Chapter 4

Wang-Landau Monte Carlo simulation of nematic-isotropic transition in liquid crystal elastomers

4.1 Introduction

Nematic liquid crystals possess long-range orientational order, and hence elasticity associated with the deformations of that order. Rubbers are weakly-crosslinked polymers with very low shear modulus, $\mu$. They can be deformed at practically constant volume and the deformations can be as large as 1000% [1, 2]. Both these materials inhabit the grey area between liquids and solids. In 1975, de Gennes [3] envisaged that the cross-linked polymers made of liquid crystals would lead to very fascinating properties due to the coupling between anisotropic properties of liquid crystals and the elastic properties of the rubbers. It was conjectured that spontaneous alignment
of constituent liquid crystal molecules at NI transition would lead to dramatic effects in stress-strain relation. Due to these extreme thermo-mechanical effects, these materials are considered to be good candidates to function as actuators in applications like artificial muscles, etc., [1, 3].

Fundamentally, irregular cross-links and chemical heterogeneity in a LCE network provide source of quenched random disorder [1, 4] similar to that observed in nematics with sprinkled silica nanoparticles [5, 6] or random anisotropy [7]. Consequently, LCE too, are characterized by a complex free energy landscape leading to glassy ordering ([37] and references therein). While in spin glassy systems quenched disorder can be overcome by a strong enough magnetic field, in LCE this can be achieved mechanically by stretching the sample [8]. LCE can be theoretically described in continuum description, by the neo-classical theory based on anisotropic rubber elasticity [1], by Ginzburg-Landau approaches [9, 15, 27], as well as by 2D modelling [10].

In liquid crystal elastomers, the cross-link density is a crucial parameter since it gives a measure of coupling between the NI transition in orientational parameter space to the elastic degrees of freedom. If the density is more, orientational order is frozen-in since the local mesogenic units are rigidly held at the cross-links. If the density is very less, elastomers behave like melts. The answer to the question as to how many cross-links are sufficient to transform a visco-elastic polymer melt into an elastomer (which is a solid) still remains unanswered [11, 12]. Moreover, as the cross-link density is increased, the transition temperature, $T_{NI}$ increases with gradual smoothening of the order parameter variation from discontinuous to continuous transition, finally tending to a non-singular cross-over from ordered phase to disordered phase. The elastic energy response of the LCE’s can be accounted for employing the continuum description which is a simple extension of the elastic theory of polymers. The rubber-elastic response to deformation of any polymer network stems from the entropy change
when the number of conformations allowed for the chains is reduced on stretching their end-to-end distance between the cross-links. According to the classical elastic theory of rubbers, the free energy due to the elongation of the polymer by an amount $\lambda$ along one of the coordinate axes is given by:

$$F = \frac{1}{2} \mu \left( \lambda^2 + \frac{2}{\lambda} \right)$$  \hspace{1cm} (4.1)

where $\mu$ is the shear modulus. Here, we have assumed incompressibility of volume of the system, and hence in undeformed state, $\lambda = 1$. In liquid crystal elastomers, the end-to-end distance distribution becomes anisotropic. The uniaxial anisotropy of polymer chains has a principal axis along the nematic director $n$. The ability of this principal axis to rotate independently under the influence of network strains makes the rubber-elastic response non-symmetric. Thus, we have

$$F_{et} = \frac{1}{2} \mu \text{Tr}(\lambda^T \cdot l_0^{-1} \cdot \lambda \cdot l_0) + \frac{1}{2} \tilde{B}(\text{Det}[\lambda] - 1)^2$$  \hspace{1cm} (4.2)

Here, $l$ is the uniaxial matrix representing chain step length before ($l_0$) and after ($l_\theta$) the director is rotated by an angle $\theta$. The last term in the above equation 4.2 represents the contribution from bulk modulus $\tilde{B}$ ($(10^{10} - 10^{11} Jm^{-3})$, which is much greater than the shear modulus and independent of the chain conformations. This large energy penalty constrains the system to become physically incompressible. From these equations it is clear that the strain components will now have non-trivial effect on the system, in contrast to the isotropic rubbers. The uniqueness of nematic rubbers stems from the competing microscopic interactions and there exists two levels of characteristic length scales: one is the anisotropy on monomer (small) scale of nematic coherence length, while the strains are defined on a much greater length scale of polymer end-to-end chain length. This length scale separation calls for the need to carry out multi-scale modelling to understand various underlying phenomena exhibited by liquid crystal elastomers.
4.2 NI transition in liquid crystal elastomers

Experimental observations on liquid crystal elastomers show that both the orientational order parameter and strain vary continuously at the nematic-isotropic transition [17, 18, 21, 22]. The NI transition is neither first-order nor continuous but rather a non-singular crossover from disordered to ordered phase [13–16]. There were several attempts to explain the nature of NI transition and study the effect of relevant factors like cross-link density, history of cross-linking, number of monomers present in between neighbouring crosslinks, monomer-monomer interaction strength, the coupling between the mesogenic units and the elastic degrees of freedom, etc., on the transition. Basically there are two radically different points of view to explain the underlying phenomena. First explanation is based on the effect of aligning stress on the transition. Unless special precautions are taken during the network fabrication, the low temperature phase of nematic elastomers is always an equilibrium polydomain director texture [23, 24]. This is in contrast with a kinetic 'polydomain' texture often referred to as Schilieren texture [25], which is the consequence of nucleation and growth mismatch in a system undergoing the first-order transition [26]. LCE samples prepared during the Kupfer and Finkelmann’s two-step procedure [8] involve imposing an aligning field above the critical value to align the polydomain sample with centres at crosslinks into a monodomain sample. According to the classical theory of phase transitions the behaviour of strain order parameter versus temperature is as shown in the figure 4.1.

There exists a critical stress below which the strain is discontinuous with respect to temperature. As the stress is increased beyond this critical value, the transition becomes continuous and softens gradually to super critical regime, where the strain varies continuously without any singularity as the temperature is varied. This aligning
stress can be either due to the external aligning fields as in the Finkelmann’s procedure or internal aligning fields due to the cross-links present in the anisotropic nematic medium.

In order to understand the underlying phenomena which causes the LCE systems to exhibit non-singular behaviour, Selinger, et. al., [27] performed experiments and attempted Landau-like free energy expansion as a function of both strain and orientational order parameters to fit the data. They derived Landau’s free energy in terms of orientational order parameter, $S$ and elongation $e$ in the presence of aligning stress, $\sigma$ as shown below:

$$F = \frac{1}{2} \alpha'(T - T_0)S^2 - \frac{1}{3} b' S^3 + \frac{1}{4} c' S^4 - u e S - \sigma e + \frac{1}{2} \mu e^2$$  \hspace{1cm} (4.3)$$

where $T$ is the temperature and $\sigma$ is the effective stress which is a combination of applied stress and the internal stress due to anisotropic cross-linking. Averaging over $S$, we obtain free energy in terms of $e$ alone

$$F = \frac{1}{2} \alpha(T - T_0)e^2 - \frac{1}{3} be^3 + \frac{1}{4} ce^4 - \sigma e.$$ \hspace{1cm} (4.4)$$

The above equation is minimized over $e$ and the resulting predictions are fitted with the experimental data. They found that the fits do not agree well with the experimental data at the transition temperatures, leading to their conclusion that the
experimental observations are not consistent with the super-critical evolution between isotropic and nematic phases. They thus consider, as a consequence, a heterogeneous model for the elastomer.

There can be two ways in which heterogeneities can be introduced in the system. The polymerization process and the crosslinks induce quenched disorder into the system. For example, polydispersity in the chain length gives one type of disorder. This may lead to distribution of regions with different nematic-isotropic transition temperatures. At any given temperature, a sample would have a coexistence of isotropic and nematic domains. As the temperature decreases, it would cross over from mostly isotropic to mostly nematic phase, leading to a smooth evolution in the average orientational order parameter and in the macroscopic strain. This is the so-called random bond disorder. Another scenario is that the cross-links act as sources of random disorder where the director orientations are quenched [4]. As the domain size near each cross-link could be different, this leads to a distribution of internal fields, -the so-called random field disorder. However, recent DNMR studies on LCE’s [17, 18] synthesized using Finkelmann’s cross-linking procedure showed signatures that supercritical behaviour is predominant with relatively low heterogeneity. As the cross-link density is increased, the nature of the phase transition changes from the first order type (subcritical) to continuous (at the critical point) and then to supercritical. This is also in agreement with the general result that quenched impurities destroy long-range order, first shown by Larkin [19] and then generalized by Imry and Ma [20].

In this context, two coarse grained lattice models were proposed recently [36, 37]. The first model (Model-I) [36], considers both random-bond and random-field disorders in the Hamiltonian, the main aim being study of the effect of such disorders on the NI transition using MC simulations. Here all the interactions including the anisotropic interactions between mesogenic units, energy contribution from elastic
degrees of freedom and the coupling between the two degrees of freedom, are incorporated in the Hamiltonian as energetic terms. The contribution from elastic degrees of freedom is derived from neo-classical rubber elasticity [1] described briefly above. However, in the absence of any heterogeneity and with the particular choice of the strength of coupling interaction, the system is driven towards strong first order and hence contributions from heterogeneities (random bond and random field disorders) are found necessary to make contact with the experimental results. The second model (Model-II) [37] however considered the contributions from elastic degrees of freedom and the coupling between the orientational degrees of freedom with the global strain as entropic in nature and hence appear as pseudo Hamiltonian terms. This model, as proposed, has the mechanism to moderate the degree of interaction between the two relevant variables depending on the instantaneous global strain present in the system, and also allows for incorporating other factors (like, cross-link density, nature of polymer formation, etc) through another variable prefactor. The model was studied through canonical MC simulations, and has shown to satisfactorily account for experimental observations.

In Model-I, orientational and strain degrees of freedom are assumed to be strongly coupled, the coupling parameter being fixed at its maximum value of unity. This corresponds to prohibitively large shape anisotropy of the polymer chains. Under these conditions this model predicts, in a homogeneous sample, a strong first order transition. Our interest in this model is to understand the effect of making this coupling more realistic by assuming more practical shape anisotropies for the polymer chain, on the NI transition, and to make the treatment simple we consider a homogeneous system. Such a variable coupling strength can also arise from other factors like cross-link density, nature of polymerization, history of cross-linking, etc. We indeed find that for a typical value of coupling parameter at $\chi = 0.2$, the strain variation with temper-
ature matches well with the experimental results even in a homoneous system. We also attempted to study the effect of such variable coupling on the strain-orientational order relation for much wider range of temperature bracketing the NI transition with a high temperature resolution. To this end we employed entropic sampling technique as described in Chapter 3 [40], and we modify the algorithm suitably to accomodate the random walk in the two dimensional parameter space. Section 4.3 describes the Model-I; the simulation details and results are discussed in the subsequent sections 4.3.1 and 4.3.2.

Model-II considers the pure elastic and coupling terms in the Hamiltonian as arising from entropic considerations, with a linear temperature dependence. This model was studied by performing canonical MC simulations. The presence of temperature in the Hamiltonian (the so-called pseudo terms) present a challenge in adopting the entropic sampling methods, which basically demands determination of density of states for a given Hamiltonian. Such a concept in the presence of terms of entropic origin needs to be examined closely to devise a methodology which enables us to apply these sampling methods to pseudo-Hamiltonians as well. We propose a procedure to generate a two-dimensional DoS, and hence 2D canonical ensembles, for such models by treating differently the two types of contributions to the Hamiltonian. Model-II is described in section 4.4. The details of the simulation methodology are given in section 4.4.1 and the results are discussed in section 4.5. Finally, we make comparative comment on the two models and discuss our results.
4.3 Lattice model of a liquid crystal elastomer: Model-I

We consider an $L \times L \times L$ cubic lattice. Each lattice site holds a nematic director denoted by a unit vector $|n_i\rangle$. Each nematic director interacts with its six nearest neighbours and the interaction is described by Lebwohl-Lasher potential [43], which has head-tail flip symmetry ($|n_i\rangle$ and $-|n_i\rangle$ are equivalent). Besides, each director is coupled to global elastic degrees of freedom. A model Hamiltonian for such an interaction between local director and global strain has been derived from the neo-classical theory of rubber elasticity [1], see [36]. According to this theory the grand trace formula is given by

$$F_{\text{elastic}} = \frac{\mu}{2} \left[ Tr \left( \hat{\lambda}^T \cdot \hat{l}^{-1} \cdot \hat{\lambda} \right) + \ln \left( \frac{\text{Det}[l]}{a^3} \right) \right]$$  \hspace{1cm} (4.5)$$

where $\mu$ is the shear modulus, $\hat{\lambda}$ is the lattice distortion tensor, $\hat{l}$ is the shape tensor of the polymer chains, $\hat{l}_0$ is the shape tensor of the chains at the time of cross-linking and $a$ is the average step length of the polymer. In a lattice model, the shape tensor $l_i$ at each lattice site in a coordinate system aligned along the director $|n_i\rangle$ is given by,

$$\hat{l}_i^{-1} = \begin{pmatrix} l^{-1}_{\perp} & 0 & 0 \\ 0 & l^{-1}_{\perp} & 0 \\ 0 & 0 & l^{-1}_{||} \end{pmatrix}$$  \hspace{1cm} (4.6)$$

where $l_{\perp}$ and $l_{||}$ are the anisotropic polymer step lengths perpendicular and parallel to the local director $n_i$, respectively. The lattice distortion tensor, $\hat{\lambda}$ in a coordinate
system aligned along the strain axis, say $\bar{m}$ is given by

$$
\hat{\lambda} = \begin{pmatrix}
\lambda^{-1/2} & 0 & 0 \\
0 & \lambda^{-1/2} & 0 \\
0 & 0 & \lambda
\end{pmatrix}
$$

(4.7)

It may be noted that the shear deformations are not considered here. The resultant trace term after substituting $\hat{\lambda}$ and the step length tensor $\hat{l}$ is then given by, after certain simplifications [36]

$$
F_{\text{elastic}}(n, \lambda) = \frac{\mu}{2} \left[ (\lambda^2 + 2\lambda^{-1}) - \gamma(\lambda^2 - \lambda^{-1}) \left( \frac{3}{2} (m \cdot n_i)^2 - \frac{1}{2} \right) \right].
$$

(4.8)

In the above expression, the first term is classical elastic energy whereas the second term provides the coupling between the elastic strain and the orientational order parameter. $\gamma$ represents the coupling strength between two degrees of freedom and is given by

$$
\gamma = \frac{2l_{\perp}^{-1} - 2l_{||}^{-1}}{2l_{\perp}^{-1} + 2l_{||}^{-1}
$$

(4.9)

In the earlier work [36], $\gamma$ is set at unity, corresponding to extreme anisotropy if the line shape tensor, $l_{||} \gg l_{\perp}$. The final Hamiltonian includes

(i) Lebwohl-Lasher nearest neighbour interaction [43] of the directors, placed on the lattice sites

(ii) the interaction of each local director, $|n_i\rangle$ with

(a) the global elastic strain $e$ given by $\lambda = 1 + e$

(b) a possible inhomogeneous field, $|h_i\rangle$

(iii) an externally imposed global stress, $\sigma$

(iv) shear modulus, $\mu$ which is held constant in this model.
With this notation, one expresses the lattice Hamiltonian as

\[ F = - \sum_{(i,j)} J_{i,j} \left( \frac{3}{2} \langle n_i | n_j \rangle^2 - \frac{1}{2} \right) + \sum_{i=1}^{L^3} \left[ \frac{\mu}{2} \left( \lambda^2 + \frac{2}{\lambda} \right) - \frac{\mu \gamma}{2} \left( \lambda^2 - \frac{1}{\lambda} \right) \left\{ \frac{3}{2} \langle m | n_i \rangle^2 - \frac{1}{2} \right\} - \sigma \lambda - \langle h_{i} | n_{i} \rangle^2 \right]. \] (4.10)

In the first term the sum extends over all distinct pairs \((i,j)\) of nearest neighbours. \(J_{i,j} > 0\) measures the strength of nearest neighbour interaction. Periodic boundary conditions are imposed in all directions.

\(\lambda \geq 1\) is a scalar denoting the strain parameter, and \(\lambda = 1 + \epsilon\), where \(\epsilon\) is the strain along the distortion axis taken to be along the unit vector \(|m\rangle\). The above Hamiltonian ensures that directors at different lattice sites tend to align along the distortion axis \(|m\rangle\). The above model Hamiltonian has the flexibility to describe the liquid crystal elastomer in the presence of random bond (\(\{J_{i,j}\}\)) or random field (\(\{|h_{i}\}\) disorder, as well as under the application of external stress, \(\sigma \neq 0\).

Selinger and Ratna [36] considered first a homogeneous elastomer (\(J_{i,j} = 1 \forall (i,j)\)) in the absence of local fields (\(\langle h_{i} \rangle = 0 \forall i\)) with maximal coupling (\(\gamma = 1\)) and no external stress (\(\sigma = 0\)). Their MC simulations under these circumstances yield a strong first order NI transition, driving a first order strain transition as well. They find that the transition can be smoothened to make contact with experiment by in principle introducing external stress and driving the system into a super critical stress condition. However based on earlier observations and arguments, they rule out the presence of stress as the softening mechanism, and show that heterogeneity in the medium, either in the form of bond-disorder or random local fields can also soften this transition to the required level, by controlling the degree of disorder. Their conclusions were based on, of course, assuming that the coupling between the
orientational and strain degrees of freedom is fixed, and that too at a value which sets
the shape anisotropy of the polymer chains at perhaps an inacceptably high value. We
argue that this coupling constant itself might have a crucial role in determining the
nature of the transition, quite independent of the presence, or otherwise, of external
stress or inhomogenities within the sample. It is based on the observations that in
reality the shape tensor anisotropy depends on the nature of the polymerization and
the constituent mesogenic units, and hence setting $\gamma = 1$ (i.e., $l_\parallel \gg l_\perp$) may be
an unrealistic idealization. Secondly, we also expect that crucial properites of the
medium like cross-link density should play a role in the effective coupling between
the two interacting variables (via their relative length scales of relevance), and hence
should affect their coupling. Accordingly, we investigate the effect of this coupling
constant $\gamma$ on the predictions of this model, considering the system to be homogeneous
and experiences no stress. We employ entropic sampling method to perform random
walk in the configuration space of these two variables, and extract infromation through
reweighting procedures. We use the density of states of the system obtained from the
WL algorithm to compute free energy profiles of the system and hence to investigate
the nature of the transition. The details of this study are given in the next section.

4.3.1 Details of simulation

In the present simulation we apply modified WL algorithm described in detail in
Chapter 1 [40]. It may be noted that one exploratory work reported therein, on bulk
liquid crystal system as well as liquid crystal confined to a porous media indicated
that the modifications introduced into the WL algorithm make the entropic sampling
of these systems much more efficient, and reproduce very well the known results on
these systems. Our aim here from the simulation point of view is to apply this method
to a complex system which involves performing a random walk in a multi-parameter
space: orientational variables and strain parameter.

We consider a homogeneous lattice model of the liquid crystal elastomer eqn 4.10, with no external field and no stress: \( J_{i,j} = 1 \) \( \forall \langle i, j \rangle \) and \( h_i = 0 \) \( \forall i \), \( \sigma = 0 \) and \( \mu = 1 \). Because of the complexity involved in performing random walk with uniform distribution with respect to energy, which itself is dependent on two MC variables, we restrict the size of the lattice, to a linear size \( L=6 \). We subsequently extended the study to \( L=8 \), just to check for the consistency of these results. We take the initial microstate with \( \{ |n_i \rangle \} \) chosen randomly on each lattice site and \( \lambda = \lambda_0 = 1 \). Let \( C_0 \) denote the initial microstate and \( E_0 \) be its energy. We probe the system in an energy range \(-500\) to \(50 \) expressed in units of \( J_i \). This energy range is divided into \( 8000 \) bins of equal width. Let \( \nu \) denote the energy bin index of the initial microstate. We set \( g_i = 1 \) \( \forall i \). In each Monte Carlo step a director is chosen at random and its orientation is changed to a trial orientation employing Barker’s method \([44]\). A trial strain parameter, \( \lambda_t \) is obtained from the current strain parameter \( \lambda_0 \) randomly following the prescription \( \lambda_t = \lambda_0 + 0.01 \times (\xi - 0.5) \) where \( \xi \) is sampled from a uniform distribution \([0,1]\). These two operations correspond to taking random step involving both MC variables, and producing a new trial microstate \( C_t \) of the lattice elastomer. The acceptance of the trial microstate is based on entropic sampling criterion described earlier. Once a microstate is accepted we update \( g \) as per Wang-Landau algorithm, as before. We carry out in this fashion one Wang-Landau run; the \( g \) function at the end of a Wang-Landau run is taken as the input for the next run. The procedure is exactly as described in the earlier Chapter, and finally we get a converged density of states which can then be used to produce an entropic ensemble of microstates spanning the space of both the degrees of freedom. This is achieved by carrying out a long production run based on the DoS obtained, and let us denote this as \( g \)-ensemble. From this \( g \) ensemble, we calculate the desired macroscopic properties.
of the liquid crystal elastomer system, with a high temperature resolution, through the re-weighting scheme described in Chapter 2. For the system of size $6 \times 6 \times 6$, the time taken to generate DoS, involving MC steps in the two variable spaces on a Pentium IV (Intel based) computer (at 2.0GHz) is about 10 days, while it extends beyond 20 days for a system of size $8 \times 8 \times 8$.

4.3.2 Results and Discussions

Figure (4.2) depicts orientational order $S$ as a function of temperature $T$, while finite size effects do effect the computed results, one interest is in the differences in the relative variation of parameters as the coupling is varied. for various values of coupling parameter $\gamma = 1, 0.8, 0.6, 0.4, \text{ and } 0$ on a system of size $6 \times 6 \times 6$. For $\gamma = 1$ we find that order parameter drops sharply when temperature increases. For smaller $\gamma$, the transition becomes less sharp and occurs at lower temperature. Figure (4.3) depicts the strain parameter $\lambda$ as a function of temperature for various values of $\gamma$. At high temperature the system is isotropic and hence irrespective of the coupling strength, the strain is zero i.e $\lambda = 1$ for all temperatures. When the temperature is lowered, say below $T_i$, strain develops, see Fig. (4.3). The value of $T_i$ is higher for larger $\gamma$. For $\gamma = 1$ the strain rises rather steeply with lowering of temperature. For lower values of $\gamma$ the increase of strain with decrease of temperature for $T < T_i$, is progressively smaller. For $\gamma = 0$ the orientational and elastic degrees of freedom are completely decoupled and hence $\lambda = 1$ for all temperatures, i.e. no strain develops even when nematic order sets in on lowering the temperature. These results are consistent with experimental observations. For $\gamma = 0.2$, the elongation at lower temperatures in the nematic regime is about 14% of the original sample size, which seems to be a benchmark value typically expected in an experiment. Thus it seems equally plausible, in principle, to soften the transition and tune the model to correspond to expected
results, without invoking the presence of stress or heterogeneity. The variable nature of $\gamma$ can be attributed to many contributing factors like cross-link density, nature of polymerization, etc. But the tuning of this model Hamiltonian to make contact with an experiment may encompass contributions from all possible factors, including deviation of $\gamma$ from unity.

![Graph](image)

**Figure 4.2** Orientational order parameter $S$ versus temperature for various values of the coupling parameter $\gamma$.

Figure (4.4) depicts specific heat, calculated from the fluctuations of energy, as a function of temperature for various values of $\gamma$. For $\gamma = 1$, we find that the specific heat shows a sharp maximum at the transition temperature. For lower values of $\gamma$ the transition occurs at lower temperature and $C_V$ peak broadens. This is in agreement with the mean-field arguments Uchida [47]:

Figure (4.5) depicts the transition temperature as a function of $\gamma$. The transition temperature is taken as the value of $T$ at which the specific heat shows a maximum. As $\gamma$ increases the transition temperature increases slowly initially; when $\gamma$ increases beyond 0.6 the transition temperature increases rather steeply.
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Figure 4.3 Strain parameter $\lambda$ versus temperature for various values of the coupling parameter $\gamma$.

Figure 4.4 Specific heat $C_V$ versus temperature for various values of the coupling parameter $\gamma$; $C_V$ has been obtained from the energy fluctuations.
As seen from figures (4.2) and (4.3), both $S$ and $\lambda$ increase with decrease of temperature. To see the nature of their correlation we have plotted in figure (4.6), $\lambda$ versus $S$ for various values of $\gamma$. For $\gamma = 0$ the strain is zero ($\lambda = 1$) and is independent of $S$ as expected. For small values of $\gamma$ the strain parameter $\lambda$ scales linearly with $S$ over the full range of temperature. For $\gamma = 1$, the scaling is linear for $S \leq 0.6$ and $\lambda \leq 1.25$, which correspond to temperatures greater than about 0.8. This is consistent with the results of earlier simulations [36] performed for $T \geq 0.8$, showing linear scaling between $\lambda$ and $S$. However, we find that for lower temperatures the scaling of $\lambda$ with $S$ is nonlinear. The strain increases steeply to fairly large values as the orientational order increases and attains its maximum value of unity. Fig. (4.7) depicts $g$ function and the corresponding energy histogram. The energy histogram is fairly flat indicating the reasonable convergence of DoS to its true value. From the $g$ function we can calculate the microcanonical entropy and free energy up to an additive constant. Note that entropy or free energy calculations are very difficult if
Figure 4.6 Variation of strain ($\lambda$) with orientational order ($S$)

not impossible from conventional canonical simulations.

We show in figure (4.8) the variation of (representative) free energy with energy for $\gamma = 1$ at three temperatures bracketing the transition point. We can see clearly that the transition is first order and strong. Figure (4.9) depicts free energy versus $E$ for $\gamma = 0.8$. The transition is still first order but is relatively weak, as seen by the decreased barrier height relative to $\gamma = 1$ (for the same system size). For smaller values of $\gamma$ the transition weakens further. For $\gamma$ less than 0.4 or so, the micro-canonical free energy barrier is not discernible.
4.3 Lattice model of a liquid crystal elastomer: Model-I

Figure 4.7 (Top) Logarithm of entropy as a function of energy. (Bottom) Histogram of energy of microstates.

Figure 4.8 Free energy versus energy for temperatures above, below and at the transition point (with equal minima) for the system with $\gamma = 1.0$. 
Figure 4.9 Free energy versus energy for temperatures above, below and at the transition point for the system with $\gamma = 0.8$. The barrier height is small; the transition is still first order though weak.
4.4 Lattice model of a liquid crystal elastomer:

Model-II

Recently, Pasini, et. al., [37] suggested another coarse-grained lattice model to describe the features of NI transition in LCE's. While retaining the pure energetic nature of the contributions from interactions among orientational degrees (like Model -I), they introduce the entropic nature of the contribution from elastic degrees by presenting their explicit (linear) temperature dependence in the Hamiltonian. Consequently, the Hamiltonian has two pseudo terms. In this model, cross-links are taken to coincide with the lattice sites in a three dimensional cubic lattice. Let us consider that there are \( M \) monomers of length \( b \) each present in each polymer chain. The pseudo-Hamiltonian to mimic the entropic effect of uniform stretching of the lattice \( \lambda \) is given by:

\[
H_e = Nk_B T \alpha \left( \lambda^2 + \frac{2}{\lambda} \right)
\]  

(4.11)

where \( N \) is the number of lattice points. \( \alpha \) is the cross-link density which depends on the characteristics of the polymer chain as \( \alpha = \frac{3a^2}{2Mb^2} \), where \( a \) is the distance between two lattice points. The interaction between two mesogenic units \((i, j)\) whose average orientations are represented by directors, \((\mathbf{n}_i, \mathbf{n}_j)\) is given by Lebwohl-Lasher potential:

\[
H_n = - \sum_{(i<j)} \epsilon_{ij} P_2(\mathbf{n}_i \cdot \mathbf{n}_j)
\]

(4.12)

Here, \( \epsilon_{ij} \) represents the nearest neighbor cell-cell interaction strength. In a homogeneous system that is under consideration all the coupling coefficients, \( \epsilon_{ij} \) are equal, say \( \epsilon \). The coupling between the elastic strain and mesogenic alignment is given by

\[
H_e = -k_B T \chi Q(\lambda) \sum_{i=1}^N P_2(\mathbf{n}_i \cdot \mathbf{z})
\]

(4.13)
where $\chi$ is the coupling constant and the value $Q(\lambda)$ is the measure of anisotropy of polymer chain end-to-end tensor distribution when the sample is deformed to a value $\lambda$ along the z-axis, preserving the volume. It is defined as

$$Q(\lambda) = (4\pi)^{-1} \int \epsilon P_2(\cos \theta) d\Omega = (3\lambda^3/2) \mathcal{L}(\lambda^3 - 1) - 1/2 \quad (4.14)$$

where

$$\mathcal{L}(\zeta) = \begin{cases} 
  \frac{\text{arctanh} \sqrt{-\zeta} - \sqrt{-\zeta}}{\sqrt{-\zeta^3}}, & -1 < \zeta < 0, \\
  1/3, & \zeta = 0 \\
  \frac{\sqrt{\zeta} - \text{arctan} \sqrt{\zeta}}{\sqrt{\zeta^3}}, & \zeta > 0;
\end{cases} \quad (4.15)$$

The volume of integration as indicated in the equation 4.14 corresponds to a uni-axial ellipsoid obtained from an isovolume deformation of a unit sphere by a factor of $\lambda$ along the z-axis. In an undistorted sample, $\lambda = 1$ and hence $Q(\lambda) = 0$. On stretching along or perpendicular to the z-axis, $Q(\lambda)$ becomes either positive or negative, respectively. The important point to be noted here is that $Q(\lambda \to \infty) \to 1$, hence it is finite even for very large deformations bounded between $-0.5$ and $1.0$. In contrast, the $\lambda$-dependent contribution in the coupling interaction of Model-I diverges for extreme deformations. The total Hamiltonian of Model-II is given by:

$$H = - \sum_{i,j} \epsilon_{i,j} P_2(\mathbf{n}_i, \mathbf{n}_j) + N k_B T \alpha \left( \lambda^2 + \frac{1}{\lambda} \right) - k_B T \chi Q(\lambda) \sum_{i=1}^{N} P_2(\mathbf{n}_i \cdot \mathbf{z}) \quad (4.16)$$

This model was investigated based on canonical MC simulations [37] to compare the predicted macroscopic behaviour of the system with experimental observations. These should also include the effects of heterogeneity and stress. These investigations indicate that proposed Hamiltonian model satisfactorily accounts for the observed thermal behaviour of the LCE. In this context, the objectives of the current effort
is to look for ways of implementing entropic sampling algorithm on a Hamiltonian which itself contains parametric dependence on temperature. Estimation of DoS, construction of canonical ensembles and extraction of physical properties out of such a model is new, and is the aim of the next section.

### 4.4.1 Details of the simulation

We use the scheme of frontier sampling discussed in the earlier chapter along with Gaussian update protocol [51] to investigate this model. In brief, the key steps in the procedure are:

- When the random walker arrives at the microstate $x_0$ whose energy is say $E_0$, the logarithm of density of states $\omega(E_0)$ is not updated locally as $\omega(E_0) \rightarrow \omega(E_0) + f$, but a Gaussian kernel $k(E)$ is placed using the updating scheme:
  \[ \omega(E) \rightarrow \omega(E) + \gamma \ast k((E - E_0)/\delta) \]
  where $k(x) = exp(-|x|^2)$ [51].

  In each WL iteration we start with a certain $\gamma$ value (say 0.1) and perform 1000 or more MC sweeps (one WL run). Such WL runs are repeated by gradually decreasing $\gamma$ till it reaches at least 0.001. The value of $\delta$ is kept fixed during this simulation.

- Each frontier run consists of a learning run followed by a reference run.
  - **Learning run:** A cut-off point in the energy range is identified by examining the the constancy of the difference between $\omega(E)$ values within a chosen tolerance corresponding to two consecutive WL iterations, and $\omega(E)$ is preferentially updated inside the frontier defined by the cut-off point, to force the system to low probable regions.
  - **Reference run:** WL iteration is performed to smoothen the DoS generated from the learning run. The difference in $\omega(E)$ from reference run and
the earlier learning run is used to find a possible new (lower) cut-off in the
next learning run. Otherwise, this step is repeated until a new frontier at
a lower energy could be found.

- After the desired energy range is spanned, a long smoothening run is performed.

- Linear interpolation method among energy bins is employed while calculating
  the acceptance ratios to avoid the possibility of the system getting sometimes
  trapped in the same energy bin for too long. Indeed this trick has speeded up
  the upgrade process considerably.

Entropic sampling procedure is intuitively clear while dealing with usual Hamilto-
nians with pure energetic contributions. Such a Hamiltonian once defined, has a set
DoS. Canonical sampling based on a temperature dependent probability distribution
merely corresponds to moderation of the natural tendency of the system with a given
Hamiltonian to exist with different probabilities in different energy regions, with a
statistical necessity of complying with the given probability prescription, owing to the
energy exchanges under canonical external conditions. This somewhat clearer role of
DoS, well defined and temperature independent for a given Hamiltonian, needs a
re-examination if the Hamiltonian also contains entropic contributions with explicit
temperature dependencies. In such a case, the above picture implies temperature
dependent DoS, as the variation of temperature in effect corresponds to changing
the relative strength of the terms involved, with respect to the chosen energy scales.
Then it is not possible to directly proceed with the above procedure for Model-II. For
convenience of discussion, we write the Hamiltonian as consisting of two parts:

\[
\mathcal{H} = \mathcal{H}_{\text{energy}} - T\mathcal{H}_{\text{entropy}}
\] (4.17)
4.4 Lattice model of a liquid crystal elastomer:

Model-II

\[ H_{\text{energy}} = -\sum_{i<j} \epsilon_{ij} P_2(\mathbf{n}_i \cdot \mathbf{n}_j) \]  
\[ H_{\text{entropy}} = -N k_B \alpha \left( \lambda^2 + \frac{1}{\lambda} \right) + k_B \chi Q(\lambda) \sum_{i=1}^{N} P_2(\mathbf{n}_i \cdot z) \]  

Because of the different procedures we adopted to compute the DoS of this system, it has been possible to carry out simulations on a bigger lattice (relative to Model-I), with a linear size \( L = 20 \). We initialize the orientations of spins representing the local directors on a cubic lattice of size \( 20 \times 20 \times 20 \). The desired energy range corresponding to interactions purely among the orientational degrees (the \( H_{\text{energy}} \) term), say along the \( E \) axis is divided into 16000 bins, whereas \( \lambda \) axis is divided into 100 bins over the range \([1,1.5]\). Before presenting the results of these simulations the generic procedure for computing the DoS and construction of entropic ensemble is presented first. The total DoS of the system is to be defined over the two dimensional grid (16000 \( \times \) 100) specified by the (spin) energy bins and the \( \lambda \) bins. The choice of the number of bins is constrained by the limitations on the memory available for storage and the computational time required, (computations being carried out on a single processor). Recognizing the fact that this Hamiltonian assigns entropic origin to all interactions involving the strain variable, we split the process of computing the DoS of the total Hamiltonian into two steps. We first compute the DoS arising entirely from \( H_{\text{energy}} \), using the normal entropic sampling procedure; and this corresponds to, as far as, orientational variables are concerned, computing the DoS of the total Hamiltonian at \( \lambda = 1 \) (the third interacting term is set to zero via the factor \( Q(\lambda) \)).

Next, we note that minimization of free energy of a system with a purely energetic Hamiltonian by a random walk in the appropriate configurational space guided by a Markov chain Monte Carlo dynamics can be mapped to the present system by simply realizing that \( H_{\text{entropy}} \) is in effect the entropy of the system defined on the
two-dimensional space of \((\lambda, E)\). Of course, \(E\) is determined by the amount of orientational order of the specific microstates, and hence influences the contribution to the coupling term through the local director distribution. Thus, the construction of a 2D DoS spanning \((\lambda, E)\) space, or equivalently \((\lambda, S)\) space (\(S\) is the scalar orientational order parameter), simplifies to the evaluation of the contribution of \(H_{\text{entropy}}\) term over a chosen range of \(\lambda\), for a given state of orientational order (i.e., \(S\), and hence \(E\)), as the entropy contribution arising from \(\lambda\)-dependent part of the Hamiltonian. Thus, for every energy value of \(E\) in the range of interest, or more practically for every bin value of \(E\), the extension of DoS along the \(\lambda\)-axis can be computed using the information on the instantaneous distribution of entropy along the \(\lambda\)-axis. The 2D DoS in \((\lambda, E)\) space is thus constructed. In the absence of coupling between the two variables, a bell-shaped distribution function located at each \(E\) bin value, extending over the \(\lambda\)-axis and peaked at \(\lambda = 1\), would result. The effect of the interaction to modify this function, changing its shape as well as the location of its peak along the \(\lambda\)-axis. The thermally driven orientational order thus modifies the DoS of the system so as to yield different (canonical) averages of \(\lambda\) for different degrees of orientational order.

After checking for its convergence, the DoS is used to generate entropic ensemble of microstates in \((\lambda, E)\) space by sampling both the variables (over their respective ranges) during a long production run, the acceptance criterion being stipulated by the DoS, as usual. The quality of the entropic ensemble can be checked by plotting the distribution of these states over the \((\lambda, E)\) plane as a histogram over the 2D bin structure. Knowledge of 2D DoS, along with the entropic ensemble of microstates spanning the desired range of the parameters is sufficient to extract a 2D canonical ensemble at the chosen temperature by the reweighting procedure. Computation
4.5 Results and discussion:

The energy scale is set by choosing $\epsilon = 1$ in eqn 4.12. The cross-link density $\alpha$ is initially chosen to be 0.3, and the coupling constant $\chi$ at 0.5. The DoS corresponding to $H_{\text{energy}}$ is computed by choosing the initial and final values of $\gamma$ during a WL iteration to be 30 and 0.0001, respectively. The value of $\delta$ is kept at 35 throughout the simulation. The ranges of these values are determined by carrying out a few exploratory runs on the chosen system size ($L = 20$) to obtain a reasonably well convergent DoS along the $E$-axis ($\lambda = 1$), as verified by the flatness of the corresponding energy histogram. The DoS is thus available at 16000 distinct energy values (bins). Corresponding to each such energy bin value (or, equivalently order parameter value), a large number of microstates (corresponding to simple LL potential, since $\lambda$ is set to 1) are available representing different orientational organization consistent with the bin value. The DoS at each of the $E$-bins is now extended along $\lambda$-axis by the following procedure. For each microstate within a given bin, the contribution to DoS from $H_{\text{entropy}}$ as a function of $\lambda$ (over the range 0.8 to 1.2) is computed eqn 4.11. All such distributions along $\lambda$ arising from each of the microstates associated with the bin are now averaged to yield the coarse grained extension of the DoS of that bin along $\lambda$ ($\lambda$ being spread over 100 bins). This has been carried out over all the $E$ bins to finally compute the 2D DoS of the system. Figure 4.10 depicts the corresponding
entropy in the \((\lambda, E)\) space. A long production run is performed in the \((\lambda, E)\) space assisted by the 2D DoS, and histogram of microstates is collected as shown in figure 4.11.

![Image of two-dimensional entropy, \(S(E, \lambda)\)]

**Figure 4.10** Two-dimensional entropy, \(S(E, \lambda)\)

The reweighting of the microstates in the entropic ensemble appropriate to a chosen temperature is carried out in two steps. First, the canonical ensemble corresponding to \(H_{\text{energy}}\) part of the Hamiltonian is extracted by reweighting the microstates associated with the cross section of the DoS at \(\lambda = 1\). This yields a set of equilibrium states corresponding to LL potential at that temperature. Let this
Figure 4.11 Two-dimensional multicanonical histogram, $H(E, \lambda)$
distribution be represented by $N(E; \lambda = 1)$. Now we performed reweighting on all the states collected in the grand entropic ensemble (in the $(\lambda, E)$ plane), with variable weight factors at each E-bin set by the canonical distribution $N(E; \lambda = 1)$. This results in 2D canonical ensemble of states distributed over $E$ and $\lambda$ axes, appropriate to that temperature. Figure 4.12 shows these distributions $N(E, \lambda)$ in different temperature regions bracketing the NI transition. The physical properties of interest are now averaged over $N(E, \lambda)$.

To illustrate the effect of temperature on the distribution of microstates along the $\lambda$-axis, the E-bin corresponding to the maximum in $N(E, \lambda = 1)$ at a given temperature is chosen, and the corresponding variation of distribution at that E-bin along $\lambda$-axis is extracted. This is repeated at different temperatures covering the phase transition region, yielding probability distributions along $\lambda$-axis as a function of temperature at the corresponding most probable orientationally ordered states. Figure 4.13 shows changes in the $\lambda$ probability distribution, say $P(S, \lambda)$, as the transition temperature is crossed. The development of strain across the transition is clearly seen from this cross sectional distribution, and the locations of the maxima of the peaks practically coincide with the canonical $\lambda$ averages reported above. Figures 4.14 and 4.15 show the variation of different parameters (like energy, orientational order, strain, specific heat and nematic susceptibility) computed as a function of temperature (with a resolution of 0.001) from the canonical ensembles generated as described above. These compare very well with the corresponding variations reported based on canonical sampling method on Model-II Hamiltonian [37]. The additional computation is of course the density of states of this complete system, and the higher resolution in temperature.

This model is further investigated with this procedure to look for the effect of other parameters on the strain transition, namely the cross-link density $\alpha$ and the coupling
4.5 Results and discussion:

Figure 4.12 Canonical ensembles at different temperatures. Canonical ensembles at $T < T_{NI}$, $T \approx T_{NI}$ and $T > T_{NI}$.
Figure 4.13 Probability distribution function, \((N(E, \lambda))\) calculated using method-II as a function of \(\lambda\) at various temperatures. As the temperature decreases, the maximum value of \(N(E, \lambda)\) shifts towards larger values of \(\lambda\).
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Figure 4.14 Variation of energy, order parameter and strain with temperature
Figure 4.15 Variation of specific heat, $C_v$ and susceptibility, $\chi_S$ with temperature
4.5 Results and discussion:

strength $\chi$ (eqn 4.16). Variation of $\alpha$ will directly affect the degree of elasticity exhibited by the elastomer, and increase in this value should resist more the influence of the (spontaneous) orientational order on the consequent onset of the strain. Figure 4.16 shows the thermal behaviour of strain at these values of $\alpha$: 0.3, 0.5 and 1.0. The percentage of strain induced due to the formation of nematic order has reduced from about 15% to about 4.5%, correspondingly. Effect of $\chi$, on the other hand, is a measure of the coupling between orientational order and global strain, and variation of $\chi$ also brings about changes in the thermal behaviour. To make a comparison with the earlier figure (depicting the effect of $\alpha$), we decrease $\chi$ and compute the profile of the strain transition at these values: 0.5, 0.3 and 0.1. Figure 4.17 shows the corresponding changes in strain; in this case the strain induced reduces from about 15% to about 4% at the same low temperature (in reduced units) as in figure 4.16. Arguing that variation in $\chi$ could be viewed, besides other contributing factors, as an indication of changes in the relative length scales of the two variables, it appears plausible that variation of cross-link density (which directly affects the primary elastic property of the material) could indirectly influence the coupling strength as well. In the present simulations we however consider them to be independent, as per the original prescription of this Hamiltonian.

Finally, we present the basic results of our simulations on both the models as shown in figure 4.19. For convenience of comparison, we set the value of $\chi$ to be unity in Model-II (comparable to that of $\gamma$ in eqn 4.10) in computing these variables. As may be seen, there is a difference in the variation of orientational order itself between the two models. It may be noted in this context that simulation on Model-I proceed with the assumptions that all the Hamiltonian terms are energetic in nature. Correspondingly, the DoS of the system, in particular concerning the orientational degrees is determined by the coupling term as well. In contrast, the DoS as far as
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Figure 4.16 Effect of cross-link density, $\alpha$ on the variation of strain with temperature

Figure 4.17 Effect of coupling parameter, $\chi$ on the variation of strain with temperature
orientational degrees are concerned are primarily determined by the energetic part of the Hamiltonian \( H_{\text{energy}} \) and seem to be only marginally affected by the other terms. But, the more dramatic difference is seen in the variation of strain. While Model-II predicts even at \( \chi = 1 \) a change in strain of \( \lambda = 1.28 \), Model-I yields at a comparable temperature \((T - T_C) \sim -0.5 \) in figure 4.19) a change in \( \lambda \) of about 2.75.

Also the nonlinear variation of \( \lambda \) with orientational order from Model-I is in contrast to the corresponding variation expected from Model-II.

The above differences in the predictions of the two models can be readily appreciated by referring to the figure 4.18. Here we plot the contributions coming from the second and third terms of the respective Hamiltonians, representing the contribution to the \( \lambda \)-dependent energy. The functional dependence of elastic energy on \( \lambda \) due to pure strain variation (second terms in the two Hamiltonians) is the same, but for an adjustable prefactor. For comparison we make them look identical and plot them, as in figure 4.18. In order to evaluate the contribution from the coupling terms, we consider the case of perfectly aligned nematic for convenience in calculation. This contribution diverges, in Model-I, in the two opposite directions as \( \lambda \) is varied over the range. The equilibrium strain is determined by the location of the minimum of energy contributions from the last two (\( \lambda \)-dependent) terms. Thus in this model the orientation induced contribution to the elastic energy drives the resultant minimum asymptotically to very large values of \( \lambda \), as the orientational order builds up. In Model-II a limiting function in the form of \( Q(\lambda) \) is introduced which bounds the variation of the orientation dependent elastic contributions, resulting in asymptotically limiting variation of strain as orientational order in the system increases. In figure 4.18 the total elastic energy contribution arising from Model-II in a completely aligned nematic is shown to indicate the shift in the minimum on introduction of coupling with a maximal orientational order.
In this Chapter, we reported the extension of entropic sampling technique to LCE with two ordering parameters, requiring a more elaborate walk in higher dimensional space. The second issue dealt with is the extension of this methodology to Hamiltonians with temperature dependent terms. We applied these sampling procedures to the two lattice Hamiltonians recently proposed to capture the features of these systems, by certain coarse-graining at the microscopic level. We present the results on these systems and compare their predictions. This work has been reported recently [53, 54].

Figure 4.18 Energy contributions of coupling terms of both the models (Model-I(red) and Model-II(blue)) compared to purely elastic energy (green) and total energy term (black) as a function of strain ($\lambda$) in completely aligned nematic state.
Figure 4.19 Variation of orientational (blue) and strain order parameter (red) as a function of temperature for Model-I (left) and Model-II (right), respectively.
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Bibliography


