Chapter 1

Introduction

This chapter describes the fundamental difference between equilibrium and non-equilibrium thermodynamics and related phase transition properties, important aspects of non-equilibrium thermodynamics and their applications, concept of mixtures and its connection with non-equilibrium phase transition, possibility of finding non-equilibrium phases in nematic liquid crystals and some of the open and unresolved problems regarding the Nematic-Isotropic phase transition in liquid crystals.
1.1 Equilibrium Thermodynamics

Mechanics, either classical or quantum, deals primarily with single objects, the simplest of which is a particle. The ‘state’ of such an object is characterized by certain measurable physical quantities. Some of these are intrinsic such as mass, charge, moment of inertia, dipole and quadrupole moment, etc. While others, such as generalized coordinate and generalized momenta, define the dynamical state of the object. However, if we have to deal with systems composed of a semi-infinite number of interacting objects, a description of the dynamical state of the system requires complete knowledge of the dynamical state of each of the objects, while we may only be interested in the transaction of energy and other average measurable properties.

Thermodynamics has developed as a section of macroscopic physics to describe the transformations of energy in all its forms. It is a generalization of mechanics by introducing three new concepts:

- The concept of state, i.e., an ensemble of quantities, called state variables, whose knowledge allows us to identify any property of the system under study. It is desirable that the state variables are independent and easily accessible to experiments. For example, a motionless fluid may be described by its mass $m$, volume $V$, and temperature $T$.

- The notion of internal energy, complementing the notion of kinetic energy, which is of pure mechanical origin. Internal energy is not a directly measurable quantity: there exist no “energy meter”. It is presumed to be some function of the measurable properties of a system like mass, volume, and temperature. It can be viewed as the mean value of the sum of the kinetic and potential energies of interaction of the particles.

- The notion of entropy. Like internal energy, it is a characteristic of the system that we cannot measure directly, but merely can measure its changes. From
a microscopic point of view, the notion of entropy is related to disorder: the higher the entropy, the larger the disorder inside the system.

With time the subject of thermodynamics has been recognized as *equilibrium thermodynamics*, a branch of physics, which studies the equilibrium properties of bulk matter using macroscopic variables. It has contributed much to the understanding of a variety of physical phenomena. The strength of the discipline is its ability to derive general relationships based upon a few fundamental postulates and a relatively small amount of empirical information without the need to investigate microscopic structure on the atomic scale. Equilibrium thermodynamics is based on some variational principle (maximization of entropy or minimization of free-energy), such that if we know the free-energy of the system then we are able to predict all the properties of its, in general, unique equilibrium state[1]. The most general and conceptually amenable definition of an equilibrium state is that where the macroscopic measurable physical quantities defining the state do not change with time explicitly. Equilibrium thermodynamics has also been applied to the description of reversible processes: a special class of idealized processes considered as a continuous sequence of equilibrium states.

### 1.1.1 Phases and Phase Transitions:

As mentioned earlier, the state of a system is defined by an ensemble of quantities, called state variables, characterizing the system. The equilibrium state is ideally a state that is time independent and spatially homogeneous in the values of the variables thus being redundant of the fluxes of matter and energy. The selection of the state variables is not a trivial task and to a certain extent it is arbitrary and non-unique, depending on the level of description, either microscopic or macroscopic, and the degree of accuracy that is required. Also this concept of equilibrium does not account for presence of the fluctuation inherent to each equilibrium state and depends
also widely on the available data and degree of accuracy of our observations. Another definition of equilibrium can be made in the light of entropy. For example, equilibrium of an isolated system is characterized by the maximization of the entropy. In general, a macroscopic system has more than one equilibrium state and each of these states is called a “phase” of the system and the most convenient way to study phases is to consider a system evolving between two phases, A and B, where by definition, the state variables will not depend on the particular way taken to go from A to B. While studying phase transitions, two different situations come up: transitions (1) at or near thermodynamic equilibrium and (2) far from thermodynamic equilibrium. Phase transitions near equilibrium were initially described by thermodynamics and then were interpreted by statistical mechanics. To describe these transitions, Landau introduced the concept of order parameter to construct the free energy of the system and used the extrema of this free energy to find the phases or possible equilibrium states and the order of the transitions. However, Landau’s theory does not take into account the local fields and fluctuations around the objects in the system. These dominate near the phase transition point and the theoretical understanding of phase transitions near equilibrium is finally accomplished in the frame of renormalization group[2, 3]. If the system is near or close to equilibrium, on certain scales the concepts of equilibrium physics can still work and these systems can be treated using the so-called local equilibrium approximation[4].

1.1.2 Non-Equilibrium Thermodynamics

A system that is neither simply isolated from the rest of the universe, nor in contact with a constant temperature, and/or chemical potential bath, will be in non-equilibrium. A system that is in the transient state before reaching equilibrium is also non-equilibrium, e.g. a plasma with a non-Maxwellian velocity distribution.

The study of non-equilibrium phase transitions is an intriguing field for both ba-
sic scientific interests and potential technical application. Although the features of equilibrium phenomena are relatively easier to understand and have been extensively studied, yet biological systems and many physical systems exist in nature essentially at non-equilibrium states and true equilibrium phenomenon is rather an ideal concept. In contrast to phase transitions at thermal equilibrium which have been well studied to a large extent, especially under the frame of renormalization group methods[2, 3], phase transitions out of equilibrium is far less understood, lacking a generalized theory. Although some concepts in the modern theory of equilibrium phase transitions, like “universality”, are so successful that we believe we can apply them to non-equilibrium phase transitions, new physics could be expected to emerge.

Besides basic scientific interests, the study of non-equilibrium phase transitions can inspire and has inspired new methods in materials manufacturing and processing and other interesting methods in nano technology as it has done, like pattern formation[5], non equilibrium structures of monomolecular organic films[6], beam-induced transformations and many others[7]. In fact, new steady states belonging to the system driven out of equilibrium can exhibit intriguing or complex structures and hence may have novel properties or enhanced properties than those at equilibrium. While these new steady states and structures of a system are by themselves exciting, theoretical understanding of phase transitions out of equilibrium can also help clarify the control parameters and the underlying mechanism and hence can improve and develop hitherto unknown manufacturing methods. Self-assembly or self-organization are both crucially important topics in nanotechnology [8–12] but we need to understand the basic difference between them. According to John and Bar[13], self-organization is a phenomenon far away from thermal equilibrium while self-assembly occurs near equilibrium. Again, the diversity of shapes and forms (including living forms) in nature certainly could not be explained by equilibrium thermodynamics, and non-equilibrium thermodynamics opens up some new ways of explanation for
these phenomena. In nonequilibrium thermodynamics, history or time evolution of a process assumes importance, leading the system to a variety of states different from equilibrium states, as energy is continuously pumped into it. When the input of energy ceases, the system evolves to its equilibrium state, which is the state of death for living forms. The study of non-equilibrium phase transitions can even benefit the study of some social events, like traffic problems and population models[14].

There is nothing like a general variational principle for non-equilibrium thermodynamics. We cannot say in general that the time evolution or steady-states of non-equilibrium systems are determined by some principle like minimum dissipation of energy, or other like maximum production of entropy, though they may work in some special cases. Therefore, the usual approach to study non-equilibrium systems is to consider each case and look for some universal behaviour. Here, universal behaviour means that the time evolution and steady-states of several different real systems can be grouped and described by solutions of a particular, usually phenomenological, non-linear partial differential equation usually referred to as master equation[15].

A dynamic system can be treated as an out-of-equilibrium system in general if the principle of detailed balance is violated. The classification of systems far from equilibrium is more fundamental. According to Odor, nonequilibrium can be classified into two categories. (1)systems that have a Hermitian Hamiltonian and whose stationary states are given by the proper Gibbs-Boltzmann distribution; (2)systems without a Hermitian Hamiltonian defined by transition rates, which do not satisfy the detailed balance condition. The second class has two subclasses. One has no equilibrium counterpart, hence being called “genuine nonequilibrium systems”, while the other is refer to as “out-of-equilibrium systems”. Odors classification is consistent with that given by Marro and Dicjman[16]. According to them, non equilibrium problems can be group in three broad categories. The first category is the same as the first class of Odors definition. The system is initially prepared far from the stationary state
and then approaches equilibrium state. However sometimes it may not reach a true equilibrium. Many systems, like phase ordering systems, glasses and spin glasses belong to this class. The second category which is driven far from equilibrium roughly corresponds to the out-of-equilibrium class defined by Odor. The difference is that systems belonging to out-of-equilibrium class may not have a steady state. The rest of the non-equilibrium systems have no equilibrium analogue and hence are termed as genuine non-equilibrium systems by Odor.

1.1.3 Concept of Mixtures and its connection with Non-Equilibrium phase transition

A mixture can be looked upon as a generalization of pure substance since it brings in new processes such as diffusion\cite{17}, coalescence\cite{18}, segregation\cite{19} and stability under segregation and new quantities such as concentration, entropy of mixing\cite{20} and forces of adhesion\cite{21} as contrasted to forces of cohesion. As a result, the phase space of mixtures is much richer and their structures and dynamics are much more complex and intriguing. Mixtures also provide the concept of interface or boundary separating two phases of matter, each of which may be solid, liquid, or gaseous. An interface in real world is not a geometric surface but a layer that has properties differing from those of the bulk material on either side of it. A common interface is that between a body of water and the air, which exhibits such properties as surface tension, which makes the interface act somewhat like a stretched elastic membrane. Interfacial effects, or processes that occur at interfaces, include the evaporation of liquids, the action of detergents and chemical catalysts, and the adsorption of gases on metals. What is more important to note is that any mixture has a zone of instability in its phase space, which gives rise to the interface between its components through a non-equilibrium process. Non-equilibrium thermodynamics thus finds application for mixtures of liquids in general. This is particularly relevant for mixtures of fluids
as even for a one component fluid, using linear constitutive relations for the currents, non-equilibrium theories like the Navier-Stokes equation\[22\] and a generalization of Fourier’s equation\[23\] is required for the fluid velocity field and temperature respectively. These equations have to be supplemented, however, by boundary conditions. If the boundary is the surface between two immiscible fluids, for instance, the boundary conditions themselves may contain new phenomenological coefficients. Waldmann was the first to point out that an analysis of the boundary conditions should be incorporated within the framework of non-equilibrium thermodynamics\[24, 25\].

The theory of mixtures postulates that each point in space is simultaneously occupied by a finite number of particles, one for each component of the mixture\[26\]. In this way, the mixture may be represented as a superposition of continuous media, each following its own movement with the restriction imposed by the interaction between components. This means that each component will obey the laws of conservation of mass and momentum, incorporating terms to account for the interchange of mass and momentum between components. To obtain a rational theory, we must require that the properties of the mixture follow the same laws as a body of a single component, that is, that the mixture behaves as a single component body.

### 1.2 Liquid Crystals: Definitions, Properties and Types

Solid/crystalline materials are characterized by long range periodic order in three dimension, whereas an isotropic liquid is defined by the state of matter where the molecular properties are the same regardless of the position or direction of measurement since all positions and directions in liquid are indistinguishable. By definition, liquid crystals are the thermodynamically stable phase of some compounds characterized by anisotropy of properties but without the existence of a three-dimensional crystal
lattice, generally lying in the temperature range between the solid and isotropic li-
quid phase and strong orientational dependence or anisotropy of properties[27]. Thus,
liquid has no orientational as well as no positional ordering. By definition, liquid
crystals are those systems where a liquid like order exists at least in one direction of
space and in which some degree of anisotropy is present. The features of solid, liquid
and liquid crystal can be distinguished in a more generalized manner by understand-
ing the degree of anisotropy of these materials through density-density correlation
function as described below:

- If a pattern of atoms or molecules of a crystal is located at a point \( x_0 \) in space,
  the probability of finding the same pattern at another point \( x \) is guided by a
  periodic function of position. This pattern is called the basis. In such case
  density-density correlation function is

  \[
  \lim_{|x-x'| \to \infty} < \rho(x)\rho(x') > = F(x-x') \tag{1.1}
  \]

- In case of liquid, if some pattern is located at a given point \( x_0 \), there is just no
  way to express the probability of finding a similar one at the point \( x \) far from
  \( x_0 \), except through the average particle density \( \bar{\rho} \). In other words,

  \[
  \lim_{|x-x'| \to \infty} < \rho(x)\rho(x') > \simeq \bar{\rho}^2 \tag{1.2}
  \]

- In case of liquid crystals, unlike in crystals, the density-density correlation func-
tion does not depend solely on the modulus of \( |x-x'| \), but also on the orientation
  of \( x - x' \) with respect to the macroscopically defined axes.

Liquid crystals are intermediate phases between the solid and liquid possessing
some typical properties of a liquid (such as fluidity, inability to support shear, for-
mation and coalescence of droplets) as well as some crystalline properties (such as

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Introduction
anisotropy in optical, electrical, and magnetic properties, periodic arrangement of molecules in one spatial direction, different viscosities in different directions etc.).

Certain structural features are often found in molecules forming liquid crystal phases, and they may be summarized as follows:

- The molecules have anisotropic shape (either rod-like or disc-like). Liquid crystallinity is more likely to occur if the molecules have flat segments, e. g. benzene rings.

- A fairly rigid backbone containing double bonds defines the long axis of the molecule.

- The existence of strong dipoles and easily polarizable groups in the molecule is important.

- The groups attached to the extremities of the molecules are generally of lesser importance.

The tendency of the liquid crystal molecules to point along a particular direction in space, called the director, leads to the anisotropy. The following parameters describe the liquid crystal phases:

- **Orientational Order**: Measure of the tendency of the molecules to align along the director on a long-range basis.

- **Positional order**: The extent to which the position of an average molecule or group of molecules shows translational periodicity.

- **Bond orientational order**: Describes a line joining the centers of nearest-neighbour molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line may be observed.
Depending on the degree of molecular anisotropy or the average number of molecular alignment with respect to the director, different liquid crystalline phases (called `mesophases`) can appear. These mesophases can broadly categorized into three distinct classes:

- **Nematic Phase:** The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (orientationally ordered). It should be mentioned that nematic ordering is achieved when more than 40% of the molecules are oriented along the director.

- **Smectic Phase:** Molecules in this phase show a degree of translational order not present in the nematic. In the smectic phase, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more “solid-like” than the nematic. This describes one dimensional order in three dimensions and can be viewed as two dimensional liquid layers stacked on each other with a well defined spacing.

- **Columnar Phase:** Columnar liquid crystals are different from the previous types because they are shaped like discs instead of long rods. This mesophase is characterized by stacked columns of molecules but the gap between the discs in a stack can change freely while it remains a liquid along the column. The columns are packed together to form a two-dimensional crystalline array. The arrangement of the molecules within the columns and the arrangement of the columns themselves leads to new mesophases.

Thus depending on the class/phase of liquid crystals, varieties of phase transition can occur within the liquid crystalline substances such as **Crystalline-Smectic**, **Smectic-Nematic** and **Nematic-Isotropic**. Apart from that, glass transitions...
can also occur in some specialized glass forming liquid crystalline substance. Generally, Smectic-Nematic and Nematic-Isotropic phase transition occur between room temperature and within 100°C and thus are easier to probe. In liquid crystals which are inherently Smectic in nature, smectic phase precedes the nematic phase as the temperature is raised. Each of these phase transitions are manifested with distinct types of symmetry breaking, either positional or orientational. For example, in case of Smectic-Nematic transition, only positional ordering will break and in Nematic-Isotropic transition, orientational ordering will break.

Liquid crystals which have solely nematic ordering (lack of smectic ordering) can exhibit rich varieties of complex phenomena in phase transitions. The properties of the nematic liquid crystals are governed by a second rank, traceless quadrupolar moment tensor $Q_{ij}[28]$ defined by

$$Q_{ij} = \frac{1}{2} S (3\hat{n}_i\hat{n}_j - \delta_{ij})$$

(1.3)

where, $S$ is the scalar order parameter and $n_i, n_j$ contains information about the average molecular alignment. The scalar order parameter ($S$) is given by the equation

$$S = \frac{1}{2} < 3\cos^2 \theta - 1 >$$

(1.4)

where $\theta$ is the angle between the director and the long axis of each molecule. The brackets denote an average over all of the molecules in the sample. The nematic phase occurs when $S \geq 0.4$. In these materials enthalpic forces of cohesion are weak relative to the entropic forces, given by $T\Delta S/\Delta x$, where $\Delta S$ is the reduction of configurational entropy due to bringing the molecule close together.
1.3 Nematic-Isotropic phase transitions- some open questions

The N-I transition in liquid crystals is most widely studied and research on the N-I transition has been continuous over the past few decades[29–34], it is surprising that there are still no clear answers to some key questions concerning the nature of this phenomenon. Earlier studies include the phenomenological model of deGennes[35, 36] and the Hamiltonian approach of Maier-Saupe[37]. Yet, despite these and many subsequent efforts, there remain quite a few questions regarding the N-I transition that are not completely resolved. First of all, N-I phase transition is considered to be a weakly first order phase transition but the obvious question is what makes it so. Earlier studies reveal that director fluctuations as well as density fluctuations play important roles to determine the weakly first order nature of the transition[38, 39]. Experimental results from high precision measurements of specific heat near the N-I phase transition of the molecule with I have worked namely MBBA (N-(4-methoxybenzylidne)-4-butylaniline) show that the behaviour of this transition is near tricritical and does not appear to agree with the Landau-deGennes model. The results of early investigations (Mayer et al 1972[40], Sorai et al 1974[41], Anisimov et al 1979[42]) of the heat capacity anomaly near the N-I transition were so contradictory that sometimes they did not allow even a qualitative interpretation. Anisimov et al (1977) measured the temperature dependence of the specific heat for MBBA near the N-I transition which showed that the fluctuations of the order parameter are not small at the phase transition point indicating features of a continuous phase transition. Concerning the specific heat phenomena, Anisimov et al (1977, 1979)[42, 43] gave a strong argument in favour of the tricritical hypothesis, fitting their data from very precise specific heat measurements on MBBA and other compounds. Recent studies by Rzoska et al[44] give an adequate description of the pre-transitional ef-
fecteds near the N-I transition. Furthermore, their studies on the pressure dependence of the clearing temperature and the low-frequency nonlinear dielectric effect in the isotropic phase of MBBA strongly support the above theoretical analysis. Their experimental results show the close relationship between the pretransitional behaviour in the isotropic phase of nematogens and that in the homogeneous phase of critical solutions. This pretransitional phenomena near the first-order phase transitions can reveal the physical reasons for their closeness to the second order[39].

However the most important questions which have not been addressed by any of these authors are that regarding the driving force of the N-I transition (whether it is entropic/enthalpic) and that whether this phase transition exhibit equilibrium/non-equilibrium behaviour in nature. The theoretical models as well as some of the experimental results discussed above raise a high doubt above the equilibrium behaviour.

1.4 Possibility of finding non-equilibrium phases in Room Temperature Nematic Liquid Crystals:

One way of addressing this question is to notice that phase transitions of liquid crystals, especially the Nematic-Isotropic (N-I) phase transition, is unique as it is governed by a continuously variable quadrupole moment second rank tensor which is the measurable order parameter in N-I phase transition. As is generally true of second rank tensors, it is a function of two molecular orientations shown in Eqn. 1.4 and thus can easily be tuned by applying external perturbing force and thus is highly dependent on history. Several theoretical models have been put forward by various researchers which point towards the fact that the N-I phase transition is guided by the entropic rather than enthalpic forces. This history dependence of N-I phase transition on the entropic force is ultimately related to the non-equilibrium behaviour.
1.4. Possibility of finding non-equilibrium phases in Room Temperature Nematic Liquid Crystals:

of this transition. The well-known theoretical models all point towards the entropic origin of the N-I transition. The statistical mean field theory by Onsager assumes that N-I transition originates from effective repulsion of the molecules, which connect entropy with excluded volume. It proposes that the increase in translational entropy with decreasing excluded volume is the probable origin for the N-I transition which thus bears an entropic origin. The phenomenological model proposed by Landau-deGennes also predicts a temperature range between the isotropic and nematic phase where these two phases can grow at the expense of each other which gives rise to the dynamic nature of the nematic-isotropic interface. Theoretical study of the dynamic nematic-isotropic interface was done by De Mesquita which incorporates a spatially varying order parameter in the original Landau-deGennes theorem and verifies that N-I transition is indeed a non-equilibrium transition.

If the N-I transition is indeed non-equilibrium in nature the question then arises regarding the probable origin of this non-equilibrium behaviour. According to Tolman's interpretation[45, 46]regarding transitions in molecular systems, any change in molecular conformation changes the conformational entropy and this conformational entropy can give rise to the non-equilibrium nature of the transition. For liquid crystalline molecules with two benzene rings connected by a bond, the plausible source of the conformational changes is the dihedral angle between the rings. With increase in temperature this angle also increases and the ring co-planarity is destroyed through disorientation of the benzene rings as they can undergo large amplitude motion which also destroys the quadrupolar axis making the quadrupole go from linear to non-linear and thus increasing the number of molecular states corresponding to the same value of the quadrupolar order parameter. This large amplitude motion increases the cross-sectional area of the molecule which allows higher levels of out-of-plane distortions of the rings. The ultimate outcome is the net increase in the conformational states available to the molecule and thus increase in the conformational entropy. This in-
crease in the conformational entropy will lead to the non-equilibrium behaviour in the transitions in the nematic liquid crystal.

1.5 Outline

This dissertation is focussed on addressing some of these questions regarding the nature of the nematic-isotropic phase transition of a liquid crystal, where only the nematic ordering exists at room temperature. I have chosen a typical organic molecule MBBA[N-(4-methoxybenzylidene)-4-butylaniline] as a model compound for my experiment as this compound has a convenient nematic range which is from room temperature to just above the room temperature (292-318 K), has a simple molecular structure and is the most widely studied nematic liquid crystal compound. My primary object is to understand whether the N-I transition of this typical nematic liquid crystalline molecule possesses an entropic or an enthalpic activation barrier. The best possible way to understand this is to measure any physical property of a material as a function of temperature, extract the Arrhenius plot, and from the nature of the plot determine whether the transition of interest contains an enthalpic activation barrier (fixed activation barrier which does not change with temperature) or an entropic activation barrier (activation barrier which changes with temperature). If the slope of the Arrhenius plot is linear, it can be regarded as activated type phase transition, i.e phase transition of constant activation energy and can be considered to be an equilibrium phase transition. Such situations appear where the system dynamics is related to crossing of an activation barrier much larger than the ambient temperature and in overwhelming majority of cases this plot exhibits Arrhenius feature. On the contrary, if the slope of the Arrhenius plot vary in no-linear fashion with temperature, then the activation energy is no longer constant and varies with temperature. The phase transitions where this type of conditions appear are considered as non-Arrhenius phase transitions and both convex and concave Arrhenius features are observed in these
cases. Non-Arrhenicity is subjected to the system dynamics crossing of an activation barrier which is comparable or even lower at room temperature. If the activation barrier is sufficiently low, it may not correspond to a minima of the free energy but rather to a saddle point and thus to non-equilibrium behaviour. I have dealt with the N-I phase transition and glass transition of MBBA from macroscopic and microscopic points of view using Differential Scanning Calorimetry (DSC) and Infrared and Uv-Vis absorption /fluorescence spectroscopy respectively. I have shown both to be essentially non-equilibrium. I have also mixed MBBA with other molecules that interact enthalpically or entropically with MBBA and have found that while the former takes the transition to an equilibrium transition, the latter presents the non-equilibrium nature.

In my experiments, I have measured the N-I phase transition temperature as a function of heating/cooling rate through differential scanning calorimetry measurements. In Chapter 4, I have shown through a detailed heating/cooling rate dependent differential scanning calorimetry study around the vicinity of the N-I phase transition of MBBA that pristine MBBA exhibits a non-Arrhenius feature in its N-I transition. N-I transition was considered to be a weakly first order phase transition since the corresponding change in the transitional parameters such as density, specific heat etc was found to be small. Yet, the transition was considered to happen in between two stable equilibrium phases where Arrhenius plot is expected to occur and the non-Arrhenius behaviour is highly unexpected. This non-Arrhenious behaviour signifies the activation barrier of the N-I phase transition of MBBA is controlled by entropic forces. I assume that the possible origin of such entropic forces comes through the disorientation of the two differently substituted benzene rings bridged between the imine (-C=N) bond above the room temperature. At room temperature, the orientation of the benzene rings are nearly co-planar with the imine bond. Above the room temperature as the N-I transition is approached, the large amplitude torsion
leading to the increase in the dihedral angle between the benzene rings may increase, thereby disorienting the co-planarity of the molecule and increase the average cross sectional area available to the molecule. The net effect of this is the net increase in the “configurational entropy” and gives the vindication of the Tolman’s theory of configurational entropy as the basis of the non-Arrhenius behaviour in this case. To test these possibilities and to understand the molecular basis of non-Arrhenius behaviour in a single component system, I have employed a detailed Fourier Transform Infrared Spectroscopy of MBBA molecule from room temperature to the vicinity of its N-I transition temperature. From FTIR spectroscopy, it transpires that my assumption regarding the increase in the net intensity of the out-of-plane distortion vibrations of the benzene rings is indeed true. Additionally, I observe that with increasing temperature the stretch intensity of imine bond reduces pointing towards a temperature induced softening of the stretch bond (backbone of MBBA molecule) which further provides room for the large amplitude motions of the benzene rings and by increasing the molecular cross-sectional area, enhance the probability of the out-of-plane distortion vibrations of the rings. Also from these two independent measurements, I am able to predict a reference temperature close to 60 K, where true co-planar arrangement of the MBBA molecule is achieved through the freezing out of the large amplitude motion. I am able to show a quantitative consistency between DSC and FTIR results and the role of the conformational/configurational entropy on the physical basis of the non-Arrhenius transitional nature of a single component system in a generalized way, where the transition occurs even between two stable phases.

This non-Arrhenius behaviour gives me the first clue regarding the non-equilibrium nature of the N-I transition considering the fact that equilibrium phase transition is manifested through the constant activation energy or linearity in the Arrhenius plot. Deviations from the linearity in the slope of the Arrhenius plots happen when the
system has a shallow free energy minimum or sometimes even have a saddle point which is an essential condition for the non-equilibrium phase transition to occur. The important characteristic feature of the non-equilibrium phase transition is that process history presumably plays an essential role here. Keeping this in mind, I have performed an initial temperature dependent DSC study at different ramp rates to probe the N-I transition and I found that the peak position of the N-I transition and associated change in enthalpy is not fixed but rather vary with the initial temperature. This indicates that thermal history plays an essential role to determine the final evolution of the N-I transition and establishes the direct experimental evidence regarding the non-equilibrium nature of the N-I transition in nematic liquid crystals. In order to have a better insight from the molecular level, I have performed the fluorescence spectroscopy of neat MBBA and measure the variation of the order parameter (anisotropy factor in this case) as a function of temperature. In any order-disorder transition, the order parameter almost remains fixed in the ordered state and then jumps abruptly at the transition point. In case of MBBA, I observe that the order parameter is constant and well-behaved just below the N-I transition and then abruptly jumps at the isotropization temperature. However, well into the nematic phase the value of the order parameter is not constant and decreases linearly with temperature indicating that the nematic ordering is pretty much sensitive to the initial temperature which corroborates with my finding through DSC study. This change in the molecular ordering from nematic to isotropic phase has further been confirmed through FTIR spectroscopy. In the vicinity of the N-I transition, spontaneous breakdown of the nematic ordering leads to the increase in the uncorrelated, out-of-plane motions of the benzene rings resulting in blue shift in the out-of-plane distortion vibrations of benzene rings due to non-coplanarity. The non-equilibrium behaviour of the N-I transition of MBBA has been discussed in the light of the modified Landau-deGennes extended theory of dynamic nematic-isotropic interface.
Apart from a detailed study regarding the non-equilibrium nature of the N-I transition, **Chapter 4** also discusses another non-equilibrium transition of MBBA, namely glass transition which occurs at much lower temperature ($\sim 210 K$). Although it is well known that glassy phase of MBBA occurs at a cooling rate faster than 40 K/min, the signature of which is observed through a change in the baseline in the DSC thermograms (not a peak formation). The kinetic behaviour and some of the important questions regarding glass transition such as (1) what happens if we approached the glass transition at much lower ramp rate and (2) whether the glass transition of nematic liquid crystal possesses an enthalpic/entropic activation barrier remained addressed. Also, the molecular conformation of the nematic liquid crystal around its glass transition temperature has never been studied rigorously. In **Chapter 4**, I attempt to answer these issues by employing a detailed heating rate dependent DSC study to understand the kinetic behaviour of the glass transition and FTIR spectroscopy to investigate the role of conformational entropy on the activation barrier of the glass transition. Kinetic study exhibits one interesting phenomenon about the glass transition of MBBA. At lower heating rate ($\leq 5 K\min^{-1}$), I observe peak formation rather than a plateau which is indicative of a order-disorder transition. This means that if MBBA is heated sufficiently slowly then it will not exhibit any glass transition but rather an order-disorder transition. Kinetic study of the glass transition of MBBA exhibits non-Arrhenius feature and an entropic activation barrier as I found previously in case of N-I transition. In order to have a better insight of the molecular conformation, FTIR spectroscopy is employed around the glass transition of MBBA. As the glass transition in any materials occur due to the sudden freezing of the vibrational and rotational movement of the molecules. I expect a change in the molecular spectra of MBBA especially in the range where the out-of-plane distortion vibrations of the benzene rings occur. I observe a number of peaks instead of one peak around this region, each of which signifies arrested conformational dynamics of
1.5. Outline

the benzene rings in the glassy state. Moreover, I observe that the peak intensity of these arrested conformers reduces significantly and they are significantly red shifted. Additionally, the peak intensity of the imine stretch enhances without any change in the position. All these data clearly confirm partial ordering in MBBA around its glassy phase due to the tendency of the benzene rings to have a co-planar arrangement with the imine bond. However, even in the glassy phase complete co-planarity is not achieved as predicted by me that the physical lower limit of temperature at which this will be achieved is $\sim 60K$. This results in the observed non-Arrhenious behaviour around its glass transition temperature.

In Chapter 5, my primary object is to understand whether the non-Arrhenius nature of the N-I transition of MBBA can be tuned in presence of external forces such as entropic and enthalpic forces. In order to examine this, some known materials should be incorporated within the nematic liquid crystal molecule that are miscible and sustainable (remain as a single phase in two component system) in long term. One of the simplest possible ways to bring these forces into the liquid crystalline system is to incorporate organic, low-molecular weight, non mesogenic solvents. Depending on the proper choice of solvents, they can introduce dominant forces which may be entropic/enthalpic in origin within liquid crystalline molecule. The dominant role of such forces can be recognized through the changes in the phase transition temperature and related thermodynamical parameters such as enthalpy, specific heat etc of the liquid crystalline material through the screening phenomenology by virtue of which the inter-molecular potential of the liquid crystalline material decreases.

Screening mediated through the entropic solvents are referred as the “entropic screening” and through the enthalpic solvents are referred as the “enthalpic screening”. Both these phenomena come up with their unique characteristic features which has been elaborately discussed in Chapter 5. To be more precise, while in entropic screening I observe a continuous decrease in the N-I transitional temperature with
increasing solvent concentration, a saturation behaviour is observed after an initial decay in the phase transition temperature in case of enthalpic screening indicative of the self-screening behaviour of the enthalpic solvents owing to the presence of the permanent dipole moment within them. However, the major outcome that has come through this experiment is that while the entropic screening preserves or even intensify the non-Arrhenius behaviour of the N-I transition of MBBA, enthalpic screening completely destroys this feature to follow Arrhenius behaviour. Through spectroscopic investigations I am able to explore the molecular basis of tunability in the phase transition of nematic liquid crystalline molecule in presence of these forces. All these experiments clearly point towards the fact that nematic ordering can sense what kind of perturbing force (enthalpic/entropic) the molecule is subjected to and it will modulate the phase behaviour accordingly.

Chapter 5 also discusses the tunability in the macroscopic N-I phase transition of nematic liquid crystalline molecule and the molecular basis in presence of a strong enthalpy driven system, i.e. Room Temperature Ionic Liquids (RTILs). RTILs are charge driven system which contains poorly coordinated cations and anions and the coulombic attraction between these constituent ions provides the strong enthalpic force. As a consequence of this, the screening which occurs at comparatively higher concentration of dipolar solvents this happens at much lower concentration in presence of RTILs. Also owing to the large molecular arrangement, the self-screening also occurs at much low concentration of RTIL. Based on this, I propose a simple charge screening model which assumes that the quadrupolar charge of nematic liquid crystalline molecule gets screened by the presence of the RTILs, where all other interactions were neglected. This simple charge screening model fits well with my experimental data points. Also, due to the strong enthalpic interaction, the transitional behaviour of nematic liquid crystal changes from non-Arrhenius to Arrhenius at a comparatively lower RTIL concentration compared to the organic dipolar sol-
vents. The molecular basis in the change of such transitional behaviour in presence of RTILs is investigated through molecular spectroscopy (FTIR Spectroscopy) which again exhibits reduction in the out-of-plane distortion vibrations in the benzene rings accompanied by increase in the molecular ordering through the imine bond of the nematic liquid crystal.

The experimental techniques chosen for the above mentioned work are usually selected on the basis of their appropriateness for a particular task. These are discussed in detail in Chapter 2. The samples used in this work are all liquid in nature and they either taken as its neat form or in mixtures with organic solvents at a particular molar concentration. For the detection of the phase transition temperature and relevant thermodynamical parameters, Differential Scanning calorimetry (DSC) is employed for the neat liquid crystal and its related mixtures. Fourier Transform Infrared (FTIR) Spectroscopy is used to detect the change in the molecular conformational states in neat nematic liquid crystal with temperature and the change due to the presence of organic solvents at room temperature and provides the molecular basis of the information that I acquire from DSC. Occasionally, I have also used UV-Visible (UV-Vis) and fluorescence spectroscopy to understand change in the molecular behaviour of nematic liquid crystal in presence of solvents or change in the order parameter in its neat form as a function of temperature.

In Chapter 3, I discuss the theoretical background essential for the understanding of my experimental results. It mainly consists of well established statistical mean field and phenomenological description of the Nematic-Isotropic phase transition put forward by many authors, Arrhenius law and Tolman’s theory regrading the convex Arrhenius plot in a generalized manner and well established theory of the glass transition which are essential for the interpretation of my experimental observation.

In Chapter 6, I have summarized my work and drawn conclusions pertaining to the whole dissertation. I have also drawn attention that how nematic liquid crystal
can be a useful template for the growth of anisotropic noble metal (Au/Ag) nanostructures. I have discussed the growth evolution of these nanostructures, self organization of the nematic liquid crystal during the nano structure growth and the macroscopic and microscopic evidences of this self organization.