Chapter 7

Summary and Conclusions

Advances in measuring relaxation rates at very low frequencies through innovative methodologies like field cycling technique have made the dynamic range of these experiments cover nearly five decades of frequency especially making it possible to focus on very low frequency dynamic processes. This work takes advantage of this capability to investigate slow dynamic processes. These investigations yielded profitably on various molecular processes like order director fluctuations (ODF), self diffusion (SD), and molecular reorientations (R) in the nematic phase, pre-transitional effects just below and above isotropic nematic transition in certain liquid crystals. An attempt is made to probe $^{19}$F spin relaxation paths which are qualitatively different from proton by an appropriate choice of the liquid crystal system. This seems to be the first attempt to carry out NMRD study with different nuclei reporting differently about the dynamics of the same molecule. Further this technique is used to probe protein-denaturant interactions to understand protein folding paths and their stability.

In general terms, the results provided reasonable insight into the role of molecular structure on the dynamic organization of liquid crystals, sensitivity of spin-rotation interactions in probing novel slow processes in liquid crystals not reported by dipolar couplings, and finally the role of denaturants in initially stabilizing the tertiary structure of protein xxx earlier by other investigations.

The tow systems chosen for this purpose have interesting and fairly characteristic and well time-scale separated dynamic phenomena. The interpretation of these detailed results require equally elaborate molecular dynamic models, whose applications can be satisfactorily tested by demands. Consistency of the experimental data with model parameters are the two dimensional space of both frequency and temperature. The present studies thus report such xxx in liquid crystal and protein solutions making use of the state of the art NMR methodology tailored for slow processes, and
applying very interesting models to interpret this data.

The PMRD studies on 4O.m liquid crystals proved to be successful in bridging the earlier high frequency studies in these systems with complimentary results. It is found that the cutoffs of ODF modes are sensitive to the end chain length (m) and lower cutoff wavelengths increase as the alkyl chain length increases. These studies bring out the effect of underlying layered smectic phases on the dynamic organization of nematic medium. The signatures of the presence of layered structure diminish as the order of the underlying smectic phase increases. It becomes transparent from the observations that in 4O.2, where the underlying $S_B$ did not form cybotactic clusters in the nematic medium, unlike liquid crystals like 8OCB with underlying $S_A$ phase, on the other hand it showed a $R_1$ dispersion similar to the case where there is no underlying smectic phase. In general in the homologous series the observed anisotropic physical properties show odd-even effects, but in the present case the cutoffs did not show such effect where as a monotonic variation of lower cutoff wavelength is observed as m-value goes from 2 to 4. The cutoffs observed in 4O.4 and the mixture of 4O.2 and 4O.4 are represented the nature of the underlying smectic phases in these samples.

Just below $T_{NI}$ the fluctuations in the nematic order parameter are caused by the fluctuations in the magnitude of the long-range orientational order. The time scales of these nematic order parameter fluctuations and their slowing down, as the nematic phase stabilizes, are observed in 4O.m liquid crystals.

While the $^1$H studies on 4OTOLFm and 4OFTOL are consistent with earlier studies in the isotropic phase showing the critical slowing down of short range nematic order fluctuations as $T_{NI}$ is reached, the $^{19}$F relaxation studies disclose a slow mechanism, which has qualitatively different temperature dependence in the experimental frequency range. In this context the emphasis is made on the presence of single fluorine on the core of liquid crystal molecule, noting that the only effective relaxation mechanism is due to the spin-rotation interaction. Data were analyzed classifying the dispersions into conventional region and overlapping region (altra low freqency, ±0.5 MHz).

In the conventional region dispersion is sensitive to short range nematic order fluctuations in addition to a slower process modeled as cage dynamics (slowly relaxing local structures). Nuclear spins, coupled with lattice by Spin-rotation interaction, modulated by fluctuating torques provides the relaxation path in this case. Whereas the critical fluctuations of short range nematic order are prone to both the nuclei
$^1\text{H}$ and $^{19}\text{F}$. It is confirmed from the consistent data at different temperatures with comparable time scales obtained for this mechanism.

The two nuclei have nearly equal gyromagnetic ratios, and hence their line shapes overlap at low enough Larmor frequencies providing a cross relaxation path. Such effects are clearly seen in the dispersion profiles below 500 kHz. This observation provides an opportunity to infer at least qualitatively about the changes in spectral line-widths near the phase transition. The temperature dependent studies of the relaxation rates further lend support to the models proposed in connection with the dispersion behaviour of the respective nuclei. In conclusion, singly fluorinated molecules in such complex fluids are seen to be exclusively sensitive to angular momentum time-correlations directly, and seem to offer a unique opportunity to probe very slow molecular processes, arising out of other cooperative modes in the system. The temperature dependant data showed in these results shows that below $T_{NI}$ also this cooperative phenomenon provides the relaxation paths to $^{19}\text{F}$ nuclei. This initial comparative study of the dynamics with multinuclear NMRD technique seems to indicate a new potential to probe new dynamic process which were not reflected in in the time modulation of dipolar interaction as is evidenced by the proton relaxation data.

The PMRD investigations, made on aqueous solutions of lysozyme and bovine serum albumin (BSA), in the presence of mild dosages of guanidine hydrogen chloride (GdnHCl), point out the increased orientational order of the interior waters in the protein. And further, in support of the well-known hydrophobic effect, these results seem to support the hypothesis of initial stiffening and stability of the protein at these small concentrations of denaturants. These results are inferred from a model dependent analysis of relaxation data, where the protein-water system is dynamically classified into three different time scales. The consistent correlation times obtained in the analysis and matching of these results with those obtained by complementary probes strongly support this hypothesis. The similar observations made on two different prototypes of protein samples here, in support of recent studies on protein-denaturant interactions, enforcing to conclude that the protein stiffening effect is general behaviour of all globular proteins.

In conclusion, nuclear spin-lattice relaxation measurements carried out over a wide frequency range, and supplemented with appropriate temperature dependent studies, seem to provide a powerful experimental probe to directly probe low frequency features of spectral densities of molecular dynamics in different soft materials. These experiments, supported by theoretical models of various molecular processes, prove
to be very valuable in informing on a variety of phenomena, characteristic of the materials investigated. In particular, the work reports a contrasting experiment wherein two very similar nuclei located on the same molecule report differently on the underlying processes, due to their differing sensitivity to the time correlation functions. These experiments indicate the possibility of exploring dynamic processes in different phase of the liquid crystal via angular momentum time correlations, and possibly uncovering molecular processes hitherto not reported through NMR techniques. In conclusion it is evidenced that the wide-dynamical range offered by NMR methods, coupled with detailed temperature dependent studies or in certain cases in support with the structural information are rich sources of dynamics in complex fluids. Correlating the physical properties with dynamics under the influence of external variable is a rewarding exercise. The strength of NMRD powered by field-cycling technique is highly appreciated in this context.