

Preface

Liquid crystals are interesting soft materials which develop variable degree of both orientational and positive ordering with the variation of suitable control parameters, usual the ambient temperature. The simplest of these phases is the nematic phase, with an appreciable orientational order, but otherwise liquid like in its mechanical behavior. The symmetry of the nematic phases could be uniaxial or biaxial, depending on the interactions between the different components of a molecular tensor. Being soft materials, the structure of liquid crystals can be relatively easily influenced by their interaction with the surfaces, and hence the physical properties of anisotropic medium can be readily manipulated by bounding surfaces and applied fields. This feature of liquid crystals has made them eminently suitable to many optical applications, the striking feature being display devices are an important step to look for novel applications. The confining geometries share a common feature: the competing boundary conditions imposed in the geometrical structures or through bounding conditions that induce new features in the free energy profiles leading to a sequence of novel phases with interesting the equilibrium structures, the control variable being either temperature, or the size of the system, or the anchoring influence at the surface. The different aspect of such behavior can be simulated by modeling these scenarios using simple lattice – based Hamiltonian models. The most known and widely used pair-wise additive lattice Hamiltonian is the Lebwohl - Lasher model, $U = -\varepsilon_{ij}P_2(\cos(\varepsilon_{ij}))$, based on Maier – Saupe theory. An extension of the LL model is used to describe a liquid crystal with biaxial molecules. Prediction of expected behavior of liquid crystals through Monte Carlo simulations modeled on such Hamiltonians, under the influence of differing geometrical confinements and as a function of temperature, is the primary objective of this thesis. With this objective Chapter - 1 sketches a brief review of liquid crystal physics relevant to the work reported.

A brief review of Metropolis algorithm and extension to non - Boltzmann methods is presented in chapter 2 to indicate the methodology adopted in the present work. The efficiency and applicability of such canonical sampling methods is put to severe test in certain physical conditions where the free energy profiles of the system under considerations either develop very shallow minima, or even barriers between two such minima. In such cases, the guided random walk (with simple Metropolis method with 'simple flip') become very inefficient, or is restricted to a single, then more efficient algorithms like non - Boltzmann

sampling methods are used. Finally, different physical properties relevant to the present study and details of the computation from the knowledge of canonical ensembles are presented.

The results of Monte Carlo simulations carried out on different liquid crystal systems are presented in the subsequent chapters. Chapter 3 presents the effect of confinement on thin films of liquid crystals comprising of uniaxial molecules. In this context, the extensive Monte Carlo simulations (based on canonical sampling methods) carried out on planar hybrid films using Lebwohl-Lasher model are supplemented by investigating this film with entropic sampling techniques. This permits a relatively error-free estimation of different properties of the medium with very fine variation of temperature. These simulations have supplemented the earlier conclusions, in helping to look for additional features of the director configurations in this film as a function of temperature. While confirming the presence of an intermediate biaxial phase over a small temperature range, this study specifically reported on the fluctuations in these order parameters particularly in different layers (in terms of their variance), to serve as possible signatures of the onset of the biaxial phase. It may be noted that the onset of the intermediate phase leaves only a weak signature C_v profile, as a shoulder. The low temperature phase with a bent director structure was further investigated by varying the thickness of the film.

Motivated by the role of hybrid boundary conditions to induce phase biaxiality in a confined system of uniaxial molecules, a thin cylindrical film embedded between two concentric cylindrical substrates was investigated with the two bounding surfaces inducing axial (along the axis of the cylinder) or radial (within each plane perpendicular to the axis of the cylinder). The interest here is that, unlike the case of the planar films, the two bounding surfaces have unequal surface area and have different curvatures, thus leading to different energy costs per unit area at the two surfaces. Under these conditions looking for possible creation of intermediate cylindrical layers of molecules which experience a competing and balanced effect of the hybrid anchoring influences from the two cylindrical surfaces required initial experimentation with different anchoring regimes assigned to the surfaces. It is found that this cylindrical film also has, under appropriately chosen anchoring conditions with specific geometry, an intermediate stable phase over a small temperature. There are striking similarities between the behavior of this specifically tailored cylindrical film and the hybrid planar film as far as phase biaxial symmetry is concerned. The thesis reports simulational results on this film based on canonical sampling methods.

The next two chapters focus on the macroscopic behavior of canonical ensembles of biaxial molecules, as reported by Markov Chain Monte Carlo simulations. The lattice Hamiltonian chosen for this purpose incorporates the interactions of both uniaxial as well as biaxial components of (second rank) tensorial attributes of neighboring molecules. This imparts to the system, the principle possibility of inducing biaxial symmetry, arising both from the phase biaxiality (from the biaxial organization of uniaxial components of the molecules) and molecular biaxiality (non-zero average contributions from the molecular

biaxial components directly). In addition such a model also generates a small contribution to order in the direction of the primary director arising from the self organization of the biaxial components of the molecules. Thus there are four order parameters which characterize the medium, and a study of these parameters and their fluctuations, along with the average energy and its fluctuations (specific heat) as function of temperature is the objective of these studies. In this context, Chapter 4 reports MC studies on a general Hamiltonian incorporating the above interactions with two variable parameters. These two in effect control the ability of the biaxial properties at the molecular level to influence the otherwise uniaxial phase obtained by the self organization of the essentially long rod like molecules. While the mutual interactions of two interacting molecules through their pure biaxial components (Term-A) create a macroscopic biaxial symmetry referred to as molecular biaxiality, the interactions involving mixed terms (Term-B) lead to the other two order parameters mentioned above. The earlier MC simulations showed that interaction between pure biaxial components (i.e. Term-A) only is responsible for the onset of a biaxial phase. Subsequent studies, based on bifurcation analysis of the general model taking into account both the above terms (i.e. Term-A and Term-B), led to an appreciation of the role Term-B in influencing the sequence and nature of thermally induced phases in such systems. In this context, the present work focuses on carrying out systematic study of the phase diagrams obtainable while spanning the two-parameter space of the interaction. Essentially one tries to change the relative importance of the above two Terms, and see it has a qualitative effect on the phase sequence that can be generated by varying the temperature of the system (control parameter). This work presents detailed phase diagrams, which one hand readily agree with the results reported earlier in certain limiting cases of choice of these parameters, and on the other indicate the progressive development of an intervening stable uniaxial nematic phase over a wide parameter space. Further study of these phase diagrams with interest on the molecular aspects of these choices could prove to be very interesting.

Chapter-5 describes the effect of confining such biaxial systems in planar geometries with hybrid anchoring conditions, much like the known case of hybrid planar film of uniaxial molecules. The major difference in this case however is that the geometric confinement applies to two axes of molecules, and is qualitatively different from uniaxial case, - it is more restrictive. This leads to two possibilities: 1. one can study the effect of such anchoring (employing equal, but variable, anchoring strengths at both the surfaces) on the thermally induced phase sequences and director configurations within each such phase through layer-wise computations; and 2. for a given choice of intermolecular interaction strengths, one can fine tune the relative importance of boundary conditions by varying the anchoring strength with a view to looking for a possible surface induced structural transition. This Chapter presents the results of MC simulations on such a film based on the biaxial Hamiltonian (satisfying the London dispersion approximation), and reports the existence of two interesting low temperature biaxial phases, as well as a structural transition within the lower temperature biaxial phase with changes in anchoring strength. These aspects

have been illustrated by computing the four different order parameters and their fluctuations (with spatial resolution), and specific heat under different experimental conditions.

The LL Hamiltonian implies that the three elastic constants for the splay, bend and twist distortions are set equal to one another ($K_1 = K_2 = K_3 = K$), and corresponds to the so-called spherical approximation. However in real nematics they are never equal, and their relative values do play an important role in determining the visco-elastic properties of the nematic medium. An interesting attempt has been made some time back to derive a lattice based Hamiltonian (with nearest neighbor coupling), starting with continuum elastic energy expression. The result is that there is now such a model lattice Hamiltonian whose interaction parameters have functional dependence on the three elastic constants (called elastic Hamiltonian, for convenience). This in turn permits tuning of the Hamiltonian to a specific liquid crystal system. However there is an important caveat in applying this Hamiltonian reliably, and originates from the fact that the space discretization of the energy to allow for the convenience of the lattice model demands that the spatial resolution so imposed should be consistent with the implicit assumption of the ability of the model to account for observed distortions through the variations of director fields only. Making use of the flexibility allowed by this model to investigate the influence of the elastic properties on the observable properties, the polymer dispersed liquid crystal (PDLC) droplets are revisited. There were earlier studied with different boundary conditions, based on LL model Hamiltonian. In the present case, the droplets were considered with radial boundary conditions, and this leads to the simplification that the relevant distortion which matters is restricted to splay only. These droplets are investigated with the elastic Hamiltonian as a function of the anchoring strength at the polymer interface. The results indicate that there is a sharp anchoring induced transition from a uniaxially ordered droplet to an essentially radially ordered droplet, and the anchoring characteristics are, as expected, influenced by the value of the splay elastic constant (K_1). The behavior is studied by computing the radial as well as axial order parameters (including layer-wise variation in different concentric spherical shells making up the droplet), and their fluctuations. The transition shows a very strong hysteresis. The validity of the model is checked by changing the spatial resolution in the model (which in effect translates to simulations at different reduced temperatures). The results show that this is a wetting transition, and is dependent only on the relative importance of the effects of splay distortion versus radial anchoring at the surface.

In conclusion, the thesis attempts to investigate liquid crystals under different conditions. These include study of assembly of interacting uniaxial (cylindrically symmetric) molecules under different confining conditions of geometry and anchoring, of assembly of interacting biaxial molecules under different conditions of mutual interactions of such molecules. These latter studies are also extended to confined biaxial systems to look for novel features, as were observed earlier in confined uniaxial systems. Finally, PDLC systems were studied with a relatively new Hamiltonian which incorporates the elastic properties as parameters of the model. It appears that confined liquid crystals are emerging as

very useful soft materials capable of exhibiting novel structures, on one hand conveniently tunable by the Hamiltonian parameters (properties inherent to the LC system) and external boundary conditions, and on the other suitably prepared to have the necessary free energy profiles by choice of the temperature of the medium.

