Chapter 4

Convex Arrhenius behaviour in the Nematic-Isotropic and glass transition: Signature of non-equilibrium behaviour

This chapter describes the macroscopic and microscopic evidence of the convex Arrhenius behaviour in the Nematic-Isotropic and glass transition of MBBA which is ultimately found to be linked with the non-equilibrium nature of these transitions.

Related publications

4.1 Outline

In this chapter, I will focus on the convex Arrhenius behaviour, a rare phenomenon in transitions between equilibrium phases of pure systems, observed in neat nematic liquid crystalline molecule MBBA through heating rate dependent differential scanning calorimetry measurements. The molecular basis of such behaviour is explained through Fourier Transform Infrared Spectroscopy in terms of the increase in out-of-plane distortion vibrations of the benzene rings in MBBA with increasing temperature and thereby increase in the configurational entropy through disorientation of the molecular quadrupole. The results obtained from this study were interpreted in the light of Tolman’s definition of configurational entropy and thus generalized the fact that any change in the molecular behaviour which is strictly conformation dependent would exhibit convexity in the Arrhenius plot. This non-Arrhenius behaviour gives the indication of the non-equilibrium nature of the \( N-I \) transition in MBBA which has been further experimentally verified through the dependence of the transition temperature and other parameters on the initial temperatures in the DSC results. I also provide the molecular basis of such non-equilibrium behaviour through molecular spectroscopy. The theoretical basis of such non-equilibrium behaviour was explained in terms of the modified Lanadau-deGennes theory of dynamic nematic-isotropic interface. Apart from that, this chapter also includes the some interesting features and the kinetic behaviour of another non-equilibrium phase transition in nematic liquid crystal, namely the glass transition which appears at much lower temperature (\( \sim 200K \)) along with the molecular basis of such transition.
4.2 Motivation for studying nematic Liquid Crystal as a model compound:

Nematic liquid crystals, as discussed earlier in Chapter 1, constitutes an intermediate phase between solid and liquid, where only orientational ordering persists and properties of the phase are governed by a second rank, traceless quadrupole moment tensor. These molecules are of general anisotropic shape of an elongated rod like structure having a backbone that contains bonds having strong dipole moments those define the long axes of the molecule. A pair of benzene rings are either bridged between this bond or appear side by side keeping the dipolar bond at the extreme end of the molecule. Depending on the position of the benzene rings relative to the dipolar bond, smectic/nematic ordering will appear in the liquid crystal. For example, in most of the liquid crystals where the benzene rings align side by side and the dipolar bond is situated at one of the extreme end of the molecule, smectic ordering will appear (for example, 5CB or 8CB) and where the benzene rings are bridged by the dipolar bond (for example MBBA and PAA) nematic ordering will be present. In MBBA, the molecular axis is defined along the C=N-C line due to the net dipole and the quadrupole moment stays along this line. The benzene rings are attached on either sides of the C=N (imine) bond and these rings can undergo flexible out-of-plane movements upon thermal excitation around the imine bond. This can happen even through the weakest thermal perturbation, as the energy needed for increasing the probability of the large amplitude motion $\sim meV$. Hence even at room temperature, the energy gained by these rings is sufficient enough to undergo such motions. The effect of such behaviour is to move the benzene rings out of coplanarity. This will lead to two simultaneous effects- the imine bond dipole and the molecular quadrupole will no longer remain coplanar thus leading to a vast increase in conformational states. On the other hand, the consequent increase in cross-sectional area of the molecule

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will also allow higher levels of out-of-plane distortions of the rings. This increase in the number of conformational states may increase the configurational entropy which makes the activation barrier of the \( N-I \) transition of \( MBBA \) highly entropic in origin. This makes the activation barrier non-linearly depends on temperature. The existence of the entropic activation barrier provides a physical basis of the non-Arrhenius behaviour in the \( N-I \) transition of \( MBBA \). This also renders fundamental insight regarding the non-equilibrium nature of the \( N-I \) transition.

From the above mentioned discussion it transpires that the \textit{nematic} liquid crystal can be recognized as a versatile system for studying the non-equilibrium phase transitions. Especially, the \( N-I \) transition in \textit{nematic} liquid crystal has rich possibilities of exhibiting non-equilibrium behaviour as this transition is guided by the entropic forces. It is notable that, in liquid crystals where smectic like ordering is predominant, \( N-I \) transitions exhibit equilibrium behaviour as manifested through the constant activation energy in the Arrhenius plot. Smectic phase is more positionally ordered than \textit{nematic} phase as it can form layers or planes unlike in \textit{nematic} phase and hence the number of conformational states for smectics will be significantly reduced. This vindicates Tolman’s idea that the number of conformational states/entropy is the key factor for determining the nature of the \( N-I \) phase transition or more specifically determines whether it is guided by the entropic/enthalpic forces. Onsager’s statistical interpretation regarding the \( N-I \) transition as described in \textbf{Chapter 3} is based on the excluded volume effect between the elongated rod like molecules and predicts that in the \textit{nematic} phase, the excluded volume decreases and this gives rise to the translational entropy of the system. In the phenomenological model proposed by Landau, there also exists an temperature interval over which \textit{nematic} and \textit{isotropic} phase can grow at the expense of each other. Thus a dynamic \textit{nematic-isotropic} interface can be a useful model to describe the actual phase transition behaviour. De Mesquita incorporates a spatially varying term within the original Landau-deGennes theory to

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describe the moving interface dynamics of $N$-$I$ phase transition.

Despite of all these theoretical efforts, direct experimental evidence regarding the non-equilibrium nature of the $N$-$I$ transition is still not provided by any of the researchers. Also, the molecular basis of such behaviour is also far from completely understood. Here, I provide a simple approach to demonstrate the direct experimental evidence regarding the non-equilibrium behaviour of the $N$-$I$ phase transition in $MBBA$ through heating rate dependent differential scanning calorimetry measurement and also explain the molecular basis of such behaviour through detailed molecular spectroscopy study. Apart from the $N$-$I$ transition, I will also discuss the kinetic behaviour and some of the important aspects of the glass transition as well as the molecular behaviour of $MBBA$ around the glass transition temperature in this chapter.

### 4.3 Materials and Characterization Tools

Pure $MBBA$ \([N-(4$-methoxybenzylidene)$-4$-butylaniline] of quoted purity 98\%, of the molecular formula $CH_3(CH_2)_3C_6H_4N = CHC_6H_4OCH_3$, having the molecular weight of 267.37 Da and density 1.027 g/ml was procured from Sigma-Aldrich. The $MBBA$ sample was used from a single batch that had been degassed under vacuum about 2 h in the isotropic phase before use. Differential Scanning Calorimetry (DSC) study was done using a NETZSCH 204 F1 calorimeter at the different ramp rates from 0.5-30 $K \text{min}^{-1}$ during heating and cooling scans around the vicinity of the $N$-$I$ transition as well as the glass transition of $MBBA$. The details of the calorimeter and operating principles are discussed in Chapter 2. The samples ($\sim 5$ mg) were loaded in alumina crucibles (diameter $\sim 8$ mm and thickness $\sim 0.5$ mm) and placed in the DSC chamber along with a empty reference pan. The samples were first annealed at 323 K for 5 min and then immediately quenched to 243 K and equilibrated for about 15 min. The heat flow was recorded along with temperature during heating and cooling scans.

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For determination of $T_g$, the standard definitions of extrapolated onset and inflection points are used and these values were obtained using the Proteus analysis software provided with the instrument. For the \(N-I\) phase transition, the peak temperatures were taken as representative.

FTIR spectroscopy was done for the detection of different stretch and out-of-plane distortion vibrations of \textit{MBBA} at room temperature and around the vicinity of the glass transition temperature using Perkin Elmer Spectrum 400 FTIR spectrometer. The operating principle and the details of the FTIR spectrometer has been discussed in Chapter 2. I have used sealed, heatable liquid cell accessory from Specac which is equipped with a pair of NaCl windows acting as a vacuum jacket. For maintaining the vacuum, this temperature controlled cell is attached with a vacuum pump which ensures the maximum air pressure of 26 mm of Hg. The liquid cell is completely leak proof and the details about this liquid cell can be found elsewhere[103].

Fluorescence anisotropy measurement was done using Hitachi F-7000 fluorescence spectrophotometer. The spectrometer is attached with two rotating polarisers, one with the exciting and the other with the emitted light. The operating principle and the details of the spectrophotometer has been discussed in \textbf{Chapter 2}. Temperature controlled measurements were done using a temperature controller attached to the fluorimeter which controls temperature using ethylene glycol-water mixture from 298 to 323 K. The resolution of the temperature controller is 0.1 K.

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4.4 Convex Arrhenius Behaviour in \textit{Nematic-Isotropic} Phase transition

4.4.1 Rate Dependent Differential Scanning Calorimetry Measurements:

In order to substantiate my proposed conjecture of N-I transition as discussed in the motivation section, I have performed a detailed heating/cooling rate dependent DSC study around the vicinity of the N-I phase transition of MBBA. In Figure 4.1 (a) and 4.1 (b), the excess specific heat capacity $C_p$ (kJ mol$^{-1}$K$^{-1}$), determined from the ratio of DSC signal (W g$^{-1}$) and scan rate (K min$^{-1}$), is plotted against temperature during heating and cooling scans respectively. The plots show a progressive shift in the N-I phase transition temperature ($T_{N-I}$) to the higher (lower) values with increasing heating (cooling) rates ($\beta$) for scan rates varying from 0.5 to 30 K min$^{-1}$ with different representative symbols. In Figure 4.2 (a) $T_{N-I}$’s are plotted with the heating (up triangles)/cooling (down triangles) scans, where the data points are best fit by the linear curves. In Figure 4.2 (b), the representative Arrhenius plot (natural logarithm of the ramp rate vs inverse of temperature) for the heating (up triangles) and cooling (down triangles) scans are shown. Data indicates a pronounced deviation from the linearity and exhibits convex Arrhenius behaviour. Data points in both heating and cooling scans can be best fit by a monomolecular growth functions given by

$$\ln \beta = A (1 - e^{-T_0}(1/T - 1/T_{qs}))$$  \hspace{1cm} (4.1)

For a generalized temperature dependent Activation Energy equation (1) reduces to

$$\ln \beta = \ln \beta_0 - E_a(T)/RT$$  \hspace{1cm} (4.2)

Unlike the Arrhenius equation, $\ln \beta$ in equation (4.1) becomes $A$, i.e., $\ln \beta_0$ at $T = \ldots$
4.4. Convex Arrhenius Behaviour in *Nematic-Isotropic* Phase transition

Figure 4.1: The *N-I* transition of MBBA: Specific Heat capacity $C_P$ (kJ/mol) vs Temperature (K) is extracted from Differential Scanning Calorimetry and shown for the heating (a) (cooling (b)) rates (all in $K min^{-1}$) of 0.50(black solid), 0.75(purple .), 1.00(Navy -), 2.0(Olive.-), 5.0(Dark cyan --.), 8.0(orange --), 10.0(pink ----), 12.0(green .-), 15.0(wine open circle), 17.0(red open up triangle), 20.0(magenta down open triangle), 22.0(cyan open square), 25.0(dark yellow star), 27.0(Violet diamond) and 30.0(Royal hexagon) respectively.
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Figure 4.2: (a) Summary of heating (up triangles) and cooling (down triangles) data from DSC for N-I transition of MBBA. (b) Arrhenius plot of $1/T$ ($K^{-1}$) vs natural logarithm of $\beta$ for heating and cooling along with fits (red line) following Mono-Molecular growth model. (c) Calculated Activation energy $E_a$ (kJ/mol) plot with following eqn (5) during heating and cooling.
4.4. Convex Arrhenius Behaviour in *Nematic-Isotropic* Phase transition

0 K. Again, equation 4.1 has two more ‘reference temperatures’, $T_{qs}$ and $T^0$. While the former corresponds to $\ln \beta = 0$ or $\beta = 1 \text{ K min}^{-1}$, and hence can be called the temperature for the quasi-static situation, the latter is more difficult to interpret. Its value from the fit comes out to be $\approx 60 \text{ K}$ and $\approx 85 \text{ K}$ from the heating and cooling curves, respectively. These values are characteristic of the energies required for large amplitude motions such as torsion of the benzene rings around single bonds and they possibly represent the ‘physical’ lower limits of $T$.

Comparing with equation (4.2), we then have

$$E_a(T) = RT \ln \beta_0 e^{-T^0 (1/T - 1/T_{qs})} \quad (4.3)$$

This Activation Barrier is shown as a function of temperature in Figure 4.2 (c). At $T = 0 \text{ K}$, the Activation Energy vanishes and the system passes smoothly from one phase to another, at $T^0$ the Activation Barrier is very small, and at $T_{qs}$ it acquires its maximum value of $RT \ln \beta_0$. Hence, near $T_{qs}$ the energy transfer is slower than any molecular processes in the system and the Arrhenius plot can be considered as linear. This clearly indicates (a) the role of conformational entropy in raising the Activation Barrier and (b) the role of large amplitude motions in raising this entropy. It is to be noted that MBBA lacks a smectic phase, pointing to the subservient role of *inter*-molecular forces to *intra*-molecular forces that control conformational entropy.

The configuration of the ground state of MBBA (Figure 4.3 (a)), generated through *ab initio* energy minimization,[104] shows that the benzene rings are almost co-planar and can undergo torsional vibrations about the N-C and C-C single bonds while these bonds, along with the C=N double bond, maintains a plane that nearly coincides with the plane of the rings. Thus the ground state, where vibrational motions are frozen out below 60 K, corresponds to a planar or at least a near planar structure. In this structure the net molecular dipole and quadrupole are along the same line defined by C=N-C, and this line can be denoted as the ‘molecular axis’. In absence of the

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Figure 4.3: Ab initio structure of *MBBA* in (a) ground vibrational state when two benzene rings are nearly co-planar with each other and in (b) excited vibrational state when this co-planarity is disturbed. The Nitrogen and carbon atom is depicted by the blue color and the atom adjacent to the double bond, where the oxygen atom is demonstrated by the red color symbol.

intramolecular entropy due to the conformational variation coming from vibrations, most of the molecules are configurationally oriented along their axes, and free energy minimization for the bulk system is achieved mainly through minimization of enthalpy as intermolecular forces orient the axes spontaneously along the director to create *nematic* order. This is the probable explanation of the above results at the molecular level.

I note that the vibration modes along the axis are the C=N and the C-N stretches, of which the C=N stretch mode is known to have a larger intensity and therefore is easier to probe. In contrast, the large amplitude motions to cause the benzene rings to become non-coplanar as shown in Figure 4.3 (b), increasing not only the configurational entropy and thereby disorienting the molecular quadrupoles about the axis but also increasing the average cross-sectional area available to the molecule. One of the major consequences of this area increase is that it allows the out-of-plane distorting vibrations of the two (inequivalent) rings of *MBBA* to take place. Hence increase in the large amplitude motion and therefore the configurational entropy causes more molecules to have these distorting vibrations and the intensity of these modes to in-
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Figure 4.4: (a) Fourier transform Infra Red (FTIR) results from MBBA; relevant bands at 836 and 888 cm\(^{-1}\) marked with arrows, are distortion modes of two differently substituted benzene rings and 1254 and 1626 cm\(^{-1}\) represents the stretch modes of C-N and C=N respectively. (b) Variation of IR absorbance with Inverse of Temperature (1/T, K\(^{-1}\)) for C-N (filled squares), C=N (Open squares) stretches and filled circles and open circles for the distortion bands at 836 and 888 cm\(^{-1}\) respectively along with fits to eqn(6).

On the other hand, the same disorientation of the molecular quadrupoles will cause a lowering of the overall intensity of the C-N stretch band due to the absence of the quadrupolar terms in the transition moment and this decrease will be continued as more molecules go into the disoriented configuration.

The above discussion suggests that with increase in temperature the increase in large amplitude motions will decrease the intensity of the C-N stretch and increase the intensities of the out-of-plane distorting vibrations of the two rings. To investigate this molecular picture MBBA was drop cast on Si (111) till it spread over the entire surface of the substrate and infrared spectra over the 700 - 3000 cm\(^{-1}\) range were taken with bare Si (111) as a reference. Infrared peaks were observed at around 836 cm\(^{-1}\) and 888 cm\(^{-1}\), marked with arrows in Figure 4.4 (a). They were fit with gaussians and assigned tentatively to the vibrational modes corresponding to out-of-plane ring distortions of the two benzene rings with different substituents[104].
4.4. Convex Arrhenius Behaviour in *Nematic-Isotropic* Phase transition

Table 4.1: Activation Energy associated with different bonds

<table>
<thead>
<tr>
<th>MBBA Bonds</th>
<th>$E_{a}^{M}$ (in units of T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=N</td>
<td>62.16</td>
</tr>
<tr>
<td>C-N</td>
<td>73.51</td>
</tr>
<tr>
<td>Benzene ring (1)</td>
<td>40</td>
</tr>
<tr>
<td>Benzene ring (2)</td>
<td>39.87</td>
</tr>
</tbody>
</table>

Intensities of these peaks were monitored around the *N-I* transition temperature of 42°C. Spectra were taken from 29°C to 50°C, i.e. from *Nematic* phase to well into the *Isotropic* phase. It was found that benzene ring out-of-plane distorting vibration intensities are monotonically increasing functions of temperature with a slow (fast) increase below (above) $T_c$, thus confirming the increase in the out-of-plane disorder due to the rings as the transition temperature is approached, while for C=N bond, the intensities are monotonically decreasing function of temperature. The plot of Intensity vs inverse of temperature, shown in Figure 4.4 (b), depicts these results that provide a preliminary vindication of our molecular model for the non-Arrhenius behaviour. This temperature induced intensity fall or rise allows us to extract the activation energy for a single molecule excitation in the form of an equation:

$$I(T) = I_0[1 + C \exp(-\frac{E_{a}^{M}}{kT})]^{-1}$$  \hspace{1cm} (4.4)

where, $E_{a}^{M}$ is the activation barrier of the particular excitation for a single molecule, C is a constant which takes care of the ratios of optical collection efficiencies, $k_B$ is the Boltzmann constant and $I_0$ represents the intensity at lowest temperature. Data for C-N, C=N and two benzene rings fit well with equation (4.4)(lines in fig 4.4(b)) and the activation barriers are shown in Table 4.1.

Table 4.1 clearly indicates that below 60 K, as determined by DSC results, the stretch bands are frozen out and the probability of the ring distortions are also much reduced, making the configuration in Figure 4.3(a) more probable. Thus a quantitative

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consistency between the DSC and IR results is achieved, giving a vindication of Tolman’s theory of conformational entropy\[46\] as the basis of non-Arrhenius behaviour by extending it to transition between equilibrium phases in a single component system.

4.5 Evidence of non-equilibrium nature of $N$-$I$ transition

As it is a very well known fact that equilibrium phase transitions occur in between two stable phases where the system dynamics is related to the crossing of an activation barrier which is much larger than the ambient temperature\[105\]. The activation barrier is in general a constant in these cases and a linearity in the Arrhenius plots is expected to occur. In systems where this condition no longer holds true, i.e. where the activation barrier between two phases is comparable or even lower than the ambient temperature, a deviation from this linearity of the Arrhenius plots is expected to occur and in general these transitions can be regarded as non-equilibrium transitions.

The convexity of the Arrhenius plots in MBBA gives me the primary clue regarding the non-equilibrium nature of this transition. As the non-equilibrium phase transitions are characterized by the time scale of observation and depends on the thermal history, I have performed a detailed initial temperature ($T_i$) dependent DSC study for two different heating rates ($\beta = 10 \text{ K min}^{-1}$ and $8 \text{ K min}^{-1}$ ). For $\beta = 10 \text{ K min}^{-1}$, the $N$-$I$ transition was studied for different $T_i$’s of 100 K, 143 K, 173 K, 213 K and 273 K, set much away from the $N$-$I$ transition temperatures ($T_{NI} = 318 \text{ K}$) to give the system sufficient room for equilibration. $T_{NI}$ and the associated enthalpy change ($\Delta H_{NI}$) were monitored for these scans as shown in Figure 4.5 (a). If $T_i$ is far from $T_{NI}$, the shift in transition is towards lower temperature. With increasing $T_i$’s,a non-linear shift in the $T_{N-I}$’s towards higher temperature is observed.

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4.5. Evidence of non-equilibrium nature of $N$-$I$ transition

indicated in Figure 4.5 (b), where the right y axis denotes the obtained $T_{N-I}$’s (triangles) for various $T_i$’s. The variation in $(\Delta H_{N-I}$ (kJ/mol)) with various $T_i$’s is also demonstrated in the same figure where the left y axis denotes the scale for $\Delta H_{N-I}$’s (circles). In order to rule out the possibility of any experimental error that effects the $N$-$I$ phase transition temperature and its associated enthalpy, DSC scans for MBBA for various $T_i$’s, 173 K, 233 K and 273 K were taken at another $\beta = 8$ K min$^{-1}$ and the representative plot along with the variation of $T_{N-I}$ and $\Delta H_{N-I}$ for different $T_i$’s are shown in Figure 4.5 (c) and (d). The plots show similar dependence of the variation of $T_{N-I}$ and $\Delta H_{N-I}$ with $T_i$’s as in the previous case. These results indicate well reproducibility of this similar behaviour repeatedly. The variation of the $N$-$I$ phase transition temperature and its associated enthalpy change with varying initial temperatures under the same ramp rate and experimental condition confirm the non-equilibrium nature of $N$-$I$ phase transition.

The above-mentioned feature clearly indicates that thermal history and time scale of observation play an essential role in defining the non-equilibrium behaviour of $N$-$I$ transition. At present, any well defined theory for explaining this unusual behaviour of the $N$-$I$ transition is lacking. However, I would like to discuss this behaviour in the light of the existing Landau-deGennes (LdG) phenomenological mean field theory [106] and works based on this theory. As introduced in Chapter 3, LdG description on the $N$-$I$ phase transition assumes the value of the order parameter to be small close to the transition point and free energy can be expanded in the powers of the order parameter as

$$F = F_0 + \frac{1}{2} A Q_{\alpha\beta} Q_{\beta\alpha} + \frac{1}{3} B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + ..... \quad (4.5)$$

where, $F_0$ is the free energy in the isotropic phase, $Q_{\alpha\beta}$ are the quadrupole moment tensors acting as the order parameters, and $A$, $B$ etc are the constant coefficients. For
4.5. Evidence of non-equilibrium nature of \(N-I\) transition

Figure 4.5: Excess specific heat capacity (kJ/mol K) vs Temperature (K) plot for MBBA at (a) fixed \(\beta = 10\) K/min with different initial temperatures \(T_i = 100\) K (diamonds), 143 K (down triangles), 173 K (squares), 213 K (up triangles) and 233 K (circles), and (b) for \(\beta = 8\) K/min with \(T_i = 173\) K (circles), 233 K (up triangles) and 273 K (squares). (c) \(T_{N-I}\) (right ordinate, triangles) and \(\Delta H_{N-I}\) (left ordinate, circles) vs \(T_i\)'s for (c) \(\beta = 10\) K/min and (d) \(\beta = 8\) K/min.
MBBA the order parameter reduces to a scalar $Q$ and hence the expansion becomes

$$F = F_0 + \frac{1}{2} A Q^2 - \frac{1}{3} B Q^3 + \frac{1}{4} C Q^4$$

(4.6)

where, $A$, $B$, $C$ are phenomenological co-efficients reduced from the $C_i$'s under the above transformation, where at $B = 0$, the above expression predicts a second order phase transition at $T^*$ if $A = a(T - T^*)$ is the dominant temperature dependent term.

The LdG description leads to the fact that the stability/metastability of nematic and isotropic phase are dependent on how the N-I phase transition is approached. For $T(T_i$ in our case) $> T_{NI}$, the nematic phase ($Q \neq 0$) has a local minimum (metastable phase) while the isotropic phase ($Q = 0$) has an absolute minimum (stable phase), while for the opposite limit of $T < T_{NI}$, the nematic phase is stable while isotropic is the metastable phase. At $T = T^*$, $\frac{\partial^2 F}{\partial Q^2} = 0$ for $Q = 0$ and isotropic phase becomes unstable. We can also define a temperature $T^+$ such that

$$T^+ - T_{NI} = \frac{1}{8} (T_{NI} - T^*)$$

(4.7)

with $\frac{\partial^2 F}{\partial Q^2} = 0$ and $Q^+ = \frac{3}{4} Q_{NI}$, where the nematic phase becomes unstable. Since $T_{NI} - T^* \sim 2 \text{ K}$, $T^+ - T_{NI} \sim 0.25 \text{ K}$.

The LdG model accounts only for the homogeneous phases where spatial variation of the order parameter is ignored. However, recent studies on domain instability of liquid crystals[107–109] which displays a variety of new dynamical phenomena and a scenario of spatio-temporal chaos demands a moving nematic-isotropic interface as a model system to study complex dynamics and pattern formation[110, 111]. This dynamic nematic-isotropic interface requires a spatially varying term to incorporate into the original LdG equation. De Mesquita[112] has incorporated this term into the LdG equation along with the other term which is $\frac{1}{2} a \zeta_0^2 T^* (\frac{\partial Q}{\partial z})^2$, where $\zeta_0$ is the ‘bare’ (temperature independent) quadrupole correlation length with dimension of the order
of the molecular size and has built a non-equilibrium theory regarding the moving nematic-isotropic interface based on this idea, where both N and I phase can grow at the expense of other and in between the limit \( T^* \leq T \leq T^+ \), the nematic-isotropic interface can exist. I propose that this dynamic interface is the probable origin of the dependence of \( N-I \) phase transition temperature on the initial temperatures.

4.5.1 Change in molecular ordering from \( N \) phase to \( I \) phase

To investigate the change in molecular ordering from the nematic to isotropic phase in MBBA I have used the anisotropy in fluorescence measurements, which in recent years has been recognized as a promising tool for the study of the reorientation dynamics of probe molecules[113, 114], as the order parameter of the transition. The fluorescence anisotropy \( r \) is defined by[115] where \( I_\parallel (t) \) and \( I_\perp (t) \) are the fluorescence intensities measured parallel and perpendicular to the polarization of the excitation light. I designated these quantities as \( I_{VV} \) and \( I_{HH} \) for \( I_\parallel \) and \( I_\perp \) respectively. The excitation polariser (\( Ex \)) and emission analyser (\( Em \)) are set as 90\(^\circ\) and 90\(^\circ\) for \( I_{VV} \) and at 90\(^\circ\) and at 0\(^\circ\) for \( I_{VH} \), respectively. Additionally the deviation from the 90\(^\circ\) angle beam geometry inside the sample chamber due to the refractive index difference between sample and quartz covering has to be accounted for by a correction factor \( G \) defined as

\[
G = \frac{\int I_{HV}(t)dt}{\int I_{HH}(t)dt}
\] (4.8)

where, \( I_{HV} \) and \( I_{HH} \) are the measured intensities along \( E_x = 0^\circ \), \( E_m = 90^\circ \) and \( E_x = 0^\circ \) and \( E_m = 0^\circ \) respectively. With these definitions, anisotropy can be defined as

\[
r(t) = \frac{[I_{VV}(t) - GI_{VH}(t)]}{[I_{VV}(t) + 2GI_{VH}(t)]}
\] (4.9)

\( G \) is given by the ratio of the intensities \( I_{HV} \) and \( I_{HH} \) and as measured by the instrument.
4.5. Evidence of non-equilibrium nature of $N-I$ transition

Pristine $\text{MBBA}$ exhibits double hump absorption peaks at 320 and 280 nm which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. The first peak is attributed to the electronic transitions of the lone pair electrons of imine bond and second peak is attributed to the electronic transitions of the bonded electrons. At 330 nm excitation, I observe weak fluorescence band at around 550 nm which does not change its position upon changing the excitation wavelength. Hence, I take this band as our probing band for measuring fluorescence anisotropy. In Figure 4.6 (a), the fluorescence spectra of MBBA various temperatures vis-a-vis from room temperature nematic phase to well into the isotropic phase are shown at a particular combination of excitation and emission polariser angle ($E_x=90^\circ$, $E_m=0^\circ$) which indicates drastic decrease in the intensity of the 550 nm peak with increasing temperature. Also, the peak position was found to be significantly blue shifted around $N-I$ transition temperature. It clearly shows that the fluorescence intensities at parallel and perpendicular directions are not equal indicating optical anisotropy in MBBA. Optical anisotropy has been measured and plotted as a function of temperature in Figure 4.6 (b). I observe that this order parameter is well-behaved in the interval 310-325 K around $T_{NI}$ (318 K), i.e., it has a constant, non-zero value below $T_{NI}$ and vanishes above $T_{NI}$. However, below 310 K this order parameter is no longer constant but decreases linearly with increase in temperature, showing that for MBBA nematic ordering is sensitive to the initial temperature during heating, pointing to the non-equilibrium nature of this phase transition as consistent with the DSC results.

The change in the molecular ordering from Nematic phase to isotropic phase is further investigated through FTIR spectroscopy. In the vicinity of the $N-I$ transition, breakdown of nematic ordering will lead to 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. In Figure 4.6 (c), FTIR spectra of MBBA around the out-of-plane distortion vibration of the benzene rings at room
temperature and around the vicinity of the N-I transition indicates blue shift in the respective band positions from 836 cm\(^{-1}\) to 839 cm\(^{-1}\) and from 887 cm\(^{-1}\) to 889 cm\(^{-1}\). This again provides evidence of the decrease in the molecular ordering from nematic to isotropic phase.

Calorimetric and spectroscopic investigations clearly transpires that the N-I transition is indeed a non-equilibrium phase transition. N-I phase transition occurs just above the room temperature and even at ambient it exhibits non-equilibrium characteristics. Earlier people have reported the existence of many metastable phases in MBBA which occurs much below the room temperature. These phases are not true thermodynamic phases and can grow at the expense of each other. Thus these phases can be regarded as the “polymorphic phases” as they are composed of different conformational states of MBBA having equal or nearly equal energy. Some of the authors have also verified that the so called “Solid” phase in MBBA which occurs prior to the nematic phase at low temperature below 273 K is not a truly solid in nature and they referred this phase as “plastic crystalline” phase. Another transition of MBBA that occurs much away from the room temperature region and well into the low temperature region (\(\sim 210\) K) is the glass transition. As it was observed previously by various authors that during cooling at heating rate \(\geq 40K\ min^{-1}\)\[100\], the glassy state of MBBA is formed which involves only a change in the baseline for \(C_P\ vs T\) curve and not a proper peak formation and it is further followed by a broad recrystallization peak. It is therefore second order transition and most probably, a glass transition. Furthermore, the absence of such a transition and recrystallization peak in case of slow cooled sample also supports this conclusion. Transition at 200 K for MBBA has been detected by other techniques and different interpretations about this nature have been put forward. Some authors considered to be a glass transition\[101, 102\], while others consider it as an evidence for the formation of a metastable state. The positron annihilation studies (PAT) carried out by Jain and Kafle also indicate that

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Figure 4.6: (a) Fluorescence spectra of MBBA at a particular combination of polariser and analyser angle ($E_x = 90^\circ$ and $E_m = 0^\circ$) for various temperatures of 304 K (circles), 308 K (up triangles), 312 K (diamonds), 316 K (left side triangles) and 323 K (right side triangles) respectively. (b) Fluorescence Anisotropy ($r$) vs Temperature (K) plot for MBBA around the $N$-$I$ transition. See text for details. (c) FTIR spectra of MBBA in the vicinity of out-of-plane distortion vibrations of the benzene rings at 298 K (down triangles), 310 K (diamonds), 318 K (up triangles) and 323 K (circles).
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this is indeed a glass transition. Typical defreezing of various molecular motions on heating is clearly indicated by these studies. However, the kinetic behaviour and some important aspects of glass transition in liquid crystals are far from completely understood. In the forthcoming section, I attempt to elucidate the kinetic behaviour and some unique features of the glass transition of $MBBA$ through differential scanning calorimetry measurements and provide molecular insight regarding the role of conformational entropy on the glass transition of $MBBA$ through FTIR spectroscopy.

4.5.2 Change in the nature of ‘glass transition’ at lower heating rate

In Figure 4.7, the DSC thermograms for $MBBA$ around 200 K at $\beta = 2$ K - 30 K min$^{-1}$ are shown, where the DSC signal (mW/mg) is replaced by the excess specific heat capacity ($\Delta C_P$) (J mol$^{-1}$ K$^{-1}$), by taking the ratio of heat flow ($dQ/dt$) and scan rate ($dT/dt$), and $\Delta C_P$ is plotted with temperature. In Figure 4.7 (a), I have separately shown the low $\beta$ curves, where the plots are shown in the same figure with the left (right) axis denoting $\Delta C_P$ scale for $\beta = 2$ K min$^{-1}$ (5 K min$^{-1}$) by black (blue) squares. In Figure 4.7 (b), I present the curves for the higher ramp rates.

Figure 4.7 (a) clearly indicates a prominent peak at these low ramp rates. This is inconsistent with a glass transition and rather indicates an order-disorder transition. In contrast, for $\beta \geq 10$ K min$^{-1}$, only a change in the baseline of $C_P$ vs $T$ curve is observed in Figure 4.7 (b) - a characteristic feature of glass transition. This shows that if heated sufficiently slowly this system does not show a glass transition but passes from one ergodic state to another, as in a continuous order-disorder transition. The peaks obtained at 2 and 5 K min$^{-1}$ were fit with gaussians (shown inset) to obtain $\Delta C_P$ at this transition (height of peak) as 401.5 J mol$^{-1}$ K$^{-1}$ for 2 K min$^{-1}$ and 144.4 J mol$^{-1}$ K$^{-1}$ for 5 K min$^{-1}$. Hence, $\Delta C_P$ at transition was decreased, for $\beta = 5$ K min$^{-1}$, to 36% of its value for $\beta = 2$ K min$^{-1}$. According to Angell[116],

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Figure 4.7: (a) Excess specific heat capacity ($\Delta C_P$, J/mol K) vs temperature ($T$, K) plot around glass transition temperature ($T_g$) of MBBA for heating rates ($\beta$) of 2 (left ordinate, black) and 5 (right ordinate, blue) K min$^{-1}$ showing peak formation. Right Inset: Jump in $\Delta C_P$ along with gaussian fit (red line) for $\beta = 2$ K min$^{-1}$. Left Inset: Jump in $\Delta C_P$ along with gaussian fit (red line) for $\beta = 5$ K min$^{-1}$. (b) Kinetic behaviour of glass transition at 10 (dash), 15 (dot), 20 (dash-dot), 25 (dash-dot-dot) and 30 (short dash) K min$^{-1}$.

a reduction of the $\Delta C_P$ value at higher $\beta$ to 30-40% of the value at lower $\beta$ can be regarded as the primary signature of the transition from ergodic to non-ergodic states. Hence, most probably the initiation of the glass transition occurs for $\beta \geq 5$ K min$^{-1}$.

4.5.3 Evidence of glass transition through change in the molecular ordering

Glass transition in complex liquids occurs due to sudden freezing of the vibrational and rotational movement of the molecules[116]. For MBBA, as discussed previously that the out-of-plane motions of the benzene rings are responsible for the different molecular conformational states and these large amplitude motions destroy the co-planarity of the benzene rings. They increase with temperature, giving rise to the convexity in the nematic-isotropic ($N-I$) phase transition of MBBA. They also allow

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space for the out-of-plane distortion vibrations of these rings. As glass transition of \textit{MBBA} occurs at much lower temperature ($T_g \sim 200$ K), around $T_g$ the distortion vibrations of the benzene rings may decrease considerably leading to nearly co-planar arrangement of the benzene rings and the imine (-C=N) group. This co-planarity is expected to reduce the intensity of the out-of-plane distortion vibrations as well as cause red shift in the corresponding vibrational band. On the other hand, this co-planar arrangement may also give rise to increase in the intensity of the stretch mode of imine (-C=N) group through increase in the orientational order.

To look for these signatures of partial order due to the ‘arrested’ conformational dynamics in the glassy state, I have employed Fourier transform infrared (FTIR) spectroscopy study of \textit{MBBA} at room temperature and around $T_g$. At room temperature (298 K) \textit{MBBA} exhibits its imine stretch at 1625 cm$^{-1}$[117] and at 836 and 887 cm$^{-1}$ for out-of-plane distortion vibrations of the benzene rings attached to the imine group and the methoxy (-OCH$_3$) group, respectively. In Figure 4.8 (a), the FTIR spectra of \textit{MBBA} around the vicinity of $T_g$ (around $T_g$ and in the glassy phase, 223 K and 203 K, respectively) indicates that the 836 cm$^{-1}$ peak is not only reduced in intensity but is split into a number of peaks as a direct evidence of the different conformers arising out of the arrested large amplitude out-of-plane motion. Again the peak at 887 cm$^{-1}$ is reduced considerably in intensity and also significantly red shifted to 882 cm$^{-1}$. Besides, I also observe enhancement in the imine stretch intensity of \textit{MBBA} in the glass phase of \textit{MBBA} compared to its \textit{nematic} phase without any shift (Figure 4.8 (b)). Thus the enhancement in the molecular ordering due to sudden freezing of out-of-plane motions of benzene rings in the glass phase of \textit{MBBA} compared to its room temperature \textit{nematic} phase is evident from these observations.
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Figure 4.8: Fourier Transform Infrared (FTIR) spectroscopy of pristine \( MBBA \) around the vicinity of the out-of-plane distortion vibration of benzene rings (800-920 \( cm^{-1} \)) at room temperature (298 K, circles), around the glassy phase (223 K, triangles) and well into the glassy phase (203 K, diamonds). The out-of-plane distortion vibrations of the benzene rings at these temperatures are marked by arrows. Figure indicates significant blue shift in these vibrations accompanied by diminishing in the intensity providing the molecular insight for the co-planar arrangement of \( MBBA \) at glass state. (b) FTIR spectroscopy at these temperatures around the vicinity of stretch vibration of imine bond (1600-1650 \( cm^{-1} \)) with the symbols have the same meaning. Figure indicates enhancement in the imine stretch intensity around glass phase with negligible shift in the position of the stretch frequency.
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4.5.4 Kinetics of glass transition

The kinetic behaviour of the glass transition of MBBA was studied during heating scans using the ramp rates of 5, 10, 15, 20, 25 and 30 K min$^{-1}$ (Figure 4.7(b)). Strong dependence of $T_g$ on the heating rate and sigmoidal variation in $\Delta C_P$, the signatures of glass transition, are observed. Three different definitions of $T_g$ were used by Moynihan et al [118] that are the extrapolated onset, the inflection point and the maximum of the DSC output curve (end point) obtained on heating. In our case, only the onset and inflection points are taken as the representative $T_g$ for all heating rates. One way to express the kinetic behaviour of glass transition is the dependence of heating rate, $\beta$, on $T_g$ given by Lasocka’s relationship[119] as

$$T_g = A + C \ln \beta$$  \hspace{1cm} (4.10)

where $A$ and $C$ are constants for a given glass composition. According to Eq. (4.10), a useful assignment of $T_g$ can be obtained by extrapolating the heating rate to $\beta = 1$ K min$^{-1}$, when $T_g = A$ and I assign $A$ as $T_g^{(1)}$. The constant $C$ reflects the rate dependence of the configurational changes of the supercooled liquids [120]. This dependence can provide information on the kinetics of glass transition [121]. Hence our first effort was to fit the $T_g(\beta)$ above $\beta = 5$ K min$^{-1}$ to this linear relation.

Figure 4.9(a) shows the plot of $T_g$ vs $\ln \beta$, with the lower set from the onset point and the upper set from the inflection point and the best fit with Lasocka’s relations. It is clear that the equation does not fit the data and a non-linear relation exists between the transition temperature and the natural logarithm of the heating rate indicating a variation in the configurational states throughout glass transition region. This clearly shows the existence of degenerate ground states of MBBA that make the system non-ergodic and drive the glass transition[122].

This non-ergodicity results in non-linear response in the Arrhenius behaviour and,
as I have previously shown, such non-linearity in the Arrhenius plot is ultimately linked to an entropic activation barrier leading to a strong dependence on temperature. In Figure 4.9(b), the Arrhenius plots for different $T_g$ assignments are obtained by plotting $\ln(\beta)$ vs $(1/T_g)$. The data show pronounced deviation from linearity.

Extending the main idea of the previous chapter, I express the activation energy of MBBA glass transition as

$$E_a(T) = RT e^{-k(\frac{1}{T} - \frac{1}{T_g})\ln\beta}$$  \hspace{1cm} (4.11)

This functional dependence of $E_a$ on $T$ is shown in Figure 4.9(c) for the two thermodynamically defined temperatures. If I put this expression for $E_a$ in a generalized Arrhenius law of the form

$$\ln\beta = \ln\beta_0 - \frac{E_a(T)}{RT}$$  \hspace{1cm} (4.12)

I obtain the final form of the Arrhenius expression for this transition as a sigmoidal Sigmoidic function given by

$$\ln\beta = \frac{A}{1 + exp(-k(\frac{1}{T} - \frac{1}{T_g}))}$$  \hspace{1cm} (4.13)

where $\ln\beta \rightarrow A = \ln\beta_0$ at $T \rightarrow \infty$ as I find in case of Arrhenius equation. This equation gives excellent fit to the data as can be seen in Figure 4.9 (b), vindicating our model for entropic activation barriers, and the extracted fit parameters are given in table 4.2.

The functional form of $E_a(T)$ for the two different $T_g$’s is shown in Figure 4.9(c).
Figure 4.9: (a) Natural logarithm of ramp rate ($\ln \beta$) vs $T_g$(K), defined as ‘onset’ (down triangles) and ‘inflection point’ (up triangles) temperatures (refer text for details), along with two linear ‘fits’ (lines). Figure clearly indicates significant deviation from linearity. (b) $(1000/T_g) (K^{-1})$ vs $\ln \beta$ plots, fit (lines) with Eq.(4) for the same definitions of the temperatures. (c)Calculated activation energy ($E_a$ (kJ/mol)) vs Temperature (K) plot for these temperatures ‘onset’ (left ordinate,down triangles) and ‘inflection point’ (right ordinate, up triangles)) from Equation 4.11.
4.6. Concluding Remarks

According to our model, entropic activation energies are decreasing functions of temperature and heating rates which means relatively low energy is needed during high heating rates to overcome the activation barrier of glass transition. It was previously shown that during cooling scan glass transition can be achievable at cooling rate higher than 40 K/min [100], which means cooling rate lower than that is insufficient to provide necessary energy to overcome the activation barrier leading to glass transition. In our case, as expected from this model, there exists no such limit for the ramp rates during heating if MBBA is quenched rapidly to very low temperature and then reheated. Sharp decrease of activation barrier with increasing heating rate is vindicated by similar findings during cooling scan of MBBA.

4.6 Concluding Remarks

Calorimetric and spectroscopic investigations clearly indicate the role of the conformational entropy on the convex Arrhenius as well as non-equilibrium behaviour of N-I phase transition of a typical nematic liquid crystalline molecule where the transition occurs in between two thermodynamically stable phases. The N-I transition was previously regarded as a weakly first order phase transition and considered as equilibrium phase transition but many of the queries regarding this transition such as the type of the activation barrier has not been addressed previously. Through simple calorimetric investigations, I have verified that the activation barrier of N-I transition in nematic liquid crystal is indeed entropic in origin and this leads to the non-equilibrium nature of this transition. Based on many spectroscopic techniques, I have provided the molecular basis of such non-equilibrium behaviour. I have also tried to provide the theoretical basis of such behaviour incorporating the concept of the dynamic nematic-isotropic interface in the light of the modified Landau-deGennes theory. Besides, I have also investigated the kinetic behaviour of another non-equilibrium phase transition in the nematic liquid crystal namely the glass transition which again
exhibits an entropic activation barrier. A side light of my study on glass transition is that if the rate of supply of heat is maintained sufficiently low, then instead of manifesting the glass transition, *nematic* liquid crystal will exhibit a continuous order-disorder transition. Kinetic study also exhibits variation in the configurational states throughout the glass transition region of *nematic* liquid crystal. The molecular conformations of the *nematic* liquid crystal around the glass transition region is investigated through molecular spectroscopy. My study provides an insight into the role of the conformational entropy on the phase transitions which are mainly entropy driven. Entropy driven phase transitions are becoming increasingly important in the study of soft material and especially in mixtures. Since the discovery of the depletion force\[123\], different entropic forces are found to be the driving forces behind micro-phase segregation\[124\] and self-organization. Tolman’s theory gave the first hint that entropic forces in phase transition may manifest themselves through non-Arrhenius behaviour. Our result shows that the entropic nature of the activation barrier is related to the convexity of the Arrhenius plot through a specific functional dependence on temperature and is involved by the absence of the barrier below a temperature. The generality of these results, especially for other field parameters and for multi-component systems has been taken up in the next chapter.

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