

Chapter 2

Brief Introduction to Computer Simulations

A simple model can shed more light on Nature's workings than a series of ab-initio calculations of individual cases, which, even if correct, are so detailed that they hide reality instead of revealing it. ... A perfect computation simply reproduces Nature, it does not explain it.

P.W. Anderson

2.1 Computer Simulation - An Integrating Tool

Computer simulation is a convenient technique to estimate, as accurately as possible different physical properties of a model system. It is one of the tools available for investigating mesogenic behavior. However, a relative newcomer compared to the many experimental and theoretical approaches available, and its role is often complementary. Computer simulation studies can yield unique insight into molecular ordering and phase behavior and so inform the development of new experiments or theories. Molecular simulations can provide systematic structure property information, through which links can be established between molecular properties and macroscopic behavior. Alternatively, simulation can be used to test the validity of various theoretical assumptions.

Computer simulations are a bridge between theory and experiment. Given a particular model based on a theoretical concept, it can be used to mimic a phenomenon. Different parameters that are acquired experimentally can be compared with those obtained through simulations. The exactness of a computer simulation – a computer experiment – depends on the model used. These models are mostly proposed based on a particular theory, that

tries to explain the system. A well-focused simulation helps one to understand what happens in an experiment and test the underlying postulates at the fundamental level. For a better understanding of experiments some of these results can also be simulated by imposing on the system the required conditions, one simple example being the simulated NMR spectrum in LC system to appreciate different director configurations [1]. A study aimed at examining the role of a simulation as a research aid that has the potential to bridge the gap between theory and reality in the case of electric circuits was undertaken [2]. It was seen that simulations can provide unique advantages for enhancing understanding of the theoretical principles, by bridging the gap between the theoretically idealized models and their formal representations of reality.

In their application to problems of statistical physics, computer simulations serve as a bridge between microscopic and macroscopic properties. The microscopic models proposed are based on molecular interactions, and it is required that the macroscopic properties of the system be predicted. Simulations provide the hidden truths behind macroscopic properties. The importance of computer simulation is 1. measure of extreme conditions that are experimentally prohibitive or difficult. 2. Details of molecular motion and structure impossible or difficult to study experimentally. 3. Molecular motions that are too fast or slow to be captured using experimental methods. In general, a computer simulation approach requires, the setting up of appropriate models of the molecules of interest and the determination of the equilibrium state of a sufficiently large system of these particles at the chosen external (thermodynamic), like conditions of temperature, pressure etc. by numerical simulation methods.

Computer simulation is a convenient technique to obtain different parameters and to study the relevant phase transitions. The study of the correlation between molecular interactions and the macroscopic properties obtained is of primary interest in computational statistical physics. The molecular complexity in liquid crystals makes computer simulations a convenient tool to study them. They are anisotropic materials, experimental techniques like NMR, polarization techniques liquid crystals have been used to study their

properties and their transitions. Continuum models based on phenomenological elastic constants and hydrodynamic transport coefficients are of great success in modeling. Molecular Modeling and Computer Simulation techniques have recently seen major progresses, due to the continuous impressive increase in the availability of high performance computing resources at affordable resources.

Confined liquid crystal systems are the interest of study in this thesis. These can be investigated using simulation methods like Molecular dynamics (MD) and Monte Carlo (MC) methods. There are qualitative differences between molecular dynamics and Monte Carlo simulations. Molecular dynamics requires finalizing approximate numerical solution of Newton's equations of motion of the macroscopic system. It employs on this context the known algorithms to solve ordinary differential equation to the required approximation. These methods correspond to actual evolution of the system with a given dynamic perception, and has advantages in examining the time evolution of the system. Both thermodynamic and kinetic data can be generated by appropriate prescription of the equilibrium condition on the distribution of velocities. Monte Carlo can be thought of as a prescription for sampling configurations from a statistical equilibrium ensemble. This principle of Monte Carlo is based on the equivalence of averages over equilibrium ensemble of microstates to the long time averages on a given macroscopic system in equilibrium. Energy is the primary physical property to prescribe the probabilistic distribution of microstates belonging to a given canonical ensemble. The choice of either MC or MD for a given simulation largely depends on the type of information to be extracted from the model system, and in the case of equal suitability the computational effort needed essentially decide the choice. This thesis employs MC methods to study confined liquid crystal systems. A brief introduction to the MC methods is presented encompassing to Metropolis algorithm and non-boltzmann sampling methods in the next sections of this chapter.

In 1945 the building of the first computer brought about a renaissance of a mathematical technique known traditionally as statistical sampling; in its new formulation and owing to its nature, such problems have come to be known as the Monte Carlo method. During this

wartime period, a team of scientists, engineers, and technicians were working furiously on the first electronic computer. N. Metropolis suggested an obvious name for the statistical method a suggestion not unrelated to the fact that Stan had an uncle who would borrow money from relatives because he just had to go to Monte Carlo. A well written history *i.e.* account of the development of the Monte Carlo method was presented in [4].

2.2 Monte Carlo Simulations

Monte Carlo method is a numerical technique that depends on random numbers. It provides approximate solutions to a variety of mathematical problems by performing statistical sampling experiments on a computer, and applies to problems with no probabilistic content as well as to those with inherent probabilistic structure. Monte Carlo technique belongs to a class of computational algorithms that rely on repeated random sampling and relies on our ability to generate in principle, a truly random sequence of numbers. These methods are often used to simulate physical system based on mathematical models. Because of their reliance on repeated computation and random (or pseudo-random) numbers, Monte Carlo techniques are most suited for calculation on a computer, and offer an efficient valuable and acceptably approximate methodology particularly, when an exact solution with a deterministic algorithm is not feasible.

An experimentally measured equilibrium macroscopic property is a time averaged quantity of a given system over a larger period of observation time [5]. This experimental time average can be equated to an average over a suitable static Gibbs ensemble of microstates, provided the time evolution is ergodic. When in equilibrium the macroscopic properties of a system do not change. These corresponds to the physical properties averaged over the equilibrium ensemble. However, the physical properties do fluctuate under equilibrium conditions, and are less prominent the larger the system is. The associated fluctuations are inversely proportional to the square root of the system size and are not observable under normal condition in macroscopic system. The task of computing the thermal average

over many-particle systems is thus reduced to the job of sampling microstates from an appropriate canonical ensemble through MC sampling technique and computation of statistical properties of different physical parameters over this ensemble. Different algorithms were proposed to obtain a large enough ensemble over which the thermal properties can be averaged, of which Metropolis algorithm is widely used.

2.3 Metropolis Algorithm

This algorithm was introduced by Nicolas Metropolis and his coworkers in a paper on simulations of hard-sphere gases in 1953 and is essentially an importance sampling algorithm based on a long sequence of random numbers.

Consider a closed system, and let the set of all the microstates of the system be represented by Ω_{CS} . Starting from an arbitrary initial state C_0 , a Markov chain of microstates is represented as

$$C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow \dots C_k \rightarrow C_{k+1} \rightarrow \dots \quad (2.3.1)$$

The sequence of the micro-states appearing in the Markov chain is probabilistic condition. A Markov process is defined as a random evolution of a memoryless system, the future state depends only on the present, and not on the past, states. For example the state C_2 depends on C_1 and not on C_0 . The probability of such a process is given as

$$P(C_k, C_{k-1}, C_{k-2}, \dots, C_3, C_2, C_1) = P(C_k|C_{k-1}) \quad \forall \quad k = 1, 2, \dots, n. \quad (2.3.2)$$

The past has no influence over the future once the present is specified. Restricting the decision to a Markovian process, one needs to specify thus only conditional probability of the following type to predict the evolution of the system as a Markov sequence:

$$P(C_k|C_{k-1}) = W_{ij} \quad \forall \quad k = 1, 2, \dots, n \quad (2.3.3)$$

where W_{ij} defines the transition probability from the state C_i to state C_j in a single step. W_{ij} is a $(i \times j)^{th}$ element of a $\Omega_{CS} \times \Omega_{CS}$ square matrix. By insisting on the ergodicity of the system, and by imposing conservation of probabilistic measure (sum of all elements

in a row of W is unity), W becomes a stochastic matrix with very special properties. The principle of ergodicity is the possibility to attain every configurations of the system starting from any arbitrary initial configuration.

The sequences of states follow a time ordered path, here the time is referred to as 'Monte Carlo time'. The time dependent behavior is described by a master equation

$$\frac{\partial P_n(t)}{\partial t} = - \sum_{n \neq m} [P_n(t)W_{n \rightarrow m} - P_m(t)W_{m \rightarrow n}], \quad (2.3.4)$$

where $P_n(t)$ is the probability of the system in being in state n at time t . In equilibrium $(\partial P_n(t)) / \partial t = 0$ and so,

$$\sum_{n \neq m} P_n(t)W_{n \rightarrow m} = \sum_{n \neq m} P_m(t)W_{m \rightarrow n} \quad (2.3.5)$$

This is called the detailed balance condition corresponding to the stationary nature of equilibrium distribution function. A more stricter condition results, known as microscopic detailed balance, by demanding that this balance be satisfied by any pair of states separable *i.e.*

$$P_n(t)W_{n \rightarrow m} = P_m(t)W_{m \rightarrow n} \quad (2.3.6)$$

The probability of the n^{th} state occurring in a classical canonical system is given by

$$P_n(t) = \frac{e^{-E_n/k_B T}}{Z} \quad (2.3.7)$$

where Z is the partition function. Hence,

$$\begin{aligned} \frac{W_{n \rightarrow m}}{W_{m \rightarrow n}} &= \frac{e^{-E_m/k_B T} / Z}{e^{-E_n/k_B T} / Z} \\ &= (E_n - E_m)\beta \\ &= \Delta E \beta \end{aligned} \quad (2.3.8)$$

where $\beta = 1/(k_B T)$. The probability is usually not known because the denominator is not known, but this is avoided in the Metropolis method by generating a Markov chain of states which depends only on the ration of the probabilities of the states involved. If we

produce the n^{th} state from the m^{th} state, the relative probability is the ratio of the individual probabilities and the denominator conveniently cancels.

In a simple way the Metropolis algorithm can be summarized as:

1. Consider an initial arbitrary state C_o from the set of micro-states Ω_{CS} . $E(C_o)$ is the energy of this initial configuration C_o .
2. The orientation of a selected molecule (spin) changed resulting in a trial state C_t . $E(C_t)$ is the energy of this trial state.
3. Compute $\Delta E = E(C_t) - E(C_o)$.
4. Accept the trial state as the next state in the Markov chain, i.e. $C_t \rightarrow C_1$, if $\Delta E \leq 0$. Otherwise accept C_t with a probability $\exp(-\beta\Delta E) \geq \xi$. ξ a random number generated.

It may be seen that this is a generalized form of importance sampling with the importance function impartially chosen as the canonical distribution function at the chosen temperature. The actual flipping of the microstate in step 2 depends on the system of study. In the Ising model the spin has only two orientations either it is up or down and hence the random steps involving a given step in the configurational spin has only two possibilities. In this thesis the system studied comprises of liquid crystal molecules, and they have continuous orientational degrees of freedom yielding a continuum of configurations to sample from. For such systems, the orientation is changed randomly by a suitable algorithm, like for example the procedure suggested for such systems by Barker and Watts [6].

2.4 Boltzmann sampling

Boltzmann sampling refers to the construction of a canonical ensemble of microstates, in contrast to the non – Boltzmann sampling (see following section) wherein the microstates are ideally generated by making a uniform random walk in energy space. In the first sampling procedure unbiased steps are proposed in the configuration space, and are accepted

or otherwise depending on the relative probabilities of the two microstates according to metropolis prescription. The system of interest is the thermotropic LC, often confined to a specific geometry and boundary conditions; and the phenomenon of interest is the nature of the phase transition between an isotropic state and nematic state. Because only the orientational degrees of freedom are relevant, lattice Hamiltonians are preferred to investigate these problems. This section describes details of MC simulations carried out in this work.

Initially a micro-state is chosen at random, – the initial state C_o , and the energy of this state is computed as $E(C_o)$ using the chosen Hamiltonian. The energy of this configuration is changed by changing the orientation of the LC molecules (spin) using Barker Watts [6] algorithm. The energy of the new trial micro-state (C_t) is referred to as $E(C_t)$. The difference between the energies of the two microstates is computed as $\Delta E = E(C_t) - E(C_o)$. If $E(C_t) \leq E(C_o)$ then $C_t \rightarrow C_1$. If not, then the state C_t is accepted with Boltzmann probability $\exp(-\beta\Delta E)$, where $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T is the temperature). We generate a random number ξ , and check if $\xi \leq \exp(-\beta\Delta E)$, so that $C_t \rightarrow C_1$. If $\xi > \exp(-\beta\Delta E)$, then we reject the trial state, include C_o in the ensemble and proceed with the random walk to generate another trial state C_t . This is the Metropolis algorithm, and the probability with which the state C_t is accepted depends on the desired type of ensemble. The energy of the microstates is plotted as a function of Monte Carlo steps to check for equilibration. It is expected that, starting from an arbitrary initial microstate, the system evolves through a series of transient states towards equilibrium, and the macroscopic properties in equilibrium are computed after the sequence of microstates in the Markov chain respectively follow canonical distribution. These microstates rejection of the initial transient states, and collect data only subsequently referred to as production run. During the production run, the physical quantities of interest show fluctuations about a mean value which is a constant. The larger the number of microstates collected in the production run, the better is the reliability of the average. An average of a parameter A can be computed as

$$\langle A \rangle = \frac{A_{sum}}{N} \quad (2.4.1)$$

Here, N is the number of microstates collected during the production run and A_{sum} is the addition of the physical parameter A over all the production run. Such MC simulations can be repeated at every desired temperature, and thus all relevant physical properties can be computed as a function of temperature. This way every parameter can be computed and plotted as a function of temperature. Computation of various order parameters will be discussed in detail as a subsequent section in this chapter. The canonical ensemble can be visualized as a result of competition of two probability distributions in the phase space. The first arises from the density of states $D(E)$ and is a consequence of the Hamiltonian and boundary conditions imposed. This is normally an increasing function of microstate energy. The second probability distribution is due to equilibrium with the surrounding at a given temperature and is described by Boltzmann factor. This is a decreasing function of microstate energy. A given microstate has a resultant probability of existence, decided by the product of these two distributions evaluated for that microstate. The equilibrium distribution will thus be a sharply peaked function in phase space, its location being determined by the canonical distribution function through the temperature. This is illustrated in the figure 2.1. The error in these simulations is avoided by considering an ensemble of about 1 million microstates in the production run over which the different physical parameters are computed. The energy distribution in a canonical ensemble is thus described as $P(E) \propto D(E)exp(-\beta E)$. However, such Boltzmann sampling is not efficient in certain physical conditions and requires considerable computational effort to yield reliable MC estimates of physical properties. These may be summarized as [7]:

1. In second order transitions, very large correlations among microstates are present at the transition. Single step algorithms are not suitable to overcome these correlations, cluster algorithms were proposed. First order transitions (thermally driven) pose a challenge even to cluster algorithms, as the free energy profile could develop significant barriers between the two co-existing phases, making canonical algorithm inefficient due to quasi-ergodic regions in the configuration space connection the two

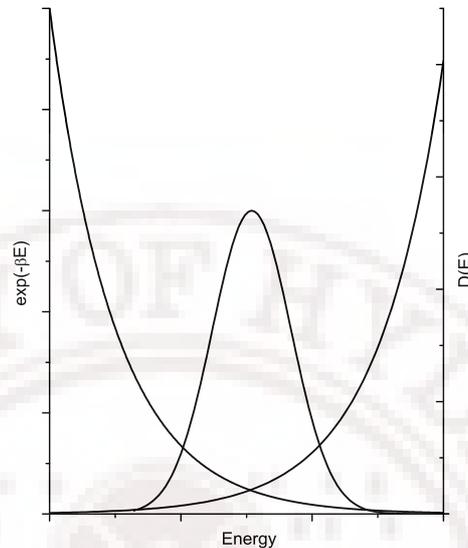


Figure 2.1: An illustrative plot for Boltzmann sampling

sets of microstates.

2. The correlation time τ diverges as $T \rightarrow T_C$ (transition temperature), and this means that finite sample Monte Carlo estimates of macroscopic properties of the system tend to become unreliable when the temperature of the system is very close to the critical value. The divergence of τ as $T \rightarrow T_C$ is called critical slowing down. This can be overcome by using non-Boltzmann sampling methods.
3. In studying critical phenomenon in detail, one needs to compute physical properties at several closely spaced temperatures and canonical sampling techniques require that each such ensemble be constructed separately. This is a very computer intensive exercise, and canonical methods are not very efficient in this respect.
4. Even though obtaining estimate of entropy and hence free energy, as a function of relevant control parameters is not within the reach of canonical sampling technique, it would be useful if this issue can be addressed by suitable algorithm, and such an exercise provides valuable insight into the physics of the system.

2.5 Non-Boltzmann Sampling

In view of importance of non – Boltzmann sampling technique as mentioned above, a brief account of methodology of constructing entropy ensemble is given below. Canonical ensemble at the desired temperature can be extracted from the microstates of the non – Boltzmann ensemble through the so – called reweighting procedure. We start this discussion by noting that the partition function is given by

$$\begin{aligned} Z(\beta) &= \sum_C \exp[-\beta E(C)] \\ &= \sum_E \exp\left[\frac{S(E)}{k_B} - \beta E\right] \end{aligned} \quad (2.5.1)$$

where $S(E)$ is the micro-canonical entropy. Here the first summation is over all the microstates, while the second is over the energy range. The probability for the closed system to be in a microstate C is given by

$$P(C) \sim \exp[-\beta E(C)]. \quad (2.5.2)$$

The probability of the system to have an energy E is given by

$$P(E) \propto \exp\left[\frac{S(E)}{k_B} - \beta E\right]. \quad (2.5.3)$$

The Metropolis algorithm helps to sample from the above distribution and obtain a canonical ensemble. If the interest is to sample from another distribution given by say,

$$P_\alpha(E) \propto \exp\left[\frac{S(E)}{k_B} - \alpha(E)\right] \quad (2.5.4)$$

then the local updation of a current state C to a trial state C_t is accepted with the probability

$$p = \min(1, \exp[-\{\alpha(E(C_t)) - \alpha(E(C))\}]). \quad (2.5.5)$$

If $\alpha(E) = \beta E$ then canonical sampling is recovered. For any other choice of $\alpha(E)$, an ensemble, not satisfying the Boltzmann distribution results and is called the non – Boltzmann ensemble. Entropic sampling is obtained when $\alpha(E) = S(E)/k_B$, which renders $P(E)$

the same for all E . Such a sampling corresponds to random walk uniform with respect to energy. Such a choice $\alpha(E)$ entropic function, is not known *a priori*. A special algorithm has to be devised to build this $\alpha(E)$ in an iterative way, depending on the microstates visited during a relatively short run. In entropic sampling, a simple random walk is done in energy space, where the energies are uniformly sampled over the energy range. Since unweighting - reweighting is done extracting the canonical ensemble of microstates, even a reasonable approximate estimate of the entropic function $\alpha(E)$ would suffice: $\alpha(E)$ should be as close to $S(E)/k_B$ as possible. A histogram of microstates generated with the above prescription leads to a fairly flat distribution with respect to energy.

Let (E_{max}, E_{min}) be the energy range over which a uniform distribution of energy microstates is to be obtained. This range of energy is split into bins of equal energy. Let E_i be the energy of the i^{th} bin, and $\alpha(E_i) = f_0$, some initial value chosen at the beginning of the simulation. The modification factor f is reduced in a particular way, can be for example $f_1 = \sqrt{f_0}$ or $f_1 = f_0/2$, until $f = 0.00000001$. For continuous systems like liquid crystal this process is repeated a large number of times in order to obtain a fully formed density of states [8].

After the density of states is obtained a production run is done to obtain an ensemble of equally sampled states in the energy space. We get an entropic ensemble of microstates $C_i : i = 1, N$. The canonical ensemble average of a macroscopic property say $O(C)$ at a desired temperature $T = 1/[k_B T]$ can be obtained by from the entropic sample unweighting (divide by $\exp[-\alpha(E(c_i))]$) followed by reweighting (multiply by $\exp[-\beta E(C_i)]$) *i.e.*

$$\langle O_\beta \rangle = \frac{\sum_{i=1}^N O(C_i) \exp[-\beta E(C_i) + \alpha(E(C_i))]}{\sum_{i=1}^N \exp[-\beta E(C_i) + \alpha(E(C_i))]} \quad (2.5.6)$$

Using the above method, all the physical parameters can be obtained at any chosen temperature. Free energy profiles and entropy may also be computed using the non - Boltzmann methods [7].

2.6 Computer simulations of Liquid Crystals

In liquid crystal context key quantities such as order tensor or the composition profile are the strength of simulations [9]. These are often difficult to resolve experimentally and are only accessible to relatively coarse-grained theories. At continuum length scales, LCs are characterized by a large number of experimentally observable parameters: viscosities, determined by the Leslie coefficients; orientational elasticity, controlled by the Frank constants; substrate - LC orientational coupling, governed by anchoring coefficients and surface viscosities. Given a full set of these parameters, mesoscale simulations are now able to incorporate much of this complex behavior into models of real systems.

LCs are fascinating systems to study because, like much of soft-condensed matter, their behavior is characterized by the interplay of several very different effects which operate over a wide range of time and length-scales. These effects range from changes in intramolecular configurations, through molecular liberations to many-body properties such as mass flow modes and net orientational order and ultimately to the fully equilibrated director field observed at the continuum time and length-scales. The extent of the associated time and length-scale spectra dictate that no single computer simulation model will ever be able to give a full atom-to-system description for even the simplest mesogen.

Computer simulation can contribute to our understanding of liquid crystals by relating detailed molecular structure to observed phase behavior and properties. It also helps in testing, in a microscopic way, the basis of theories of phase transitions, structure and dynamics. Using molecular dynamics and Monte Carlo techniques, and employing simple molecular models, one can hope to get insight into general features of phase equilibria, structure, and dynamics of liquid crystals. Different from the case of ordinary fluids, a simulation of liquid crystal systems should be able to yield the various phases of interest (isotropic, nematic, smectic etc.) and their transitions and to provide relevant anisotropic properties (that would reduce to a scalar for normal liquids), for a certain choice of molecular features.

Simulations of liquid crystals reported so far are carried out using two kinds of widely

divided models. Firstly, the off-lattice models, where the particles are free to move and can have any orientations [10]. The Gay-Berne (GB) potential that represents molecules as uniaxial or biaxial ellipsoids, can be regarded as a generalized anisotropic and shifted version of the Lennard-Jones (LJ) interaction which is commonly used for simple fluids, with attractive and repulsive contributions that decrease as 6 and 12 inverse powers of the intermolecular distance [11]. Extensive simulations of the Gay - Berne family of molecular models, in which potential parameters are adjusted to vary the molecular length-to-width ratio in a systematic way are studied. Simulation study of the approach to the isotropic nematic phase transition, using a large system size and lengthy runs on the T3D parallel supercomputer were reported earlier [12]. Such flexible modeling of liquid crystal gave rise to models with molecules that are biaxial in shape [13]. The progress towards accurate atomistic modeling of nematics has been discussed [14], pointing to improvements in force fields made recently and discussing the progress towards accurate prediction of material properties.

The second widely used and simple models are the lattice models, where the position of the molecule is fixed, but it can have any random orientation. Such models are useful only to describe a nematic–isotropic transition. Lattice models have a advantage over the off – lattice model when it comes to computing time [15]. These are simpler models to simulate and are adequate to study the relevant parameters at the nematic-isotropic transition. Lattice spin models are systems of simple interacting spins placed at every lattice point of say a cube. These spins are represent as unit vectors, with a continuously varying orientation. One model that is most widely used for the study of liquid crystals is the LL model [16], and has been extensively investigated in confined liquid crystals with specific effect on isotropic – nematic transition. Many modifications were suggested to this Hamiltonian to make it realistic and more appropriate in the context of a liquid crystal [17]. LL model is discussed in detail in the previous chapter of this thesis. Lattice models were also proposed for the study of more complex systems like biaxial liquid crystals [18].

Using these models the thermal averages of various physical parameters are computed

using the algorithms discussed previously. This thesis mainly deals with lattice Hamiltonians and the different parameters required for our study of liquid crystal systems are vividly discussed in some detail below.

2.7 Computation of the different parameters

2.7.1 Period Boundary Conditions

One of the ubiquitous problems is the choice of the boundary conditions, i.e. of what to surround the simulated sample with. Tackling it is unavoidable since computer simulations are usually performed on relatively limited number of particles. Even for lattice models, typical number of particles is of the order $10^3 - 10^6$, in comparison to a real bulk system with numbers as the to the Avogadro scale. Then, apart from choosing a lattice size as large as possible, it is very important to adopt some artifact at the sample surfaces so as to minimize the effects of finite size system. The appropriate choice of the boundary conditions becomes then essential, especially when small systems are investigated. The most often used constraints are the so called periodic boundary conditions (PBC), where the sample box is surrounded by exact replicas of itself. Although this kind of boundary conditions introduces a non-existent periodicity and thus some spurious correlations. PBC effectively reduce the effect of the finite size of the sample surfaces as long as the sample size is larger than the correlation lengths that can develop in the system during different simulation conditions. Due to greater correlation among sites it is expected that periodic boundary conditions might overestimate the transition temperature (T_C). The opposite case arises when the correlation between the sites is underestimated as in the case of free boundary surfaces. Consequently periodic and free boundaries yield, respectively, upper and lower bounds for the transition temperature.

2.7.2 Average Energy and Specific Heat (C_V)

The total configuration energy is taken as the sum of the intermolecular pairwise interactions. The average energy at every temperature is computed as the average of the energy

of all microstates in the ensemble. These microstates are collected during the production run of the Monte Carlo simulation, after neglecting the initial transient states (i.e. after equilibration). Thus, the average energy is computed as

$$\langle E \rangle = \frac{E_{total}}{N_p}. \quad (2.7.1)$$

Here, E_{total} represents the sum of the energy E over the ensemble and N_p the number of microstates collected during the production run.

The specific heat capacity (at constant volume) is obtained when the average energy is differentiated with temperature under constant volume. This can also be expanded in terms of the square mean fluctuation of energy.

$$\begin{aligned} C_V &= \left(\frac{dU}{dT} \right)_V \\ &= \frac{1}{k_B T} (\langle U^2 \rangle - \langle U \rangle^2) \end{aligned} \quad (2.7.2)$$

where k_B is the Boltzmann constant, T is the temperature. As mentioned earlier, the temperature is always measured in the units of the coupling between the neighbors and hence one employs the reduced temperature T^* instead, expressed in dimensionless units as,

$$T^* = \frac{k_B T}{\varepsilon}. \quad (2.7.3)$$

The temperature at which the peak occurs is considered as the transition temperature and this peak defines the transition in these Monte Carlo simulations.

2.7.3 Order parameters

The second rank Legendre polynomial $\langle P_2 \rangle$ is calculated by averaging $P_2(\cos \beta)$ over the probability $P(\beta)$ of finding the molecule at orientation β with the director. This method is useful if the director orientation \hat{n} is known *a priori*. In the present MC computations, we work in an arbitrary laboratory frame with no applied aligning field. Thus we do not know the orientation of the director in each configuration and it changes with the evolution of the microstate. This means that computation of $\langle P_2 \rangle$ requires *a priori* knowledge of the principal axes system in which the ordering tensor is diagonal.

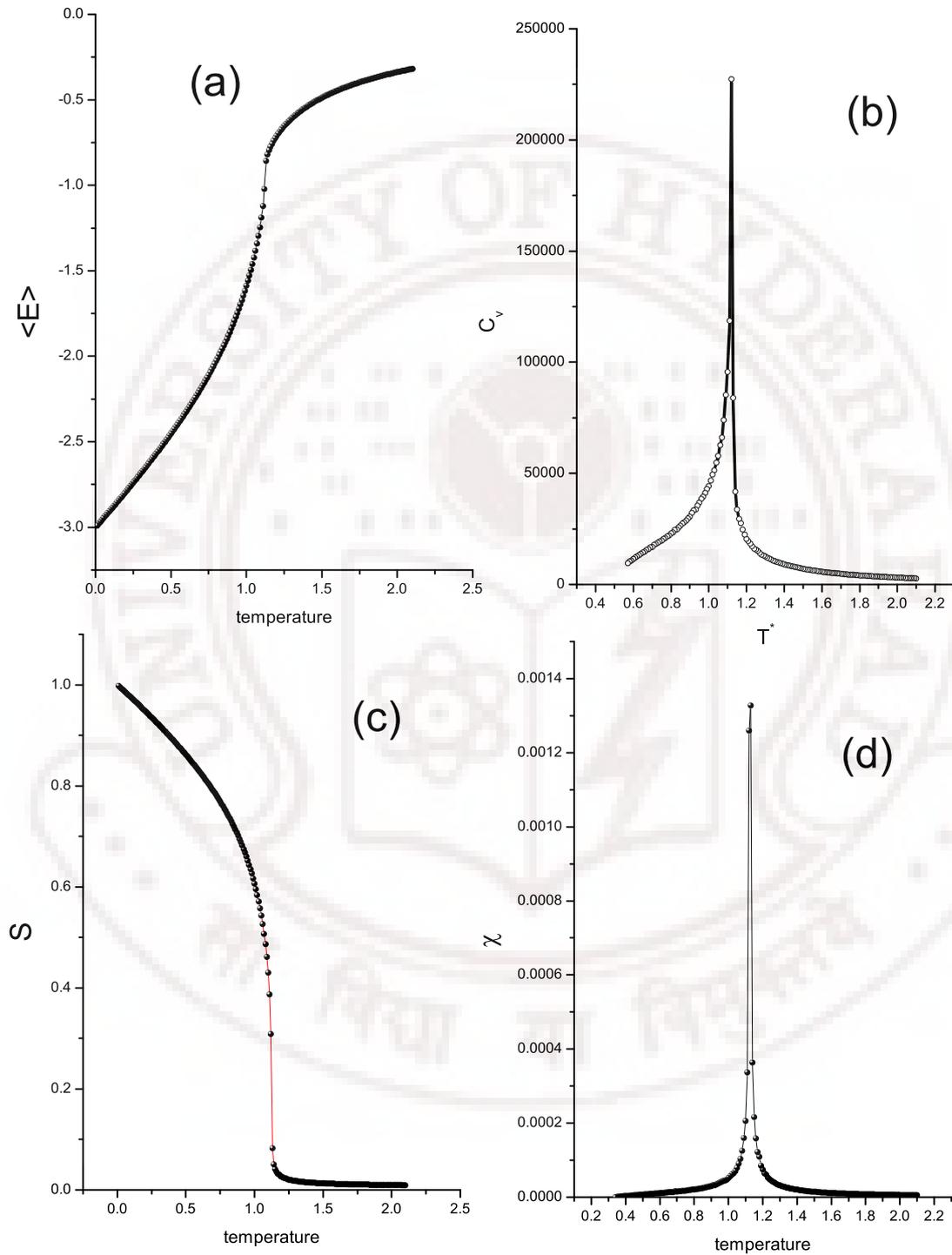


Figure 2.2: The different parameters computed for a $25 \times 25 \times 25$ cubic LL system with the variation in temperature: (a) average energy (b) specific heat (c) The order parameter (d) the nematic susceptibility (fluctuations in S) (χ)

To model such molecules we need an orthonormal set of vectors say $e_x, e_y,$ and $e_z,$ which represent the geometry of the molecules. The system considered has N number of particles, so N orthonormal sets are to be considered, $e_x^{(i)}, e_y^{(i)}, e_z^{(i)}$ for $i = 1, \dots, N$. Order parameter of the system, a second rank tensor, is built by taking a direct product of the vectors in every direction. Consider $e_z^{(i)}$ axis to be the long axis of the molecule. $e_y^{(i)}$ and $e_x^{(i)}$ lie in a common plane ($X - Y$ plane) but define a preferred axis each. Considering each axis of every molecule we define three order parameters Q_{xx}, Q_{yy}, Q_{zz} where Q_{zz} defines an ordering tensor considering the $e_z^{(i)}$ s, similarly Q_{yy} from $e_y^{(i)}$ s and Q_{xx} from $e_x^{(i)}$ s.

For symmetrical molecules

Let \mathbf{A} be a molecular matrix property whose only non vanishing component is along the molecule symmetry axis e_x [19]

$$A_{ab}^{MOL} = \delta_{az}\delta_{bz}. \quad (2.7.4)$$

Now, considering molecules that are rotationally symmetric about their long axes $e_z,$ *i.e.* $e_x = e_y,$ the relevant ordering matrix is Q_{zz} averaged over the sample, and is given by

$$Q_{zz} = \frac{1}{N} \sum_{i=1}^N \begin{pmatrix} e_{zx}^2 - \frac{1}{3} & e_{zx}e_{zy} & e_{zx}e_{zz} \\ e_{zx}e_{zy} & e_{zy}^2 - \frac{1}{3} & e_{zy}e_{zz} \\ e_{zx}e_{zz} & e_{zy}e_{zz} & e_{zz}^2 - \frac{1}{3} \end{pmatrix}. \quad (2.7.5)$$

Here, Q_{zz} is symmetric and traceless. The average of A is obtained by relating the components of A to the molecular frame fixed components and summing over all the particles *i.e.*

$$\langle A_{ab}^{MOL} \rangle_S = Q_{zz} + \frac{1}{3}\delta_{ab}. \quad (2.7.6)$$

The diagonalization of Q_{zz} with respect to rotation matrix U identifies the director frame. Rotating and diagonalization of $\langle A^{LAB} \rangle$ is equivalent to defining the director frame of Q . The director itself is defined by the eigenvectors corresponding to the maximum eigenvalue λ_{max} . The second rank order parameter is given as $\langle P_2 \rangle_\lambda = \frac{3}{2}\lambda_{max}$. The difference in the other two eigen values is the measure of the macroscopic biaxiality due to orientational ordering of the uniaxial molecule, called the phase biaxiality.

For molecules without rotational symmetry

To define the overall director of the system, we find the dominant eigen values of each Q_{xx}, Q_{yy}, Q_{zz} (say W_{xx}, W_{yy}, W_{zz}) and their associated eigen vectors ($\varsigma_{xx}, \varsigma_{yy}, \varsigma_{zz}$). The eigen vector of the most dominant eigen value W_1 from among (W_{xx}, W_{yy}, W_{zz}) defines the direction of the primary director. This is labeled as ' Z '. The most dominant eigen value W_1 provides the primary order parameter of the system. For rod – like molecules, the directions correspond to the average direction of alignment of the long axes of the molecules.

To define the second relevant axis of the system, we construct a right handed orthonormal system with axis X, Y, Z . The direction of Z is already defined as above. The other two preferred directions X and Y are obtained from Q_{xx} and Q_{yy} . The second direction Y is obtained by considering the eigen vectors of Q_{xx} and Q_{yy} (corresponding to the respective dominant eigen value of these tensors) and projecting the on to a plane orthogonal to the system director. The eigen vector so projected orthogonal to Z is taken as ' Y ', the eigen vector of the next dominant eigen value. The ' X ' direction is obtained by completing the set of axes to a right handed orthogonal system.

The measure of biaxiality is given by

$$B = R_{22}^2 = \frac{1}{3}[X^T Q_{xx} X + Y^T Q_{yy} Y - X^T Q_{yy} X - Y^T Q_{xx} Y] \quad (2.7.7)$$

where $X^T Q_{xx} X$ measures the extent to which the molecules x-axis are aligned along laboratory X , similarly $Y^T Q_{yy} Y$. $X^T Q_{yy} X$ gives the extent to which molecules y-axis aligned along X similarly $Y^T Q_{xx} Y$. A non-zero value of B indicates degree of biaxiality in the system.

Hence the different order parameter can be defined as

$$R_{00}^2 = Z^T Q_{zz} Z \quad (2.7.8)$$

the system order parameter, the most dominant eigen value.

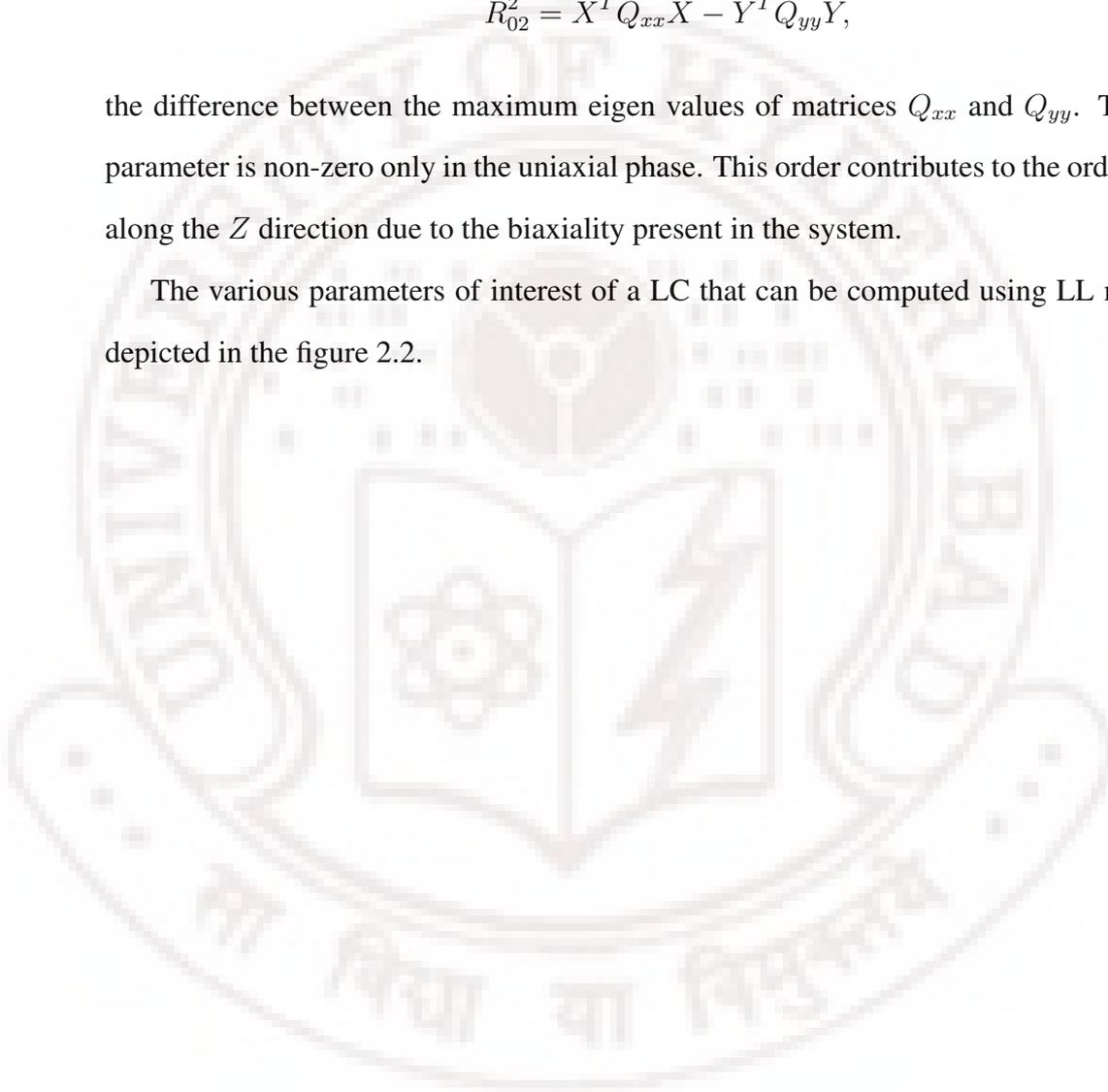
$$R_{20}^2 = f_2^T Q_{zz} f_2 - f_3^T Q_{zz} f_3 \quad (2.7.9)$$

the phase biaxiality, non-zero only in the biaxial phase. This order parameter is computed as the difference between the other two eigen values of Q_{zz} ordering matrix, f_2 and f_3 , the eigen values of Z . The molecular biaxiality is given as

$$R_{02}^2 = X^T Q_{xx} X - Y^T Q_{yy} Y, \quad (2.7.10)$$

the difference between the maximum eigen values of matrices Q_{xx} and Q_{yy} . This order parameter is non-zero only in the uniaxial phase. This order contributes to the order present along the Z direction due to the biaxiality present in the system.

The various parameters of interest of a LC that can be computed using LL model are depicted in the figure 2.2.



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