Influence of Confinement on Relaxation of Director Orientational Fluctuations in Nematic Liquid Crystal

by
Edwin X. Arroyo Félix

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science

Masters Program
University of Puerto Rico
Faculty of Natural Sciences
Department of Physics
Río Piedras, Puerto Rico
May 2009
# Table of Contents

Acknowledgements ................................................................. iii  
Dedication .............................................................................. iv  
List of Figures ........................................................................ v  
List of Abbreviations ............................................................. vii  
Thesis Approval Page ............................................................... viii  
Abstract ................................................................................ ix  
Authored and co-authored publications and presentations ........... x  
I  Introduction .......................................................................... 1  
II  Basic Information about Liquid Crystals ............................... 3  
   2.1  General Information about Liquid Crystals ....................... 3  
   2.2  Influence of Confinement on Physical Properties of the Liquid Crystals ......................................................... 6  
III  Phase Transitions in Liquid Crystals ..................................... 9  
   3.1  Basics of Phase Transitions ........................................... 9  
   3.2  Phase Transition in Liquid Crystals ................................. 15  
IV  Light Scattering and Relaxation in Liquid Crystals ................. 17  
   4.1  Basic Light Scattering Concepts .................................... 17  
   4.2  Dynamics of Fluctuations of Director Orientations .......... 20  
V  Experimental Method ........................................................... 27  
   5.1  Experimental Details .................................................... 27  
   5.2  Data Analysis ............................................................... 30  
   5.3  Samples ........................................................................ 31
VI Dynamic Light Scattering in Bulk MBBA and MBBA Confined in 100 nm and 10 nm Random Pores ........................................... 34

6.1 Dynamic Light Scattering in Bulk MBBA ..................... 34

6.2 Dynamic Light Scattering in MBBA Confined to 100 nm Random Pores .......................................................... 38

6.3 Dynamic Light Scattering in MBBA Confined to 10 nm Random Pores .......................................................... 45

VII Conclusions .............................................................. 53

References ........................................................................ 55
Acknowledgments

The work presented on this thesis was supported by:

NASA grant # NCC3 – 1034

NASA grant # NNX08BA48A

I would like to thank the Center for Nanoscale Materials and the Center for Advance Nanoscale Materials for the academic and financial support they gave me during this investigation. I thank the research group, the thesis advisor Prof. Fouad M. Aliev, Vladimir Dolidze, Manuel Rivera, and, Iván López. I would also like to thank Prof. Wilfredo Mattos Cintrón for teaching me the beauty of physics. Especially I would like to thank my family. My mother and father, Marina Felix and Luis Edwin Arroyo, for the help and love they have given me all my life. You have always been a blessing and inspiration. My cousins, Laura and Matilde García for the love and fun they have shared with me all my life. Thanks for those wonderful Christmases that you made so special. To my family in Humacao, Titi Tere, Titi Carmen, Carmín and Lily for making every summer one to remember and for the wonderful memories that you have given me. To my wife, Myriam for all your love and support. I would also like to acknowledge three wonderful women who are not physically with me, but they left an imprint in my life forever. My two grandmothers, María Méndez and Consuelo Avilés and my aunt, Titi Matil. I am sure that you are enjoying this moment with me as much as I am thinking of you three.
Dedicado a mi esposa Myriam por todo tu amor y comprensión
y a Fanny por la alegría y amor que traes a mi vida.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBBA</td>
<td>4-methoxybenzylidene-4-butylaniline</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>PCS</td>
<td>Photon Correlation Spectroscopy</td>
</tr>
<tr>
<td>QELS</td>
<td>Quasi – Elastic Light Scattering</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional Integral Derivative</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Phase Transition Temperature</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Order Parameter</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Director</td>
</tr>
</tbody>
</table>
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBBA</td>
<td>4- methoxybenzylidene-4-butylaniline</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>PCS</td>
<td>Photon Correlation Spectroscopy</td>
</tr>
<tr>
<td>QELS</td>
<td>Quasi – Elastic Light Scattering</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional Integral Derivative</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Phase Transition Temperature</td>
</tr>
<tr>
<td>Ω</td>
<td>Order Parameter</td>
</tr>
<tr>
<td>ν</td>
<td>Director</td>
</tr>
</tbody>
</table>
Dedicado a mi esposa Myriam por todo tu amor y comprensión
y a Fanny por la alegría y amor que traes a mi vida.
ABSTRACT

Dynamic light scattering (DLS) was applied to study the influence of confinement on dynamic properties of 4-methoxybenzylidene-4-butylaniline (MBBA) nematic liquid crystal dispersed in random porous matrices with mean pore sizes of 10 and 100 nm.

In DLS experiments we observed for confined MBBA in 100 nm random pores at nematic phase two relaxation processes. The first relaxation process is attributed to bulk like orientational fluctuations of director in the portion of liquid crystal located in the central part of the pores. The second process is associated with fluctuations of director orientational fluctuations in liquid crystal at pore wall - liquid crystal interface. This second relaxation process is slower than the first relaxation process. For confined MBBA in 10 nm random pores in nematic phase a slow and a broad relaxation process is present which is absent in the bulk nematic liquid crystal.

The result obtained for MBBA confined in random porous matrices suggested that the main differences in the dynamical behavior from that of bulk are due to the existence of the liquid crystal pore-wall interface and the slow process is surface related relaxation.
Authored and co-authored publications and presentations

Publications:


Presentations:

1. Dynamics of Director Fluctuations in Confined Liquid
   Sarmistha Basu, Edwin Arroyo and Fouad Aliev
   Materials Research Society Meeting – Boston, MA, 2005

2. Dynamics of Director Fluctuations in Confined and Filled Liquid Crystals
   Edwin Arroyo, Sarmistha Basu, Fouad Aliev
   American Physical Society Meeting – Baltimore, MD, 2006

3. Basics of Photon Correlation Spectroscopy
   Edwin Arroyo
   Seminar given in Physics Department, April 2007 – UPR Río Piedras

4. Relaxation Processes and Phase Transitions in Nanoconfinied Liquid Crystals
   Edwin Arroyo, Sarmistha Basu and Fouad Aliev
   American Physical Society Meeting – Denver, CO, 2007

5. Relaxation Processes and Phase Transitions in Nanoconfined Liquid Crystals
   Edwin Arroyo, Sarmistha Basu, Fouad Aliev
   PR-EPSCOR Annual Meeting, San Juan, PR, 2008

6. Relaxation Processes and Phase Transitions in Nanoconfined Liquid Crystals
   Edwin Arroyo, Sarmistha Basu, Fouad Aliev
   Annual Puerto Rico NASA Meeting, Humacao, PR, 2008
Chapter I

Introduction

Liquid crystals are materials important both in many recent scientific developments in chemistry and physics, and in applications such as computer displays. Liquid crystals have been a fascinating subject of investigation since their discovery for different reasons. For example, liquid crystals possess a variety of phases and different degrees of orientational and translational order (Jones, 2002). Also heterogeneous systems based on liquid crystals such as liquid crystals dispersed in inorganic porous matrices are materials important as model systems of materials used for applications and fundamental physics.

Confined liquid crystals and matrices form heterogeneous and anisotropic materials characterized by a well develop interface. Different aspects of the dynamic behavior of confined liquid crystals can be investigated by dynamic light scattering.

In this thesis we showed results of dynamic light scattering investigations of the influence of confinement on the behavior of a nematic liquid crystal 4-methoxybenzylidene-4-butylaniline (MBBA). The experiment shows changes in relaxation properties of MBBA confined in different porous sizes (10 nm, 100 nm). The appearance of a slow relaxation process, absent in the bulk phase of this liquid crystal, was observed in confinement.
In Chapter Two a general description of liquid crystals is presented followed by a
description of phase transition in liquid crystals in Chapter Three. In Chapter Four there
is a description of light scattering and relaxation processes in liquid crystals. Chapter Five
is a discussion about the experimental method used in this investigation which is dynamic
light scattering (DLS). In Chapter Six the results of this investigation are presented.
Chapter Seven has the conclusions of this investigation.
CHAPTER II
Basic Information about Liquid Crystal

2.1 General Information about Liquid Crystals

The term liquid crystal describes a phase of matter that is intermediate between a solid crystal and isotropic liquid. It refers to a phase that possesses a degree of order intermediate between the molecular disorder of a liquid and the ordered structure of a crystal (Chandrasekhar, 1992). One important property of liquid crystal phases is that these phases have long range orientational order. For this to be possible the molecules must be anisotropic, whether this results from a rod-like or a disc-like shape. Molecules that are capable of forming liquid crystal phases are called mesogens. Figure 2.1 represents an illustration of a crystal, nematic liquid crystal, and isotropic liquid.

Liquid crystals can be divided into two classes: thermotropic liquid crystals and lyotropic liquid crystals. The prefix thermo refers to a phase transition in which heat is generated. In contrast, lyotropic liquid crystals phases form in solution, and thus concentration controls the liquid crystallinity in addition to temperature (Collings & Hird, 1997). Lyotropic liquid crystal phases are formed by amphiphiles in solution. The vast majority of thermotropic liquid crystals are composed of rod-like molecules. They are classified broadly in three types: nematic, cholesteric, and smectic.

The nematic liquid crystal has a certain degree of long range orientational order of the molecules, but no long range translational order, just as in a normal isotropic liquid. This is the simplest liquid crystal phase. The nematic phase can thus
be considered to be an anisotropic liquid. Presence of long range orientational order in a nematic liquid crystal is characterized by a unit vector called director ($\mathbf{\nu}$) (Stephen & Straley, 1974). Figure 2.2 represents the molecules of a nematic liquid crystal phase and the director.

The states of the director ($\mathbf{\nu}$) and ($-\mathbf{\nu}$) are indistinguishable. The degree of alignment of the molecules along the director ($\mathbf{\nu}$) is characterized by order parameter ($\Omega$). The positional order of the molecules in nematic phase is close to the order of an isotropic liquid; it is thus characterized by short-range density correlation.

The nematic phases are constituted of rod-shape molecules which are identical to their mirror image (achiral molecules). Examples of such molecules are the ones that compose the liquid crystal 4- methoxybenzylidene-4-butylaniline (MBBA).

In this work the focus will be on the phase transition of liquid crystals, specifically isotropic – nematic transition, and on the relaxation of fluctuations of director orientations processes in nematic phase.
Fig. 2.1 – Illustration of a solid, nematic liquid crystal and isotropic liquid.

Fig. 2.2 – Schematic representation of molecules in a nematic liquid crystal. The dashed arrow shows the direction of preferred orientation (director).
2.2 Influence of Confinement on Physical Properties of the Liquid Crystals

The investigations of the effect of confinement on physical properties and behavior of condense matter has brought a great deal of achievements and controversies over the past years.

Liquid crystals are soft systems and the energy responsible for long range orientational order is small. Therefore, the influence of the interface and confinement effects should be very strong in the case of liquid crystals.

Confinement has at least two impacts on a given material: the interaction of the material with the cavity surface and the finite sizes effects. In studying the dynamics of confined systems some trouble issues might show up: separation of the role of random field effects from that of finite size effects and the influence of the pore solid surface on liquid crystal properties. Liquid crystals are interesting because they exhibit a variety of phases and different degrees of orientational and translational order (Chandrasekhar, 1992).

They also have different kinds of phase transitions such as first and second order. What happens with the structure and dynamics of liquid crystals near the interface is relevant for liquid crystals applications and for basic purposes.

For a nematic liquid crystal the interaction between the surface and the liquid crystal results in the appearance of preferred orientation of the director at the surface called the easy direction, for which the surface energy is minimal. The strength of the liquid crystal solid surface interaction is described by the quantity called anchoring strength (de Gennes & Prost, 1993). The static and dynamic properties of the liquid crystals are influenced strongly by the interfaces. The effects of the interfaces play a
dominant role when the liquid crystals are dispersed in a solid matrix. Because the liquid crystal is confined in a small cavity the volume to surface ratio approaches some characteristic length of the liquid crystal phase. Due to the long range orientational order in liquid crystals the length scale where this confinement phenomena are expected to play a role is much larger than in ordinary liquids. New effects which are not observed in the bulk liquid crystals are expected to be seen in confined liquid crystals due to their nanoscale confinement, geometry, and large area of interface interactions (Bellini, Clark, & Shaefer, 1995).

Porous media are good systems to use for the description of the surface interactions on the physical properties of liquid crystals. The size of the pore in the random porous media dictates the relative role of these effects. If the size of the pore is small, the finite size effects dominate and the transition temperature from the isotropic to nematic phase is lowered (Mertelj & Copic, 1997). To study the size effects and ordering in confined liquid crystals different geometrical cavities are used, for example spherical, plane, parallel, and cylindrical (Kuzma & Labes, 1983).

Several techniques have been used to study the nature of the isotropic-nematic phase transition of liquid crystals confined in a random porous media such as differential scanning calorimetry, nuclear magnetic resonance, and dynamic light scattering. Armitage and Price (1976) were one of the first researchers who investigated aspects of the influence of confinement on thermodynamic properties of confined liquid crystals.

Dynamic light scattering (DLS) is a powerful and convenient method to study the dynamics of orientational fluctuations of director in different liquid crystalline phases and orientational order parameter in isotropic phase. A large number of investigations on
porous sizes and interface interaction have an influence on the ordering of the liquid crystal. One of the more important investigations done on this area was done in 1992 by Goldburg, Wu, Liu and Xue. In their dynamic light scattering experiments of a liquid crystal named 4-n-octyl-4-cyanobiphenyl (4CB), they reported that when the liquid crystal is confined in a random porous media (silica gel) the fluctuations of the orientation order parameter relax at a much slower rate than in the bulk liquid crystal. According to the authors, the order parameter fluctuation is the mechanism that describes the fluctuations of scattered light. These fluctuations in the nematic phase are slow and resemble glass dynamics. The phase transition between isotropic and nematic phase is smeared out by the random porous media. The authors attribute some of the dynamic features of this system to the idea that porous medium imposes a random uniaxial field on the liquid crystal, whereas in Goldburg, Aliev and Wu (1995) some problems have been summarized which are still unsolved. DLS was also applied for investigations of nematic phase of liquid crystals in aerogel systems (Bellini, Clark, Muzny, Wu, Garland, Schaefer, & Oliver, 1992). It was concluded that the orientational fluctuations in small pores are dominated by surface properties (Mertelj & Copic, 2000).

Dynamic light scattering experiments were done to study the influence of confinement in a liquid crystal in isotropic and nematic phase dispersed in random porous media. In this research the main objective is to study the intensity of scattered light related to the fluctuations of director orientations. This goal can be achieved by measuring the intensity-intensity autocorrelation function. Dynamic light scattering is a useful technique to measure director fluctuations of director orientations away from the surface as well as the fluctuations of liquid crystal layers that are close to the surface.
CHAPTER III

Phase Transitions in Liquid Crystals

3.1 Basics of Phase Transitions

Phase transitions are physical phenomena that have been known for a very long time. They are found in nature or daily life, for example condensation of water. They are also present in numerous technical systems or industrial processes. For example, evaporation of water in the steam generator of a nuclear power plant is the physical process to activate the turbines in electric generators. Any substance of fixed chemical composition can exist in homogenous forms whose properties can be distinguished; these are called the states. For example, water exists as a gas, liquid, and solid matter. These three states of matter differ in density, heat capacity, and other physical properties. Phase transitions manifest by the appearance of new properties of matter, for example ferromagnetism and superconductivity (Pabon, Leblond, & Meijer, 2007). In general, a transition is manifested by a series of associated physical events. There are two kinds of phase transitions: first order and second order.

The physicist P. Ehrenfest proposed a classification of phase transition based on the thermodynamic potentials in 1933.

Ehrenfest proposed the following:

a) First – order transitions which are accompanied by discontinuities of thermodynamic quantities such as the entropy (S) and density, associated with the first derivatives of thermodynamic potential (G). Such derivatives as:

\[ S = \left( \frac{\delta G}{\delta T} \right)_P \quad \quad \quad V = \left( \frac{\delta G}{\delta P} \right)_T \]
The latent heat is associated with discontinuity of the entropy.

b) Second – order transitions for which the thermodynamic potentials and their first – order derivatives are continuous, while some second derivatives with respect to state variables are reduced to zero or approach infinite asymptotically at the transition point. The heat capacity \( C_p \) at constant pressure is related to the entropy of the system by the relationship

\[
\frac{C_p}{T} = - \left( \frac{\delta^2 G}{\delta T^2} \right)_p = \left( \frac{\delta S}{\delta T} \right)_p.
\]

Figure 3.1 represents the variations of different thermodynamic quantities with temperature for first-order and for second-order phase transitions.

For a phase transition one can define an order parameter, which typically takes a zero value in the disorder phase and a finite value in the ordered phase. The way the order parameter varies with temperature provides information about the nature of the transition (Collings, 1990).

Therefore, to describe phase transitions we must use theories that describe the ordering in the system. This is often done approximately, using the average order parameter within the mean field theory. In simplest case, the order parameter is a function of the thermodynamic state of the system and is uniform throughout the system and at equilibrium is not time dependent. Now we will discuss a general model that has broad applicability to phase transition in soft materials, the Landau theory (Hamley, 2007). The Landau theory describes the ordering at the mesoscopic level. The Landau theory is based on an expansion of the free energy in a power series of an order parameter. In our discussion we will consider it in the context of a phase transition in a soft material.
Fig 3.1 – Examples of phase transitions. (a) first-order phase transitions; potentials such as $G$ are continuous in the transition, but the first derivatives and associated quantities are discontinuous. (b) Second-order phase transitions; the first derivatives of $G$ are continuous, but some second derivatives diverge, for example $C_p$. 
forming a low symmetry phase at a low temperature and a high symmetry phase at a high
temperature.

Such transition is characterized by a change in an order parameter, denoted \( \Omega \),
examples of which include an orientational order parameter for nematic liquid crystals,
which will be discussed in the next section. Figure 3.2 shows temperature dependence of
the order parameter for a first order phase transition where phase transition temperature
\( (T_c) \) changes discontinuously. Landau associated the order parameter with the changes in
symmetry that accompanied a phase transition. The order parameter is a physical quantity
of extensive character which is zero in the most symmetric state or disorder state and
non-zero in the least symmetric state or order state. This notion of order parameter
imposes qualitative meaning, when the temperature decreases, the order of the system
increases (Chaikin & Lubenski, 1995).

The Landau theory was created for second order phase transitions. A second order
phase transition is one where the order parameter changes continuously.

The Landau theory considers changes in the free energy at the phase transition. As
mentioned above, the essential idea of the theory is that under these conditions the free
energy can be expanded as a power series in the order parameter as:

\[
f(\Omega, T) = f_o(T) + A(T)\Omega + B(T)\Omega^2 + C(T)\Omega^3 + D(T)\Omega^4 + \ldots.
\]

Where \( f_o(T) \) is the free energy of the high temperature phase, with respect to
which the free energy is defined. The symmetry of the phases under consideration
imposes constraints on the number of non-zero terms in this expansion.
Figure 3.2 – Temperature dependence of order parameter for the first order phase transition. \( T_c \) – phase transition temperature.
The odd terms in formula (3.1) are equal to zero, then we have:

\[ f(\Omega, T) = f_o(T) + B(T)\Omega^2 + D(T)\Omega^4 + \ldots \]

The order parameter \( \Omega \) is associated with a particular state of the system, the equilibrium value of \( \Omega \) is defined by the minimum free energy.

At the transition \( B(T = T_c) \) must vanish, and the simplest function to satisfy these condition is:

\[ B(T) = b(T - T_c). \]

Although \( D(T) \) varies with temperature, it is usually assumed that this dependence is weak, so that \( D(T) \) can be taken to be constant. The term \( f_o(T) \) is not strongly temperature dependent in the vicinity of the transition. Then the temperature dependence of the free energy is determined only by \( B(T) \). To find the equilibrium states, the minimal value in the free energy is determined by differentiating it with respect to the order parameter and setting this equal to zero. The resulting equation:

\[ 2b (T - T_c)\Omega + 4D\Omega^3 = 0. \]

Below \( T_c \), the solution which has physical meaning is,

\[ \Omega = \pm \left( \frac{b}{2D}\right)^{\frac{1}{2}} (T - T_c)^{\frac{1}{2}}. \quad (3.2) \]

Above \( T_c \), the only real solution is \( \Omega = 0 \). This corresponds to the state with an equilibrium value \( \Omega = 0 \). For temperatures below \( T_c \), \( \Omega = 0 \) corresponds to a maximum in the free energy. The magnitude of the equilibrium order parameter in the low temperature phase therefore decreases with increasing temperature according to the formula (3.2). The critical exponent \( \frac{1}{2} \) for the temperature dependence is characteristic of mean field behavior.
Landau theory provides basic information for understanding soft materials. This theory is important because of its generality in describing, at least qualitative, phase transition in weakly ordered systems (Chaikin & Lubenski, 1995). However, Landau theory has a weakness which is that this theory did not take into account fluctuations interactions. Unfortunately, many soft materials such as liquid crystals are strongly fluctuating especially near the phase transition. Therefore, Landau theory breaks down in the vicinity of the transition.

3.2 Phase Transition in Liquid Crystals

As mentioned above, phase transitions are characterized by symmetry changes, by transformation in orientational and translational ordering in the system. The transition from the isotropic phase of a liquid crystal to an ordered phase (nematic phase) is said to be a symmetry breaking transition because the symmetry at the isotropic phase with full rotational and translational symmetry is broken at low temperatures. Now let us describe the degree of order in liquid crystals. In a liquid crystal, in nematic phase, the anisotropic molecules tend to point along the same direction. The long-range orientational order of the constituent molecules is the defining characteristic of liquid crystals. It is, therefore, important to be able to quantify the degree of orientational order. To do this an orientational order parameter is introduced that describes the average orientation of the molecules. In nematic phases with mirror plane symmetry normal to the director, orientational order is described by the order parameter:

\[ \Omega = \frac{1}{2} < (3 \cos^2 \theta - 1) >. \]
In a system where there is perfect orientation $\Omega = 0$. If all molecules are perfectly aligned $\Omega = 1$ (de Gennes & Prost, 1993). In isotropic phase all orientations are equally probable and $<\cos^2 \Theta> = 1/3$. Therefore, order parameter in isotropic phase is equal to zero.

For liquid crystals although the isotropic-nematic phase transition is a weak first-order phase transition it resembles a variety of pre-transitional phenomena that it might be interpreted to be a second-order transition. It can be modeled by the Landau-de Gennes mean field theory (Chandrasekhar, 1992). According to the mean field theory, the transition temperature from isotropic to nematic phase is an apparent transition temperature. In practical case the isotropic-nematic transition is first order and occurs at an actual transition temperature which is about 1.5°C above the apparent transition temperature.

In this chapter an introduction to phase transitions on liquid crystals was presented. On the following chapter the discussion will be devoted to light scattering in liquid crystals and to the dynamics in liquid crystals, specifically fluctuations of the director orientations.
CHAPTER IV

Light Scattering and Relaxation in Liquid Crystals

4.1 Basic Light Scattering Concepts

Light scattering is recognized as a powerful and useful method of investigation of condense matter. Light scattering is caused by optical inhomogeneities due to fluctuations of physical quantities coupled to refractive index in the material. These inhomogeneities can be either static or dynamic. The intensity of scattered light describes the magnitude of the fluctuations.

In a light scattering experiment a monochromatic polarized laser beam falls on a sample and collected into a detector placed at a scattering angle $\Theta$. Assume that in the light scattering experiment we have a plane electromagnetic wave, then the electric field has the form

$$E (r, t) = E_0 \exp [j (k \cdot r - \omega t)]. \quad (4.1)$$

Here $E_0$ is the amplitude of the electric field, $k$ is the incident wave vector, and $\omega$ is the angular frequency. If the local dielectric tensor $\varepsilon(r,t)$ of the medium is divided into an average and a fluctuation term, one can write:

$$\varepsilon (r, t) = <\varepsilon> + \delta \varepsilon (r, t). \quad (4.2)$$

Where $<\varepsilon>$ is the average value of the dielectric permittivity and $\delta \varepsilon$ is the fluctuating term.

According to Berne and Pecora (2000) it can be shown by classical electrodynamics that the component of the scattered electric field at a large distance $R$ from the scattering volume $V$ and polarization along the unit vector $a$ is:
\[ E_s(t) = \left( E_0 / 4\pi R \right) \exp \left[ i(k_i R - \omega t) \right] \int \exp(iq \cdot r) \left\{ a \cdot (k_f \times k_i) \right\} \delta \varepsilon(r, t) \, dr. \]  \hspace{1cm} (4.3)

The scattering vector \( q \) is defined in terms of the scattering geometry as:

\[ q = k_i - k_f. \]  \hspace{1cm} (4.4)

Where \( k_i \) is the incident wave vector and \( k_f \) is the scattered wave vector.

If we consider light scattering in an isotropic liquid, then these magnitudes are identical which gives,

\[ k_i \cong |k_f| = |k_i|, \]

\[ q = 2k_i \sin(\theta/2) = (4\pi n/\lambda) \sin(\theta/2). \]  \hspace{1cm} (4.5)

The angle between \( k_i \) and \( k_f \) is called the scattering angle \( \Theta \), \( n \) is the refractive index of the medium and \( \lambda \) is the wavelength of the laser beam in vacuum. Due to the optical anisotropy of the liquid crystals, the refractive index depends on the orientation of polarization (Sheffold & Schutenberger, 2003). Figure 4.1 shows a basic scattering geometry, where \( k_i \) is the incident wave vector and \( k_f \) is the scattered wave vector for light polarized. Since the magnitude of the wave vector is related to the refractive index, the wave vectors \( k_i \) and \( k_f \) have different values and it becomes necessary to evaluate the scattering vector \( q \) in each specific case, to be in accordance with formula (4.4).

Introducing the spatial Fourier transform of the dielectric fluctuation, formula (4.3) can be expressed as:

\[ E_s(t) = (k_f^2 E_0 / 4\pi R) \exp[i(k_i R - \omega t)] \delta \varepsilon_{if}(q, t). \]  \hspace{1cm} (4.6)

Then the average intensity of scattered light is obtained by the following formula,

\[ I_s(q) = \langle E_s^* (t) E_s(t) \rangle = (k_f^4 I_0 / 16\pi^2 R^2) \langle \delta \varepsilon_{if}^2(q, t) \rangle. \]  \hspace{1cm} (4.7)
Fig. 4.1 – Light scattering geometry, which demonstrates the wave vectors of incident $k_i$ and scattered $k_f$ light and the scattering vector $q$. 
4.2 Dynamics of Fluctuations of Director Orientations.

The first measurements on light scattering in nematic liquid crystals phases were made by Chatelain in 1948. The experiment showed that the scattering of light was more intense in the nematic phase in comparison to the isotropic phase by a factor of $10^6$ in magnitude. This strong scattering in nematic phase is due to the spontaneous fluctuations of the director orientations (de Gennes & Prost, 1993).

In a nematic liquid crystal the molecules tend to be aligned along a certain direction determined by director ($\mathbf{u}$). However, there are thermal fluctuations of director orientations. The spontaneous orientational fluctuations of director are responsible for the fluctuations in the dielectric tensor. As a result the light that passes through the liquid crystal strongly scatters on these fluctuations (Ho, 2001). In the nematic phase, the contributions from director orientational fluctuations to the intensity of scattered light dominated the contributions associated with the order parameter and density fluctuations. The dynamics of the director fluctuations is probed by dynamic light scattering (de Gennes & Prost, 1993).

De Gennes and Prost (1993) provided a theory to describe fluctuations in alignment, as well as deformations resulting from boundary constrain; it is convenient to use a continuum theory, in which the detailed order on a molecular scale is ignored and the local director ($\mathbf{u}$) is treated as a continuous function of the position ($\mathbf{r}$). Therefore,

$$\mathbf{u}(\mathbf{r},t) = \mathbf{u}_o + \delta \mathbf{u}(\mathbf{r},t).$$  \hspace{1cm} (4.8)

Where $\mathbf{u}_o$ is the equilibrium director and $\delta \mathbf{u}$ is the fluctuation of $\mathbf{u}(\mathbf{r})$ from its equilibrium position. The director fluctuations are related to the three fundamentals types of deformations in nematic liquid crystals: splay, twist and bend. These deformations are ...
shown in figure 4.2. Assuming uniformity in order parameter, the elastic energy of
distortion per unit volume of a nematic liquid crystal $F_d$ according to de Gennes & Prost
(1993), can be written as

$$F_d = \frac{1}{2} K_1 (\nabla \cdot \mathbf{u})^2 + \frac{1}{2} K_2 (\mathbf{u} \cdot \nabla \times \mathbf{u})^2 + \frac{1}{2} K_3 [\mathbf{u} \times (\nabla \times \mathbf{u})]^2. \quad (4.9)$$

Where $K_1$, $K_2$, $K_3$ are the elastic constants. The first $K_1$ is associated with a splay
deformation of the director; $K_2$ is related to a twist deformation and $K_3$ with bend
deformation. These three elastic constants are termed the Frank elastic constants of the
nematic phase which have been calculated by means of extensions of the Onsager
theories (Stephen & Straley, 1974).

The director in a nematic liquid crystal is oriented in the $X – Z$ plane. So we can
conclude that it has two components which will represent as $\delta \mathbf{u}_1$ and $\delta \mathbf{u}_2$ along the $X$ and
$Z$ axis respectively. If we substitute formula (4.8) in formula (4.9) and assume that the
equilibrium director is oriented along the $Z$ axis then we have,

$$F_N = \frac{1}{2} \{K_1(\partial_1 \mathbf{u}_1 + \partial_2 \mathbf{u}_2)^2 + K_2(\partial_2 \mathbf{u}_1 - \partial_1 \mathbf{u}_2)^2 + K_3[(\partial_3 \mathbf{u}_1)^2 + (\partial_3 \mathbf{u}_2)^2]\}, \quad (4.10)$$

where $\partial_a = \partial / \partial X_a$, and 1,2,3 stand for $x,y,z$.

Each component of director fluctuations in the scattering volume $V$ can be written
in terms of its Fourier series like,

$$\delta \mathbf{u}_a(\mathbf{r}) = V^{-1} \sum_q \delta \mathbf{u}_\rho(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{r}). \quad (4.11)$$

Where $\rho = 1, 2, 3$.

Here $\mathbf{q}$ is the scattering vector oriented in the $X – Z$ plane like the director and
therefore is perpendicular to the $Y$ axis. Taking the coordinates for an arbitrary $\mathbf{q}$ in
formula (3.11) and integrating over the scattering volume we can write,

$$\int_V F_N \, d\mathbf{r} = \frac{1}{2} \sum_q (K_1 q_\perp^2 + K_3 q_{ll}^2) \delta \mathbf{u}_1^2(\mathbf{q}) + (K_2 q_\perp^2 + K_3 q_{ll}^2) \delta \mathbf{u}_2^2(\mathbf{q}). \quad (4.12)$$
Here the components of \( \mathbf{q} \) oriented along the X and Z axis are \( q_\perp \) and \( q_\parallel \) respectively. Application of the equipartition theorem of classical statistical physics to formula (4.12) yields the mean square amplitudes of the two director modes for the wave vector \( \mathbf{q} \) (Stephen & Straley, 1974), which are described by the following formulas:

\[
< |\delta n_1(\mathbf{q})|^2 > = \frac{k_B T}{K_1 q_\perp^2 + K_3 q_\parallel^2}, \tag{4.13}
\]

\[
< |\delta n_2(\mathbf{q})|^2 > = \frac{k_B T}{K_2 q_\perp^2 + K_3 q_\parallel^2}. \tag{4.14}
\]

The combinations of elastic constant entering in formulas (4.13) and (4.14) showed that the first mode related to \( \delta \nu_1 \) is a combination of splay and bend, and the second mode associated with \( \delta \nu_2 \) is a combination of twist and bend distortions.

In the case where \( \mathbf{q} \) in the direction of the equilibrium director then the fluctuations associated with bend distortions are present. Formulas (4.13) and (4.14) provide the amplitudes of the director modes which are responsible for the intensity of scattered light. To interpret the frequency spectrum of scattered light it is required to study the dynamics of director orientational fluctuations which relates to the viscosity coefficients. In the liquid crystal phase the motions associated with the translation of molecules are coupled with the orientational motions. To analyze the director orientational dynamics it is necessary to take into account new transport parameters associated with the director field \( \mathbf{u}(\mathbf{r},t) \) in addition to those associated with the velocity field that are used in ordinary liquids. According to the macroscopic approach proposed by Ericksen, Leslie and Parodi cited in Ho (2001) and Stephen and Straley (1974) among all the viscosity coefficients for a homogenous nematic liquid crystal only five are independent.
Fig 4.2 - The three basic types of deformation in liquid crystals: splay, twist and bend.
A simple case is in which a liquid flows in the X direction with a velocity gradient oriented in Y direction. In this case it can be shown that the velocity gradient can align the director at an angle $\Theta$ to the direction of flow. The most commonly viscosity coefficients used are the Miesowicz viscosities $\eta_1, \eta_2, \eta_3$, the Leslie coefficients $\alpha_1, \alpha_2$ and $\alpha_3$. Considering the viscosity constants and Frank elastic constants, relaxation rates for two director fluctuations modes can be written as:

\[
\Gamma_1(\mathbf{q}) = \frac{(K_1 q_\perp^2 + K_3 q_\parallel^2)}{\eta_1(\mathbf{q})},
\]

\[
\Gamma_2(\mathbf{q}) = \frac{(K_2 q_\perp^2 + K_3 q_\parallel^2)}{\eta_2(\mathbf{q})}.
\]

Where $\eta_1(\mathbf{q})$ and $\eta_2(\mathbf{q})$ are the effective viscosities defined as:

\[
\eta_1(\mathbf{q}) = \gamma_1 - \frac{(\alpha_3 q_\perp^2 - \alpha_2 q_\parallel^2)^2}{\eta_2 q_\perp^4 + (\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) q_\perp^2 q_\parallel^2 + \eta_2 q_\parallel^4},
\]

\[
\eta_2(\mathbf{q}) = \frac{\gamma_1 - \alpha_2^2 q_\parallel^2}{(\eta_2 q_\perp^2 + \eta_2 q_\parallel^2)}.
\]

By choosing the corresponding direction of the scattering vector $\mathbf{q}$ and the polarizations relative to the optical axis one can study the individual Frank elastic constants of distortion. Consider the scattering plane normal to the optical axis and the direction is such that the scattering vector $\mathbf{q}$ is perpendicular to the polarization; this is shown in Figure 4.3 (a). Then the formula (4.15) yields to single – mode relaxation rate,

\[
\Gamma_{\text{splay}}(\mathbf{q}) = \frac{K_1 q_\perp^2}{\gamma_1 - \alpha_3^2/\eta_2}.
\]

In a similar manner if the optical axis lies on the scattering plane and $\mathbf{q}$ is chosen to be normal to the optical axis and to the polarization, Figure 4.3 (b), then formula (4.16) leads to a single twist mode relaxation rate,

\[
\Gamma_{\text{twist}}(\mathbf{q}) = \frac{K_2 q_\parallel^2}{\gamma_1}.
\]
In the case that the optical axis lies on the scattering plane and the scattering vector \( \mathbf{q} \) is normal to the polarization and parallel to the optical axis, Figure 4.3 (c), then from formula (4.16) has single bend mode relaxation rate.

\[
\Gamma_{\text{bend}}(\mathbf{q}) = K_3 q^2 / \left( \gamma_1 - \alpha_2^2 / \eta_c \right). \tag{4.21}
\]

In the single elastic constant approximation \((K_1 = K_2 = K_3 = K)\), if we assume that the five viscosity coefficients have the same order of magnitude and are denoted by \(<\eta>\) (where \(<\eta>\) represents the average viscosity) then the relaxation time of director fluctuations is,

\[
\tau = <\eta>/Kq^2. \tag{4.22}
\]

Since in the formula (4.22) the elastic constant and the viscosity coefficient are functions of temperature one can conclude that the variations of relaxation time of director orientational fluctuations with temperature depends on the temperature dependence of the ratio of the viscosity coefficient and the elastic constant.

Fundamental knowledge of the Frank elastic constant is valuable for the development of technologies based on liquid crystals displays. For example, in high resolution liquid crystals displays the ratio of bend to splay elastic constant is required to be small. In chapter six we will turn our attention to the influence of confinement on liquid crystal properties. The fundamental question will be: “What happens with the structure and dynamics of liquid crystals near the solid liquid crystal interface?”
Figure 4.3 - Light scattering geometries for the (a) splay, (b) twist and (c) bend modes.
Chapter V

Experimental Method

5.1 Experimental Details

The measurement of the intensity/intensity autocorrelation functions of scattered light intensity can be done by using a method called photon correlation spectroscopy (PCS). It is sometimes known as dynamic light scattering (DLS) or quasi-elastic light scattering (QELS). It involves measuring the temporal fluctuations of the intensity of scattered light. The number of photons entering a detector are recorded and analyzed by a digital correlator. This technique becomes preferable when the process to be examined has relatively slow relaxation times (~ $10^{-7}$ s or longer). In contrast, optical spectroscopy to examine processes faster than ~ $10^{-7}$ s would require the use of frequency-filtering techniques based on either a diffraction grating (for Raman scattering) or a Febry-Perot interferometer (for Brillouin scattering).

The dynamic light scattering experimental set used in this thesis is presented in Figure 5.1. It has the following components: the laser and optics elements used in the experiment, light scattering cell in thermostat and photon detection system with single mode optical fiber. The computer has the ALV-5000 correlator (This device correlates intensities at any time, operates all devices and evaluates measured data.) and digital temperature controller from Poly science allowing exposure of the sample temperatures from $-10^\circ$C to $+100^\circ$C with $0.05^\circ$C stability and very short settling times.
We are using helium-neon laser from Melle Griot, which has a power of 15 mW and wavelength of 632.8 nm as the source of light for dynamic light scattering experiments. The incident beam is vertically polarized.

The thermostat is a hollow copper cylinder that has an opening in the middle. This allows for a metallic cell to be placed tightly inside. The sample is mounted on a sample holder inside this metallic cell. Both the thermostat and the sample cell have a space so that vertically polarized incident laser light falls on the sample. This allows measuring the scatter light at different angles. To keep the temperature constant inside the cell Silicon oil is circulated through the hollow portion of the thermostat. By controlling the temperature of the liquid around the hollow part of the thermostat and keeping to a minimum heat exchange with the surroundings one can control the temperature of the sample inside the cell. Away of the phase transition temperature the time required to obtain temperature stabilization is about 30 minutes. A digital temperature controller is used to maintain the temperature of the circulating liquid, which is responsible of maintaining the set temperature inside the cell. A temperature probe is placed inside of the sample cell.

The photon detection system consists of a photomultiplier tube, an amplifier discriminator and a single mode optical fiber which allows collecting light scattered from the first coherence zone and gives the best theoretical value for the signal to noise ratio (Dhadwal, Khan, & Suh 1993). The output end of the single mode optical fiber is integrated with the output lens connected to the photomultiplier tube. We are using Thorn EMI photomultiplier tube model QL30FIS/RIF with PM28B power supply.
Experimental Setup

Fig 5.1 – Experimental set up for dynamic light scattering.
The output of the photomultiplier is connected to the ALV amplifier discriminator with a short rigid connector to limit noise due to electronics. In our laboratory we are using ALV-5000/FastE time digital correlator that measures intensity/intensity autocorrelation function.

When fast fluctuations are to be investigated, it is necessary to have the highest temporal solution. The ALV-5000/Fast is designed for this purpose. The device of the board allows an initial sampling time of 12.5 ns.

This makes the ALV-5000 the very efficient correlator for dynamic light scattering experiments.

The intensity-intensity auto correlation function is defined as

\[ g_2(t) = \frac{<I(t)I(t + \Delta t)>}{<I(t)>^2}. \]  

(5.1)

For scattered light that obeys Gaussian statistics, \( g_2(t) \) can be expressed in terms of a square of the normalized electric field auto correlation function \( g_1(t) \), which is related to the properties of the system (Shaumeyer, Briggs, & Gammon, 1993) to be investigated and is defined as,

\[ g_1(t) = \frac{<E^*(t)E(t + \Delta t)>}{<E(t)E^*(t)>}. \]  

(5.2)

Then,

\[ g_2(t) = B + A |g_1(t)|^2. \]  

(5.3)

Here B represents the baseline, A the coherence factor determined by the signal to noise ratio.

5.2 Data Analysis

After obtaining the experimental data the next step is to determine quantitatively physical parameters and understand the nature of the processes. The data is analyzed by
fitting a relaxation function with the intensity-intensity autocorrelation function measured. Fitting the intensity-intensity autocorrelation function provides information on the relaxation time of the system.

We use the Sigma Plot software for the analysis of data. We write the functions with the initial parameters that best provide the description of the results obtained in the experiments. Then we fit the experimental curve with the fitting values provided by the software and compare results. Usually for bulk liquid crystal the fitting has a reliability of 99 percent.

III. Samples

We have investigated the liquid crystal MBBA (4-methoxybenzylidene-4-butylaniline) from Aldrich and it was used as received. Figure 5.2 represents the molecular structure of MBBA. Bulk MBBA has a nematic phase in the temperature range of 23°C to 43°C. To study the effect of randomness and confinement on relaxation of director orientational fluctuations, matrices with thoroughly interconnected and randomly oriented pores of two different sizes (100 nm and 10 nm) were used. We used porous silicate glasses distinguished by their uniform chemical composition, purity and mechanical strength. Before impregnation with liquid crystal, the matrices were heated to eliminate all impurities that it might had.

This was done using the Carbolite eurotherm temperature control oven, model 3216P1. This model is a digital temperature controller which uses proportional integral derivative (PID) algorithms to provide excellent temperature control. This type of control uses a complex mathematical control system to adjust the power being sent to the elements and to hold the oven at the desired temperature.
Fig 5.2 - Molecular structure of MBBA.
This controller can store and run a single program of eight ramp/dwell segments. It can also be used as a simple temperature controller. Using the program features of this oven we use the following program for the annealing of the matrices of 100 nm and 10 nm:

1) Heat at a rate of 2 degrees per minute until 150 °C is reached.
2) Dwell at 150 °C for 20 minutes.
3) Heat at a rate of 5 degrees per minute until 300 °C is reached.
4) Dwell at 300 °C for 30 minutes.
5) Heat at a rate of 5 degrees per minute until 600 °C is reached.
6) Dwell at 600 °C for 120 minutes.

After this program finished, we then move the samples to the Fisher Isotemp Vacuum Oven, model 281A for further sample preparation. We impregnated matrices with liquid crystals at temperature 60 °C. Usually the samples stay in the fisher oven at a temperature of 60 °C under vacuum for at least 24 hours. This enables us to be sure that pores were completely impregnated with liquid crystal.
Chapter VI
Dynamic Light Scattering in Bulk MBBA and MBBA Confined in 10 nm and 100 nm Random Pores

6.1 Dynamic Light Scattering in Bulk MBBA

Define $\delta n$ as the fluctuations in refractive index; the intensity of scattered light can be expressed as:

$$I_{sc} \propto (\delta n)^2. \quad (6.1)$$

Since $\delta n$ means the deviation of refractive index $n$ from its equilibrium value $n_0$, we have:

$$n(t) = n_0 + \delta n(t). \quad (6.2)$$

As mentioned earlier, dynamic light scattering experiments measure the intensity-intensity autocorrelation function which contains information about the dynamics of refractive index fluctuations. In the nematic phase of a liquid crystal light is scattered due to director orientational fluctuations, order parameter fluctuations, and density fluctuations. The intensity of scattered light due to director fluctuations is stronger by many orders of magnitude that the ones associated with order parameter and density fluctuations. Therefore, in nematic phase, the contributions of density and order parameter fluctuations can be neglected. Normally the scattered light in nematic phase is approximately $10^6$ stronger than in isotropic phase.

We have investigated the dynamics of director orientational fluctuations in bulk MBBA and confined MBBA in 100 nm and 10 nm random pores. Figure 6.1 shows the intensity-intensity autocorrelation function and its fitting for MBBA bulk liquid crystal at a temperature of 300.7 K in nematic phase. The contrast of the autocorrelation function is
99.2% which is a value close to the theoretical limit of 100%. The autocorrelation function shown in Figure 6.1 was fitted with single stretched exponential decay function. This function has the following form:

\[ g_1(t) = A \cdot \exp\{-t/\tau\}^\beta \]. \quad (6.3)

A is the amplitude of the function, \( \tau \) is the relaxation time of the process, and \( \beta \) is a parameter which determines the degree of stretching. This stretching in the decay function is present because we used multidomain sample of MBBA. Figure 6.2 shows the intensity-intensity autocorrelation functions for two different temperatures (\( T = 314.0 \) K, \( T = 299.0 \) K) of MBBA in nematic phase. From the Figure 6.2 we see a shift of \( \tau \) for the autocorrelation functions on time scale with temperature. This shows that with the decrease in temperature the process becomes slower; therefore, the values of the relaxation time should increase. Table 6.1 shows the fitting parameters obtained for these two temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>A</th>
<th>( \tau ) (ms)</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>314.0</td>
<td>0.999</td>
<td>0.0781</td>
<td>0.62</td>
</tr>
<tr>
<td>299.0</td>
<td>0.994</td>
<td>0.1364</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Figure 6.3 shows the temperature dependence of relaxation time (\( \tau \)) for director orientational fluctuations of bulk MBBA in nematic phase. The variation of relaxation time with temperature observed in Figure 6.2 can be explained by the functional dependence of \( \tau \) on viscosity (\( \eta \)), elastic constant (K). This is described by the formula (3.22).
Figure 6.1 – Intensity-Intensity autocorrelation function for bulk MBBA in nematic phase at a temperature of 300.7 K. Symbols - experimental data, solid line – fitting.
Figure 6.2 – Intensity-Intensity autocorrelations function for bulk MBBA in nematic phase at different temperatures.
Very close to the isotropic-nematic transition there is a small increase in relaxation time with temperature, due to the fact that in this region the elastic constant (K) approaches zero and viscosity (η) is finite. However away from the phase transition the relaxation time for bulk MBBA decreases with temperature.

6.2 Dynamic Light Scattering in MBBA Confined to 100 nm Random Pores

Liquid crystals behave differently in confinement. The surface effects are pronounced for confined liquid crystals because of developed area of pore wall (Aliev, 1995). Due to the large pore size of the matrix, it was expected that some bulk-like properties would be observed in confined MBBA in 100 nm random pores.

Figure 6.4 shows the intensity-intensity autocorrelation function in nematic phase of MBBA in 100 nm random pores at a temperature of 300.3 K. If we fit this autocorrelation function with single stretched exponential decay function, as we did with MBBA bulk, data analysis shows that single stretched exponential function does not describe the experimental data. This is illustrated in the inset of Figure 6.4.

Therefore, the autocorrelation functions for MBBA in 100 nm at all temperatures were fitted with the superposition of two stretched exponential decay functions which has the following form:

\[ g_1(t) = A \cdot \exp\left[-(t/\tau_1)^{\beta_1}\right] + (1-A) \exp\left[-(t/\tau_2)^{\beta_2}\right] \]  \hspace{1cm} (6.4)

Fitting with this decay function is shown in Figure 6.5

The first relaxation time \( \tau_1 \) characterizes the first fast relaxation process; \( \tau_2 \) describes the second slow relaxation process. The first relaxation was similar to the relaxation to director orientational fluctuations in bulk MBBA and had the same physical
Figure 6.3 – Temperature dependence of relaxation times due to director orientational fluctuations of bulk MBBA in nematic phase.
origin. However this first fast decay is faster than the decay seen in bulk phase for this temperature.

This is shown in Figure 6.6. This can be due to multiple scattering present for MBBA confined in 100 nm random pores. This multiple scattering is due to the fact that in this sample there was mismatch of refractive indexes of liquid crystal and matrix material, which caused strong light scattering. The second slow relaxation process can be attributed to the relaxation of fluctuations of director orientations at pore wall – liquid crystal interface. Figure 6.7 shows three autocorrelation functions for confined MBBA in 100 nm random pores.

Relaxation processes for MBBA confined in 100 nm random pores were not frozen below the temperature of crystallization of bulk MBBA (296 K). Table 6.2 shows the fitting parameters of the three autocorrelation functions shown in Figure 6.7 at three different temperatures.

Table 6.2

<table>
<thead>
<tr>
<th>T (K)</th>
<th>A₁</th>
<th>τ₁ (ms)</th>
<th>β₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.0</td>
<td>0.65</td>
<td>0.0126</td>
<td>0.85</td>
</tr>
<tr>
<td>288.3</td>
<td>0.47</td>
<td>0.0156</td>
<td>0.87</td>
</tr>
<tr>
<td>278.8</td>
<td>0.58</td>
<td>0.0293</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Figure 6.4 – Intensity – Intensity autocorrelation function of MBBA confined in 100 nm random pores in nematic phase. Symbols - experimental data, solid line - fitting with single stretched exponential function.
Figure 6.5 – Intensity-Intensity autocorrelation function of MBBA confined in 100 nm random pores in nematic phase. Symbols - experimental data, solid line - fitting with superposition of two stretched exponential functions.
Figure 6.6 - Intensity-intensity autocorrelation functions for bulk MBBA and confined MBBA in 100 nm random pores at nematic phase. The temperature is 300.5 K
Figure 6.7 – Intensity-Intensity autocorrelation functions of MBBA confined in 100 nm random pores at different temperatures in nematic phase.
The temperature dependence of relaxation time ($\tau_1$) related to the bulk-like reorientational dynamics of director for confined MBBA in 100 nm pores is presented in Figure 6.8. Data analysis leads to the conclusion that in temperature range from $T = 293.0$ K to $288.3$ K $\tau_1$ depends on temperature as the ratio $\eta / K$. There was an increase of $\tau_1$ for $T = 278.8$ K in comparison with the previous temperatures, and it can be related to the fact that well below the crystallization temperature of MBBA (296 K) the viscosity of MBBA increases more rapidly than the elastic constant.

In Figure 6.9 the temperature dependence associated with the second slow relaxation processes ($\tau_2$) is shown. As mentioned above, because this second process is related to director dynamics in surface layers at solid pore wall - liquid crystal interface, the amplitude of the process is small. Therefore, it is difficult to obtain more precise information about temperature dependence of ($\tau_2$).

### 6.3 Dynamic Light Scattering in MBBA Confined to 10 nm Random Pores

Now we will show results of the dynamical behavior of MBBA confined in 10 nm random pores. The autocorrelation function for MBBA confined in 10 nm at $T = 300.5$ K is presented in Figure 6.10. This figure illustrates the influence of confinement in narrow pores on director relaxation. It should be mentioned that for this confined sample we observed a single very slow and extremely broad relaxation process which is absent in the bulk phase. This decay is highly non-exponential in contrast with bulk. The fitting function used to describe this relaxation process is known as activated dynamics which has the following form (Aliev & Sinha 1997; Wu, Goldberg, Liu & Xue, 1992),

$$g_1(t) = A \cdot \exp[-\left\{\ln(t/\tau_0)/\ln (\tau/\tau_0)\right\}^2]. \quad (6.5)$$
Figure 6.8 – Temperature dependence of the first relaxation time ($\tau_1$) due to bulk-like director orientational fluctuations of MBBA confined in 100 nm random pores.
Figure 6.9 - Temperature dependence of the second slow relaxation time process ($\tau_2$) due to surface effects of MBBA confined in 100 nm random pores.
Figure 6.10 - Intensity-Intensity autocorrelation function of MBBA confined in 10 nm random pores in nematic phase. Symbols - experimental data, solid line - fitting.
For our purpose $\tau_0 = 10^{-8}$ s and $z = 2$ provides a suitable fitting for confined MBBA in 10 nm random pores. The origin of this glass like decay could be related to director dynamics in surface layers formed at solid pore wall – liquid crystal interface. The relaxation time of the slow process for MBBA in 10 nm random pores strongly increases with temperature decrease from 299 K up to 284 K.

The autocorrelation functions for MBBA in 10 nm random pores corresponding to the following temperatures $T = 299.05$ K, $T = 291.30$ K and $T = 284.64$ K are presented in Figure 6.11. The relaxation times obtained from the fitting of these three functions are presented in Table 6.3 which demonstrates the drastic slowing down of relaxation processes with decrease in temperature. The temperature dependence of relaxation times for confined MBBA in 10 nm random pores is shown in Figure 6.12. This graph confirms the increase in relaxation time as the temperature decreases.

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|}
\hline
$T$ (K) & $\tau$ (ms) \\
\hline
299.05 & 0.01 \\
291.30 & 3.2 \\
284.64 & 310.3 \\
\hline
\end{tabular}
\end{table}

A comparison of the dynamical behavior of bulk MBBA and confined MBBA in 10 nm random pores is shown in Figure 6.13. In small pores the volume fraction of the molecules in core region of the pore is very small; therefore, the bulk properties are weak and the contribution due to this relaxation process is negligibly small compared to the amplitude of the slow decay.
Figure 6.11 – Normalized intensity-intensity autocorrelation functions of MBBA confined in 10 nm random pores at different temperatures in nematic phase.
Figure 6.12 – Temperature dependence of the relaxation times of MBBA confined in 10 nm random pores.
Figure 6.13 – Intensity-intensity autocorrelation functions for bulk MBBA and MBBA confined in 10 nm random pores in nematic phase. The temperature is 300.6 K
Chapter VII

Conclusions

In this investigation the influence of confinement on the relaxation of fluctuations of director orientations of a liquid crystal (MBBA) were studied by dynamic light scattering. The following conclusions are made from the present studies:

1. Samples of nematic liquid crystal (MBBA) confined in random porous were prepared.
2. Relaxation of fluctuations of director orientations at different temperatures was investigated for bulk nematic liquid crystal and confined in random pores of two pore sizes: 10 nm and 100 nm.
3. Dynamic Light Scattering Experiments showed that two relaxation processes (fast and slow) were observed for confined MBBA in 100 nm random pores. The first relaxation process was associated with bulk like director orientational fluctuations. The second slow relaxation process was caused by relaxation of director orientational fluctuations in surface layers of liquid crystal formed at liquid crystal – pore wall interface.
4. Away from the isotropic-nematic transition, the temperature dependence of relaxation time of director orientational fluctuations for bulk MBBA and the first relaxation time for MBBA confined in 100 nm random pores was determined by temperature dependence of viscosity to elastic constant ratio $[\eta (T)/K (T)]$.
5. For MBBA confined in 10 nm random pores a single and very slow relaxation process, which is absent in the bulk phase, was present. The origin of this slow
decay could be related to director dynamics near surface layers of the liquid crystal interface.

6. The influence of confinement on relaxation process was pore size dependent, and it was much stronger for smaller pores.

7. Confinement results in supercooling of liquid crystal and relaxation processes were not frozen below the bulk crystallization temperature.

8. Glass like behavior (broad spectrum) of relaxation time of director orientational fluctuations was observed for MBBA confined in 10 nm random pores.

9. The temperature dependence of relaxation time of MBBA confined in 10 nm random pores shows that with the decrease in temperature there is a strong increase in relaxation time. This relaxation time is strongly influenced by surface of the pore wall – liquid crystal interface.
References


