biaxiality due to the bent-core molecules. After the above discussion about the coupling of two vibrational
modes, we choose Coupling Method 1 to derive the intensities expression. The expressions of intensities are shown in eqs.5.13 and 5.14:

\[ I_\parallel = \frac{2}{15} (5(1 + 2r + 3 r^3) + (-1 + r)^2 \cos 2\Omega) \]

\[ - \frac{1}{42} \langle P_{200} \rangle (-1 + r)(5 + 9r - (-1 + r) \cos 2\Omega + 3(3 + 4r) \cos 2B_0 \]

\[ + 3(3 + 4r) \cos 2(B_0 + \Omega))(1 + 3 \cos 2\theta) \]

\[ + \frac{1}{17920} \langle P_{400} \rangle (-1 + r)^2(6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) \]

\[ + 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega))(9 + 20 \cos 2\theta + 35 \cos 4\theta) \]

\[ + \frac{2}{7} \langle P_{220} \rangle (-1 + r)(5 + 9r - (-1 + r) \cos 2\Omega + 3(3 + 4r) \cos 2B_0 \]

\[ + 3(3 + 4r) \cos 2(B_0 + \Omega)) \sin^2 \theta \]

\[ + \frac{3}{224} \langle P_{420} \rangle (-1 + r)^2(6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) \]

\[ + 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega))(5 + 7 \cos 2\theta) \sin^2 \theta \]

\[ + \frac{1}{32} \langle P_{440} \rangle (-1 + r)^2(6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) \]

\[ + 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega)) \sin^4 \theta \]  

\[ (5.13) \]

\[ I_\perp = \frac{1}{30} (-1 + r)^2(5 + 3 \cos 2\Omega) \]

\[ + \frac{1}{84} \langle P_{200} \rangle (-1 + r)^2(1 + 3 \cos 2\Omega + 6 \cos 2B_0 + 6 \cos 2(B_0 + \Omega)) \]

\[- \frac{1}{17920} \langle P_{400} \rangle (-1 + r)^2(6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) \]

\[ + 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega))(-3 + 35 \cos 4\theta) \]

\[ + \frac{1}{14} \langle P_{220} \rangle (-1 + r)^2(1 + 3 \cos 2\Omega + 6 \cos 2B_0 + 6 \cos 2(B_0 + \Omega)) \]

\[ + \frac{1}{896} \langle P_{420} \rangle (-1 + r)^2(6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) \]

\[ + 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega))(1 + 7 \cos 4\theta) \]

\[ + \frac{1}{128} \langle P_{440} \rangle (-1 + r)^2(6 \cos 2\Omega + 5(6 + 8 \cos 2B_0 + 7 \cos 4B_0 + 8 \cos 2(B_0 + \Omega) \]

\[ + 7 \cos 4(B_0 + \Omega) + 14 \cos 2(2B_0 + \Omega)) \sin^4 \theta \]  

\[ (5.14) \]

Following the same approach as in Chapter 4, the effect of each phase biaxial order parameters on the depolarization ratio can be discussed as shown in Fig.5.17. In these discussions, the bend angle and tilt angle are kept constant as 140° and 20°
respectively. The uniaxial order parameters $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ are also kept constant at 0.5 and 0.2 respectively. Then for each plots in Fig.5.17, one biaxial order parameter is allowed to change while others are set to zero. Fig. 5.17a) shows the effect of $\langle P_{220} \rangle$ on the depolarization ratio. By increasing $\langle P_{220} \rangle$, the depolarization ratio around $\theta=90^\circ$ and $\theta=270^\circ$ decreases dramatically while the depolarization ratio value around $\theta=0^\circ$ and $\theta=180^\circ$ increases.

Fig. 5.17 The effect of different order parameters on the behaviour of the depolarization ratio plots. In these calculations, $\langle P_{200} \rangle=0.5; \langle P_{400} \rangle=0.2; \ r=-0.12; \ B_0=20^\circ$ and $\Omega=140^\circ$. a) dependence on $\langle P_{220} \rangle = 0$ (black), 0.1 (red) and 0.2 (blue); b) dependence on $\langle P_{420} \rangle = 0$ (black), -0.01 (red) and -0.02 (blue); and c) dependence on $\langle P_{440} \rangle = 0.005$ (black), 0 (red) and -0.005 (blue).

So in general, $\langle P_{220} \rangle$ makes the depolarization ratio graph flat. A more pronounced effect is seen on varying $\langle P_{420} \rangle$ as shown in Fig.5.17b). By increasing $\langle P_{420} \rangle$ value, the depolarization ratio increase dramatically at $\theta=90^\circ$ and $\theta=270^\circ$ while the depolarization ratio value around $\theta=90^\circ$ and $\theta=270^\circ$ is decreased. So $\langle P_{420} \rangle$ reduces the oscillation around $\theta=90^\circ$ and $\theta=270^\circ$. In addition, the depolarization ratio around $\theta=0^\circ$ and $\theta=180^\circ$ are also increased slightly with the increasing $\langle P_{420} \rangle$. Thus $\langle P_{420} \rangle$ makes the
depolarization ratio graph fluctuate less when it increases. Finally Fig.5.17c) shows the effect of \( \langle P_{440} \rangle \) on the depolarization ratio. With increasing \( \langle P_{440} \rangle \), the depolarization ratio around \( \theta = 90^\circ \) and \( \theta = 270^\circ \) are dramatically decreased and it is worth noticing that the depolarization ratio value around \( \theta = 0^\circ \) and \( \theta = 180^\circ \) is almost constant. All the discussion shows a good agreement with the Gleeson’s work in 2010\(^4\) even though the discussion in this paper depends on Southern’s method. This indicates the modification in this chapter only has effects on the value of order parameters but will not change the effects of each order parameter on the depolarization ratio graph.

### 5.7.2. Fitting Taking Phase Biaxiality into Consideration

With the biaxial order parameter taken into consideration, the fitting is a hard process due to the large number of the fitting parameters. It is impossible to robustly fit so many parameters at same time to a single data fit. So only the phase biaxial order parameters were used as the fitting parameters. As a first step, the accuracy of the fitting results was examined following the method shown in blue from Fig. 5.18. At first, a set of parameter values from eqs.5.7 and 5.8 was obtained with the condition that the bend angle is 140° and tilt angle is 20°. Then the value of \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) were modified to two set of random values while keeping the other fitting values of the parameter in first step as constant. Finally, substitute these values into eqs.5.13 and 5.14 and fitting for the phase biaxial order parameters.

![Flow diagram of the fitting method](image)

Fig. 5.18 Flow diagram of the fitting method. The blue section is for the accuracy check. The red section is for the final fitting procedure.
As shown in Fig. 5.19, two sets of fitting values of $\langle P_{220} \rangle$, $\langle P_{420} \rangle$ and $\langle P_{440} \rangle$ can be obtained depending on $P_{200}$ and $P_{400}$ values and both of them show a good fitting quality. Thus it can be concluded that the biaxial order parameter values have a strong dependence on the uniaxial order parameters. Besides, the standard error is large for the fitting. So it is clear that robust fitting values cannot be obtained according to eqs. 5.13 and 5.14. However, we will still discuss a final fitting using the phase biaxial order parameters as shown in the red section in Fig. 5.18. It is worthy of note that the fitting value of $r$ has an obvious difference due to the bend angle. This fact raises a question that whether $r$ should be independent of bend angle or not. According to the discussions by Southern, the $r$ value depends on the vibrational mode, temperature and liquid crystal phase. Thus the change in fitting value of $r$ due to the bend angle should be avoided. Therefore, the fitting value of $r$ from the uniaxial molecular model was used. More discussion will be given later.

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Fig. 5.19 Two set of biaxial order parameter fitting values dependent on the different uniaxial order parameter values.

Fig. 5.20a) shows the fitting results if the confinements in eq. 5.15 are ignored as what Southern did in his work. VBG93 is uniaxial nematic phase when $T/T_{NI}>0.922$ which means the biaxial order parameter should converge to zero in this region. However, the biaxial order parameter fitting results in Fig. 5.20a) do not show this behaviour. Instead there is an obvious jump of the phase biaxial order parameter values around $T/T_{NI}=0.922$. Moreover, according to the definition of the phase biaxial order parameters, the values of phase biaxial order parameters must be confined by the condition in eq. 5.15:

$$0 \leq |\langle P_{220} \rangle| \leq 0.25; \ 0 \leq |\langle P_{420} \rangle| \leq 0.0536; \ 0 \leq |\langle P_{440} \rangle| \leq 0.0625.$$ (5.15)
The fitting result following the condition as eq.5.15 is shown in Fig.5.20b. It can be seen that the fitting is even worse especially for $\langle P_{440} \rangle$ which always reach the lower boundary.

![Fig. 5.20 Fitting result of the phase biaxial order parameters $\langle P_{420} \rangle$ (square), $\langle P_{440} \rangle$ (circle) and $\langle P_{220} \rangle$ (triangle). The fitting values are not confined by the conditions in eqs.5.15 in a) while they are confined in b).](image)

It is reasonable to see the unusual fitting values of the phase biaxial order parameters. We know that both $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ have a strong effect on the fitting value of the phase biaxial order parameters. In our fitting method, the values of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ come from fitting results according to eqs.5.8 and 5.9 wherein the phase biaxial order parameters are not considered. Thus the values of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ already include the correction for ignoring the phase biaxial order parameters. So the fitting results that depend on eqs.5.13 and 5.14 are not reliable in biaxial phase $(T/T_{NI}<0.922)$. However, despite this fact, bad fitting results still obtained in uniaxial phase $(T/T_{NI}>0.922)$. Two possible explanations are considered. Firstly, the large error bar reveals the fluctuation on each of the fitting values. Secondly, we modify the differential polarizability ratio $r$ during the fitting process. This modification is debatable since according to the previous investigation done by Southern$^{2,17}$, different liquid crystal phases will affect $r$ value. This means the different molecular arrangement will affect the $r$ value. So there is no doubt that the uniaxial molecule and bent-core molecule will have different molecular arrangement even in the same phase. This will lead to the possible conclusion that $r$ will change in different molecular models. However we do not have a robust evidence to support this. Thus, it is still a challenge to derive order parameters from the fitting method for the bent-core systems using PRS.
5.8. Investigations of a Polar Biaxial Smectic A Phase Material

5.8.1. Introduction to Polar Biaxial Smectic Phase

As mentioned in Section 5.1, a variety of phase structures such as $B_1$ to $B_8$ have been found with a wide variety of phase transitions in the bent-core systems\textsuperscript{1,11}. Within these phases, the columnar $B_1$ and biaxial smectic-like $B_2$ phases are the most widely observed and investigated. In this section, we will mainly concentrate on a material with the $B_2$ phase, in particular, the biaxial smectic A (SmA) phase that was first observed in 1991\textsuperscript{18}. The biaxial SmA phase has a small structural difference compared to the uniaxial SmA phase, namely that the rotation of the molecules around the molecular long axis is confined to one preferred direction which is defined as the molecular short axis. There are two possible arrangements in the biaxial SmA phase according to the arrangements of the molecular short axes. As shown in Fig.5.21a), the antiferroelectric biaxial smectic A (SmAP$_A$) phase has the anti-parallel arrangement of the molecular shorts axes within the adjacent layers. This phase has been reported by many researchers\textsuperscript{19-21} and has been regarded as the ground state structure of the biaxial smectic A phase\textsuperscript{11,22}. On the contrary, the ferroelectric biaxial smectic A (SmAP$_F$) phase has a parallel arrangement of the molecular short axes within adjacent layers as shown in Fig.5.21b). It is usually obtained by aligning the molecular short axes of a SmAP$_A$ phase with an electric field. SmAP$_F$ is metastable and if the electric field is removed, it will relax to the SmAP$_A$ phase\textsuperscript{11}.

Fig. 5.21 The typical structure of: a) the antiferroelectric biaxial smectic A phase (SmAP$_A$). The short axes in layer 1 and layer 3 are in the same direction while it is in the opposite direction for layer 2. b) the ferroelectric biaxial smectic A phase (SmAP$_F$). The short axes are in same direction for all the layers 1, 2 and 3.
The material that was investigated in this section was synthesized by the H. N. S. Murthy and B. K. Sadashiva from the Raman Research Institute and is named SmOC\textsubscript{18}NO\textsubscript{2} (or BK) with molecular structure and phase transition temperatures shown in Fig.5.22\textsuperscript{21}. The molecule is asymmetric with a long alky chain on one arm and a nitro functional group on the other arm. Since this material shows a transition from the uniaxial SmA\textsubscript{d} phase to the biaxial SmA\textsubscript{d}P\textsubscript{A} phase\textsuperscript{21}, it can provide information on the transition between the uniaxial phase and the biaxial phase. Note that the subscript \textsubscript{d} in SmA\textsubscript{d} and SmA\textsubscript{d}P\textsubscript{A} indicates a partial bilayer structure in that the adjacent layer is inter-digitated. In this experiment, several typical experimental techniques including polarizing microscope measurements and dielectric permittivity measurements were carried out to investigate the BK material. Furthermore, we also tried to investigate the phase transition by using PRS.

\[\text{C}_{18}\text{H}_{37}O\]

\(\text{Crystal} \rightarrow 141^\circ \text{C} \rightarrow \text{SmA}_d\text{P}_A \rightarrow 155^\circ \text{C} \rightarrow \text{SmA}_d \rightarrow 171^\circ \text{C} \rightarrow \text{Isotropic}\)

Fig. 5.22 The molecular structure of the BK material and transition temperatures according to Ref.21

5.8.2. Experimental Setup

It is worthy of note that the material is light sensitive due to the presence of the nitro group at the molecular end. The samples were prepared and stored in a dark room and the exposure time was minimized during the experiment. In this experiment, the 5 and 20 µm thick AWAT cells were used for homeotropic aligned samples and the 5 µm thick AWAT cells were used for homogenous aligned samples. Since the BK material shows a crystalline phase at room temperature, the empty cell was heated to 180°C and the BK material was then filled into the cell in the isotropic phase. Polarizing microscopy measurement was carried out using the Leica optical polarizing microscope. A heating stage (Linkam LTS350) was mounted onto the rotating stage and controlled \textit{via} a
temperature controller (Linkam TMS94) with an accuracy of ±0.1 K. The dielectric permittivity measurements were carried out via a LCR meter (Agilent E4980A).

The depolarization ratio was calculated using the data obtained from a polarized Raman system. A solid state laser (Spectra-Physics) with 515.32 nm wavelength and 50 mW output power was used. The Raman spectra were collected with a Raman spectrometer (Renishaw RM1000) and a Leica optical polarizing microscope with 50× ultra-long working distance objective lens (Olympus, N.A.0.5). The temperature controlling system on the polarized Raman system consists of a heat stage (Linkam HFS91) and temperature controller (Linkam TMS93) to maintain the temperature with an accuracy of ±0.1 K. The heating stage was mounted onto the rotating stage of the microscope and the depolarization ratio was determined by recording the Raman scattering intensity as a function of rotation angle, under the different polarizer and analyzer arrangements.

5.8.3. Optical Polarizing Microscopy Measurement

The optical polarizing microscopy measurements had shown an interesting phenomenon, i.e. in a homeotropic cell which remained homeotropic aligned initially for the first half an hour, later, after several heating and cooling cycles, the alignment changed to a homogenous texture which grows with time as shown in Fig. 5.23. Within 4-5 hours, a homogenous texture appeared in the homeotropic cell. Therefore, in the same homeotropic cell, both the homeotropic as well as the homogenous textures can be observed at the same time as shown in Fig.5.23.

![Homeotropic Texture](image)

Fig. 5.23 Growth of the homogenous texture in the 5 µm thick homeotropic cell at 164°C

The textures observed in a 5µm thick homeotropic cell at various temperatures are shown in Fig.9.4. The transition temperature was shifted in this cell from that quoted
above (Ref.21) to Iso-179 °C-SmA_d-161 °C- SmA_dP_A -148 °C-Crystals. In our measurement, the SmA_dP_A phase exists for 13 °C compared with 14 °C in Ref.21 and the SmA_d phase exists for 18 °C compare with the 16 °C in Ref.21. So considering the temperature range of each phase, all transition temperatures are shifted almost equally and thus the transition temperature result is still reliable when considering the relative temperature. According to Fig. 9.4a)-c), the homeotropic area shows two domains with the Schlieren textures in the SmA_dP_A phase as shown in the circled area of Fig.5.24b). Notice that the contrast in these figures is modified to show a clear difference between the two domains. This phenomenon was also reported by Murthy^{21}. These two domains are not seen in SmA_d phase as shown in Fig.5.24d). The homogenous texture shows some tiny stripes in the fan-shape texture in SmA_dP_A phase and these stripes disappear after heating up to SmA_d phase. So according to the textures obtained from optical polarizing microscope, the uniaxial SmA_d phase and biaxial SmA_dP_A phase show an obvious difference especially within the homeotropic alignment.

![Fig. 5.24 Polarizing microscopy textures of the BK material at different temperatures in a cooling process with the SmA_dP_A phase shown in (a)-(c), (e)-(g) and SmA_d phase in (d), (h). Plots a-d are the homeotropic textures while e-h are the homogenous textures.](image)

Conoscopic texture measurements were also carried out in the homeotropic aligned 20 µm thick cells as shown in Fig.5.25. In this sample, the transition temperatures are Iso-172 °C- SmA_dP_A-156 °C- SmA_d-140 °C-Crystal which again is shifted from the recorded values in Ref.21, but the temperature range for each phase is still similar. A clear Maltese cross is observed as shown in Fig.9.5a) when the material is in the uniaxial SmA_d phase. At 155°C (Fig.5.25b)), the Maltese cross could be seen split into two isogyres which indicates the transition to the biaxial SmA_dP_A phase. As the temperature is
further lowered, the two isogyres are seen in Fig. 5.25c) which confirms the phase biaxiality. This result also agrees with the results reported by Murthy et al.\textsuperscript{21}.

Fig. 5.25 Conoscopic textures at different temperatures. a) uniaxial SmA\textsubscript{d} phase with clear and sharp Maltese cross. b) biaxial SmA\textsubscript{d}P\textsubscript{A} phase 1 °C below the transition, two isogyres. c) biaxial SmA\textsubscript{d}P\textsubscript{A} phase 6 °C below the transition (two blurred isogyres).

### 5.8.4. Dielectric Permittivity Measurements

The dielectric permittivity and absorption was determined from a 5 µm thick homogenous cell and the results are plotted as a function of frequency as shown in Fig. 5.26. The real part $\varepsilon_1'$ and imaginary part $\varepsilon_\perp''$ are shown in Fig. 5.26a) and b) respectively. The dielectric permittivity increases in the uniaxial phase and reaches a maximum and then decreases in the biaxial phase as seen in Fig. 5.26a) (as well as in Fig.5.27a)). Figure 5.26b) shows the dielectric absorption as a function of frequency at different temperatures. A relaxation frequency can be seen around 100 kHz which it is strongly temperature dependent. Similar relaxation behaviour has been observed in another bent-core material which has exactly same bend core structure reported by Guo et al.\textsuperscript{23}.

Fig. 5.26 Dielectric permittivity for a) the real part $\varepsilon_1'$ and b) the imaginary $\varepsilon_\perp''$ as the function of frequency at various temperatures. Data come from the 5 µm thick homogenous cell.
Fig. 5.27 The a) perpendicular \( (\varepsilon_\perp) \) and b) parallel \( (\varepsilon_\parallel) \) components of the dielectric permittivity as a function of relative temperature \( T - T_{\text{I-SmA}} \) at a frequency of 10 kHz in 5 µm thick homogeneous and homeotropic cells respectively. Data come from a) the 5µm thick homogenous cell, b) the 5 µm thick homeotropic cell.

Figure 5.27a) and b) show the perpendicular \( \varepsilon_\perp \) and parallel \( \varepsilon_\parallel \) components of the dielectric permittivity at a frequency of 10 kHz throughout the temperature range. The temperature is shown as a relative temperature \( (T - T_{\text{I-SmA}}) \), where \( T_{\text{I-SmA}} \) is the transition temperature from the isotropic phase to the SmA\(_d\) phase in a cooling process. Figure 5.27a) shows a large increase (about seven times) in \( \varepsilon_\perp \) values from the high to the low temperature in the uniaxial SmA\(_d\) phase. \( \varepsilon_\perp \) reaches a maximum at the phase transition \( (T - T_{\text{I-SmA}} = -16 ^\circ \text{C}) \) and then starts decreasing in the biaxial SmA\(_d\)P\(_A\) phase. Figure 5.27b) shows \( \varepsilon_\parallel \) at 10 kHz as a function of the relative temperature obtained from a 5 µm thick homeotropic cell. Unlike the large change observed in the both the uniaxial SmA\(_d\) and the biaxial SmA\(_d\)P\(_A\) phases in the homogeneous geometry, the change in \( \varepsilon_\parallel \) in both phases is only \( \sim 2\% \). However, both graphs in Fig. 5.27 again show a clear distinction between the SmA\(_d\) and the SmA\(_d\)P\(_A\) phases.

5.8.5. PRS Measurements

PRS measurements were carried out with a 20 µm thick homeotropic cell. Due to the interesting phenomenon mentioned in section 9.1.3, this homeotropic sample also exhibited a fan-shape homogenous texture in the experiment. The 20 µm thick cell was used to ensure a good Raman spectrum intensity. The Raman spectra were collected with 6 mW laser power at the sample position and 60s collecting time. Since it was reported
that the Jones et al.’s method would provide a good approximation for obtaining the uniaxial order parameters \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) from a smectic phase, the method introduced in Section 5.6.1 (evolved from Jones et al.’s method), should also give reasonable fitting results.

In the data analysis of the BK material, all biaxial order parameters were ignored, as has been discussed in Section 5.7.2, the large number of fitting parameters will introduce huge uncertainty on the fitting results. By setting the tilt angle to be 30° and the bend angle to be 120° (according to the molecular structure), the order parameters can be obtained by fitting the depolarization ratio graph using eqs.5.7 and 5.8. Fig. 5.28 shows the fitting results for \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) as the function of reduced temperature \( (T/T_{l-SmA_d}) \). The values of \( \langle P_{200} \rangle \) and \( \langle P_{400} \rangle \) increase with decreasing temperature when \( T/T_{l-SmA_d} \) is between 0.986 to 0.963.

![Fig. 5.28 The uniaxial Raman fitting of BK material at different temperature. Order parameters values for both SmA\(_d\)P\(_A\) (before 156° C, \( T/T_{l-SmA_d}=0.963 \)) and SmA\(_d\) (after 156° C, \( T/T_{l-SmA_d}=0.963 \)) are shown in this plot.]

However, the uniaxial order parameters show an unusual decrease when the temperature is lower than 155 °C (\( T/T_{l-SmA_d} = 0.963 \)). This temperature agrees with the transition temperature from SmA\(_d\) to SmA\(_d\)P\(_A\). So this unusual decrease of the uniaxial order parameters suggests the existence of a biaxial phase transition. It is worthy of note that this does not mean that the uniaxial order parameters decrease in the SmA\(_d\)P\(_A\) phase. In fact the order parameters should increase since the liquid crystal structure becomes more ordered in the SmA\(_d\)P\(_A\) phase. In the biaxial SmA\(_d\)P\(_A\) phase, the phase biaxial order parameters are no longer zero compared with zero in the uniaxial SmA\(_d\) phase, which will affect the depolarization ratio values as discussed in Section 5.7.1. Due to the lack of
phase biaxial order parameters in the fitting process, the effects caused by the phase biaxial order parameters are all reflected on the fitting values of the uniaxial order parameters which lead to an unusual decrease on uniaxial order parameters. To prove the effect of phase biaxial order parameters, a fitting process with phase biaxial order parameters was carried out. However, as the conclusion of Section 5.7.1, the phase biaxial order parameter values have a strong dependence on the uniaxial order parameters. Thus to reduce this effect, uniaxial order parameters need to be constants during the fitting. Combining the fact that uniaxial order parameters should not at least decrease in the SmA_dP_A phase, the uniaxial order parameters values at $T/T_{T_{1-SmA_d}} = 0.963$ will be used and assumed as constants in SmA_dP_A phase. By doing this, the effect of the phase biaxial order parameters can be obtained. Detail procedure of the fitting process is shown in Fig.5.29.

Fig. 5.29 The flow chart of the fitting process.

![Flow chart of the fitting process](image)

Fig. 5.30 Fitting result of the phase biaxial order parameters $\langle P_{420} \rangle$ (square), $\langle P_{440} \rangle$ (circle) and $\langle P_{220} \rangle$ (triangle) in SmA_dP_A phase.
The fitting results are shown in Fig. 5.30. An increasing tendency of the phase biaxial order parameters can be observed when temperature is decreasing. This indicates that the phase biaxial order parameters indeed have effect in the SmA_dP_A phase. But there is an important thing to mention. In the SmA_dP_A phase, one of the basic assumptions of these fitting method, \( \hat{n} = -\hat{n} \), is invalid due to the ferroelectricity property. As a consequence, it is doubtable whether these fitting values are reliable in the SmA_dP_A phase. But nevertheless, the fitting results still provide a clear indication of the phase transition from the uniaxial phase to the biaxial phase.

5.9. Summary

In this chapter, some of the background for the bent-core systems has been reviewed in the first section. Then we reviewed and discussed the theoretical approach to derive order parameters using PRS in a bent-core system. The discussion reveals some problems in Southern’s approach. Thus a modified molecular model was carried out by introducing the bend angle \( \Omega \) and tilt angle \( B_0 \). With this molecular model setup, we can achieve uniaxial molecular model with the setting that \( \Omega = 180^\circ \) and \( B_0 = 0^\circ \) to represent rod-like molecules or represent bent-core molecules with a combination of tilt angle and bend angle. During the discussion of deriving depolarization ratio expression, two different coupling methods of two arms of the molecules are discussed without considering all biaxial order parameters. The discussion leads to the conclusion that the best way to express Raman tensor in bent-core system is using the total Raman tensor which is the sum of two tensors form each arms. This coupling method of the two arms gives a reasonable fitting result on the uniaxial order parameters in bent-core molecular system. During the discussion, we have checked both the bent-core molecular model and the uniaxial molecular model. The lower fitting values obtained from uniaxial molecular model shows the bend angle in the bent-core systems is an important value in fitting process. Moreover, the fitting value of differential polarizability ratio is different according to the molecular model. Finally, we introduced the phase biaxial order parameters into the discussion. The effect of each biaxial order parameter on the depolarization ratio was discussed. It can be concluded that \( \langle P_{440} \rangle \) has opposite effect on the depolarization ratio graph comparing to the effect of \( \langle P_{220} \rangle \) and the \( \langle P_{420} \rangle \) is used to
make the depolarization ratio graph fluctuate. However, it is disappointing that the fitting still did not give reasonable results. Too many fitting parameters and the dependence between the order parameters raise the uncertainty in the fitting process. The difference on the differential polarizability ratio $r$ was discussed again and we tend to believe the differential polarizability ratio $r$ should be different according to molecular shape. But this is not supported by any experimental data and need carefully check and investigation in the future.

The experimental results on the BK material have been reviewed in the last section. According to the experimental results, the biaxial SmA$_d$P$_A$ phase can be identified from uniaxial SmA$_d$ phase by using optical polarizing microscopy. The split of Maltese cross was observed in the SmA$_d$P$_A$ phase according to the conoscopic texture measurements which agree the previous literature$^{21}$. The dielectric permittivity measurements show a clear distinction between the SmA$_d$ and the SmA$_d$P$_A$ phases. Beside, a relaxation frequency can be seen around 100 kHz which agrees the discussion from the previous literature$^{23}$. Moreover, the PRS was also applied on identifying the transition between the SmA$_d$ and the SmA$_d$P$_A$ phases. The measurement results indicate that the PRS can also provide a clear indication of the phase transition between the uniaxial and biaxial phases. Further, a possible indication of the effect of phase biaxial order parameters in the SmA$_d$P$_A$ phase was discussed according to the experimental data. But limited by the fitting method, this discussion is not assured.
References


Chapter 6

Graphene and Graphene Oxide

The discussion on the investigation of applying Polarized Raman Spectroscopy (PRS) in different systems has been shown in previous chapters. As a brief review, the basic theory and background of PRS was reviewed in Chapter 2 and 3. In Chapter 4 we had put forward two possible explanations of the problem that different order parameters are obtained with PRS using different vibrational modes. Then in Chapter 5, a modified PRS analysis method for bent-core systems based on Southern’s work had been shown. Now we will continue our discussion onto the second main topic of this project which investigates the dispersion of graphene or graphene oxide in liquid crystals. In this chapter, we will firstly review what is graphene and graphene oxide and why they are attractive to scientists (Section 6.1). Since Raman spectroscopy is the main experimental technique of the project, the features of Raman spectrum of graphene will be reviewed in Section 6.3. In the last section, we will briefly introduce the graphene and graphene oxide samples that will be used for the discussions in the following chapters.

6.1. Introduction

A one-atom thick planar sheet of sp²-hybridized carbon atoms that are densely packed in a perfect hexagonal lattice, called graphene as shown in Fig.6.1, has become a hot topic recently. The term graphene was initially used to describe the individual carbon layers in graphite by Boehm et al.¹. The history of graphene research can be traced back
to 1947 when the band theory of graphite was discussed by Wallace. In 1962, detailed experimental studies of few layers of graphite were reported. However, the research was still largely based on graphite layers (a few layers of graphene) instead of graphene, due to the limitation of synthesis methods. The true one atom thick material, graphene, was firstly synthesized in 2004 by Geim and Novoselov. This sparked a revolution in graphene research which leads it to become the hot-topic in condensed matter research. Graphene is the thinnest known material due to the one atom layer structure and strongest material with a Young’s modulus 1 TPa. Such properties enable graphene to become a prime material for mechanical applications. Optical measurements show a high opacity, absorbing about 2.3% of white light even in one atomic monolayer. The thermal conductivity is 2000 to 4000 Wm⁻¹K⁻¹ depending on temperature which is much higher than other materials such as carbon nanotubes and graphite. So graphene is an excellent thermal conductor. As well as the examples above, graphene shows excellent electric properties. Firstly, the electron mobility at room temperature can exceed 15000 cm²V⁻¹s⁻¹. Secondly, the resistance of graphene is 10⁻⁶ Ω·cm which is less than the resistance of silver (1.59×10⁻⁶ Ω·cm). These properties enable graphene to be an excellent candidate for the new generation electrical devices. Graphene can be prepared with four main methods: chemical vapour deposition (CVD); separating graphene from graphite; exfoliation of graphite in solvents; and reducing the graphene oxide dispersion (Details can be found in Appendix A.5).

Graphene oxide is a compound of carbon, oxygen and hydrogen as shown in Fig.6.2. Similar to the relationship between graphene and graphite, graphene oxide can also be regarded as one layer of graphite oxide. In our discussion, the phrase “graphene oxide” will be used instead of the graphite oxide for comparison to graphene. The history of graphene oxide can be traced back to 19th century when a chemist, Brodie, from Oxford obtained graphite oxide by treating graphite with nitric acid and potassium.
Historically, graphene oxide is named “oxide”, however, strictly speaking, graphene oxide is not the oxide of graphene. Some other functional groups such as carbonyl (C=O) and hydroxyl (-OH) can also be found in graphene oxide. Due to the hydrophilic functional group, graphene oxide can be dissolved in water. It is worthy of note that graphene oxide is usually an semiconductor or even insulator. Graphene oxide is also attractive in recent years since it can be easily obtained from graphite and can be used for graphene synthesis. Graphene oxide is mainly obtained by treating graphite with strong acid and oxidant (Details can be found in Appendix A.5).

![Fig. 6.2 Structure of graphene oxide](image)

### 6.2. Raman Spectrum of Graphene

It is widely believed the Raman spectroscopy is a good technique for identifying graphene and the layered structure of graphene. Details of the Raman Spectrum can be found in Ferrari’s paper in 2006. So here we summarise some of the important features of the Raman spectrum of graphene.

The priority task of Raman spectroscopy is identifying graphene and clearly distinguishing it from graphite. A comparison of the Raman spectrum of graphene and graphite is shown in Fig.6.3a). There are two important peaks in these two spectra. Firstly, the G peak is located at 1580 cm⁻¹ due to the E₂g mode. Secondly the 2D peak locates at around 2700cm⁻¹ which is also known as G’ peak since it is the second strong peak in the graphite Raman peaks. 2D peak comes from the second order of zone-boundary phonons. There is an obvious shift on 2D peak from graphite to graphene and this shift can be related to the layers of graphene (up to 5 layers) as shown in Fig.6.4. Thus the 2D peak is useful in identifying graphene as well as identifying the layer.
structure of graphene. Another graphene peak locates at 1350 cm\(^{-1}\) which is labelled as D as shown in Fig.6.3b). This D peak is related to defects. If the structure is perfect, the D peak is invisible. Thus there is no D peak in Fig.6.3a) since the spectrum is collected in the graphene/graphite layer centre. If the material is in powder form, or the focus is at the edge of graphene layer, the D peak will appear. The D peak in graphite is broader than the one in graphene since the D peak in graphite has two components while there is only one in graphene\(^3\).

![Graphene and Graphite Raman Spectra](image)

Fig. 6.3 a). a comparison of Raman spectra of graphite and graphene. The G peak (~1580 cm\(^{-1}\)) and 2D peak (~2700 cm\(^{-1}\)) are shown in the spectrum. The spectra are collected from the graphite/graphene layer centre. So no D peak appears. Notice that the spectrum is rescaled to give a similar magnification of 2D peaks. The original spectra show a similar height of the G peak. (Plot comes and modified from Ferrari’s paper: Ref.29). b) the Raman spectrum of graphene flakes coagulation. The D peak can be identified at 1350 cm\(^{-1}\).

![Graphene Multilayer Raman Spectra](image)

Fig. 6.4 Evolution of the spectra at a) 514 nm and c) 633 nm laser with the number of layers (Plots come and modified from Ferrari’s paper: Ref.29)
6.3. Graphene and Graphene Oxide Samples Used in the Project

6.3.1. Graphene Sample

The graphene sample we used was graphene dissolved in N-methyl-2-pyrrolidone (NMP) provided by Dr. Rahul Raveendran-Nar. The graphene flakes have an average size of 200 nm×200 nm and 0.06 mg/mL. Since we didn’t prepare the graphene NMP dispersion, a brief synthesis method is shown according to the work by Geng\textsuperscript{33}. As the first step, graphite powder is added into NMP with small amount of porphyrin-3 and tetrabutylammonium hydroxide (TBAH). Then apply ultra-sonication method on the mixture for 30min according to Ref.3. After sonication, the mixture is left for 1 week to allow the graphite to be fully exfoliated by the TBAH and porphyrin. In the final step, the mixture is centrifuged in 500 rad/min to separate the coagulation and unexfoliated graphite and the supernatants are collected as the graphene dispersion in NMP. The appearance of the graphene dispersion in NMP is shown in Fig.6.4. It is worth notice that the graphene in the mixture could be several layers or very tiny graphite particles since the method is based on exfoliating which makes it is hard to control the quality of the graphene sample.

![Fig. 6.5 Photo of the graphene dispersion in NMP](image)

6.3.2. Graphene Oxide Sample

The sample of graphene oxide dissolved in distilled water is prepared via the modified Hummers method\textsuperscript{27} and provided by Dr. Rahul Raveendran-Nar. Since the graphene oxide was prepared from oxidisation with strong acid and oxidant, the pH value
of the dispersion is around 4. So before use, a dialysis procedure to the graphene oxide sample was carried out to increase the pH value of the graphene oxide sample. The dialysis membrane we used is Spectra/Por 1 Dialysis Membrane. The Molecular Weight Cut-off (MWCO) is 6-8000 which is ideal for the graphene oxide distilled water dispersion\textsuperscript{34}. Detail of the dialysis experiment setup is shown in Fig.6.5.

![Fig.6.5. Dialysis experimental setup.](image)

A large volume of distilled water which was around 100 times of the volume of the graphene oxide water dispersion was filled in a beaker. This large volume of distilled water can guarantee a good efficiency of the dialysis process. A dialysis membrane tube was cut into the appropriate length allowing an extra length for a small head space for air (about 10% of total sample volume). This ensures that the tube with sample can float in the beaker and will not be damaged by the rotating magnetic stirring bar. One end of the dialysis membrane tube was clamped leaving approximately 3 to 5 mm to the end. Then the graphene oxide water dispersion was filled into dialysis membrane tube through the open end and sealed the open end with another clamp. Then the dialysis membrane tube with graphene oxide water dispersion and a clean magnetic stir bar were placed into the beaker. The beaker was placed on the stirring stage and the distilled water was stirred by the magnetic stir bar. The dialysis process lasted for three days and the distilled water in the beaker was replaced every 6 hours. After the dialysis process, the graphene oxide sample was transferred to a clean container. The final sample obtained after the procedures is shown in Fig.6.6 and the pH value is around 7. The concentration of the graphene oxide is hard to estimate due to the dilution process.
6.4. Summary

In this chapter, we have reviewed the history of graphene and graphene oxide as well as their properties. This has led a multitude of research, and especially for graphene, due to the excellent mechanical, optical, thermal and electrical properties. It is expected that graphene will alter many industries in the future. In the end of this chapter, we have given a brief introduction to the samples and materials used in our project. The experimental results of our attempts in combining graphene or graphene oxide with liquid crystal system will be discussed in Chapter 7.
References


B. C. Brodie, Philosophical Transactions of the Royal Society of London 149, 249 (1859).


Chapter 7

Investigation of Graphene and Graphene Oxide Dispersions in Liquid Crystal Environments

As has been discussed in Chapter 6, the graphene and graphene oxide have many interesting properties in different application areas which have become a hot topic in recent years. These amazing materials also attract attentions in liquid crystal research. Liquid crystals, with their fluidity and self-organization, are attractive hosts for the dispersion and manipulation of macro- and nanoparticles, allowing the realization of their ordered assemblies. In addition, new functional materials can be created owing to the particle properties. From this point of view, it will be interesting if one can combine graphene or graphene oxide with a liquid crystal system. This supports a possible approach to changing the properties of liquid crystal or rearranging the structures of graphene in a liquid crystal by either forming a liquid crystal phase directly with graphene or graphene oxide, or by dispersing them into a liquid crystal environment. In this chapter, the up to date research progresses will be reviewed as well as our research results of forming liquid crystals with graphene directly (Section 7.1). Then the second possible approach, forming a graphene or graphene oxide dispersion in liquid crystal environments will be discussed. In this study, the tests of graphene and graphene oxide dispersions in the most commonly used liquid crystal type, calamitic liquid crystal, will be shown in Section 7.2. Then we will show the results of forming dispersions based on discotic liquid crystals (Section 7.3) since this type of liquid crystal has a similar shape to graphene or graphene oxide flakes. Finally, some trials based on the chromonic liquid
crystal (Section 7.4), are again inspired because chromonic liquid crystals can be treated as the discotic equivalent of lyotropic liquid crystals.

7.1. Forming Liquid Crystal Phases with Graphene and Graphene Oxide

7.1.1. Review of the Existing Research Literatures

As mentioned in the introduction, the first possible pathway to combine liquid crystals and graphene materials (graphene and graphene oxide) together is to produce a liquid crystalline state with the flakes of graphene material directly. The only possibility of a liquid crystalline phase that graphene can form directly is a lyotropic liquid crystal. Such a system was first reported by Behabtu et al. who observed that liquid-crystalline phases can be formed in high concentration (about 2~3 wt%) dispersions of graphite in a super acid of chlorosulfonic acid\(^1\). Birefringence was observed with optical polarizing microscopy, with a liquid-crystalline Schlieren texture formed that is very similar to that of a typical chromonic nematic liquid crystal sample.

It is known that both graphene and graphite sheets are hydrophobic thus it is hard to form a dispersion in a polar solvent such as water without extra dispersing agents. However, there is an exception: graphene oxide which is decorated by hydrophilic functional groups can be dispersed in water simply by sonication and the concentration can reach a high value depending on the preparation method\(^2\), \(^3\). This fact makes it possible to find a lyotropic liquid crystal phase with graphene oxide. Some progresses have been reported in this area, for example, Xu and Gao who investigated graphene oxide sheets in a water environment, which is produced via a modified Hummers method by including an additional oxidization step to enhance the solubility of graphene oxide sheets. An isotropic-nematic (I-N) phase transition in the liquid-crystalline phase was found in the graphene oxide/water dispersion\(^4\). They also plotted a phase diagram for the liquid-crystalline phase of graphene oxide. Kim and co-workers have also demonstrated the liquid crystalline properties of graphene oxide aqueous dispersions\(^5\). They arranged the graphene oxide material using a modified Hummers method. According to their work, the liquid crystal phase can be maintained by either decorating the graphene oxide with
nanoparticles or mixing a polymer component in the solvent. With this kind of modification, a variety of different material compositions and functionality of graphene oxide lyotropic liquid crystals can be made. The new progress of the lyotropic liquid crystal formed by graphene oxide dispersion indicates that the graphene oxide lyotropic liquid crystal is hard to align (the largest region of uniform alignment is around 0.5 mm width and 50 µm thickness) with no observed switching in fields (no response to the electric fields up to 1000 V/mm). Meanwhile, it is also reported by Shen et al. that a graphene oxide isotropic dispersion itself shows interesting properties including extremely large Kerr constant (up to $2 \times 10^{-5}$ m/V²) and it can react to an external field change (2.5 V/mm).

7.1.2. Brief Review of Our Experiments

The work discussed in Section 7.1.1 mainly focuses on the graphene oxide/water dispersions since they are easier to achieve and the dispersion concentration can reach a high value (0.75 wt% according to Kim et al.) to enable the formation of liquid crystal phase. However, it is reported that graphene can form a good quality of dispersion in NMP (up to around 0.05 mg/mL and 0.06 mg/mL for our material). This provides a possibility of forming lyotropic liquid crystal based on the graphene/NMP dispersion. Our experiment is undertaken by removing NMP from the graphene/NMP dispersion at temperature as high as 100 °C in an oven. However, the result is disappointing. The material after NMP removal exhibited a large degree of coagulation as shown in Fig.7.1 and the mixture with coagulation did not show any birefringence texture when studied with a polarizing optical microscopy. The reason is that the concentration is too low to form liquid crystal phase. Sonication was also applied to the sample. However, the coagulation are not re-dispersed in the NMP. This result is reasonable since the highest concentration of graphene/NMP dispersion reported by Geng et al. is 0.05 mg/mL and our material has a concentration of 0.06 mg/mL which has already reached a high value. In the heating process, the concentration of graphene in NMP reaches and exceeds the maximum value, thus graphene flakes separate from the dispersion and the coagulated particles can’t be re-dispersed. So we abandoned this approach in the end and turned to the one of dispersing graphene or graphene oxide into a liquid crystal environment.
7.2. Graphene and Graphene Oxide Dispersion in Calamitic Liquid Crystals

As mentioned, another possible approach to combine liquid crystals and graphene together is dispersing graphene into liquid crystals. The research into this approach is a blank and no previous literature has been published. However, considerable research has been done on carbon nanotubes (CNTs) in liquid crystals\(^9\)\(^{-13}\). The conclusions and results of such work can provide us with some background for our approach. It has already been proved that CNTs can be dispersed into liquid crystals, especially the calamitic nematic phase, and aligned by the liquid crystal system\(^9,\)\(^{11,}\(^{13}\). Following the same approach, the first trial was based on the idea of dispersing graphene into calamitic nematic liquid crystals. As mentioned in previous chapters, 5CB is the most widely studied calamitic nematic liquid crystal. Since it is easy to obtain and its properties are well known, 5CB was chosen as a host for the graphene dispersion and several experimental approaches were examined for making the dispersion.

7.2.1. Direct Dispersing Experiment

The sample preparation procedures of direct dispersing were as follows. Firstly, 5CB (about 40 µL) was dropped on a piece of glass and then mixed with 20 µL of graphene/NMP dispersion. The sample was mixed well with a spatula and then heated to
around 100 °C to remove the NMP. Finally, covered the mixture with a cover glass and then cooled the sample to the room temperature. An example of the sample (we call this kind of sample as simple sample since no alignment layer and no spacer used) is shown in Fig.7.2. Coagulations and stains in the sample can be identified by eye (circled area in Fig.7.2) which indicates a poor dispersing quality of graphene in 5CB.

![Substrate Glass and Stain Area](image1)

Fig. 7.2 A simple sample of a graphene and 5CB mixture

![Stain area](image2)

Fig. 7.3 Microscopy images of the graphene coagulation in 5CB sample at room temperature without crossed polarizers.

A microscopy observation of the sample showed quite a lot coagulations in the mixture which could flow within the liquid crystal. However, after about 1 hour, most of the coagulations formed stains on the glass surface as shown in Fig.7.3. The Raman spectra, shown in Fig.7.4, were collected with 13 mW laser power at the sample position and 30s collecting time using a Renishaw RM1000 Raman system. There is a peak shown at around 2695 cm\(^{-1}\) which is the location of graphene 2D peak, so combining the discussion in Section 6.2 and Fig.6.4, it can be concluded that the stain is formed from graphene. The large D peak in the spectrum at around 1350 cm\(^{-1}\) indicates the existence of graphene flake boundaries in the coagulation.
Fig. 7.4 Raman spectra of the stained area (Red line). Since the stained area contains 5CB and graphene coagulations, the Raman spectra are the combination of 5CB and graphene. Thus the pure 5CB spectrum (Black line) is used for comparison. The intensities of the stain are amplified by 5 times to show a clear comparison.

A graphene oxide/5CB dispersion was also tested with a similar preparation process as discussed above with a difference in the heating process such that the mixture is heated to 80 °C since a graphene oxide/water dispersion was used for the preparation. The same coagulation phenomenon can also be obtained from the graphene oxide/5CB mixture as is shown in Fig.7.5. The coagulations and stains are even larger due to the larger amount of graphene oxide in the dispersion, since the concentration of the graphene oxide/water dispersion is much higher than the graphene/NMP dispersion.

Fig. 7.5 A simple sample of graphene oxide and 5CB mixture

Fig. 7.6 Microscopy images of the graphene oxide coagulation in a 5CB sample at room temperature without crossed polarizers.
Microscopy observation also proves that larger coagulation occur in the
dispersion, as shown in Fig.7.6. The Raman spectrum was also collected as shown in
Fig.7.7. The Raman peaks of graphene oxide are similar to graphite and graphene. It has
been reported that graphene oxide has three main Raman peaks which are the D peak (at
around 1350 cm\(^{-1}\)), the G peak (at around 1580 cm\(^{-1}\)) and the 2D peak (at around 2700
cm\(^{-1}\)) with larger peak width compared to graphite or graphene\(^{14}\). According to Fig.7.7,
the Raman peaks are indeed wider than in Fig.7.4. However, graphene oxide Raman
peaks are very weak and hard to identify compared with the strong 5CB peaks.

![Fig. 7.7 Raman spectrum of the graphene oxide dispersion in 5CB on the stain area (Red line). Since the stain area contains 5CB and graphene oxide coagulations, the Raman spectra are the combination of 5CB and graphene oxide. Thus the pure 5CB spectrum (Black line) is used for comparison. The intensities from the stain are amplified by 1.5 times to show a clear comparison.]

So in conclusion, direct dispersing of graphene or graphene oxide into a
calamitic liquid crystal cannot provide a good quality of dispersion, thus some
modification of the dispersing method is needed to improve the dispersion quality.

7.2.2. Sonication and Stirring Assisted Dispersion Experiments

It is known that sonication is a typical method of dispersing nanoparticles into a
liquid crystal environment, so we modified the preparation process and added a
sonication procedure to the dispersing process. In the experiment, a large graphene flake
formed by several layers of graphene as shown in Fig. 7.8a) was mixed with 5CB. Then the mixture was put into a sonication bath for 6 hours and a gray dispersion was obtained. No obvious coagulations could be judged by eye as shown in Fig. 7.8b). Finally this dispersion was filled into a 5 μm thick homogenous cell and checked with optical polarizing microscope. The texture is typical homogenous texture of 5CB but with tiny coagulation/stain areas as shown in Fig. 7.9. It is good that the coagulations are much smaller and the size is uniform when compared to the sample discussed in Section 7.2.1. Moreover, this dispersion is stable and can be maintained as a dispersion for about 12 hours before coagulations settlement. No further coagulations formed during the phase transition from the isotropic phase to the nematic phase. Further, the phase transition temperature does not have any obvious difference in the dispersion from the pure 5CB mentioned.

Fig. 7.8 a) Graphene multi-layer flake used for sonication. b) graphene/5CB dispersion after sonication.

Fig. 7.9 Optical polarizing microscopy textures of the graphene sonication dispersion in 5CB at different temperatures.
In order to reduce the coagulations in the mixture, a centrifuge process was applied to the dispersion obtained in the beginning of this section. In the centrifuge process, two speeds, 500 rad/min and 1000 rad/min were suggested to be used for comparison. After centrifuging, two layers were obtained. The upper layer was almost as white as the original 5CB and the lower layer contained the coagulation deposition. 5 µm thick homogenous aligned cells were filled with the upper layer mixture. After checking the samples via microscope, the coagulations are seen to be fewer in 500 rad/min sample while the coagulations have completely gone in the 1000 rad/min sample. Then experiments were carried out to check whether any graphene was still dispersed in the mixture after the centrifuge process. Firstly, Raman spectroscopy was applied to the mixture. However the Raman spectra for the mixtures are exactly the same as the 5CB spectrum. The graphene flakes, if they exist, are too small to be identified by the Raman spectroscopy, especially compared with the strong signal of 5CB. Secondly, PRS was used to check whether the order parameters are changed or not compared with the pure 5CB sample. The phenyl stretching mode was still used to get depolarization ratio, ignoring the dipole tilt in the order parameter analysis, thus only uniaxial order parameters \(P_{200}\) and \(P_{400}\) exist in the result. The order parameters at the same relative temperature \((T-T_{NI})\) were obtained and shown in Table 7.1. It can be concluded from Table 7.1 that the difference on the order parameter values is negligible. So this approach can’t provide evidence for the existence of graphene flakes in the mixture. According to these experiments, it is hard to obtain the evidences for that graphene was dispersed into 5CB via sonication process, since most of the graphene flakes were still coagulated which lead to a very low concentration of graphene flake in 5CB. However, the smaller amount of coagulation in the dispersions compared with previous method mentioned in Section 7.2.1 indicates a possibility of the existence of graphene dispersion.
Table 7.1 The table of the fitting values of the order parameters for the 500 rad/min, 1000 rad/min and pure 5CB sample. Three measurements and the mean value of the three measurement results are shown. The depolarization ratio data are collected at $T-T_{NI} = -2 \, ^\circ C$.

The experimental results of graphene oxide dispersion with stirring process will be discussed below. In this test a larger amount (about 5 mL) of 5CB was filled in a small bottle. Then added the graphene oxide/water dispersion into it. A clear separation of the layers from each other appeared immediately and they did not mix well as shown in Fig.7.10a). The sample was then stirred and heated at around 50 °C for 3 days to remove the distilled water. At the beginning of this process the graphene oxide/water dispersion was located above the 5CB but as the water removed from the mixture, the graphene oxide/water dispersion became denser and eventually lay below the 5CB. Moreover, the graphene oxide/water dispersion formed oil-like bulbs in 5CB when water concentration was decreased as shown in Fig.7.10b). Finally some coagulation, observed as stains, was formed as shown in Fig.7.10c). Further, similar to the graphene/5CB dispersion discussed above, a grey dispersion was obtained which indicated the existence of graphene oxide flakes or coagulations. The sonication process was applied to the dispersion, but the coagulations still existed. The microscopy observation as shown in Fig.7.11 also indicates coagulations in the mixture but the coagulation size is much smaller compared with the result from Section 7.2.1.
Fig. 7.10 Graphene oxide/water dispersion mixed with 5CB. a). The initial state after mixing. The brown layer is graphene oxide and the white layer is 5CB. b). The sample state after 2 hours stirring and heating. The oil like bulbs of graphene oxide in water appears in the circle area. c). Sample state after stirring and heating for 3 days.

Fig. 7.11 Microscopy images of the graphene oxide coagulations in 5CB sample at room temperature without crossed polarizers.

After these discussions, it is clear that 5CB is not a particularly good choice as the host liquid crystal in which the graphene or graphene oxide are dispersed. Even though the sonication and stir process can reduce the coagulation size, we still can’t guarantee the quality of the dispersion and we didn’t find a robust evident to prove the dispersion of graphene flake. These simple treatments are not enough to achieve the graphene/graphene oxide dispersion in a calamitic liquid crystal system and more investigation is necessary in the future.

7.2.3. Direct Dispersing Graphene into E7

It has been reported that E7 is a better dispersion medium for CNTs comparing to 5CB because of the longer alkyl chains in E7\textsuperscript{15,16}. So in this section, E7 will be examined as the dispersing medium. On the other hand, 5CB has a well-known property that the 5CB molecules form an antiparallel ordering structure in liquid crystal phase\textsuperscript{17-19}. But E7
does not show antiparallel ordering due to different local interaction (g factor is different from 5CB)\textsuperscript{20}, thus E7 can also be used to check the effect of different local arrangement on the dispersion.

As shown in Fig.7.12, the main component of E7 is 5CB, so the main properties of E7 are the same as 5CB\textsuperscript{20}. However, the existence of the extra components breaks the antiparallel structure, thus the effect of an antiparallel structure can be checked after comparing the result of dispersing in E7 and 5CB. E7 samples were made with direct dispersing method with graphene/NMP dispersion. But unfortunately, the graphene/E7 dispersion results also indicate a bad dispersion quality as shown in Fig.7.13. The coagulations and stains still exist and graphene flakes are not well dispersed in E7. This indicates that the longer alkyl chain does not or only have a weak effect on improving the dispersion quality of graphene in E7. Besides, the effects of antiparallel ordering cannot be checked since both E7 and 5CB shown a bad dispersion quality.

So after the discussions above, it can be concluded form these experiments that the calamitic liquid crystals are not good candidates as the host of graphene or graphene oxide dispersions with simple dispersing methods. So in the next section, the discotic liquid crystal will be checked as the dispersing medium for graphene/graphene oxide.
7.3. Graphene Dispersion in Discotic Liquid Crystals

It has already been shown that the calamitic liquid crystals are not a good dispersion host for graphene and graphene oxide, even though it was reported to be a good dispersion host for carbon nanotubes (CNTs)\textsuperscript{13, 15, 16}. The different performances may due to the calamitic liquid crystal molecular shape with respect to the graphene and graphene oxide geometry. The CNTs have a rod-like structure that is similar to the calamitic liquid crystal molecules which are also rod-like. Thus the CNTs can be dispersed and aligned in calamitic liquid crystals. Graphene and graphene oxide, on the other hand, have a large planar structure which is different from the calamitic liquid crystal molecules which can only provide limited planar area. Thus a large planar molecular structure may be a better choice as the host liquid crystal for graphene or graphene oxide dispersions. This reminds us of the discotic liquid crystals mentioned in Chapter 1 which are formed by disk-like molecules. Experimental results will be given on dispersing graphene and graphene oxide into discotic liquid crystals in this section.

7.3.1. Introduction to HAT-6

As the first stage of this section, the basic properties of HAT-6 will be given in this section\textsuperscript{21}. The molecular structure of HAT-6 is shown in Fig.7.14. The HAT-6 has a core part formed by triphenylene and the 6 side chains are exactly same which form a symmetrical structure. Our HAT-6 is provided by York University. The HAT-6 is crystalline at room temperature and the crystal phase can maintain up to around 65 °C then columnar phase appears. Then the columnar phase will changes to isotropic phase at around 125 °C.

\begin{center}
\includegraphics[width=0.5\textwidth]{fig7_14.png}
\end{center}

Fig. 7.14 The molecular structure of HAT-6 and the transition temperatures.
Fig. 7.15 Microscopy textures of HAT-6. The textures are collected on heating within 5 µm thick homeotropic cell (a,b,c) and 5 µm thick homogenous cell (d). a. crystal phase at 50 °C (homeotropic cell); b. columnar phase at 70 °C; c. columnar phase at 120 °C; d. crystal phase at 50 °C (homogenous cell).

The alignment layer is a useful tool to confine the molecular arrangement in calamitic liquid crystals. However, it is worthy of note that according our experiment results, this alignment layer doesn’t work well for HAT-6 (as seen in Fig.7.15a) and d). This is because HAT-6 molecules prefer to stack homeotropically which the director is perpendicular to the cell surface no matter whether homeotropic or homogenous alignment layers were applied. On the other hand, the viscosity in the HAT-6 liquid crystal phase is high since it shows a hexagonal columnar phase\textsuperscript{22}. The appearance of liquid crystal phases will be affected by the state where it generated from i.e. paramorphism phenomenon will appear. The textures of HAT-6 in the different phases in a 5 µm thick homeotropic cell are shown in Fig.7.15a)-c). Fig.7.15a) indicates the crystal structure of HAT-6 which shows a dendritic crystal growth\textsuperscript{23}. There are three main axes (indicated by the arrows in Fig.7.15a) that the crystal phase grows with the angle between any two of them is about 60°. This texture reflects the hexagonal crystal geometry\textsuperscript{23}. Since the crystal phase is formed from cooling the liquid crystal phase, combining the fact that paramorphism phenomenon appears in HAT-6, it can be concluded that the liquid crystal phase is hexagonal columnar phase. However, the hexagonal columnar texture is hard to identify at low temperature as shown in Fig.7.15b)
after heating from crystal phase due to paramorphism. By increasing the temperature, the texture of columnar phase is increasingly obvious as shown in Fig.7.15c) which is the pseudo focal conic fan-shaped texture\textsuperscript{24}. Another thing that is worthy of note is that the rate of cooling from the isotropic phase to the liquid crystal phase also has strong effect on the structure of liquid crystal sample\textsuperscript{25, 26}. In our experiment, if the rate is as high as 10 °C/min (3~10 °C/min according to Bouligand\textsuperscript{26}), defects from non-homeotropic arrangement will generate as shown in Fig.7.16a). The defects show a fan shape texture with the maximum angle around 25° according to Bouligand\textsuperscript{26}. On the contrary, if the cooling rate is 1°C/min, a dendritic growth pattern will generate as shown in Fig.7.16b)\textsuperscript{24} and it reflect the six-fold symmetry of the hexagonal columnar phase\textsuperscript{26}.

Fig. 7.16 Different textures observed during cooling processes in HAT-6. a): the columnar phase texture with crossed polarizers at 120 °C after a 10 °C/min cooling process. The columnar texture is dominated by a uniformed homeotropic aligned area which is black between crossed polarizers. A few defect areas appear with a birefringent texture. b): the texture formed at the transition from isotropic phase to the columnar phase without crossed polarizers. The columnar phase expands and forms a dendritic growth pattern.

Fig. 7.17 Raman spectrum of HAT-6 at isotropic phase

The typical HAT-6 Raman spectra were collected at 3 mW laser power at the sample for 30s with an Olympus ultra-long work distance 50×objective lens (N.A.0.5).
The Raman spectrum is shown in Fig. 7.17 with two large Raman peaks at around 1380 cm\(^{-1}\) and 1616 cm\(^{-1}\) and it agrees well with the experimental data from the work done by Burhanudin\(^{27}\). Although, the Raman spectrum of HAT-6 is quite different compared to what we obtained from a calamitic liquid crystal phase, the phenyl stretching peak can be readily found in Fig. 7.17. Unsurprisingly, the peak intensity does not change if the sample is rotated since the sample is not homogenously aligned. Thus we can’t obtain the depolarisation ratio and hence order parameters in a HAT-6 sample using PRS.

7.3.2. Graphene Dispersion in HAT-6

In this section, the experimental results of graphene dispersion in HAT-6 will be discussed. HAT-6 can be dissolved in many solvents such as Hexane, CH\(_2\)Cl\(_2\), Tetrahydrofuran (THF) and NMP\(^{28}\). Notice that graphene oxide was not used in the experiment of this section. This is because the HAT-6 can’t be dissolved in distilled water. If we apply graphene oxide/water dispersion to HAT-6, separation will happen as shown in Section 7.2 and coagulations will appear in the end. In this experiment, the graphene/NMP dispersion was used to mix with HAT-6. Several different methods were tried and they are discussed in this section.

**Dispersing Method 1:**

In Dispersing Method 1, 3 mg of HAT-6 was used to mix with 100 μL of graphene/NMP dispersion. The mixture was dripped on the substrate glass in the first step. Then the NMP was removed by heating the mixture at 100 °C on the substrate glass for 10 min and graphene/HAT-6 dispersion sample was obtained. Covering the sample with another piece of glass formed a simple sample. Fig. 7.18 shows three textures without crossed polarizers at different temperatures in a heating process. Fig. 7.18a) indicates the texture from crystal phase. It is worthy of note that some dark areas appear on the right of the plot, indicating some stain structures and it does not move or grow in Fig. 7.18b) and c) indicating they were formed in sample preparation process. It is hard to judge whether graphene/HAT-6 dispersion has formed due to the large area of the stain. Further, the transition temperature is reduced to around 120 °C. This is most probably due to the NMP remaining or possibly graphene in the mixture.
Fig. 7.18 Microscopy textures of graphene HAT-6 dispersion following Dispersing Method 1. Crossed polarizers were removed and the temperatures are: a. 50 °C (crystal); b. 70 °C (columnar phase); c. 120 °C (isotropic phase)

**Dispersing Method 2:**

In Dispersing Method 1, quite lot stains were obtained on the substrate glass in the preparing process. In order to reduce the stain amount, a transfer process was applied in Dispersing Method 2. Similar to Dispersing Method 1, the graphene/NMP dispersion and HAT-6 mixture was dropped onto a clean glass slice. The mixture was stirred with a spatula during the heating process to remove the remaining NMP, and then the graphene/HAT-6 dispersion was transferred to another clean glass substrate slice. Finally, a simple sample was made by covering the graphene/HAT-6 mixture with a cover glass slide. With the additional transfer process, the stains which appeared in the preparation process in Dispersing Method 1 can be avoided.

Fig. 7.19 Microscopy textures of a graphene/HAT-6 dispersion following Dispersing Method 2 (first trial). Crossed polarizers are removed in b), c) and d) and the temperatures are: a). 26.2 °C (crystal); b). 70 °C (columnar phase); c). 110 °C (columnar phase); d). 120 °C (isotropic phase).
In the first trial, 3 mg HAT-6 was still used to mix with 100 μL graphene/NMP dispersion and the mixture was heated at 100 °C for 10min. The microscopy textures from a heating process are shown in Fig.7.19. From Fig.7.19b) and 7.19c), the stains are much fewer. The reason is that the coagulations were left as stains on the first glass substrate. However, it was still not a stable dispersion. The graphene will finally form stains and attach to the surface of glass as shown in Fig.7.19d). Another thing worthy of note is that most coagulations were formed after transferring to the isotropic phase after comparing Fig.7.19c) and d) which also happens in CNTs dispersion experiment due to the zone refining in the phase transition\textsuperscript{15,16}. 

In the second trial, two samples were made for comparison. In the first sample (Sample 1), the graphene/HAT-6 dispersion obtained with Dispersing Method 2 was filled into a 5 μm thick homogenous cell. As the comparison, in another sample (Sample 2), the HAT-6 and NMP mixture was used and NMP was removed with Dispersing Method 2. After this process, Sample 2 is actually HAT-6 and is filled in a 5 μm thick homogenous cell. With these two samples, the effect of the graphene on the texture and transition temperature can be checked, ensuring that any effects seen are not due to the remaining NMP solvent.

The crystal textures of these two samples are shown in Fig.7.20. As seen from Fig.7.20a), the crystal texture of Sample 1 is very messy and it is hard to find the regular growth of the crystal texture. On the other hand, as shown in Fig.7.20b), the crystal texture from Sample 2 is not as regular as was seen in Fig.7.15d). However, Fig.7.20b) can roughly be separated into three main areas by the dashed straight lines. Within these areas, the dendritic crystal growth can be identified. Thus the crystal texture from Sample 2 is more regular compared with the crystal texture from Sample 1. The possible reason is that the graphene flakes or coagulations in Sample 1 disrupt the growing of the regular texture and randomizes the crystal texture.
Fig. 7.20 Optical polarizing microscopy texture of the crystal phase of a).Sample 1 (graphene/HAT-6 sample) and b).Sample 2 (HAT-6 sample) at 26.2 °C. The texture in Sample 1 is irregular while the texture in Sample 2 can be divided to three reigns showing dendritic crystal growth pattern.

A comparison of the phase transition from the isotropic phase to the columnar phase with a cooling rate of 1 °C/min is shown in Fig.7.21 and the difference is obvious. In Sample 1, the dendritic growth patterns (shown in Fig.7.16b)) do not appear and the shape is not regular. On the contrary, Sample 2 shows the same dendritic growth patterns that appeared in pure HAT-6 sample. So the graphene flakes or coagulation in the HAT-6 indeed affects the properties of the HAT-6. Besides, the transition temperature of Sample 1 is 115 °C from the measurement, which is much lower than Sample 2 at 123.7 °C. Such a huge difference may lead to the assumption that graphene flakes or coagulation in HAT-6 will affect the transition temperature. But no further evidence was observed to support this assumption.

Fig. 7.21 Microscopy texture of phase transition of a) Sample 1 (with graphene) and b) Sample 2 (pure HAT) at: Sample 1: 115 °C; Sample 2: 123.7 °C
By using Dispersing Method 2, an unstable graphene liquid crystal dispersion may probably be obtained, but further checks are necessary to prove the existence of graphene in the liquid crystal. On the other hand, the graphene still coagulates in the liquid crystal, significantly, when the liquid crystal is heated into the isotropic phase.

**Dispersion Method 3:**

The graphene/NMP dispersion and HAT-6 mixture used in this test has a high concentration with 7mg HAT-6 and 100 μL graphene/NMP dispersion. Instead of heating the mixture, we just dripped about 30 μL of this mixture on a piece of glass and left it at room temperature for 24 hours to remove the NMP. In this test, no cover glass was used on the sample. This kind of sample with a free surface is defined as an “open sample”. Fig.7.22 shows the microscopy texture after the drying process which looks quite different from the previous HAT-6 crystal texture (e.g.Fig.7.15a) and d)). In Fig.7.22, the crystal shows a stripe texture and the growing direction is random compared with three preferred directions in Fig.7.15a). Further, some holes can be observed as shown in the dashed circle areas in Fig.7.22b) and c) which are also quite different. This difference is due to the different ways that the crystal structure generated. Since the crystal texture was generated from liquid crystal phase via temperature change in Fig.7.15a), the textures maintained some structural features of the liquid crystal. However, the crystal texture in Fig.7.22 was formed from the mixture via evaporation. So it is not surprising that the crystal textures are different. From Fig.7.22, very few graphene stains can be identified. This may be because of the existence of defects where the graphene flakes/coagulations are probably distributed in making the flakes/coagulations hard to find. Besides, a large amount of NMP may be left in the mixture providing a good solubility of graphene flakes.

![Fig. 7.22 Microscopy textures of the crystal phase of graphene HAT-6 mixture at room temperature. a), texture with crossed polarizers on; b), and c), are two different areas without crossed polarizers.](image)

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Fig. 7.23 Microscopy textures of graphene HAT-6 mixture. Crossed polarizers are removed in f), and the temperature are: a). room temperature; b). 50°C; c). 70°C; d). 90°C; e). 110°C; f). 120°C. The foggy picture in e) is due to the NMP vapor from the open sample.

The phase transition was checked on heating, the textures are shown in Fig.7.23. It is obvious that the NMP vapour comes out of the mixture, indicating the existence of NMP in the open sample. Besides, the coagulations eventually appeared in the dispersion and formed stains in the sample. Notice that the structure in Fig.7.23 will not reoccur again after cooling from the isotropic phase since this crystal phase comes from a liquid crystal phase instead of a solution. The crystal texture after cooling from isotropic phase is shown in Fig.7.24a). It is very different since no dendritic crystal growth was seen. Instead, some dish-like texture was found in the crystal state. Besides, interesting textures also appear after reheating the mixture to liquid crystal phase as shown in Fig.7.24b) and c). The textures show a fan-shape texture which is very similar to the fan-shaped texture of Smectic B phase in calamitic liquid crystal\textsuperscript{24,29} which agrees with the previous experimental results done on the discotic droplets with free upper surface\textsuperscript{26}. Thus this phenomenon is because of that no cover glass slice was used in the open sample. So the molecular arrangement at the free surface is no longer homeotropic, instead, both homeotropic and homogenous alignment appears\textsuperscript{26}. Further, according to Fig.7.24d), the graphene coagulation is still problematic to the graphene dispersion in liquid crystals.
Fig. 7.24 Microscopy textures of graphene HAT-6 mixture in a heating process. Cross polarizer are removed in a) and d). The temperatures are: a) 40 °C; b) 70 °C; c) 100 °C and d) 125 °C.

Fig. 7.25 Microscopy textures of the crystal texture of graphene/HAT-6 dispersion in an open samples. Cross polarizer were removed in a) and c). a) and b) are textures from pure HAT-6 open sample; c) and d) come from a graphene/HAT-6 dispersion sample.

It is interesting to compare the crystal textures of the graphene/HAT-6 dispersion to the pure HAT-6 in open samples. The pure HAT-6 open sample was prepared using Dispersing Method 3 with NMP instead of graphene/NMP dispersion to rule out the effect of NMP. From Fig.7.25a) and b), it is found that the crystal is very regular with two domains: in the first domain, dendritic crystal growth was seen while in the second domain, the crystal forms a dish-like structure. However, in Fig.7.25c) and d), it is hard to see the dendritic crystal growth and only small disc-like structures can be found. The crystal texture is dominated by random structure in Fig.7.25c) and d). Since the crystal textures will indicate the structure of liquid crystal phase, it is again indicated that the
graphene in the sample will randomize the liquid crystal structure. However, it can’t be assured whether this random texture is because of the graphene flakes in the liquid crystal or the graphene stains.

As a summary of this section, three different sample preparation methods were tested, but only unstable graphene dispersions in HAT-6 can be obtained. Some evidence has been given to supporting that graphene in the graphene/HAT-6 dispersion has some effect on the HAT-6 properties. However, it is not yet been proved whether these effects are because of the graphene flakes dispersed or coagulations. So it is worth finding some evidence to support the existence of graphene flakes in the mixture. In next section, Raman measurements to the graphene/HAT-6 dispersion will be shown in order to find some evidence of the graphene flakes in the dispersions.

7.3.3. Raman Spectroscopy Investigations of the Graphene Dispersion in HAT-6

In the same way as in Section 7.2.1, we will compare the Raman spectra obtained from the stain areas and non-stain area to seek the evidence of graphene flakes in the graphene/HAT-6 dispersions. The sample made with Dispersing Method 2 in 5 μm homogenous cell (Sample 1 in Section 7.3.2) was checked. In this test, the laser power is 6 mW at the sample and the collecting time is 30s. Two different measurements were applied: with the laser focused on the non-stain area and with laser beamed on the stain area. The Raman spectra are shown in Fig.7.26. Similar to the spectrum obtained in Section 7.2.1, No Raman peak of the graphene can be seen in the non-stain area. After making a subtraction of HAT-6 spectrum (non-stain area spectrum) from the stain area spectrum, as shown in Fig.7.27, the graphene peaks are obtained at 1351 cm\(^{-1}\) (D peak), 1580 cm\(^{-1}\) (G peak) and 2697 cm\(^{-1}\) (2D). The data again show that the stain is formed from multi-layered graphene flake coagulations. So unfortunately, we still can’t prove the existence of graphene flakes in the dispersion by Raman spectroscopy. The reason is that, the graphene flakes, if they exist, are too small to generate a strong enough Raman peak in the non-stain area. So the Raman spectroscopy is not very helpful on finding graphene flakes in the dispersion.
Fig. 7.26 Raman spectrum of the graphene oxide dispersion in HAT-6 on the stain area (Red line). Since the stain area contains HAT-6 and a graphene oxide coagulation, the Raman spectra are the combination of HAT-6 and graphene oxide. The spectrum for non-stain is shown with black line and it is the spectrum of the pure HAT-6.

Fig. 7.27 Raman spectrum obtained after subtract the spectrum of HAT-6 (non-stain area) from the stain area spectrum. There Raman peaks of multi-layered graphene is seen.

For HAT-6, sonication can’t be used to improve the dispersion quality as HAT-6 is crystal at room temperature and the viscosity is high in the columnar liquid crystal state. Thus we didn’t test sonication approach. So after the discussion of this section, even though the idea of using HAT-6 as dispersion medium is attractive, in reality, it is still a hard task to disperse graphene into HAT-6 with simple methods. Even though the microscopy observation showed some indications of the effect of graphene, it is not assured whether these indications are owing to graphene flakes or coagulations. In next chapter, a different liquid crystal, knowing as chromonic liquid crystal will be tested as the dispersion medium.
7.4. Graphene and Graphene Oxide Dispersion in Chromonic Liquid Crystals

In section 7.3, the discotic thermotropic liquid crystal has been examined as a host material for graphene dispersion. However, the experimental results are not exciting since the graphene tends to coagulate in the discotic liquid crystal environment. Thus we need to seek other possibilities. Chromonic liquid crystals attract our attention since they also have board-like molecules which can form liquid crystal phases similar to discotic liquid crystals, but they belong to the class of lyotropic liquid crystals hence are solvent based (usually water). Details have been gone through with the basic description of chromonic liquid crystals in Chapter 1, so in this section, we will mainly concentrate on the chromonic liquid crystal material as the graphene/graphene oxide dispersion medium and show the experimental results.

7.4.1. Introduction to Sunset Yellow (SSY)

The chromonic liquid crystal used in this section is called Sunset Yellow (SSY). It is commonly used as a food dye even though there is a debate whether it should be used in this way due to allergic reactions. The chemical structure of SSY is a disodium salt of 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid.

![Molecular structure of Sunset Yellow](image)

The molecular structure of SSY is shown in Fig. 7.28. As mentioned in Chapter 1, chromonic liquid crystal molecules have a solubilizing group and rigid aromatic core part. In the SSY molecule, the solubilizing groups are the sulfonate groups that are attached to both sides of the molecule. The rigid aromatic core part is formed by phenyl and naphthyl rings combined via an azo group. The properties of SSY were initially discussed in two PhD theses^{30, 31} and later discussed by Horowitz^{32}, Park^{33} and Edwards^{34}. The chromonic
liquid crystal structure is well established in SSY compared with other chromonic liquid crystals, thus SSY is widely used in chromonic liquid crystal research. The phase diagram of SSY is shown in Fig.7.29. There are three phases in SSY which include the isotropic phase, the nematic phase (N) and the hexagonal-like columnar phase (M). As a lyotropic liquid crystal, the phase is not only determined by temperature, but also the concentration. The broad coexistence regions of different phases also exist in the SSY phase diagram. In our research, we mainly concentrate on the nematic phase and the SSY concentration is around 30 to 35 wt%.

![Phase Diagram of SSY](image)

**Fig. 7.29** The phase diagram of SSY in water (Figure from Ref.34, Edward’s paper)

Microscopy observation indicates a clearly birefringent texture in the SSY sample as shown in Fig.7.30, which is a typical nematic texture (the textures are not perfectly uniformed due to the lack of alignment layer). The transition temperature of the SSY chromonic phase to the isotropic phase depends on the concentration. Generally speaking, a higher concentration indicates a higher condensed phase at the same temperature. Our Raman system cannot be used for the measurements on SSY liquid crystal due to the strong fluorescence of SSY under 515.32 nm laser.

![Textures of SSY](image)

**Fig. 7.30** Textures of SSY chromonic liquid crystal at different temperatures. The SSY solvent concentration is 33 wt%.
7.4.2. Direct Dispersion of Graphene Oxide and Graphene in SSY

As discussed above, SSY can form a chromonic liquid crystal phase in distilled water. This fact attracts our attention since the graphene oxide can also form dispersions in water, so graphene oxide and SSY can be mixed in a water environment and it may be possible to obtain a graphene oxide dispersion in a chromonic liquid crystal environment. So in the first stage, the dispersing of graphene oxide into SSY will be examined. The SSY sample comes from Tokyo Chemical Industry. The purity is >90%. No purification process was applied since the SSY can form a good liquid crystal phase even with some impurities. To prepare the SSY liquid crystal, a certain amount of SSY sample was weighed and mixed with distilled water according to the concentration (wt%), then stirred and heated the sample to around 120 °C to get an even solvent. Then the mixture was cooled to room temperature to obtain the SSY liquid crystal sample as shown in Fig.7.31.

![Fig. 7.31 Image of sunset yellow (SSY) liquid crystal at room temperature](image)

In the direct dispersing experiment, the graphene oxide/water dispersion is mixed with 35 wt% SSY chromonic liquid crystal. After a stirring treatment, the mixture showed an orange colour as shown in Fig.7.32 which is same as the SSY chromonic liquid crystal. A lot of small coagulations appeared which could be identified by eye. A simple cell was obtained by placing a drop of this graphene oxide/SSY water mixture on the substrate glass surface and covering it with a cover glass slice. The microscopy observation results are shown in Fig.7.33.
According to Fig.7.33, coagulations can be identified in both the isotropic and nematic phase. The coagulations can flow in the mixture at the beginning, but then form stains on the glass surface. A reasonable explanation for this phenomenon can be suggested as followed. As discussed in Chapter 6, there are carbonyl function groups attached to the graphene oxide. The carbonyl group carries a positive charge. On the other hand, SSY molecules have sulfonate groups on each end of the molecule which carry negative charge. Thus, the SSY molecule will attach to the graphene oxide flake surfaces and act as the “glue” between the graphene oxide flakes, so the interaction between graphene oxide flakes is stronger than in water. As a consequence, the graphene oxide forms coagulations in the mixture. So the possibility of dispersing graphene oxide into SSY to achieve a graphene oxide/liquid crystal dispersion can be ruled out.

Now a mixture of graphene/NMP dispersion with SSY will be discussed. Since the NMP is miscible in water, no separation should happen. The mixing procedure was same as discussed in the graphene oxide/SSY water mixture which simply mixed the graphene/NMP dispersion with 35 wt% SSY chromonic liquid crystal with stirring. A very different mixture was obtained, as shown in Fig.7.34. The dispersion showed a mud-like appearance compared with the orange solvent for pure SSY chromonic liquid
crystal. Interestingly, the mud-like appearance disappeared after a heating. A simple cell was made for the microscopy observations and the results are shown in Fig.7.35.

Fig. 7.34 The graphene NMP dispersion and SSY chromonic liquid crystal mixture (left) compared with pure SSY chromonic liquid crystal (right).

Fig. 7.35 The textures of the graphene/NMP dispersion with the SSY chromonic liquid crystal mixture. a). the texture in the isotropic phase (80 °C) without crossed polarizers. b). the texture at 40 °C with crossed polarizer. c). the transition to the mud-like appearance in a cooling process.

As shown in Fig.7.35a), coagulations are still a problem in the mixture. Thus dispersing graphene into SSY chromonic liquid crystal is still not properly achieved with a direct mixing method. Moreover, Fig.7.35b) shows a very different texture compared with the texture in Fig.7.33b). This is no longer a nematic phase since no birefringent texture can be observed over a large area. Small areas such as within the dashed circle in Fig.7.35b show a liquid crystal focal conic texture. This phenomenon maybe due to the NMP in the mixture since the NMP may affect the solubility of SSY. Further, since the SSY molecules separate from the mixture, the concentration is lower which destroys the chromonic liquid crystal phase. Thus some crystal like structures and liquid crystal areas can be identified while the dominant area shows no birefringence in Fig.7.35b) and c). The transition to the mud-like appearance seems to be a result of crystallization of SSY. This is supported by the fact that the mud-like appearance disappears after heating the dispersion since the heating will increase the solubility of SSY.
It can be concluded that the direct dispersion does not work for graphene dispersion in SSY chromonic liquid crystal. So a method to improve the solubility of graphene in SSY and to decrease the interaction between graphene flakes is the key to the problem.

### 7.4.3. Dispersing Graphene in SSY with Surfactant

In this section, we will discuss the effect of surfactant on a graphene dispersion within the chromonic liquid crystal. Adding a surfactant is a commonly used method in the CNTs dispersions in liquid crystals\textsuperscript{13,35,36}. The surfactants are usually amphiphilic molecules which can also be used to form the lyotropic liquid crystals. As discussed in Chapter 1, the amphiphilic molecules have a solubilizing group which is hydrophilic and an attached chain which is hydrophobic. It is reported that many different surfactants including SDBS, CTAB, SDS and Triton X-100 were used in carbon nanotube dispersions in nematic liquid crystals\textsuperscript{35,36} since the hydrophobic end of the surfactant can attached to the carbon nanotube, leaving the hydrophilic end outside\textsuperscript{35}. This will form an ion shell on the carbon nanotube which increases the repulsive force between the carbon nanotubes, thus avoiding the formation of coagulations. On the other hand the surfactant decorated carbon nanotubes also have a better solubility in water. This research result attracts our attention since graphene can be thought of as an unwrapped carbon nanotube, so the surfactant will also attach to the graphene surface and increase the repulsive force to avoid coagulation.

![CTAB](image)

**Fig. 7.36** The molecular structures of an amphiphilic surfactant, CTAB.

In the experiment, CTAB was tested. As shown in Fig.7.36, the long alkyl chain will attach to the graphene and the positive charge will increase the repulsive force. The CTAB solvent we used in this experiment is 15 wt% CTAB in water. A experiment is conducted on a graphene/NMP dispersion in SSY with the addition of CTAB. Two samples were made for the experiment. The components of these two samples are shown
in in Table 7.2. All components were mixed together and heated to around 80 °C to fully dissolved. Then the mixture was cooled to the room temperature to obtain the mixtures.

<table>
<thead>
<tr>
<th></th>
<th>SSY (mg)</th>
<th>15wt% CTAB water solvent (µL)</th>
<th>Distilled water (µL)</th>
<th>Graphene/NMP dispersion (µL)</th>
<th>SSY concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>108.85</td>
<td>150</td>
<td>150</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>Sample B</td>
<td>103.55</td>
<td>300</td>
<td>/</td>
<td>50</td>
<td>35.8</td>
</tr>
</tbody>
</table>

Table 7.2 The component in the test samples.

It has been discussed in Section 7.4.2 that the existence of NMP will affect the mixture property. However, the graphene dispersion quality can still be checked at high temperature when all the SSY are dissolved. The microscopy observation results are shown in Fig. 7.37. It is disappointing that CTAB does not improve the dispersion quality of graphene since quite a lot of coagulations still exist in the sample no matter what the concentration of CTAB is in the mixtures. After reviewing the experiment, the reasonable explanation could be suggested as follows. Even though the CTAB increases the repulsive force between graphene flakes, the amino group of CTAB can combine to the SSY molecule. Thus the SSY molecule will again act as the “glue” and helps graphene coagulation formation in the graphene oxide/SSY dispersion.

![Fig. 7.37 The textures without crossed polarizers at 80 °C from a) Sample A (150µL CTAB solvent +150 µL distilled water), b) Sample B (300 µL CTAB solvent distilled water).](image)

After these experiments, it again indicates that we cannot get a good quality graphene dispersion in SSY with a simple method. After reviewing the whole experiment, adding surfactant is still a possible approach since the surfactant with negative charge, e.g. SDBS as shown in Fig. 7.40 was not tested. The SDBS molecule also has the alky chain which can be attached to the graphene flake surface. On the other hand, both SDBS and SSY have the sulfonate groups connected to benzene ring. So a sandwich structure may probably generate with the graphene flake, SDBS molecule and SSY molecule, which
make it possible to form a graphene dispersion in SSY. Thus more work is still needed on this approach in the future.

Fig.7.40. The molecular structure of SDBS.

7.5. Summary

In beginning of this chapter, the up-to-date research results on a graphene oxide-based lyotropic liquid crystal and our attempts on forming liquid crystal phase with graphene NMP dispersion were reviewed. After these discussions, a large number of attempts to disperse graphene or graphene oxide into different liquid crystal materials, including calamitic, discotic and chromonic liquid crystal systems, were examined. The results are listed in Table.7.3. Unfortunately, a reliable approach to obtain stable and good quality dispersions of graphene or graphene oxide in a liquid crystal environment was not achieved.

<table>
<thead>
<tr>
<th>Material</th>
<th>Graphene NMP dispersion</th>
<th>Graphene oxide water solvent</th>
<th>Large Graphene flake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct dispersing</td>
<td>Direct dispersing</td>
<td>Dispersing with sonication.</td>
</tr>
<tr>
<td>SCB</td>
<td>Coagulate</td>
<td>Coagulate</td>
<td></td>
</tr>
<tr>
<td>ET</td>
<td>Coagulate</td>
<td>/</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3 Experimental results summary
However, according to the experimental results, several highlights based on the experiment can be summarized.

- A high temperature and phase transition (especially the transition from liquid crystal to isotropic phase) will introduce a large amount of coagulation into unstable graphene dispersions in liquid crystal systems.

- Sonicating graphene flakes in a liquid crystal is a useful method to improve the dispersion quality. However, this approach is limited by the dispersion medium (e.g. we can’t apply this method on HAT-6 due to the high melting temperature).

- Even graphene flakes are indeed dispersed in a liquid crystal system, their concentration is very low, thus Raman spectroscopy can’t give a reliable check on the existence of graphene flakes.

- There is no evidence to support that the longer alkyl chain in E7 comparing to 5CB improves the dispersion quality even though it was reported having effects in CNTs dispersions\textsuperscript{15,16}.

- Graphene coagulations or graphene flakes have effects on the texture of the graphene/HAT-6 dispersion revealed by the polarizing microscopy measurement.

- NMP will affect the solubility of SSY in water which leads to separation in the SSY chromonic phase and the formation of a mud-like appearance of the dispersion.

Since the literature research on graphene dispersions in liquid crystal is extremely sparse, there are many attractive ideas that are unproven. Thus our experiments which contain many different attempts with cursory experimental details and simple treatment offer some new and important insight. Even though the results are not exciting, several areas seem worthy of pursuing for more investigations in the future based on simple treatment methods. Firstly, sonication gives a relatively good dispersion of graphene flakes in 5CB, further work must be done to prove the existence of graphene flake in the mixture. Secondly, since sonication is a helpful technique in improving the dispersion quality, it is worth checking the graphene dispersions in some discotic liquid crystals that exhibit liquid crystal phases at low temperature where sonication could be tried. Thirdly, as discussed in Section 7.4.3, SDBS may be a good candidate as the surfactant for graphene dispersions in SSY chromonic liquid crystals.
Meanwhile, the experimental results also indicate that complex treatments are needed to obtain graphene or graphene oxide dispersion in liquid crystal system. In next chapter, the interactions between liquid crystal molecules and graphene will be examined using on Raman spectroscopy since understanding the interaction will give some guidance on controlling and optimizing the dispersion quality.
References

Chapter 8

Observing the Interaction between Liquid Crystal Molecules and Graphene using Raman Spectroscopy

The graphene and graphene oxide dispersions in different liquid crystal environments have been discussed in Chapter 7 with some simple methods of producing dispersions. The experimental results prove it to be a hard task to disperse graphene or graphene oxide into liquid crystal environments. Understanding the interaction between liquid crystal molecules and graphene will help in controlling and optimizing the dispersion quality, so acquiring the interaction information between liquid crystal molecules and graphene is of great importance. Thus in this chapter, we will discuss the experimental results on examining the interaction between liquid crystal molecules and graphene. In Section 8.1, a brief introduction will be given on the experiments which have already been carried out on examining the interaction between carbon nanotubes (CNTs) and liquid crystals using Raman spectroscopy. Inspired by this approach, a modified experimental method used for checking the interaction between liquid crystal molecules and graphene will be given. The experimental results for calamitic liquid crystal systems including 5CB, E7 and ZLI-1695 will be reviewed in Section 8.2. Following the same investigation method, the results for the discotic liquid crystal (HAT-6) will be presented in Section 8.3.
8.1. Background Review and Experimental Method

As mentioned in Chapter 7, CNTs dispersion in liquid crystals have been investigated by many researchers\textsuperscript{1-8}. Within this work, it has been reported by Scalia that the Raman peak of the radial breathing mode of 5CB has a peak shift after dispersing CNTs in the liquid crystal material\textsuperscript{6}. This fact suggests an interaction between CNTs and the 5CB molecule, specifically, the interaction between the aromatic cores of 5CB molecules and the CNT surface \textit{via} non-covalent interactions such as \textpi-\textpi interactions\textsuperscript{6,9}. Scalia’s experiment attracts our attention since it suggests a method of checking the interaction between liquid crystal molecules and graphene.

According Scalia’s paper\textsuperscript{6}, CNTs dispersion in liquid crystal was used in their study. However, since the experimental results, mentioned in Chapter 7, indicate a poor dispersion of graphene in liquid crystals, such an approach is not appropriate to study the interactions in graphene systems. Indeed, even for the unstable dispersions, due to the low concentration of the graphene flakes, no Raman signal of graphene is obtained. The spectra obtained (e.g. Fig.7.4) show the typical spectra of the pure liquid crystals unless measured from the stain area of graphene coagulations. In our experiment, we use these areas of graphene coagulations (stains) in the liquid crystal to check the interaction since the coagulation has small spaces which are filled with the liquid crystal as shown in Fig.8.1. In the experiment, we will use the simple sample of the liquid crystal with a substrate of graphene coagulations as shown in Fig.8.1.

To prepare the sample, a small amount (20~40 μL) of the graphene/NMP dispersion was dried on a substrate glass in vacuum at 87 °C. After this drying process,
the NMP in the dispersion was removed and stains were formed by the graphene coagulations on the glass surface. Then a drop of liquid crystal was placed on the substrate glass and covered with a cover glass to form a simple sample. The structure of the sample and the two different measurements regions used for comparison are shown schematically in Fig.8.1. The graphene coagulation measurement in Fig.8.1 focuses on the area with graphene coagulations while the liquid crystal measurement focuses on the non-coagulation area. Raman spectra were collected by the Raman system with a Renishaw Raman spectrometer (RM1000) with a 50 mW output power, 515.32 nm solid state laser (Spectra-Physics) and Olympus ultra-long working distance 50× objective lens (N.A.0.5) on the Raman microscope as mentioned in Chapter 3. The laser power obtained at the sample stage after the scattering in the Raman system is around 13 mW. Different experimental parameters were applied according to the different materials. For the 5CB and E7 measurements, 30s collecting time was used. For ZLI-1695 and HAT-6 measurements, 60s collecting time was used to guarantee a good quality of spectra.

According to the experimental results in Chapter 7 (e.g. Fig.7.4), the Raman spectra obtained from the graphene coagulation measurement will be the liquid crystal spectrum combined with a graphene spectrum, while the Raman spectra obtained from the liquid crystal measurement will be the pure liquid crystal spectrum. After comparing these two measurements, it is possible to obtain information on the interaction between the liquid crystal and graphene from any Raman peak shifts observed in the liquid crystal spectra.

![Schematic optical arrangement of the confocal detection system.](image)

Fig. 8.2 Schematic optical arrangement of the confocal detection system.

It is worth noticing here that the Raman system used in this experiment is capable of the confocal measurement with a schematic optical arrangement shown in
Fig. 8.2. From Fig. 8.2, the information from the focal plane will reach the spectrometer as indicated by the green light path. On the other hand, the light from the area out of the focal plane (indicated by the red light path) will be blocked by the pinhole, thus all the information out of the focal plane is blocked by the pinhole. Fig. 8.2 only shows a brief structure of an ideal confocal system. In reality, the focal area is not a plane but a volume. Thus Raman spectrum of about 1 \( \mu m^3 \) volume can be detected\(^\text{10}\). With the advantage of the confocal measurement, a depth scan measurement can be done by changing the focus position as shown in Fig. 8.3\(^\text{11}\). In this measurement, the objective lens was firstly focused on the substrate glass. Then the stage that holds the sample was moved downward so the focus volume moved upward with respect to the sample. The relative position of the focus volume within the sample was recorded with the reading on the fine focus adjustment of the microscope with one step equals to 1 \( \mu m \). By this method one can scan through the whole sample from the bottom to the top and record the Raman spectra at the different relative positions.

![Depth Scan Measurement Diagram](image.png)

**Fig. 8.3 Illustration of the depth scan measurement**

As shown in Fig. 8.3, at Focus Position 1, the focus volume is located in the substrate glass. At this position, only Raman spectrum of glass can be observed. Then the focus volume moves upward to Focus Position 2 which locates on the interface of the substrate glass and the graphene coagulations. The Raman spectrum will reflect the liquid crystal and graphene coagulation in the focus volume. Moreover, the peak position will show a shift due to the graphene coagulation if the interaction exists. After the focus volume moves into the graphene coagulation area (Focus Position 3 in Fig. 8.3), the spectrum obtained will be the liquid crystal spectrum with any effects from the graphene coagulation. Then the focus position will move to the interface of the graphene coagulation area and the liquid crystal as Focus Position 4 in Fig. 8.3. Since more liquid...
crystal now appears in the focus volume, the peak shift will decrease. Finally, the pure liquid crystal spectrum will be obtained at Focus Position 5. So this depth scan measurement will provide information on how the Raman peak position changes on the liquid crystal spectrum due to the graphene coagulation which gives a better illustration of the interaction.

The following sections will discuss the experimental data obtained for several different liquid crystals including calamitic liquid crystals (5CB, E7 and ZLI1695) and discotic liquid crystal (HAT-6).

8.2. Calamitic Liquid Crystal Experimental Results

8.2.1. 5CB Experimental Results

The 5CB sample was prepared with the method mentioned in Section 8.1. In this experiment, three coagulation areas and three non-coagulation areas (liquid crystal areas) were picked from different area of the sample as the test points. The spectra obtained at these test points are shown in Fig.8.4. The test areas with graphene coagulations show the graphene Raman peaks at at 1350 cm\(^{-1}\), 1580 cm\(^{-1}\) and 2700 cm\(^{-1}\). The peak position shifts of the four important peaks of 5CB at 1182 cm\(^{-1}\), 1285 cm\(^{-1}\), 1606 cm\(^{-1}\) and 2226 cm\(^{-1}\) (peak position refer to the data from a pure 5CB sample) will be discussed. In this discussion, the Raman peak positions were obtained by using Lorentz fitting and the results are shown in Fig.8.5.

Fig. 8.4 The Raman Spectra of 5CB obtained from different test points
Fig. 8.5 Comparison of the peak position from different Raman peaks at the coagulation areas and the non-coagulation areas in 5CB. a) 1182 cm\(^{-1}\) peak, b) 1285 cm\(^{-1}\) peak, c) phenyl stretching peak 1606 cm\(^{-1}\) and d) cyano stretching peak 2226 cm\(^{-1}\).

From Fig.8.5a), the peak at 1182 cm\(^{-1}\) may have some shift due to the graphene substrate, but considering the uncertainty, this is not assured. Fig.8.5b) and c) indicate that the graphene coagulations do not have strong effect on the vibrational modes at 1285 cm\(^{-1}\) and 1606 cm\(^{-1}\), since the peak positions only show random variations which do not depend on the existence of the graphene coagulation. However, according to Fig.8.5d) the peaks at 2226 cm\(^{-1}\) shows an obvious shift around of approximately 0.4 cm\(^{-1}\) due to the existence of the graphene substrate. This Raman peak is related to the cyano stretching mode of 5CB molecules.

The depth scan measurements were also conducted, focusing on the cyano stretching peak (2226 cm\(^{-1}\)) with coagulation area and the non-coagulation area. According to Fig.8.6, the peak intensity change as a function of the relative position within the sample is plotted. The intensity of the graphene (2D peak at 2700 cm\(^{-1}\)) and
5CB (reflected by the cyano stretching peak) are both very weak at the interface of the graphene coagulations and the glass where is located at -45 µm. From -45 µm the intensity of 5CB and graphene both grow as the focus volume moves into the coagulations. The graphene peak intensity reaches a maximum value at about 20 µm, then decrease dramatically after the focus volume moves close to the interface of the graphene coagulation and liquid crystal (~35 µm) while the intensity of the 5CB peak keeps increasing as more liquid crystal is included. After the focus volume moves out of the coagulation region, the graphene peak intensity decreases until it vanishes at 55 µm. On the other hand, the 5CB signal keep increasing until it reaches the maxium intensity at around 55 µm and then decreases since the focus volume moves close to the cover glass.

Fig. 8.6 The intensity changes of the cyano Raman peak (squares) and the graphene 2D peak (circles) at different sample postions in the depth scan measurement.

Since it is shown that the cyano stretching peak is affected by the graphene coagulation as shown in Fig.8.5d), the peak shifts at the different relative postions in the sample was checked with depth scan measurement. In Fig.8.7, the peak postion versus focus postion is shown. For the coagulation area, it is clear that the peak position start to shift from -45 µm where is the interface of the graphene coagulations and the glass. Then the peak shift reaches its maximum value (~1.5 cm⁻¹) between 5 µm to 25 µm which is exactly the area where graphene peak reaches the maximum values in Fig.8.6. After 30 µm, the peak shift start to decrease until it returns to the exactly same peak position as the non-coagulation area at 70 µm. On the other hand, the peak postion from non-coagulation area is almost constant. This difference provides envidence for the interaction between the cyano group and the graphene surface. As discussed in Chapter 4, the cyano group is
located at the end of 5CB molecule, implying that it is the end of the 5CB molecule that interact with the graphene surface, causing the Raman peak shift.

![Graph showing Raman peak shift]

Fig. 8.7 The Raman peak shift plot of the cyano Raman peak in the coagulation area (black square) and in a non-coagulation area (red dots) from the depth scan measurement in 5CB.

However, it is worthy of note that the cyano Raman peak can be identified below the graphene coagulation (1000 a.u at -50 µm in Fig.8.6) and it shows a peak position coincident with a pure 5CB material. The focus volume should be located in the substrate glass at the moment, if the measurements are confocal, it should not give any liquid crystal peaks which is contrary to the experimental results. This discrepancy is because even though the Raman system used is capable of confocal measurements, the optics path within the Raman system were not perfectly set up for such confocal measurements in these experiment\textsuperscript{12}. The axial resolution along laser beam path of the Raman system in fact takes a value between 1 µm (obtained in an idealy confocal system) to 2.5 µm (limited by the depth of focus of the objective lens used in the Raman system). Further, all parts of the sample within the laser beam path are exited by the laser in the microscope system, leading to a background on the Raman spectrum. Even though the Raman system used is an approximately confocal system, this background cannot be completely removed. As a consequence, a very weak liquid crystal signal appears even though there is no liquid crystal in the focus volume. Combined with the fact that the sample is dominated by the liquid crystal, the background Raman spectrum will be the pure 5CB spectrum. Nevertheless, this is not very important for the measurement. It is still good to see the strong peak shift of the cyano stretching mode which indicates the existance of the interaction.
8.2.2. E7 Experimental Results

As discussed in Chapter 7, E7 is a nematic liquid crystal mixture with 5CB as the main component (~51 wt%) and shows similar Raman spectrum to 5CB\textsuperscript{13}. According to the investigation results from CNTs experiments, E7 is a better dispersion medium for CNTs than 5CB\textsuperscript{11,9}. This may indicate a stronger interaction to graphene in E7 compared with 5CB. Thus it is worthwhile checking E7 as a comparison. As the first check in the E7 experiment, two coagulation areas and two non-coagulation areas are checked and the peak positions of the different peaks are compared in Fig.8.8.

![Fig. 8.8 Comparision of the peak position of different Raman peaks at coagulation area and non-coagulation area in E7. a). 1182 cm\textsuperscript{-1} peak, b).1285 cm\textsuperscript{-1} peak, c).phenyl stretching mode peak 1606 cm\textsuperscript{-1} and d). cyano stretching peak 2226 cm\textsuperscript{-1}.](image)

According to Fig.8.8a), the peak shift for 1182 cm\textsuperscript{-1} is obvious (about 1 cm\textsuperscript{-1}) compared with 5CB experiment which only indicates a possible shift of 0.3 cm\textsuperscript{-1} in Fig.8.4a). The peak at 1285 cm\textsuperscript{-1} does not show any shift according to Fig.8.8b) which is
similar to the 5CB results. It is hard to conclude the peak at 1606 cm\(^{-1}\) is shifted since the Coagulation Test 1 data is almost not shifted and the shift on Coagulation Test 2 is only 0.4 cm\(^{-1}\) which is not very reliable as shown in Fig.8.8c). Finally, it is again seen that the Raman peak at 2226 cm\(^{-1}\) is also shifted (about 0.7 cm\(^{-1}\)) in E7 in Fig.8.8d) as happened in 5CB.

It can be summarised that E7 has two obvious peak shifts (1182 cm\(^{-1}\) and 2226 cm\(^{-1}\)) and one possible peak shift (1606 cm\(^{-1}\)) compared with the one obvious shift (2226 cm\(^{-1}\)) and one possible peak shift (1182 cm\(^{-1}\)) observed in 5CB. Since E7 is made mainly from 5CB, the 5CB simulation data from Chapter 4 can be used here. According to the simulation results, the vibrational modes related to 1182 cm\(^{-1}\), 1606 cm\(^{-1}\) and 2226 cm\(^{-1}\) are shown in Fig.8.9. It is interesting to see that both 5CB and E7 have interactions with graphene via the end of the molecules since the 2226 cm\(^{-1}\) peak is related to the cyano stretching mode. The 1182 cm\(^{-1}\) peak relates to a C-C stretching vibration which is located close to the rigid core as shown in Fig.8.9. It shows a shift in E7 and possible peak shift in 5CB. Finally, only E7 shows evidence of an interaction in the core which is related to the phenyl stretching mode 1606 cm\(^{-1}\) peak. So the interaction is through the molecular ends while the core has little interaction.

![Image](image_url)

Fig. 8.9 Vibrational modes related to the Raman peaks in 5CB

The results indicate that E7 has a stronger interaction with graphene compared with 5CB since the interaction is probably happened in the rigid core in E7 as only an
interaction at the molecular end is definitely observed in 5CB. On the other hand, the different interaction strength may due to the antiparallel structure since it is the most important difference between 5CB and E7. However, this conclusion is not assured since it is also reported that the longer alky chains in E7 will also help to improve the interaction to CNTs$^9,^{14}$.

We also did a depth scan measurement concentrating on the cyano stretching mode at 2226 cm$^{-1}$ on E7, shown in Fig.8.10. The result is the same as the 5CB result, the existence of graphene coagulations also leads to a peak shift (~1 cm$^{-1}$ between 60µm to 70 µm) which indicates the existence of the interaction.

![Raman peak shift plots](image)

**Fig. 8.10** The Raman peak shift plots of the cyano Raman peak at coagulation area (black squares) and non-coagulation area (red circles) in the depth scan measurement in E7.

### 8.2.3. ZLI-1695 Experimental Results

We have considered two calamitic liquid crystals based on a biphenyl core structure. It is interesting to check another category of liquid crystals based on a different core structure. ZLI-1695 is a nematic calamitic liquid crystal mixture with a cyano bicyclohexyl structure, as shown in Fig.8.11. This material was chosen for comparison is because all the four components of the mixture share exactly the same rigid core but with different lengths of the alky chain. Both ZLI-1695 and 5CB have a cyano group at one
end of the rigid core and an alkyl chain on the other end. This choice of material offers a
good comparison to exam the effect of the rigid core on the interaction with graphene.
The typical Raman spectrum is shown in Fig.8.12. In the spectrum (Fig.8.12), the cyano
stretching peak is still easy to identify, but the peak position is shifted to around 2240cm\(^{-1}\),
in agreement with previous experimental results\(^{15}\). Since the goal of the experiment is to
check the relative position shifts of certain peaks, this change of the original peak position
will not affect our conclusions. As in the 5CB and E7 experiments, the cyano stretching
mode will again be checked with a depth scan measurement.

![Molecular structure and mixture components of ZLI-1695](image)

**Fig. 8.11** Molecular structure and mixture components of ZLI-1695

![Raman spectrum of ZLI-1695](image)

**Fig. 8.12** Raman spectrum of ZLI-1695

As shown in Fig.8.13, the depth scan measurement result is very different from
the results for 5CB and E7 (Fig.8.7 and Fig.8.10). The cyano stretching mode does not
show any peak shift in both coagulation areas and in the non-coagulation area. This
means that the cyano stretching mode does not interact with the graphene coagulation or
the interaction is too weak to generate peak shift on the Raman spectrum.
The Raman peak shift plots of the cyano stretching peak at coagulation area (black square and red circle) and non-coagulation area (blue triangle) in the depth scan measurement in ZLI-1695.

A possible explanation for this phenomenon can be suggested according to the molecular structure. In 5CB molecules, the rigid core is a biphenyl structure. Even with a tiny (about 12°) twist between the two phenyl rings as shown in Fig. 8.14a), evidence has been given by Scalia et al. that this biphenyl structure can interact with CNTs by non-covalent interactions such as the π-π interaction. This fact also supports an interaction concerning cyano stretching mode since the cyano group also have π-bond which can eventually interact with graphene surface through the π-π interaction. On the other hand, ZLI-1695 molecule has a rigid core with bicyclohexyl as shown in Fig. 8.14b). This rigid core does not have π-bond which cannot interact with graphene via the π-π interaction. Further, the hydrogen atoms will locate between the rigid core and graphene which increase the distance between them. Combining this with the fact that the typical π-π interaction occurs in the range of 3.4~3.8 Å, the π-π interaction will be affected by a larger distance. As a consequence, the peak shift cannot be observed in the experiment.

Fig. 8.14 The comparison of the core structure of 5CB and ZLI-1695 viewing from side. a). 4'-cyano biphenyl structure of 5CB; b). 4'-cyano bicyclohexyl structure in ZLI-1695.
From the experiments in this section, it is clear that calamitic liquid crystals can interact with graphene even though the dispersion experiments did not show satisfactory results in chapter 7. The Raman data provides similar conclusions as were seen in experiment on the CNTs dispersions in liquid crystals\(^1\), indicating a similar mechanism of the interaction. However this mechanism is complex and many factors can affect the interaction\(^9\). The experimental results for calamitic liquid crystals are summarized in Table 8.1. According to the experiment, it can be concluded that E7 has a stronger interaction with graphene compared to 5CB. However, it is not clear whether this difference is due to a breakup of the antiparallel ordering or the different length of the alkyl chains in E7. No shift of the cyano peak from ZLI-1695 was observed indicating that different rigid cores will have different effects on the interaction between the cyano group and graphene.

<table>
<thead>
<tr>
<th>Liquid Crystals</th>
<th>1180cm(^{-1})</th>
<th>1285cm(^{-1})</th>
<th>1606cm(^{-1})</th>
<th>2220cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CB</td>
<td>Probably shifted</td>
<td>No shift</td>
<td>No shift</td>
<td>1.5cm(^{-1}) shift</td>
</tr>
<tr>
<td>E7</td>
<td>1cm(^{-1}) shift</td>
<td>No shift</td>
<td>Probably shifted</td>
<td>0.7cm(^{-1}) shift</td>
</tr>
<tr>
<td>ZLI-1695</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>No shift</td>
</tr>
</tbody>
</table>

Table 8.1 Summary of the Raman peak shifts in different calamitic liquid crystals.

### 8.3. Discotic Liquid Crystal Experimental Results

In Section 8.2, the interaction between calamitic liquid crystals and graphene has been discussed. In this section, discotic liquid crystals will be considered through the same measurement to exam the effect of different molecular shape. The advantage of discotic liquid crystals come from their disc-like rigid core which can in principle provide a larger interaction area and have a similar shape as a graphene flake, possibly leading to a stronger interaction. HAT-6 will be used in this experiment with the basic properties were discussed in Chapter 7. Again, although HAT-6 was thought to be a good candidate as a dispersion medium for graphene or graphene oxide, the results were not good, as discussed in Chapter 7. Nevertheless, we will check the interaction between HAT-6 molecules and graphene in this section.

In the experiment, 5 coagulation tests and 5 non-coagulation tests are chosen to show how the graphene coagulation effects the Raman peak position in the HAT-6
spectrum. As shown in Chapter 7, three peaks at 1390 cm\(^{-1}\), 1431 cm\(^{-1}\), and 1616 cm\(^{-1}\) in the HAT-6 Raman spectrum were selected for the check. The peak position check results are shown in Fig. 8.15. It is interesting that all of the peaks are dramatically shifted. The peak at 1390 cm\(^{-1}\) has the largest shift which is by about 6 cm\(^{-1}\) to 1384 cm\(^{-1}\). However, this shift may be affected by the graphene peak at 1350 cm\(^{-1}\). However, considering the low intensity of graphene peaks, this data should still provide some indications of the peak shift. The peak at 1431 cm\(^{-1}\) has the smallest shift of the three peaks, by 1.3 cm\(^{-1}\). The phenyl stretching mode at 1616 cm\(^{-1}\) also has a 2 cm\(^{-1}\) peak shift. Notice that the phenyl stretching mode frequency is also different form in calamitic liquid crystals (E7 and 5CB), but as discussed in the ZLI-1695 experiment (Section 8.2.3), this difference is not important to the results. The shift of these peaks indicates a strong interaction between the HAT-6 molecules and graphene. These results are within our expectation that the larger area and flat shape of the molecule have effects on the interaction to graphene.

Fig. 8.15 Comparision of the peak positions of different Raman peaks at coagulation area and non-coagulation area in HAT-6. a). 1390 cm\(^{-1}\) peak, b). 1431 cm\(^{-1}\) peak and c). 1616 cm\(^{-1}\) peak.
Depth scan measurement results for all of the three important peaks are shown in Fig. 8.16. However, due to the lack of cyano group in the molecule, we cannot compare directly with E7 and 5CB data. Nevertheless, it is again shown that every peak has a shift due to the graphene coagulation. These experimental results indicate a strong interaction between HAT-6 molecules and graphene.

![Graphs showing Raman peak shift plots for coagulation and non-coagulation areas in HAT-6.](image)

**Fig. 8.16** The Raman peak shift plots of the cyano Raman peak at coagulation area (squares) and non-coagulation area (circles) in the depth scan measurement in HAT-6.

Now it is clear that the discotic liquid crystal does indeed have a strong interaction with graphene which is stronger than the calamitic liquid crystals. So it should be possible to disperse graphene into a discotic liquid crystal system even though the simple method didn’t give a good result, as discussed in Chapter 7.
8.4. Summary

In this chapter, the experimental methods of the investigation of the interactions between liquid crystal molecules and CNT were reviewed. This showed that by using the Raman spectroscopy, it is possible to check the interaction between liquid crystal molecules and graphene via the peak shift. Following this approach, we introduced a modified investigation method of the interaction between graphene and liquid crystal molecules based on the graphene coagulations in the liquid crystals. In the experiments, two different categories of liquid crystals, calamitic liquid crystals and discotic liquid crystals were tested. In the calamitic liquid crystal tests, 5CB, E7 and ZLI-1695 were checked. Several results were obtained from the experiment. Firstly, a stronger interaction in E7 comparing to 5CB has been proved since more peaks were shifted in E7. However, due to the complex interaction mechanism, it is hard to confirm whether this difference is due to the longer alky chains in E7 or the lacking of antiparallel ordering compared to 5CB. Secondly, there is no evidence for interaction in ZLI-1695 according to the cyano stretching mode results. This leads to the conclusion that different rigid core has different effects on the interaction between liquid crystal molecules. After the discussion of calamitic liquid crystals, the experimental results on discotic liquid crystal were shown. In the results, all the three selected Raman peaks of HAT-6 are shifted, leading to an evidence of the strong interaction between HAT-6 and graphene. These experimental results indicate the fact that although the dispersion experiment in Chapter 7 is not very good, liquid crystal molecules still interact with graphene. The dispersion of graphene in liquid crystal is still possible and controlling the graphene arrangement in liquid crystals is still an attractive topic for the future.
References

Chapter 9

Conclusions and Future Work

9.1. Conclusions

The aim of this thesis is, firstly, investigating the application of Polarized Raman Spectroscopy (PRS) in determining the liquid crystal order properties in different liquid crystal systems, and secondly, seeking a possible approach to the graphene/graphene oxide dispersion in liquid crystal systems. In this chapter, the highlights of these research areas will be summarized.

The first topic is the order parameters research in liquid crystal systems via PRS. As reviewed in Chapter 3, Jones et al.’s method\(^1\) gives a \(P_{400}\) fitting value which compares much better with theory and other experiments than the value given by Jen et al.’s method\(^2\). However, a long existing problem on Jones et al.’s method, namely that a discrepancy in order parameters values is found using data from different vibrational modes, attracts some negative opinion on whether PRS is reliable for obtaining the order parameters.

After a careful review of the theoretical approach of Jen et al.’s and Jones et al.’s approaches, two possible explanations were presented in Chapter 4. The first possible explanation is bases on adding a dipole tilt \(\beta_0\) which describes the dipole tilt of certain vibration from the molecular long axis to Jones et al.’s method. This tilt was assumed as the tilt of the vibrational symmetry centre from the molecular long axis in Jen et al.’s discussion. In this explanation, the phenyl stretching mode has no dipole tilt \((\beta_0 = 0)\), or a small dipole tilt that can be ignored. Thus the phenyl stretching mode satisfies Jones et al.’s method well and good results can be obtained from Jones et al.’s method. However,
the cyano stretching mode, on the contrary, is presumed to have a relatively large dipole tilt ($\beta_0 \sim 20^\circ$) compared with the phenyl stretching mode. This dipole tilt can’t be ignored and it introduces molecular biaxiality into consideration which was excluded in Jones et al.’s method. Thus different order parameters were obtained from cyano stretching mode showing a much higher $\langle P_{400} \rangle$ value (e.g.~0.33) compared to the one from phenyl stretching mode (e.g.~0.20).

A systematic discussion was carried out. Firstly, by checking the effect of the dipole tilt and molecular biaxial order parameters, which are introduced due to the dipole tilt, to the depolarization ratio graph, it was observed that different depolarization ratio graphs can be generated with exactly same set of order parameters only with different dipole tilts. Further, these different depolarization ratio graphs agreed well with the experimental depolarization ratios of the phenyl and cyano stretching modes. Secondly, the discussions about the effects of the molecular biaxial order parameters to the fitting values of the uniaxial order parameters showed that $\langle P_{402} \rangle$ could reduce the $\langle P_{400} \rangle$ (15% reduced at $\beta_0 = 15^\circ$, $\langle P_{402} \rangle = 0.0536$) when the dipole tilt existed. This reduction gives a better fitting value of $\langle P_{400} \rangle$ from the cyano stretching mode compared to that from Jones et al.’s method. This robust evidence has been shown to support this explanation. However, a drawback of this explanation is that the computer simulation results did not indicate the existence of vibrational symmetry centre tilt from the molecular long axis. If the simulation is correct, consequently, we suggested the redefinition of $\beta_0$ as the tilt angle between the molecular long axis and the dipole direction, with the dipole tilt different to the vibrational symmetry centre tilt. However, no robust evidence can be provided to support this redefinition. Thus a second explanation was carried out. In this explanation, the dipole tilt was ignored and different vibrational symmetries were used by assuming the phenyl stretching mode has a cylindrical symmetry while the cyano stretching mode has an elliptic cylindrically symmetric. After systematic discussion, it was found that the molecular biaxial order parameters will affect the depolarization ratio graph when the vibration shows elliptic cylindrical symmetry while has no effect when the vibration is cylindrical symmetry. Further, it was again shown the depolarization ratio plots could be obtained with the same set of order parameters but different dipole symmetries. These graph again also agreed well with the experimental depolarization ratio graphs. Based on these two explanations, we attempted to put forward a modified analysis method which satisfied different vibrational modes. However, due to large
amount of parameters in these methods, the fitting results are not robust, though the calculations do reproduce the experimental data.

The second topic in this thesis concentrates on expanding the applicable systems for PRS. A discussion on applying PRS to a bent-core system to obtain order parameters was given in Chapter 5. Inspired by the work done by Southern, a modified molecular model was proposed by introducing the bend angle $\Omega$ and tilt angle $B_0$. It is shown that the bend angle and tilt angle both have strong effect on the depolarization ratio graph. With this molecular model, different molecules including rod-like and bent-core can be discussed using a common set of equations. Followed the discussion presented in Chapter 5, the conclusion was made that the best way to express the Raman tensor in a bent-core system is to use the total Raman tensor which is the sum of two tensors from each of the arms. After applying fitting methods based on the bent-core molecular model and the rod-like molecular model to the data from bent-core system, different fitting results were obtained, indicating that the bend angle in the bent-core systems is an important parameter for the fitting process. The phase biaxial order parameters were also introduced in the analysis method and the effect of each of the biaxial order parameters were examined. However, too many fitting parameters and the inter dependence between the order parameters raises the uncertainty on the fitting process which makes the fitting results unreliable. Some constrains on the fitting parameters are still needed to allow the fitting to such data to be carried out in a robust and reliable way. Besides, a bent-core material shows both the uniaxial and biaxial smectic A (SmA$_d$ and SmA$_d$P$_A$ respectively) phases were examined with several different techniques. The optical polarizing microscopy showed a clear distinction between the biaxial and uniaxial phases. Conoscopic texture showed a split of Maltese cross indicating the biaxiality in SmA$_d$P$_A$ phase. The electric permittivity measurements also showed a clear change between the SmA$_d$ and the SmA$_d$P$_A$ phases. Besides, a relaxation frequency was observed around 100 kHz. Moreover, the PRS, again, provided a clear indication of the phase transition between the two phases reflected on the changing of order parameter values. By introducing the phase biaxial order parameters to the fitting for the biaxial phase, it showed a possible indication of the effect of phase biaxial order parameters in the SmA$_d$P$_A$ phase. But limited by the fitting method, this discussion is not assured.

The researches on the applications of PRS in liquid crystal systems are mostly theory-based. After the theory-based research, we moved to an experiment-based research
topic in which we sought the graphene/graphene oxide dispersions in liquid crystal systems. As was discussed in Chapter 7, several attempts have been made on the graphene/graphene oxide dispersions based on simple dispersing methods, e.g. direct dispersing, sonication and stirring. This work included the graphene/graphene oxide dispersions in calamitic liquid crystals (5CB and E7), discotic liquids crystal (HAT-6) and chromonic liquid crystals (SSY). Unfortunately, the experimental results indicate that the simple dispersing methods are not enough for the production of graphene/graphene oxide dispersion in liquid crystals.

Since understanding the interaction between the liquid crystal molecules and graphene will help in controlling and optimizing the dispersion quality, acquiring an understanding of the interaction information between liquid crystal molecules and graphene is of great importance. Inspired by Scalia’s method of acquiring the interaction information from the peak shift in the Raman spectrum of the carbon nanotube dispersion in liquid crystals\(^5\), a modified method was introduced based on study of liquid crystals in graphene coagulations to determine the interactions, as discussed in Chapter 8. Two different categories of liquid crystals, calamitic and discotic liquid crystals, were tested. In the calamitic liquid crystal tests, 5CB, E7 and ZLI-1695 were tested. It is shown that for the materials with biphenyl core part, 5CB and E7, the cyano group at molecular end has a clear interaction with graphene. For E7, the interaction with graphene can be observed even with the core part of the molecules suggesting a stronger interaction in E7 than 5CB. However, no obvious evidence is available to explain why this difference appears. It may either because of the antiparallel ordering which is broken in E7 or the length of the alkyl chain which increasing the interaction, or even more complex mechanisms. For ZLI-1695 measurements, no peak shifts obtained for the cyano group peak, contrary to what was observed in 5CB and E7. This suggests that the different rigid core parts will have different effects on the interaction which is seen on the cyano group at the molecular end. After the discussion of calamitic liquid crystals, a discotic liquid crystal (HAT-6) was studied with same experimental method. It is interesting to see that all Raman peaks in HAT-6 are shifted, which indicates the existence of a strong interaction between HAT-6 molecules and graphene. These experimental results indicate the fact that although the dispersion experiments are not satisfactory, liquid crystals molecule can still interact with graphene and the dispersion of graphene in liquid crystals is still possible.
9.2. Future Work

9.2.1. Liquid Crystal Alignment on the Anisotropic Substrate

As reviewed in Chapter 1, the typical way to align a liquid crystal is by using the alignment layer formed by the long chain polymers (homogenous alignment) or amphiphilic molecules (homeotropic alignment) on the substrate surface. However, it will also be an interesting idea to align the liquid crystals on the anisotropic crystal surface. Since the crystal structure is different according to the direction on the anisotropic crystal surface, this may probably provide the similar confinement effect to the liquid crystals. Besides, it was also reported by Southern that the mica surface may generate biaxial alignment to the VBG93 sample when checking with SAXS. So in this section, an anisotropic crystal substrate (mica) will be investigated as a homogenous alignment layer for liquid crystals.

In the experiment, a ruby mica disc with a thickness of 25 µm was used as a substrate. 5CB was used to check the alignment. The experimental sample was prepared by spin coating a thin layer of 5CB at 50 rad/s onto the mica disc surface. An open sample was made without cover glass slides. After the spin coating process, a uniform texture was obtained as shown in Fig.9.1. However, it is not assured that the 5CB was aligned on the mica surface since, firstly, the 5CB layer is supposed to be very thin. Thus it is hard to identify the birefringent colour change when the sample is thin. Secondly, the substrate is anisotropic crystal which will also generate a birefringent texture colour. Thus the optical polarizing microscopy measurement is not very reliable. As a consequence, PRS was applied to check the alignment of 5CB on the mica surface.

![Fig. 9.1 The thin 5CB sample on the mica surface by spin coating.](image)

The depolarization ratio data was collected at room temperature by using the PRS technique based on the phenyl stretching mode. As the typical setting for the 5CB PRS experiment, 13 mW laser power at the sample stage and 50× ultra-long working
distance objective lens (N.A.0.5) were used with 30s collecting time. As shown in Fig.9.2, the depolarization ratio plot is slightly different from what we obtained in Chapter 3. The highest value is only about 0.8 compared with 1.1 to 1.2 in the data from Chapter 3. Jones et al.’s method\(^1\) was used on the depolarization ratio data for order parameters. Three measurements at different areas of the 5CB open sample have been carried out for comparison. The order parameter fitting values in Table 9.1 shows a good agreement with each other. However, the fitting values of \(\langle P_{200}\rangle\) and \(\langle P_{400}\rangle\) is 0.3 and 0.1 respectively, compared with 0.5 and 0.2 respectively from Chapter 3, indicating a much lower order parameter values from mica surface than the values from the commercial homogenous cell. This result is not surprising since that if the alignment is due to the mica substrate, the alignment of liquid crystal only relies on the interaction between the mica surface and liquid crystal molecules; the alignment strength may not as strong as the homogenous alignment layers in the commercial cell. However, some other possibilities are not ruled out. It is not clear whether the spin coating process will introduce disorder on the liquid crystal arrangement. Further, since we didn’t use cover slides, the free surface may also introduce disorder to the molecular arrangement close to the surface\(^6\)\(^,\)\(^7\). Thus the fitting values for order parameters are smaller.

![Fig. 9.2 Depolarization ratio data (scatter squares) and fitting results (solid line) of 5CB on the mica surface at 30°C.](image)

<table>
<thead>
<tr>
<th>Data</th>
<th>(\langle P_{200}\rangle)</th>
<th>error</th>
<th>(\langle P_{400}\rangle)</th>
<th>error</th>
<th>r</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>0.03</td>
<td>0.10</td>
<td>0.03</td>
<td>-0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.27</td>
<td>0.01</td>
<td>0.10</td>
<td>0.01</td>
<td>-0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.31</td>
<td>0.02</td>
<td>0.09</td>
<td>0.02</td>
<td>-0.09</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 9.1 The uniaxial order parameter values from three different areas in the 5CB open cell on mica surface.
Thus further experiments should be carried out carefully with parameter control. In order to confirm the alignment from mica, the experiment can be designed as: 5 examples can be prepared with 5CB as shown in Table 9.2 with the order parameters obtained by PRS. Then by comparing the order parameters values for Sample No.1-3, the effect of the mica surface can be confirmed. By comparing Sample No.1 result with Sample No.4 and Sample No.5, the effect of cover slides and spin coating process can be confirmed respectively. Further, since it was mentioned from Southern’s paper that the mica surface may generate biaxial alignment to the VBG93 sample when checking with SAXS\textsuperscript{4}. It is worthy applying PRS to VBG93 in the unaxial and possible biaxial phases on mica substrate and finding evidence to support the biaxial alignment of mica surface.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Mica disc</td>
<td>Glass</td>
<td>Glass + Homogenous alignment layer</td>
<td>Mica disc</td>
<td>Mica disc</td>
</tr>
<tr>
<td>Spin coating</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Cover slides</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 9.2 Samples for the future work.

9.2.2. Investigations of Non-ionic Chromonic Liquid Crystal Phase

It has been reported that a non-ionic chromonic liquid crystal phase can be generated based on hexalkoxy-dibenzo[a,c]phenazines (HDBPs) with the molecular structure shown in Fig.9.3\textsuperscript{8}. The pure material shows a thermotropic discotic liquid crystal phase. After being dissolved in water, a chromonic nematic phase appears at room temperature at the concentration of 25~40wt% and then a higher ordered chromonic phase (M Phase) will be generated at the concentration of 40~50wt% according to Welch\textsuperscript{8}.
Inspired by the discussion of the non-ionic chromonic liquid crystal research by Welch, an attractive idea comes out. As discussed in Chapter 7, the HAT-6, which is a discotic liquid crystal, can be dissolved into NMP. So it is worth checking whether HAT-6 can form a non-ionic chromonic liquid crystal in NMP. If the non-ionic chromonic liquid crystal phase can be obtained, then it will be an exciting experiment to disperse graphene into this liquid crystal system. Since it has been proved that the interactions exist between graphene and the HAT-6 molecules in Chapter 8, combining the fact that graphene can also form a stable dispersion in NMP, dispersing graphene into HAT-6/NMP chromonic liquid crystal may be a good approach to the graphene dispersion in liquid crystal. So as the first stage, we will check whether HAT-6 can form non-ionic chromonic liquid crystal phase in NMP. In this experiment, a 13 wt% HAT-6 dispersion in NMP was prepared which showed a clear solution with no birefringence observed. Then the sample was heated at 100 °C in the oven and maintained for 40 min. After this process, the concentration reached 14wt% with no birefringence identified in this solution. So the sample was further heated at 120 °C for 60 min with the concentration reached around 16 wt%. But after this treatment, the solvent becomes yellow as shown in Fig.9.4 which indicates some change in the material and no birefringence was observed. Limited by the time, no further investigation is done on HAT-6/NMP solvent.

Fig. 9.3 Molecular structures of HDBPs which can form chromonic liquid crystal phase

Fig. 9.4 HAT-6/NMP solvent after heating treatment.
After the HAT-6 experiment, another nematic discotic liquid crystal based on the HAT structure was tested with a larger molecular structure as shown Fig.9.5. The discotic molecule dispersion in NMP with a concentration of 10wt% was prepared using sonication as shown in Fig.9.6. It is interesting that the mixture is no longer clear and after heating to around 50 °C, the mixture becomes clear. This phenomenon may because of that the solubility of the discotic molecules in NMP is increased by heating. A simple sample was prepared by dripping a drop of the solution on a substrate glass and then covering the sample with a cover glass. The simple sample was checked by optical polarizing microscopy and some interesting textures were obtained as shown in Fig.9.7
As shown in Fig. 9.7, birefringent textures can be found in the discotic liquid crystal solvent in NMP at room temperature. Definitely, this birefringence texture does not come from the discotic liquid crystal phase since the melting point of this material is 134°C as shown in Fig. 9.5. So the only possibility is that the discotic molecules form a lyotropic liquid crystal phase in NMP. This lyotropic liquid crystal phase has a high probability to be chromonic but there is no robust evidence to prove this at the moment. On the other hand, the chromonic liquid crystal phase is not stable, a crystallization process was observed from the liquid crystal phase as shown in Fig. 9.8.

The experimental results shown in this section are only based on a quick measurement. However, the result is exciting since the lyotropic liquid crystals phase (probably the chromonic phase) was formed with the discotic molecules dispersion in NMP. Further works can be carried out on finding a stable chromonic liquid crystal phase of the discotic molecules in NMP, and possibly leading to a graphene dispersion in this chromonic system. Thus this research is definitely worth pursuing in the future.
References

Appendix

A.1 Optical Axis in Anisotropic Materials

We can express an anisotropic material in a Cartesian coordinate with the refractive index along the three axes, $n_x$, $n_y$ and $n_z$. Notice that the $n_o$ and $n_e$ are different from $n_x$, $n_y$ and $n_z$ in most case. For a general anisotropic material, $n_x \neq n_y \neq n_z$, there are two optical axes as shown in Fig. A.1, thus this anisotropic material is usually called biaxial material as mentioned in Chapter 1. We assume the anisotropic material has the property that $n_z > n_y > n_x$. To derive the two optical axes, the concept of a beam surface which is defined as the surface that a beam from the origin can reach in certain time period, are used in Fig. A.1. Notice that the Cartesian coordinate in Fig. A.1 is not the refractive index ellipsoid, instead, the position vectors are expressed with the beam speed in different axes and is usually expressed in the form of $1/n$.

![Fig. A.1 The beam surface which is used to decide optical axis in a general biaxial anisotropic material. The refractive indices values $n_x, n_y$ and $n_z$ decide the scale of the long axis (L) and short axis (S) of the ellipse and radius (R) of the circle. MN₀ is the common tangent of the circle and ellipse. ON₀ and it mirror image about Z axis are the optical axes. Notice that we assume $n_z > n_y > n_x$ here.](image-url)
However, as biaxial system is usually hard to investigate, a special case is usually used for investigation. In this case, the refractive indices have the relation that \( n_z > n_y = n_x \) which is known as uniaxial system since only one optical axis exists as shown in Fig.A.2. The number of optical axis becomes one and the system is simpler compared with the biaxial system as shown in Fig.1.16.

![Diagram of uniaxial system](image)

Fig.A.2 The beam surface which is used to decide optical axis in uniaxial system. The refractive values \( n_x, n_y \) and \( n_z \) decide the scale of the long axis (L) and short axis (S) of the ellipse and radius (R) of the circle. ON\(_0\) is the optical axis. Notice that we assume \( n_z > n_y = n_x \) here.

### A.2 Relationship between \( n_\perp \), \( n_\parallel \) and \( n_e \), \( n_o \) in Uniaxial System

To analyse the birefringent properties of the anisotropic materials, a refractive index ellipsoid with \( n_x, n_y \) and \( n_z \) values as the three orthogonal axes is usually used. Notice that this refractive index ellipsoid is a mathematical tool which does not really exist. It is useful in uniaxial system since the polarization direction of O-ray and E-ray can be easily obtained alongside with the refractive indices. For a uniaxial system, if we assume \( n_y = n_x = n_\perp \) and \( n_z = n_\parallel \), the refractive index ellipsoid is shown in Fig.A.3. If a beam of light comes into this uniaxial anisotropic material from a random direction, a cross section plane which is perpendicular to the income beam direction and includes the origin point \( O \) within can be generated. The cross section is an ellipse with the long axis...
and short axis are the polarization direction of E-ray and O-ray respectively. Moreover, the length of the long axis and short axis are the refractive index value of the E-ray and O-ray respectively.

Fig.A. 3 The refractive index ellipsoid of the uniaxial anisotropic material and the O-ray and E-ray polarized direction for a certain income beam.

We can use geometry analysis method to derive the relationship between $n_\perp$, $n_\parallel$ and $n_e$, $n_o$. To achieve that, Fig.A.4 shows the cross section in XOZ plane of the beam surface in the uniaxial system as shown in Fig.A.2. The cross section of the E-ray beam surface is a ellipse with the long axis OB is equals to $1/n_\perp$ while the short axis OA is equals to $1/n_\parallel$. Combine the fact that the O-ray has a constant refractive index and along the optical axis the O-ray and E-ray share same refractive index, we can easily got eq.A.1.

**eq.1.1:**

$$n_o = n_\perp,$$  \hspace{1cm} (A.1)

Fig.A. 4 Cross section plot in XOZ plane of the beam surface in the uniaxial system as shown in Fig.A.2
Then concentrate onto \( n_e \), we set a beam of E-ray from origin and it reaches the beam surface on \( M \). The length of \( OM \) can be expressed as \( \nu_r/c \) where \( \nu_r \) is the beam speed and the angle between \( OM \) and \( z \) axis is \( \xi \). \( MN \) is the tangent line of the ellipse. Then draw a normal line of \( MN \) which also go through the origin. This line also relate to a speed which is named normal speed. This normal speed is actually the speed of wave front and the tilt angle of \( ON \) from \( z \) axis is \( \theta \). Notice that the refractive index \( n_e \) is not simply defined using the beam speed \( \nu_r \). Instead, it is defined using the normal speed \( \nu_N \).

A special case happened when the beam travelling along the \( x \) and \( z \) axes where the beam speed \( \nu_r \) is in the same directions as normal speed \( \nu_N \). Thus we can get \( n_e(\theta = 0) = n_o = n_\perp \) and \( n_e(\theta = 0) = n_\parallel \). To derive a general expression with random \( \theta \), we need to use the ellipse function which could write as eq.A.2,

\[
\frac{x^2}{n_\parallel^2} + \frac{z^2}{n_\perp^2} = 1. \tag{A.2}
\]

Got differential for both side, we can get,

\[
2n_\parallel^2xdx = -2n_\perp^2zdz. \tag{A.3}
\]

Simplify eq.A.3 the expression is obtained,

\[
-\frac{n_\perp^2z}{n_\parallel^2x} = \frac{dx}{dz}. \tag{A.4}
\]

According to Fig.A.2, we have,

\[
\frac{z}{x} = \cot \xi, \tag{A.5}
\]

\[
\frac{dx}{dz} = \tan \left( \frac{\pi}{2} + \theta \right) = -\cot \theta. \tag{A.6}
\]

Combine eqsA.4-A.6, we have,

\[
\cot \theta = \frac{n_\perp^2}{n_\parallel^2} \cot \xi. \tag{A.7}
\]

This is a very useful expression we’ll going to use.
Also according to eq.A.2, we can have the expression about beam speed $v_r$ as below,

$$n_\parallel^2 \left( \frac{v_r \sin \xi}{c} \right)^2 + n_\perp^2 \left( \frac{v_r \cos \xi}{c} \right)^2 = 1. \quad \text{(A.8)}$$

And according to the geometry, $v_r$ and $v_N$ has the relation below,

$$v_r \cos(\theta - \xi) = v_N. \quad \text{(A.9)}$$

Substitute eq.A.9 in A.8, we have,

$$v_N^2 = \frac{c^2 \cos^2(\theta - \xi)}{n_\parallel^2 \sin^2 \xi + n_\perp^2 \cos^2 \xi}. \quad \text{(A.10)}$$

Then we can start transformation using eq.A.7,

$$n_e^2 = \frac{c^2}{v_N^2} = \frac{n_\parallel^2 \sin^2 \xi + n_\perp^2 \cos^2 \xi}{\cos^2(\theta - \xi)} = \frac{n_\parallel^2 \sin^2 \xi + n_\perp^2 \cos^2 \xi}{(\cos \theta \cos \xi + \sin \theta \sin \xi)^2} = \frac{n_\parallel^2 + n_\perp^2 \cot^2 \xi}{(\cos \theta \cot \xi + \sin \theta)^2}$$

$$= \frac{n_\parallel^2 + n_\perp^2 \left( \frac{n_\parallel^2}{n_\perp^2} \cot \theta \right)^2}{(\cos \theta \frac{n_\parallel^2}{n_\perp^2} \cot \theta + \sin \theta)^2} = \frac{n_\parallel^2 + n_\parallel^4 \cos^2 \theta}{n_\perp^2 \sin^2 \theta} = \frac{n_\parallel^2 + n_\parallel^4 \cos^2 \theta}{(n_\parallel^2 \cos^2 \theta + n_\perp^2 \sin^2 \theta)^2}$$

$$= \frac{n_\parallel^2 n_\perp^2}{n_\parallel^2 \cos^2 \theta + n_\perp^2 \sin^2 \theta}. \quad \text{(A.11)}$$

So we have,

$$\text{eq. 1.2:} \quad n_e = \frac{n_\parallel n_\perp}{\sqrt{n_\parallel^2 \cos^2 \theta + n_\perp^2 \sin^2 \theta}}. \quad \text{(A.12)}$$
A.3 A Review of the Derivation for the ODF in Terms of Legendre Polynomials

This review is mainly based on Jen et al.’s deriving method in 1977 and Southern’s PhD thesis, with supplementary mathematics. First, recall the definition of the ODF in terms of the Wigner D-matrix as discussed in Section 2.3.1.

\[
eq 2 \frac{L + 1}{8 \pi^2} \langle D^L_{m',m} (\alpha, \beta, \gamma) \rangle D^L_{m,m} (\alpha, \beta, \gamma), \quad (A.13)
\]

where,

\[
D^L_{m,m} (\alpha, \beta, \gamma) = e^{-im'\alpha} d^L_{m',m} (\beta) e^{-im\gamma}
\]

Remember the fact that index \( L, m', \) and \( m \) are related to the effect of Euler angle \( \beta, \alpha \) and \( \gamma \) on the ODF. For uniaxial phase with uniaxial molecules, the ODF is not related to \( \alpha \) and \( \gamma \), thus index \( m' \) and \( m \) must be zero. Then, for uniaxial phase with non-uniaxial molecules, the distribution according to \( \gamma \) should be added in, as the consequence, the ODF is related to \( \beta \) and \( \gamma \). Finally, for biaxial phase with uniaxial molecules, the ODF only related to \( \alpha \) and \( \beta \).

- Uniaxial phase with non-uniaxial molecules

Now we are going to show how to derive the simplified ODF. First, according to the property of Wigner D-matrix, we have the basic equations below,

\[
D^L_{m,0} (\alpha, \beta) = \sqrt{\frac{4\pi}{2L + 1}} Y^m_0 (\alpha, \beta),
\]

where \( Y^m_0 \) is the spherical harmonics. Notice that in eq.A.13, \( m \) is zero, thus this equation is for biaxial phase with uniaxial molecules. But here we will use uniaxial phase with non-uniaxial molecules for example, so one more step is needed. According to eq. A.16,

\[
d^L_{m',m} (\beta) = (-1)^{m - m'} d^L_{m',m} (\beta).
\]
Substitute eq.A.16 into eq.A.14, we can get the express of $D_{0m}^l(\beta, \gamma)$,

$$D_{0m}^l(\beta, \gamma) = d_{0m}^l(\beta)e^{-im\gamma} = (-1)^{m-o}d_{m0}^l(\beta)e^{-im\gamma} = (-1)^mD_{m0}^l(\gamma, \beta). \quad (A.17)$$

Besides, we also have equations below,

$$Y_{l}^{m*}(\beta, \gamma) = (-1)^m Y_{l}^{-m}(\beta, \gamma). \quad (A.18)$$

Combine eq.A.15, A17 and A.18, we have,

$$D_{0m}^l(\beta, \gamma) = \sqrt{\frac{4\pi}{2L+1}}(-1)^mY_{l}^{m*}(\beta, \gamma) = \sqrt{\frac{4\pi}{2L+1}}(-1)^m(-1)^m Y_{l}^{-m}(\beta, \gamma) \nonumber$$

$$= \sqrt{\frac{4\pi}{2L+1}}Y_{l}^{-m}(\beta, \gamma), \quad (A.19)$$

We also have the expression of spherical harmonics related to associated Legendre polynomials,

$$Y_{l}^{m}(\beta, \gamma) = \sqrt{\frac{(2L+1)(L-m)!}{4\pi(L+m)!}}P_{l}^{m}(\cos\beta)e^{im\gamma}. \quad (A.20)$$

Here $P_{l}^{m}$ is the associated Legendre polynomial. With the property of associated Legendre polynomial as shown below in eq.A.21, we can now express $D_{0m}^l(\beta, \gamma)$ as shown below by simplify eq.A.19:

$$P_{l}^{-m}(\cos\beta) = (-1)^m \frac{(L-m)!}{(L+m)!}P_{l}^{m}(\cos\beta). \quad (A.21)$$

$$D_{0m}^l(\beta, \gamma) = \frac{(L+m)!}{(L-m)!}P_{l}^{-m}(\cos\beta)e^{-im\gamma} = (-1)^m \frac{(L-m)!}{(L+m)!}P_{l}^{m}(\cos\beta)e^{-im\gamma}. \quad (A.22)$$

As the complex conjugation of $D_{0m}^l(\beta, \gamma)$, $D_{0m}^l(\alpha, \beta, \gamma)$ in eq.A.13 can be expressed as shown below,

$$D_{0m}^{l*}(\beta, \gamma) = (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}}P_{l}^{m}(\cos\beta)e^{im\gamma}. \quad (A.23)$$
Then we can divide \( \langle D_{0m}^L (\alpha, \beta, \gamma) \rangle \) into real part and imaginary part using the Euler Equation:

\[
\langle D_{0m}^L (\beta, \gamma) \rangle = ((-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) e^{im\gamma})
\]

\[
= ((-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) \cos (m\gamma) + (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) \sin (m\gamma)) i
\]

\[
= (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} \cos (m\gamma) (P_m^L (\cos \beta)) + (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} \sin (m\gamma) (P_m^L (\cos \beta)) i
\]

\[
= A_{0m}^L + B_{0m}^L i . \quad (A.24)
\]

We can also divide \( \langle D_{0m}^L (\alpha, \beta, \gamma) \rangle \) into real part and imaginary part with same approach.

\[
D_{0m}^L (\beta, \gamma) = ((-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) \cos (-m\gamma) - (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) \sin (-m\gamma)) i
\]

\[
= C_{0m}^L - D_{0m}^L i \quad (A.25)
\]

Now substitute eqs.A.24 and A.25 into eq.A.13, we can have the expression as shown below (notice that only real terms are left in this equation):

\[
f(\beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m=-L}^{L} \frac{(2L+1)!}{8\pi^2} [A_{0m}^L C_{0m}^L + B_{0m}^L D_{0m}^L]. \quad (A.26)
\]

In this equation,

\[
A_{0m}^L C_{0m}^L = (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} \cos (m\gamma) (P_m^L (\cos \beta)) (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) \cos (-m\gamma)
\]

\[
= \frac{(L-m)!}{(L+m)!} \cos (m\gamma)^2 P_m^L (\cos \beta) (P_m^L (\cos \beta)), \quad (A.27)
\]

\[
B_{0m}^L D_{0m}^L = (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} \sin (m\gamma) (P_m^L (\cos \beta)) (-1)^m \sqrt{\frac{(L-m)!}{(L+m)!}} P_m^L (\cos \beta) \sin (-m\gamma)
\]

\[
= \frac{(L-m)!}{(L+m)!} \sin (m\gamma)^2 P_m^L (\cos \beta) (P_m^L (\cos \beta))
\]
Now we are going to check the relation between the term with \( m \) and \(-m\).

\[
A_{0-m}^l B_{0-m}^l = \frac{(L + m)!}{(L - m)!} (\cos(-m\gamma))^2 P_{L}^{m} \cos\beta (P_{L}^{-m} \cos\beta)
\]

\[
= \frac{(L + m)!}{(L - m)!} (\cos(-\gamma))^2 (-1)^m (L - m)! P_{L}^{m} \cos\beta ((-1)^m (L - m)! P_{L}^{-m} \cos\beta)
\]

\[
= \frac{(L - m)!}{(L + m)!} (\cos(\gamma))^2 P_{L}^{m} \cos\beta (P_{L}^{m} \cos\beta) = A_{0m}^l C_{0m}^l
\]  \( (A.28) \)

\[
B_{0-m}^l D_{0-m}^l = -\frac{(L + m)!}{(L - m)!} (\sin(-m\gamma))^2 P_{L}^{-m} \cos\beta (P_{L}^{-m} \cos\beta)
\]

\[
= -\frac{(L + m)!}{(L - m)!} (\sin(-\gamma))^2 (-1)^m (L - m)! P_{L}^{-m} \cos\beta ((-1)^m (L - m)! P_{L}^{-m} \cos\beta)
\]

\[
= -\frac{(L - m)!}{(L + m)!} (\sin(\gamma))^2 P_{L}^{m} \cos\beta (P_{L}^{m} \cos\beta) = B_{0m}^l D_{0m}^l.
\]  \( (A.29) \)

So the components in eq.A.26 have exactly same expression with \( m \) and \(-m\) and it can now be simplified to,

\[
f(\beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m=0}^{L} \frac{2(2L + 1)}{8\pi^2} [A_{0m}^L C_{0m}^l + B_{0m}^L D_{0m}^l].
\]  \( (A.31) \)

Also after investigating the material without ferroelectricity property which means that there is no difference on director direction \( \hat{n} \) and its opposite direction \(-\hat{n} \), thus

\[ f(\alpha, \beta, \gamma) = f(\pi + \alpha, \pi - \beta, \pi + \gamma), \]

and all terms in eq.A.31 with odd \( L \) value are zero.

Combine all these equations together; we can get the expression for \( f(\beta, \gamma) \) as below:

\[
f(\beta, \gamma) = \left( \frac{1}{8\pi^2} \right) [1 + \frac{5}{2} A_{00}^2 (3\cos^2 \beta - 1) + 5\sqrt{6}\sin\beta\cos\beta (A_{01}^2 \cos\gamma + B_{01}^2 \sin\gamma)]
\]

\[
+5 \sqrt{2} \sin^2 \beta (A_{02}^2 \cos2\gamma + B_{02}^2 \sin2\gamma) + \frac{9}{8} A_{00}^4 (35\cos^4 \beta - 30\cos^2 \beta + 3)
\]

\[
+ \frac{9}{2} \sqrt{5}\sin\beta\cos\beta (7\cos^2 \beta - 3)(A_{01}^4 \cos\gamma + B_{01}^4 \sin\gamma)
\]

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Since we assume the molecular is board like, there is two symmetry plans parallel to the molecular long axis. In other words, ODF need to satisfy $f(\alpha, \beta, \gamma) = f(\alpha, \beta, \pi - \gamma)$ and $f(\alpha, \beta, \gamma) = f(\alpha, \beta, \pi + \gamma)$. This condition eliminates items which contains $\cos \gamma, \cos 3\gamma, \sin 2\gamma, \sin 4\gamma, \sin \gamma$ and $\sin 3\gamma$. So only $A_{00}^2, A_{02}^0, A_{02}^4, A_{04}^4$ and $A_{04}^4$ items are left. Here we use $A_{02}^4$ item as an example for next stage transformation. The ODF now is as below.

$$f(\beta, \gamma) = \left( \frac{1}{8\pi^2} \right) \left[ \frac{5}{2} \sin^2 \beta (A_{02}^4 \cos 2\gamma) + \cdots \right]. \quad (A.33)$$

And $A_{02}^4$ can write as,

$$A_{02}^4 = \langle \frac{(2 - 2)!}{(2 + 2)!} \rangle P_2^2 (\cos \beta) e^{-i2\gamma} = \langle \frac{1}{\sqrt{24}} (3 \sin^2 \beta) \cos 2\gamma \rangle. \quad (A.34)$$

So now the ODF can write as,

$$f(\beta, \gamma) = \left( \frac{1}{8\pi^2} \right) \left[ \frac{5}{2} \sin^2 \beta \cos 2\gamma \left\{ \frac{1}{\sqrt{24}} (3 \sin^2 \beta) \cos 2\gamma \right\} + \cdots \right]$$

$$= \left( \frac{1}{8\pi^2} \right) \left[ \frac{5}{2} \cdot \frac{1}{4} \cdot 3 \cdot (\sin^2 \beta) \cos 2\gamma \left\{ \frac{1}{\sqrt{24}} (3 \sin^2 \beta) \cos 2\gamma \right\} + \cdots \right]$$

$$= \left( \frac{1}{8\pi^2} \right) \left[ 5 \cdot 4 \cdot \frac{1}{4} \cdot (\sin^2 \beta) \cos 2\gamma \left\{ \frac{1}{\sqrt{24}} (3 \sin^2 \beta) \cos 2\gamma \right\} + \cdots \right]$$

$$= \left( \frac{1}{8\pi^2} \right) \left[ 60 \cdot \frac{1}{4} \cdot (\sin^2 \beta) \cos 2\gamma \left\{ \frac{1}{\sqrt{24}} (3 \sin^2 \beta) \cos 2\gamma \right\} + \cdots \right]$$

$$= \left( \frac{1}{8\pi^2} \right) \left[ 60 P_{202} \langle P_{202} \rangle + \cdots \right]$$

$$= \left( \frac{1}{8\pi^2} \right) \left[ \frac{5}{2} \cdot (\sin^2 \beta) \cos 2\gamma \cdot 6 \cdot \langle P_{202} \rangle + \cdots \right]. \quad (A.35)$$
Here $P_{l0m}$ are a set of generalised Legendre polynomials and the mean values $\langle P_{l0m} \rangle$ are the order parameters. As a summary, the ODF is finally written as,

$$f(\beta, \gamma) = \left( \frac{1}{8\pi^2} \right) [1 + \frac{5}{2} \langle P_{200} \rangle (3\cos^2\beta - 1) + \frac{5}{2} \langle P_{202} \rangle 6(1 - \cos^2\beta) \cos(2\gamma) + \frac{9}{8} \langle P_{400} \rangle (35\cos^4\beta - 30\cos^2\beta + 3) + \frac{9}{8} \langle P_{402} \rangle 60(7\cos^2\beta - 1)(1 - \cos^2\beta) \cos(2\gamma) + \frac{9}{8} \langle P_{404} \rangle 70(1 - \cos^2\beta)^2 \cos(4\gamma)].$$  \hspace{1cm} (A.36)

With generalised Legendre polynomials,

$$P_{200} = \frac{1}{2} (3\cos^2\beta - 1),$$ \hspace{1cm} (A.37)

$$P_{202} = \frac{1}{4} (1 - \cos^2\beta) \cos(2\gamma),$$ \hspace{1cm} (A.38)

$$P_{400} = \frac{1}{8} (35\cos^4\beta - 30\cos^2\beta + 3),$$ \hspace{1cm} (A.39)

$$P_{402} = \frac{1}{24} (7\cos^2\beta - 1)(1 - \cos^2\beta) \cos(2\gamma),$$ \hspace{1cm} (A.40)

$$P_{404} = \frac{1}{16} (1 - \cos^2\beta)^2 \cos(4\gamma).$$ \hspace{1cm} (A.41)

- **Uniaxial phase with uniaxial molecules**

For the uniaxial phase with uniaxial molecules, the ODF does not relate to both $\alpha$ and $\gamma$, as the consequence, all the terms with $\gamma$ should be zero in eq.A.36 and only two order parameters $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ left which is the expression shown in eq.A.42,

$$f(\beta) = \left( \frac{1}{8\pi^2} \right) [1 + \frac{5}{2} \langle P_{200} \rangle (3\cos^2\beta - 1) + \frac{9}{8} \langle P_{400} \rangle (35\cos^4\beta - 30\cos^2\beta + 3)].$$  \hspace{1cm} (A.42)

**Biaxial phase with uniaxial molecules**

It is very similar to the uniaxial phase with non-uniaxial molecules case. The only difference is that we can use eq.A.14 directly. Following the same approach, we can now express $D_{m0}^L(\alpha, \beta)$ as eq.A.43
As the complex conjugation of \( D_{0m}^L(\beta, \gamma) \), \( D_{0m}^{*L}(\alpha, \beta, \gamma) \) in eq.2.20 can be expressed as shown in A.44,

\[
D_{m0}^{*L}(\alpha, \beta) = \frac{(L - m)!}{(L + m)!} P_L^m(\cos \beta) e^{-im\alpha}.
\]  

Compared with eqs.A.22 and A.23, the only difference is the \((-1)^m\) term. However, this term has no effect after substituted into \( \langle D_{m0}^{*L}(\alpha, \beta) \rangle \) term. As the conclusion, the ODF in this case is same to the uniaxial phase with non-uniaxial molecules, but with different index label.

\[
f(\alpha, \beta) = \left( \frac{1}{8\pi^2} \right) \left[ 1 + \frac{5}{2} \langle P_{200} \rangle (3\cos^2 \beta - 1) + \frac{5}{2} \langle P_{220} \rangle 6(1 - \cos^2 \beta) \cos(2\alpha)
+ \frac{9}{8} \langle P_{400} \rangle (35\cos^4 \beta - 30\cos^2 \beta + 3)
+ \frac{9}{8} \langle P_{420} \rangle 60(7\cos^2 \beta - 1)(1 - \cos^2 \beta) \cos(2\alpha)
+ \frac{9}{8} \langle P_{440} \rangle 70(1 - \cos^2 \beta)^2 \cos(4\alpha) \right].
\]  

With generalised Legendre polynomials,

\[
P_{200} = \frac{1}{2} (3\cos^2 \beta - 1), \quad \text{(A.46)}
\]

\[
P_{220} = \frac{1}{4} (1 - \cos^2 \beta) \cos(2\alpha), \quad \text{(A.47)}
\]

\[
P_{400} = \frac{1}{8} (35\cos^4 \beta - 30\cos^2 \beta + 3), \quad \text{(A.48)}
\]

\[
P_{420} = \frac{1}{24} (7\cos^2 \beta - 1)(1 - \cos^2 \beta) \cos(2\alpha), \quad \text{(A.49)}
\]

\[
P_{440} = \frac{1}{16} (1 - \cos^2 \beta)^2 \cos(4\alpha). \quad \text{(A.50)}
\]
A.4 A Review of Jones et al.’s Analysing Method

This review is based on Jones et al. paper in 2004 along side with mathematical discussion. Different from Jen et al.’s method, Jones et al. simplified the problem with the assumption that the liquid crystal molecular has uniaxial cylindrical symmetry and get the result using geometry method. As the starting point, the Raman tensor in the molecular frame has the form,

\[
\alpha'_M = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & \alpha'_{33}
\end{pmatrix}.
\] (A.51)

Consider a simplest condition that there is only one molecule in the liquid crystal, combined with the basic assumption that the vibration direction is exactly along the long axis of the molecule, the Raman scattering is in Fig.A.5.

![Fig.A. 5 The intensity of input beam is $I_0$. The Raman beam polarization direction has a tilt angle $\theta_0$ from z axis and the intensity is $I_R$. Ignore the refractive indices correction, the measurement intensity are $I_{zz}$ and $I_{xz}$. Following the assumption, the distribution function has the value of 1 at $\theta = \theta_0$ and vanished at other position since only one molecule exists.](image)

With these settings, the measurement intensities $I_{zz}$ and $I_{xz}$ could be expressed in terms of $I_0$, the director of the liquid crystal is rotated in $zox$ plane with a tilt angle $\theta_0$ from the $z$ axis. According to the knowledge in optics and the discussion of Raman scattering,

\[
I_0 = C_1 E_Z^2,
\] (A.52)

\[
I_R = C_2 P_3^2.
\] (A.53)

Here $C_1$ and $C_2$ are constants. Combine with the fact that,
\[ P_3 = \alpha_{33}E_3 = \alpha_{33}E_Z \cos \theta_0 = \alpha_{33} \frac{I_0}{A} \cos \theta_0. \]  \hspace{1cm} (A.54)

Then, combine with the conclusion in Chapter 2 the equation for \( I_R \) is changed.

\[ I_R = C_2 P_3^2 = C_3 \alpha'_{33}^2 I_0 \cos^2 \theta_0. \]  \hspace{1cm} (A.55)

where \( C_3 \) is also a constant. Then \( I_R \) goes through the analyzer in \( x \) or \( z \) direction and generating the measurement intensities. According to the Malus’s law,

\[ I_{ZZ} = I_R \cos^2 \theta_0 = C I_0 \alpha'_{33}^2 \cos^4 \theta_0, \]  \hspace{1cm} (A.56)

\[ I_{XZ} = I_R \cos^2(90^\circ - \theta_0) = C I_0 \alpha'_{33}^2 \cos^2 \theta_0 \sin^2 \theta_0. \]  \hspace{1cm} (A.57)

With eqs.A.56 and A.57, we can get the contribution on the intensities for the molecule at certain rotation angle \( \theta_0 \). So combine with the molecular distribution function, we can obtain the statistical mean value of the intensity for a material with molecules rotating in a plane. With same approach, we turn to a 3D system as shown in Fig.A.6. The director of the liquid crystal sample is rotate in the ZOX plane with a tilt angle of \( \theta \). The 1D molecule is still used in the system, the Raman tensor shown in eq. A.51 is still used.

Fig.A. 6 Two coordinate systems exist in this graph. 1) The laboratory frame (X,Y,Z). 2) The director frame (U,V,W). The director is generated from rotating laboratory frame in XOZ plane with Y axis. \( \angle AOB = \angle BDO = \angle OBC = 90^\circ \)

So referring to eq.A.56 and A.57, we just need to find the cosine expression of \( \angle AOD \) and \( \angle COD \) to calculation the intensities. According to the geometry knowledge, we have,
\[ AD^2 = AB^2 + BD^2 + 2AB \cdot BD \cos \phi, \quad (A.58) \]

\[
\cos \angle AOD = \frac{AO^2 + OD^2 - AD^2}{2AO \cdot OD} = \frac{AO^2 - AB^2 + OD^2 - BD^2 - 2AB \cdot BD \cos \phi}{2AO \cdot OD}
\]

\[
= \frac{2OB^2 - 2AB \cdot BD \cos \phi}{2AO \cdot OD} = \cos \theta \cos \beta - \sin \theta \sin \beta \cos \phi = \cos Z_3, \quad (A.59)
\]

\[ DC^2 = BC^2 + BD^2 - 2BC \cdot BD \cos \phi, \quad (A.60) \]

\[
\cos \angle COD = \frac{CO^2 + OD^2 - CD^2}{2CO \cdot OD} = \frac{CO^2 - BC^2 + OD^2 - BD^2 + 2CB \cdot BD \cos \phi}{2CO \cdot OD}
\]

\[
= \frac{2OB^2 + 2CB \cdot BD \cos \phi}{2CO \cdot OD} = \cos \theta \sin \beta \cos \phi + \sin \theta \cos \beta = \cos X_3. \quad (A.61)
\]

With these expressions, the expression of \( I_{ZZ} (\theta) \) and \( I_{XZ} (\theta) \) could be inferred from

\[ I_{ZZ} (\theta) = C_l \alpha_{33}' \int_{\cos \beta = -1}^{1} d \cos \beta \int_{0}^{2\pi} d \phi f (\cos \beta) \cos^4 Z_3, \quad (A.62) \]

\[ I_{XZ} (\theta) = C_l \alpha_{33}' \int_{\cos \beta = -1}^{1} d \cos \beta \int_{0}^{2\pi} d \phi f (\cos \beta) \cos^2 Z_3 \cos^2 X_3. \quad (A.63) \]

Combine the expression of distribution function \( f (\cos \beta) \), the depolarisation ratio can be expressed.

This is not the end of this method. More Raman tensor components can be introduced into the analysis with addition condition that \( \alpha_{11}' = \alpha_{22}' = r \alpha_{33}' \) as in eq.A.64.

\[
\alpha' = \begin{pmatrix} \alpha_{11}' & 0 & 0 \\ 0 & \alpha_{22}' & 0 \\ 0 & 0 & \alpha_{33}' \end{pmatrix} = \begin{pmatrix} r & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha_{33}'
\]

\[ = \begin{pmatrix} r & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \alpha_{33}' + \begin{pmatrix} 0 & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & 0 \end{pmatrix} \alpha_{33}' + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha_{33}'. \quad (A.64) \]

The Raman tensor can be separated to three terms as shown in eq.A.64. We can assume the 3D molecules as three independent 1D molecules. Since \( \theta \) is decided by the director, so \( \theta \) does not change. So eqs.A.62 and A.63 are available to the three 1D
molecules with different angles. To investigate these angles, the 3D system is plotted as in Fig.A.7

Fig.A. 7 Two coordinate system exist in this graph. 1) The molecular frame (1,2,3). 2) The director frame (U,V,W). OW is in the 2O3 plane and 1 axis lies in UOV plane.

The axis 3 has already been discussed. So for axis 3, we have the equation from A.59 and A.61,

\[ \cos Z_3 = \cos \theta \cos \beta - \sin \theta \sin \beta \cos \phi, \]  \hspace{1cm} (A.65)
\[ \cos X_3 = \cos \theta \sin \beta \cos \phi + \sin \theta \cos \beta, \]  \hspace{1cm} (A.66)

1) For axis 1, \( \beta \) is replaced by \( \xi = 90^\circ \) and \( \phi \) is replaced by \( \gamma = \phi + 90^\circ \),

\[ \cos Z_1 = \cos \theta \cos \xi - \sin \theta \sin \xi \cos \gamma = \sin \theta \sin \phi, \]  \hspace{1cm} (A.67)
\[ \cos Y_1 = \cos \theta \sin \xi + \sin \theta \cos \xi \cos \gamma = -\cos \theta \sin \phi. \]  \hspace{1cm} (A.68)

2) For axis 2, \( \beta \) is replaced by \( \delta = 90^\circ - \beta \) and \( \phi \) is replaced by \( \lambda = \phi + 180^\circ \),

\[ \cos Z_2 = \cos \theta \cos \delta - \sin \theta \sin \delta \cos \lambda = \cos \theta \sin \beta + \sin \theta \cos \beta \cos \phi, \]  \hspace{1cm} (A.69)
\[ \cos Y_2 = \cos \theta \sin \delta \cos \lambda + \sin \theta \cos \delta = -\cos \theta \cos \beta \cos \phi + \sin \theta \sin \beta. \]  \hspace{1cm} (A.70)

With the equation above, the integration expression is shown below,
After integrate the whole equation, the equations in the literature will come out finally as shown below

\[
I_{zz}(\theta) = C I_0 \int_{\cos \beta = -1}^{1} d \cos \beta \int_{0}^{2\pi} d \phi f(\cos \beta) [\alpha'_{zz} (\cos \theta \cos \beta - \sin \theta \sin \beta \cos \phi)^2 + \alpha'_{33} r (\sin \theta \sin \phi)^2 + \alpha'_{33} r (\cos \theta \sin \beta + \sin \theta \cos \beta \cos \phi)^2]^2 \tag{A.71}
\]

\[
I_{zy}(\theta) = C I_0 \int_{\cos \beta = -1}^{1} d \cos \beta \int_{0}^{2\pi} d \phi f(\cos \beta) \left[ \alpha'_{33} (\cos \theta \cos \beta - \sin \theta \sin \beta \cos \phi) (\cos \theta \sin \beta \cos \phi + \sin \theta \cos \beta) \right.
\]
\[
+ \alpha'_{33} r (\sin \theta \sin \phi) (-\cos \theta \sin \phi)
\]
\[
+ \alpha'_{33} r (\cos \theta \sin \beta + \sin \theta \cos \beta \cos \phi) (-\cos \theta \cos \beta \cos \phi + \sin \theta \sin \beta)]^2 \tag{A.72}
\]

After integrate the whole equation, the equations in the literature will come out finally as shown below

\[
I_{zz}(\theta) = k \left( \alpha'_{szz} \right)^2 \left( A_3 + B_3 (P_{200}) + 3 C_3 (P_{400}) - 3 B_3 (P_{200}) \cos^2 \theta - 30 C_3 (P_{400}) \cos^2 \theta \right.
\]
\[
+ 35 C_3 (P_{400}) \cos^4 \theta), \tag{A.73}
\]

\[
I_{zy}(\theta) = k \left( \alpha'_{szz} \right)^2 \left( D_3 - E_3 (P_{200}) - 4 C_3 (P_{400}) + 35 C_3 (P_{400}) \cos^2 \theta \sin^2 \theta \right)
\]
\[
, \tag{A.74}
\]

where,

\[
A_3 = \frac{8r^2 + 4r + 3}{15}; \tag{A.75}
\]

\[
B_3 = \frac{(8r^2 - 2r - 6)}{21}; \tag{A.76}
\]

\[
C_3 = \frac{(r - 1)^2}{35}; \tag{A.77}
\]

\[
D_3 = \frac{(r - 1)^2}{15}; \tag{A.78}
\]

\[
E_3 = - \frac{(r - 1)^2}{21}; \tag{A.79}
\]
A.5 Graphene and Graphene Oxide Synthesis Methods

Graphene

Since graphene has so many amazing properties, it is in high demand, to develop large scale synthesis methods for it is the aim of much currently research. Several different synthesis methods are presented in this section. Here we base the discussion of techniques mainly according to a literature review by Zhu et al.4

The most traditional method for graphene synthesis is called chemical vapour deposition (CVD). This method can be traced back to the year of 1969, and following works in 1970s6-8. However, as mentioned in the introduction section of Chapter 6. The method at that time could only produce few layers of graphite instead of graphene. So the recent progress on this method report that a large area of graphene can be obtained from silicon carbide wafer with temperature annealing in vacuum9-11. The carrier mobility reached as high as 2000cm²/Vs 11. There is another CVD method is based on copper film that produces a larger area of graphene. Attractive research area is growing graphene on a metal oxide surface to produce electronic devices.

Since graphene is single layer of graphite, separating graphene from graphite is the second method to generate graphene. The second synthesis method is usually called micromechanical exfoliation. The basic concept of this method was firstly put forward in 199912, 13. This work inspired the interests of physicists and several methods appear following this concept. The first experimental method to produce graphene by Geim and Novoselov in 2004 belongs to this category, which is often known as the Scotch tape method14. Obviously, the micromechanical exfoliation method is easy to achieve without a complex synthesis procedure. However, the disadvantage is also obvious, that only small pieces with dimensions of the order of hundred µm of graphene can be achieved with this method.

The third method, exfoliation of graphite in solvents, is inspired by the experiment that individual layers of graphene oxide are obtained in water. Graphene powder dissolved in some non-polar solvents such as dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP) is achieved by sonication15. However, even though there is significant progress in this area, the disadvantage of this method is the low efficiency
and it is hard to control the quality of the products. Further, the loss due to the coagulation in the drying process is also a challenge. Recently, it has been reported that with platinum nanoparticle decorations, graphene can be exfoliated from graphite\textsuperscript{16}.

As mentioned, graphene oxide solvent is also a hot topic for the graphene syntheses. Theoretically speaking, if the functional group on graphene oxide is removed, the graphene oxide will be reduced to graphene. However, this process is hard to achieve and, due to the hydrophobic property of graphene, the reduced graphene will coagulate in water. The current research reports that different functional groups can be removed by a variety of methods\textsuperscript{17-21}. However, it is not yet published that graphene flake is obtained from this method.

Beside these main methods, there are also some other methods been reported, such as to produce a gas phase graphene within a microwave plasma reactor\textsuperscript{22} and multi-layered graphene synthesis in arc discharge\textsuperscript{23}.

**Graphene Oxide**

Generally speaking, the procedure to produce graphene oxide is treating graphite with strong acid and oxidant. Different methods vary from each other depending on the different choice of the strong acid and oxidant. As discussed in the introduction section of Chapter 6. Graphene oxide was first synthesized by Brodie using nitric acid (HNO\textsubscript{3}) and potassium chlorate (KClO\textsubscript{3}) on graphite\textsuperscript{24}. This method was then modified by Hummers in 1958\textsuperscript{25}. In this method the nitric acid is replaced with sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) and the oxidant is sodium nitrate (NaNO\textsubscript{3}) and potassium permanganate (KMnO\textsubscript{4}). Hummers’ method is safer compared with Brodie’s method and thus it is widely used in modern research. There are some modifications on Hummers’ method. For example, the acid is replaced with a sulphuric acid and phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) was used to improve the product efficiency\textsuperscript{26}. Recently, there is also another approach on graphene oxide synthesis which is called the Tang-Lau method which is a hydrothermal method using glucose as the reagent\textsuperscript{27}. This method is interesting since it is cheap and environmental friendly.
A.6 Experiment Details Discussion

![Experimental Setup Diagram](image)

Fig.A. 8 A basic illustration of the experimental setup. The green line indicates the laser light path. The analyzer is parallel to the incoming beam polarization direction and the half wave plate is used to rotate the polarization direction by 90° to obtain the perpendicular measurement.

The experimental setup was shown in Fig.A.8. Before the measurement, a Linkam/AWAT commercial homogenous aligned cell was used for the liquid crystal sample. The alignment layer is made with polyimide and rubbed antiparallel. Homogenous cells were used since there is an obvious change at different rotation angle comparing to homeotropic cell. 5μm thickness cells were always used in order to provide a good Raman intensity as well as a good alignment quality. The effect of the ITO layers was ignored due to the very thin thickness. In fact, the ITO layers in the cell are not actually necessary to the PRS measurement since no electric field was applied on the cell. Thus for a handmade cell, normal glass with homogenous alignment layers is enough for the experiment purpose. The pre-tilt of the sample was not measured. However, the pre-tilt value for the alignment layer made with polyimide is 1° to 4°. Combined with the fact that the optical texture shows the right birefringent colour for the cell spacing, the pre-tilt should be very small. Thus it is assumed as a very tiny effect that we didn’t take into consideration. On the other hand, the effect of refractive index of glass was discussed in Chapter 2. As a summary, in Jen et al.’s method the effect was discussed using correction terms must be used and the corrected equation are shown in eqs. A.80 and A.81.

\[ R_1 = C_n r_1, \]

\[ R_2 = \frac{r_2}{C_n}, \]
Where \( R_1 \) and \( R_2 \) are the two depolarized ratio data measured in Jen et al.’s method and \( C_n \) is the refractive indices correction.

\[
C_n = \left( \frac{n_{\text{glass}} + n_{zz}}{n_{\text{glass}} + n_{xx}} \right)^2.
\]  

(A.82)

It is worthy of note that the refractive index for alignment layer is about 1.5 which is very close to that of glass, thus the effect of alignment layer is included in the indices correction. On the other hand, the thickness of glass is around 0.5mm comparing to that of ITO and alignment layers (25~65nm and around 100nm respectively), so we assume the ITO and alignment layer do not have effect.

For Jones et al.’s method, the correction is reflected on the differential polarized ratio \( r \) value. \( r \) is replaced by \( rC_n \) where \( C_n \) is a constant as defined in eq.A.82. Usually, the liquid crystal samples were sealed by UV glue and dried in UV oven. However, for UV sensitive material, a black cover slide is used to mask the liquid crystal area in UV oven. It is worthy of note the UV glue may probably contaminate the liquid crystal sample. So in some special case, the cells were not sealed and the whole measurement was finished within 36 hours to avoid effects from air.

After the sample preparation, the liquid crystal cell was fixed on the hot stage with a copper clamp. A black paper or black cap was placed between the hot stage and the liquid crystal sample. It has been proved the black background can reduce background noise dramatically. However, it is also important to mention that this black background may also introduce temperature gradient up to around 1°C which may effect on the temperature accuracy, thus using relative temperature is a useful method to get rid of this effect.

All lights around the experiment bay were switched off and the measurement was done in a darkroom to reduce the background noise from other light source. Removed all objective lens except 50x Olympus long working distance lens and fixed all wires on the stage to allowing the hot stage rotate freely for 360° without any shift due to the unattached wire.

After setting the hot stage to certain temperature, Raman spectra were collected every 10° from 0° to 360° (rotation angle values comes from the reading from the rotate stage)
for the experimental setup with analyzer parallel to the laser vibration direction (without half wave plate in). The collecting time and laser intensity is decided according to the type of liquid crystal material (e.g. 5CB can sustain 60s collecting time and 12.8mW laser power on the sample). In fact, 180° measurement (one period) is sufficient for the analysis, but we still use 360° for our experiment. There are two main reasons for this set up: firstly, by doing 360° measurement, we equally measured two period which means we have repeated the measurement twice, so the fitting result is more reliable (e.g. as shown in Table.A.1, all fitting values obtained from 0° to 360° data are the mean value of the values obtained form 0° to 180° and 180° to 360° data); Secondly, by comparing spectra at 0° and 360°, we can check the measurement quality, a good measurement should only show a small difference in these to spectra since they are actually same point. If there is a huge difference, it means either the sample shifted during the experiment or the focus changed a lot, or even worse, the liquid crystal sample degraded or contaminated.

On the other hand, to reduce the experimental error, we can actually repeat the spectra collection for several times. However, in reality, this method is time consuming. Fig.A.9 shows an example for depolarization ratio graph with error bar generated from repeating measurement. It is clear that the error bar is very tiny at around 150° and 330°. Moreover, as shown in Table.A.1 the fitting values obtained without considering the error bar only show a small value difference (~0.005 on \( P_{200} \) and \( P_{400} \)) from the fitting values obtained with considering the error bar. Combine with the fact that the experimental error is about 0.03 for the final order parameter result due to other error, this difference is negligible. Thus in our experiment, we only measure once from 0° to 360° and it can provide reasonable fitting result.

![Fig.A. 9 Example of depolarization ratio graph with error bar.](image)
Then the stage was rotate back from 360° to 0° for the experimental setup with analyzer perpendicular to the laser vibration direction (with half wave plate in). This experiment setup avoids the effect from the step shift during the rotation of the rotation stage. During the experiment process, any focus change was avoided and the stage was rotated softly to avoid shift of the stage.

More data can be collected at different temperature to investigate the effect of temperature on order parameters. Theoretical speaking the sample can be refocused in different temperature measurement since the final data used for fitting is depolarization ratio which is the intensity ratio. However, in order to avoid focusing onto different focus depth, we avoided the focus change during the whole experimental process. The fitting results (example in Fig.) show a good agreement with other measurement result.

<table>
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<tr>
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<th>( P_{200} )</th>
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<th>( P_{220} )</th>
<th>Fitting error</th>
<th>( r )</th>
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<td>0.215</td>
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<td>-0.166</td>
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Table A.1. Summary of the fitting results using different method according to Fig. A.9

Fig. A. 10 Example of the order parameters fitting result comparing to the result obtained by refractive index measurement (Ref. 28).
References of the Appendix


B. C. Brodie, Philosophical Transactions of the Royal Society of London 149, 249 (1859).


