Chapter 3

Wang-Landau Monte Carlo simulation of nematic-istotropic phase transition in liquid crystals

3.1 Application of WL algorithm to continuous systems

Wang-Landau (WL) algorithm [1] as mentioned in the chapter I was initially proposed for systems with discrete energy spectrum like Ising model, q-state Potts model, etc. It was found to be very efficient in generating density of states (DoS), and hence free energy profiles, accurately for reasonably large sizes of such discrete systems. There were also attempts to apply WL algorithm to continuous systems like simulations of proteins [3–7], fluids represented by Lennard-Jones potential [8–19], polymers [20–24], liquid crystals [25], binary Lennard-Jones glasses [26], solid-liquid equilibria [27], of Heisenberg model [28, 29], and XY model [30]. Most of the above studies suggest that the WL algorithm (in its original form) as applied to continuous systems is not
that efficient and requires certain modifications to get accurate estimates of DoS over the energy range of interest. The main issues concerned with the continuous systems are convergence of DoS within an acceptable and realistic time frame, and difficulties in accessing lower energy regions with significantly less probability. Also, there are issues connected with numerical computations like overflow errors and rounding-off errors due to truncation which limit the efficiency of the algorithm. As the system size increases these become more prominent and acute. The reason is that the number of microstates in continuous systems is prohibitively large, so much so that, the number of steps needed for the system to sample over the desired energy range tends approximately to infinity, particularly as the system size grows. Moreover, the difference between degeneracies at lower and higher entropy regions is so high that, practically system needs additional algorithmic guidance to force it towards lower energy regions.

In the original WL algorithm, the modification factor is decreased exponentially until it reaches a negligible value so as to lead to a final random walk satisfying the detailed balance condition. However in this scheme, configurations generated at different stages of the simulation do not contribute equally to the DoS. In the final stages of iteration, the factor will be so small that it practically does not contribute to the DoS estimate. Continuous systems with the above difficulties are thus less susceptible to ready application of WL algorithm, relative to discrete energy systems. To overcome such problems, there were suggestions to determine the running estimate of DoS from the configurational information rather than the energy histogram [4, 10]. In some studies it was suggested that WL algorithm has to be combined with other methods like multi-bondic cluster algorithm, multi-canonical method, broad histogram method, transition matrix method, N-fold way rather than a single spin flip, parallel tempering, etc to increase its efficiency. In the present study, we apply
WL algorithm to study liquid crystal systems which has continuous orientational degrees of freedom, with focus on the study of the nematic-isotropic phase transition. We will briefly recall in the next section the original WL algorithm as proposed in [1]. Further, certain modifications are proposed to adapt the WL algorithm to liquid crystal systems, and these are discussed in detail in the subsequent sections.

### 3.2 Wang-Landau algorithm

In order to generate an ensemble of microstates distributed uniformly with respect to energy, the random walk in the configurational space should be appropriately biased, based on the knowledge of the representative density of states. However, DoS is not known a priori, and needs to be estimated, as accurately as possible, as a part of the computation. The WL algorithm addresses this problem by including the calculation of DoS as a part of the initial learning process, made efficient so as to span very low probable states through an algorithmic guidance. This is eventually withdrawn asymptotically following a protocol, leading to the evaluation of DoS on one hand, and consequent construction of an entropic ensemble over a large enough production run.

However, to initiate the computation the DoS represented by \( g(E) \) is set to be uniform over the energy range of interest, which is conveniently divided into a large enough number of bins. It is customary to set \( g(E) \) to be unity at the beginning of the learning run. To start with, we divide the desired energy range into \( N \) number of bins. We initialize \( g(E_i) \forall i \in N \) to a positive number (say 1) or alternatively we can initialize \( \alpha(E_i) = \log[g(E_i)] \) to \( e \). Let us consider a set of molecules distributed over a cubic lattice of size \( L \times L \times L \). To map the calculation to a LC system we assume an orientation dependent nearest neighbour interaction among the molecules.
We perform a random walk in the space of the microstates of the system by randomly changing the orientation of a randomly chosen molecule. Let the energy of the initial state be $E_i$. The probability of accepting a trial state of energy, $E_t$ is prescribed in this algorithm as

$$p = \min \left[ 1, \frac{g(E_i)}{g(E_t)} \right]. \quad (3.1)$$

After every such Monte Carlo step, $g(E)$ is updated by the so-called modification factor $f$, (referred to as Wang-Landau factor in [32]), $g(E) \rightarrow g(E) \times f$. Alternatively, we can write it in terms of its logarithm as $\alpha(E) \rightarrow \alpha(E) + \ln(f)$, where $\alpha$ represents the entropy of the system. The energy histogram $H(E)$ is collected in the desired energy range. After a large number of Monte Carlo sweeps (termed as one iteration), each sweep consisting of $L^3$ Monte Carlo steps, we decrease the value $f$ monotonically until it becomes equal to 1. Wang and Landau in original work [1] suggested taking the square root of $f$ as a protocol to decrease progressively the value of $f$. But any other method which ensures $f$ to decrease monotonically to 1 can be used [31]. As $f \rightarrow 1$, long enough walk guided by the prescription in eqn 3.1 will eventually make $g(E)$ converge to the true density of states, $D(E)$. It should be noted though, that detailed balance condition is satisfied only in the final iterations when $f \approx 1$.

Once the DoS is accurately known, the relevant thermodynamic observables can be in principle be estimated via the computation of the associated partition function. But, in the case of systems with continuous degrees of freedom it has been found more practical to construct an entropic ensemble, comprising of microstates obtained by a long random walk (during a production run) guided by the DoS computed earlier. This should lead to a reasonably uniform distribution of microstates with respect to energy, the degree of uniformity reflecting the accuracy in the estimation of DoS. Though such an ensemble does not correspond to a physically observable
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macrostate, canonical ensemble at any desired temperature can now be extracted from this collection of microstates by the so-called reweighting procedure (described in Chapter 2). It essentially corresponds to accepting each microstate of energy $E$ in the entropic ensemble with a combined probability determined by the DoS, $g(E)$ and the Boltzmann factor $\exp(-\beta E)$. An interesting outcome of using the DoS for this purposes is that any minor inaccuracies involved in its estimation (which would have been reflected in a deviation from uniform distribution along the energy axis) are corrected for in the reweighting process. Thus it has been found possible to allow moderate deviations in the energy histogram without perceptibly affecting the extracted behaviour of macroscopic observables with respect to temperature.

We present the results obtained for Ising model of size $100 \times 100$ simulated using WL algorithm described above. The density of states, $g(E)$ and energy histogram describing the distribution of microstates in the entropic ensembles, $H(E)$ for this system are shown in the figure 3.1. It may be seen that the DoS has spanned the entire energy range and the energy histogram is reasonably flat.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.1.png}
\caption{Density of states, $g(E)$ (left) and energy histogram, $H(E)$ (right) for Ising model of size, $100 \times 100$.}
\end{figure}
3.3 Modified Wang-Landau method

The Wang-Landau algorithm as proposed in [1] proved to be efficient to study discrete systems, particularly involving first order transitions. The important signature of the first order transition is the existence of a free energy barrier separating ordered and disordered phases. In order for any algorithm to simulate first order phase transitions efficiently, the tunneling times between ordered and disordered phases have to be short. In simple systems, short tunneling times are considered to be a good indication for a successful flat-histogram method [33]. Canonical simulations at a fixed temperature sample the states from a peaked distribution in a very narrow region at a fixed temperature and hence the tunneling times will be very large. As the system size increases, the tunneling time increases exponentially because the barrier height scales linearly with the linear size of the system. WL algorithm, like the other flat histogram methods, samples the states from a broad range of energies and hence reduces the tunneling time. The tunneling time in WL algorithm seems to exhibit a power-law scaling with the system size [35] and hence found to be efficient to study first order transitions compared to the canonical as well as other flat-histogram based simulations. However, it has been observed that in all the flat-histogram based methods the time required to go from higher entropy regions to lower ones is longer than vice versa.

Liquid crystals as modeled by Lebwohl-Lasher potential [2] defined on a cubic lattice with free wheeling molecules at each lattice site is one such system which exhibits first order transition from isotropic to nematic phase as we reduce the temperature. Application of the Wang-Landau algorithm to this system in its original form proved to be inefficient [31], particularly beyond a typical system size of $6 \times 6 \times 6$. After examining in detail the converging trends of DoS under different protocols of
3.3 Modified Wang-Landau method

Modification process through the factor $f$ we find that a slightly different strategy works for the LC systems, and one can study systems with sizes upto $25 \times 25 \times 25$ within an acceptable time frame. We present below the details of this modified algorithm [32]. In this connection, it may be noted that there are also a number of other modifications proposed independently to improve the performance of the algorithm as applied to continuous systems. It is common experience that these modifications and improvements are mostly problem-specific.

Let us consider a cubic lattice of liquid crystals. Free wheeling spins with head-tail symmetry are placed at each lattice point. Initially we divide the desired energy range $[-3L^3, 1.5L^3]$ into $N$ number of bins. It should be noted that if the bin width is more, the system tends to get stuck in the same energy bin and the dynamics becomes slow. On the other hand, if the bin width is too narrow larger computational times are required to obtain a reasonable amount of statistics in the energy histogram. In practice, the bin width is usually chosen depending on the temperature resolution at which one would like to calculate the thermodynamic observables. In all our simulations, we have taken the total number of bins as twice the number of particles in the system. Bin width is then calculated as the desired energy range divided by the number of bins. Let us represent the orientation of each spin by polar angle $\theta$ and azimuthal angle $\phi$. We initialize the orientations of the spins on the lattice by randomly generating direction cosines from $[\cos \theta, \phi]$. $g_i(E) \forall i = 1, N$ is initialized with a positive value (say $e$). Let $C_0$ denote the initial microstate and its energy belongs to, say, $\mu^{th}$ bin. Let us now pick up a spin either randomly (or via typewriter fashion) and change its orientation by employing Barker's method [41]. In this method, one of the three coordinate axes is chosen randomly. The spin is rotated about this chosen axis by a small angle $\Delta \theta$. In all our simulations, $\Delta \theta$ varies between $-0.5$ to $+0.5$. 
Let \( C_t \) be the trial microstate so obtained and its energy belongs to \( \nu^{th} \) bin. If \( g_\nu \leq g_\mu \), then the trial state is accepted. If \( g_\nu > g_\mu \), the trial state is accepted only if \( g_\nu / g_\mu \geq r \) where \( r \) is a random number generated from the uniform distribution in the range \([0, 1]\). If \( g_\nu / g_\mu < r \) then the trial state is rejected. This constitutes one Monte Carlo step. \( L^3 \) such moves constitute one Monte Carlo sweep (MCS).

Since \( g_i \) are chosen to have the same initial value, all the moves during the first MCS will be accepted. After one such MCS, we update \( g_i \) to \( g_i \times f \). In the original algorithm [1], \( g_i \) is updated after every Monte Carlo step, rather than sweep. Since the energy difference between two consecutive Monte Carlo steps is very less in continuous systems, updation of \( g(E) \) after every Monte Carlo step would spike up the \( g(E) \) entries in a narrow energy region, thus leading to slower dynamics. We perform \( P = 10000 \) such Monte Carlo sweeps which constitute one iteration. After each iteration we update \( f \to f^{0.9} \). The final \( g_i \) obtained after each iteration is used as an initial value for the next one. We perform \( M \ (160) \) such iterations so that \( f_M - 1 = 10^{-7} \), for an initial value of \( f \), \( f_0 = 10 \). Let us call \( M \) such iterations as one Wang-Landau run. \( f \) is reset to \( f_0 \) in the next WL run. The value of \( g_i \) and the microstate obtained from each such WL run are carried forward to the next WL run as initial values. We performed a total of 50 such WL runs. The value of \( f_0 \) is 100 for the first 40 runs, 10 for the next 9 and \( f_0 = e \) for the last run. These values are chosen after some experimentation such that the final \( g_i \) spans totally the desired energy range and the final histogram in energy is almost flat. In the first sub-stage of 40 runs, \( f_0 \) is initialized to a higher value. This is required to sample a wider energy region. But the penalty we pay is in the accuracy of \( g(E) \), since error introduced in the \( g(E) \) away from the true DoS increases with increase in \( f \). Once the \( g(E) \) spans the desired energy range, then we reduce the value of \( f_0 \) in the subsequent runs. In the last stage, we perform a long smoothening run with minimum \( f_0 \) so that
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$g(E)$ converges to the true DoS. It should be noted here that the values of $f_0$ and
the number of iterations to be employed completely depend on the characteristics of
the system like system size, complexity etc and hence for a given system exploratory
computations are needed before optimizing the parameter values. A detailed flow
chart of this algorithm for one WL run is shown in the figure 3.2. A description of
the scheme of WL runs employed by us is shown in figure 3.3.

The final $g_i$ obtained after completing the required WL runs is used without fur-
ther modifications (i.e., $f = 1$) for performing a long run of about one million, or
more Monte Carlo sweeps, also called the production run. During this process, we
collect a large number of microstates constituting the non-Boltzmann ensemble ob-
tained from the entropic sampling. These microstates contain information pertaining
to all regions of configurational space encompassing all the temperatures. From this
ensemble, we extract all the thermodynamic observables like average energy ($E$), ori-
etational order parameter ($S$), specific heat at constant volume ($C_V$), orientational
susceptibility ($\chi$) and Binder’s cumulant ($V_4$) at any temperature by appropriate
reweighting procedure.

3.3.1 Flatness criteria

In this algorithm, the energy histogram is checked for flatness only after each sub-
stage of WL runs unlike in original WL algorithm where the flatness is checked after
every MCS. In the original algorithm, the energy histogram is considered to be flat if
all the accessible states were populated by more than 90% of the average number of
visits [1]. However, this flatness criterion seems to be too restrictive for continuous
systems as the system size becomes large. In many cases, it is found sufficient if there
are atleast a minimum number of visits in each energy bin particularly in the lower
energy bins [8]. The minimum value to be set, however, depends on the complexity of
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Figure 3.2 Flow chart of the basic WL algorithm

Simulation details

- Initialize lattice spins, $L^3$ with random orientations given by $(\theta, \varphi)$.
- Divide energy range into bins.
- Initialize $q_i$, $i = \text{bin#}$.

Change the orientation of the spin $(\theta, \varphi)$ randomly using Barker’s method.

$L^3$ times (1 MCS)

$p = \min \left[ 1, \frac{g(x)}{g(x')} \right]$

- yes: accept
- no: reject

Calc the bin #

$\ln(g_{\text{old}}) \rightarrow \ln(g_{\text{new}}) + f$

$\frac{f_{\text{new}}}{f_{\text{old}}} \leq 10^{-4}$

Repeat $N = 10^5$ times

Repeat $N = 10^5$ times

One WL iteration

Final $q_i$
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Figure 3.3 Scheme of WL runs employed in the modified version

The problem. Shell et. al [8] suggested a minimum value of 20, whereas, Parsons and Williams [24] suggested about 4000 samples per bin for polymer models. It has also been suggested that one can consider a histogram to be flat enough (for purposes of reweighting) in continuous systems if all the higher energy bins on the right side of the empty bins are completely filled [24]. However, the flatness criterion in continuous systems is still an open question. The reason that one can manage even with not-so-flat a histogram of states is the self-correcting opportunity afforded during the reweighting process.

We observed that there are certain numerical problems associated with this kind of iterative procedures even for moderately large systems, arising from the representation of data on computer like over flow errors and loss of precision due to the truncation errors. In order to reduce these errors we reformulated this algorithm on a log-log scale (i.e., in the representation of logarithm of entropy) and performed the simulations accordingly. These involve calculating $g_i$ in terms of $\xi = \log(\alpha) = \log(\log(g_i))$. The acceptance probability, updation of $\xi$, unweighting-reweighting procedure, etc., are
also calculated in the same log-log scale following the numerical tricks suggested by Berg [42]. The details of these numerical tricks are given in Appendix A. We find significant improvement in the efficiency of the algorithm due to this change of scale and we could attempt simulations on a $20 \times 20 \times 20$ system.

### 3.3.2 Modification factor, $f$

It has been observed that modification factor, $f$ as well as the scheme adapted to update $f$ plays a crucial role in the convergence of DoS. In a recent study [34], it was observed that the convergence of $g(E)$ to the true DoS scales as $\sqrt{\ln f}$. In other words, a good convergence criterion in simulations could be that each bin is visited at least a number of times which scales with modification factor as $1/\sqrt{\ln f}$. This scheme seems to increase the accuracy of DoS at later stages of the iterations as more time is spent in constructing the DoS. However, when the system exhibits rugged energy landscape, it takes longer time to escape from the local energy minima. Moreover, it was observed [36] that the effect of initial value $f_0$ on the accuracy of $g(E)$ is felt only for shorter times. As the number of Monte Carlo runs increases, the efficiency as well as accuracy of final $g(E)$ is not influenced much by the value of $f_0$. In the present study, we have adapted a scheme where the factor $f$ is scaled to its initial value after every few iterations, each iteration consisting of large number of Monte Carlo runs, and repeat the procedure until DoS converges satisfactorily as evidenced by successive DoS profiles. Even though in this scheme, the accuracy of DoS is compromised whenever $f$ is scaled to a higher value, it has the distinct advantage of driving the system out of local energy minima in doing so. The comparative graph between original and modified WL algorithms is shown in figure 5.18. The figure shows the updation scheme of modification factor $f$ in the two algorithms.
3.3 Modified Wang-Landau method

Figure 3.4 Updation schemes of $f$ for original and modified WL algorithms respectively

3.3.3 Results and Discussion

Figure 3.5 represents the logarithm of density of states $\log(g(E)) = \alpha(E)$ obtained after each WL run as a function of energy for a system of size, $L = 12$. From the figure, it is clear that as the iteration index increases from one WL run to another, the span in energy range increases. The increase in energy span is more for the initial stages and decreases gradually as $g(E)$ converges to the true DoS. The accumulation of $g(E)$ in later stages is very less and helps only in smoothening the DoS by removing any remaining discontinuities. This smoothening run is essential for achieving the desired accuracy of DoS, since large discontinuous deviations are introduced in the initial stages of modification protocol. As the system size increases further, the DoS becomes steeper making the low energy microstates relatively that much less probable and hence requires higher number of WL runs at different stages. The initial values $f_0$ should also be larger in order to drive the system towards low probable regions.

We calculate orientational order parameter averaged over canonical ensemble of microstates, $\langle S \rangle$ at various temperatures. The resolution in temperatures for all the macroscopic quantities is chosen to be 0.001. The advantage of WL algorithm over
Figure 3.5 Logarithm of DoS plotted against energy, after every WL run for a cubic system of size, $L = 12$
canonical simulations lies in being able to calculate all the thermodynamic observables at any desired resolution of temperature simultaneously. Figures 3.6 and 3.7 represent specific heat and Binder’s cumulant for various lattice sizes, $L=4, 6, 8, 10$ and 12, respectively. We observe that for $L = 4$ and 6 the transition is not sharp due to the finite size effects. But as the size of the system increases, we find that the specific heat profiles become sharper. The transition temperature ($T_{NI}$) obtained from the peak value of specific heat $T_{NI} = 1.126 \pm 0.005$ for a system of size $L = 12$ confirms with the earlier experimental and numerical results [43, 44].

Figure 3.8 represents the free energy profiles generated during the simulation for $L=12$. The three curves represent the profiles below, at and above the transition temperature, $T_{NI}$ respectively. It can be observed that exactly at the transition, i.e., when both the ordered and disordered phases have equal probability, the two minima are separated by a free-energy barrier. For temperatures below and above $T_{NI}$ the respective ordered or disordered phase is more probable. From the free-energy profiles, we deduce that the transition is first order. Figure 3.9 represents the scaling behaviour of transition temperatures, $T_{NI}$ obtained from specific heat profiles, nematic susceptibility and Binder’s cumulant profiles.

### 3.4 Further improvements and modifications of WL method

An important concern connected with the application of WL algorithm to even moderately large systems is that one has to sample extremely large number of microstates in the phase space to be able to span the desired energy range which may turn out to be prohibitively expensive in terms of the computational effort needed. To overcome this problem, in the original WL algorithm [1] and in several subsequent
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Figure 3.6 Specific heat profiles for a liquid crystal system of linear sizes L= 4, 6, 8, 10 and 12

Figure 3.7 Binder’s cumulant profiles for liquid crystal system of linear sizes L= 4, 6, 8, 10 and 12
3.4 Further improvements and modifications of WL method

Figure 3.8 Free energy profiles below, at and above the $T_{NI}$ for liquid crystal system of linear size, $L = 12$

Figure 3.9 Transition temperatures from specific heat, susceptibility and binder’s cumulant versus $1/L^3$ for liquid crystal system of linear sizes
studies [4, 8, 27, 29, 37, 38, 45–48], it was suggested to divide the desired energy range into a number of sub-regions and perform the WL algorithm in each energy window independently to speed-up the simulation. Each sub-region is simulated in different processors and the resulting \( g(E) \) is appropriately combined together to get the final DoS. But by restricting the random walk to a sub-energy region, the states tend to get accumulated near the right edge of the energy range (corresponding to the higher energy side) and give rise to systematic errors [1]. To reduce these so-called edge effects, Schulz et.al. [49] have suggested to update \( g(E) \) and the energy histogram, \( H(E) \) even when the trial Monte Carlo step is rejected. Moreover, in continuous systems, it is observed that during the updation of \( g(E) \), more number of Monte Carlo steps are utilized in sampling already explored energy range, while, only a fraction of that number is used in extending \( g(E) \) to unexplored regions. An innovative way of updating \( g(E) \) is given in [29] wherein \( g(E) \) is updated by a continuous global update function till the values of \( g(E) \) satisfies a pre-defined cut-off criterion, and then local updates are performed over the cut-off region (referred to as frontier). This in essence forces the system to sample from the energy regions beyond the frontier, corresponding to less visited configurational space. This global update process, conveniently referred to as \textit{frontier sampling} hereafter, is discussed in detail in the subsequent sections.

More often one needs to study the phase transitions exhibited by a system as a function of more than one parameter. This is essential when one has to investigate the system near triple points or tricritical points. Simulation of multi-dimensional DoS and hence obtaining free-energy as a function of two or more parameters simultaneously is appealing since all the information is obtained from a single simulation. For example, DoS can be obtained as a function of energy and magnetization in magnetic systems like Heisenberg model [28, 29], energy and reaction-coordinate or the
end-to-end distance in protein models [29], energy and volume while investigating solid-liquid equilibria [27], energy and number of particles in simulation of fluids [9], etc. However, calculation of such joint DoS for continuous systems is computationally very challenging and also gives rise to several numerical issues. Therefore such methods have to be restricted to small systems [8, 48] or a carefully chosen small region in the parameter space [9, 10, 27]. Less costly alternative methods have been introduced, e.g., EXEDOS [3–5], which restricts the simulation at a fixed temperature in place of at a fixed external force field. In the present work, we have generated a multi-dimensional DoS as a function of orientational order and elastic strain while investigating the nematic-isotropic transition in liquid crystal elastomers which will be discussed in detail in Chapter 3.

The DoS $g(x)$ is a continuous function (in the case of a system of any size with a continuous MC step, or even in system with a discrete MC step of sufficiently large size) and the simple binning scheme used in the above-mentioned procedure effectively approximates $g(x)$ with a piece-wise constant function. By using sufficient number of bins, as discussed above, this method can be made to work satisfactorily for smaller systems [28]. However, for larger systems and particularly while generating joint density of states, this scheme results in an excessively large number of bins to sample. This can be avoided to a certain extent by using linear interpolation among neighbouring bins [8]. Updating the $g$-function with a continuous kernel function [29, 51, 52] seems to be consistent with the continuous nature of $g(x)$. Moreover, in the frontier sampling method [29], the continuous function, $g(x)$ is updated by two alternate cycles of global and local updates, which force the system towards lower energy regions and prohibit it from visiting the higher energy regions repeatedly. This kind of algorithmic guidance is very essential to simulate systems of reasonable size as the slope of the $g(x)$ becomes progressively steeper as the system size increases,
and the disparity between the relative probabilities of lower and higher energy regions becomes significantly large. In the present study, we have adapted the frontier sampling method [29] and applied it to certain complex liquid crystal systems like confined liquid crystals in various geometries, liquid crystal elastomers, etc, which will be discussed in the subsequent chapters. In the next section, the improved WL algorithm based on frontier sampling method is discussed in detail. This is then applied to bulk liquid crystal system and liquid crystals confined to porous media to test the efficiency of the algorithm and to validate the results so obtained by comparing them with earlier known data.

### 3.5 Frontier Sampling based WL algorithm

#### 3.5.1 Frontier Sampling method

In the frontier sampling method [29], the function \( w(x) \) which is equivalent to logarithm of \( g(x) \) is updated by a Gaussian kernel function, \( k(x) \geq 0 \), where \( k(x) = \exp(-|x|^2) \) as shown below:

\[
w(x) \rightarrow w(x) + \gamma k((x - x_0)/\delta) \quad (3.2)
\]

where \( \gamma \) and \( \delta \) are scaling parameters to adjust the height and width of the Gaussian kernel, respectively. According to the above equation, the function \( w(x) \) is updated by the Gaussian, whenever random walker arrives in the bin with parameter value, \( x_0 \). The acceptance probability is expressed as

\[
A = \min \left(1, \exp[\ln \alpha(w(x_i) - w(x_f))]\right). \quad (3.3)
\]

Here, a constant \( \ln \alpha \) was inserted so that \( w(x) \) converges to \( \log_\alpha g(x) \). Hence, in this method, instead of a single modification factor, \( f \) we have a triplet \((\alpha, \gamma, \delta)\) for
3.5 Frontier Sampling based WL algorithm

updating the function $w(x)$. In [29], the authors have chosen the values of 0.0001 to 0.01 for $\gamma$, and 1/200 of energy or magnetization width for $\delta$. During the simulation, $\delta$ and $\alpha$ values are not changed. In order to force the random walker to sample the unexplored regions, a global update function is defined. Whenever the values of $w(x) \geq \kappa$ for some value of $x$ in the already explored region, it is updated with a global update function given by:

$$w_T(x) \rightarrow w_T(x) + k \exp \left[ -\frac{\lambda}{w_T(x) - \kappa} \right] \Theta(w_T(x) - \kappa)$$

(3.4)

where, $w_T(x)$ represents the values of $w(x)$ in the region $T$. From the above equation, we notice that as $w_T(x) \geq \kappa$, the value of $w_T(x)$ is shifted up by an amount $k$ and the exponential function removes the resultant discontinuity. Hence, the simulation is essentially divided into two stages:

1. **Accumulation stage**: Initialise $w(x) = 0$ and perform WL runs with the local updates given by eqn 3.2. As soon as $w(x) \geq \kappa$ for some $x$, global update is applied eqn 3.4 and accumulation is continued with the local updates eqn 3.2. $w_T(x)$ initially accumulates on the boundary of region $T$ and then extends inside the region $T$ uniformly. Once the uniform growth starts inside this region global update is again applied.

2. **Refining stage**: Once the region $T$ spreads over the entire region of interest, then we continue the simulation with only local updates eqn 3.2 untill uniform growth of $w_T(x)$ is observed in the entire region. The $w(x)$ can be refined further by reducing the value of $\gamma$ and by following the above two steps at this stage.

The cycle representing the global update and immediate local updates at the frontier is as shown in the figure 3.10, [29].
3.5.2 Modifications to the frontier sampling method

Our objective now is to adapt the frontier sampling method described in the earlier section to study liquid crystal systems, since this shows promise to force the system to span the low energy regions also with an innovative algorithmic guidance scheme. We have modified the algorithm so as to make it work satisfactorily for lattice models of liquid crystals. In [29], the cut-off in the $w_T(x)$ is chosen at a point on the energy axis, where $w_T(x) \geq \kappa$ and all $w(x)$ to the higher energy side (T region) are boosted with a positive value. In the present work, we have chosen the criterion for this frontier depending on the difference in values of $w_T(x)$ accumulated in two successive runs. We made use of the fact that the difference (as a function of $x$) between values of $w_T(x)$ from two consecutive runs will be nearly uniform if the system has already sampled the T region adequately (thereby making the DoS there nearly accurate).
Extent of such uniform region is a logical basis for defining a frontier, so as to force the system to sample away from the T region in the next iteration in the frontier sampling scheme. Initially, the system will have more tendency to sample the higher entropic regions which in our case is in isotropic phase with energies nearer to zero. So, initially the cutoff is chosen as 95% of the difference in $w_T(x)$ values in the first two runs at the bin with the highest allowed energy value. The corresponding bin number is the so-called frontier. The system is allowed to perform random walk in the usual manner and the difference in the values of $w_T(x)$ is calculated after every two iterations. This difference is compared with the earlier cut-off value. A new frontier (extending to lower energy regions) is defined whenever the above criterion leads to expansion of the T-region. In other words, as more and more higher entropic regions are adequately sampled, the frontier is moved correspondingly to lower energy regions, so as to make the system sample beyond the frontier through the updating procedures described above. This corresponds to boosting all the values of $g(E)$ towards right side of the frontier by a positive value. As the Monte Carlo runs proceed further, the frontier shifts towards lower entropic regions. This procedure is repeated till the entire energy range is sampled. The global update function in our algorithm is given by:

$$w_T(x) \rightarrow w_T(x) + k\Theta(w_T(x) - \kappa)$$

(3.5)

The values of $\gamma$ and $\delta$ are not kept constant during the simulation. We find it profitable to reduce these values progressively as the iterations proceed. Once $w_T(x)$ covers the entire energy range, a long smoothening run is performed with very low values of $\gamma$ and $\delta$ to remove discontinuities that would have naturally crept in due to the global update process. Moreover, in our simulation the scale parameters are restricted to two $(\gamma, \delta)$ (eqn 3.2). The acceptance probability is accordingly given by:

$$A = \min (1, \exp[ln[w(x_i) - w(x_f)]])$$

(3.6)
3.5.3 Details of the simulation

We initialise the cubic lattice (size $L$) of liquid crystal system with random configuration of headless spins. The interactions between the spins is given by Lebwohl-Lasher potential and restricted to nearest neighbours. We performed simulations on lattices of sizes upto $L=25$. The energy range is divided into $N$ number of bins. On a Wood-crest processor operating at 3.0GHz, the simulation on a $L = 20$ lattice takes about 30 hrs. Orientation of each spin is randomly changed either by choosing spin site randomly, or in a type-writer fashion. The acceptance probability is given by eqn 3.6. Once a Monte Carlo sweep (MCS) is completed which consists of $L^3$ Monte Carlo steps, the value of $\xi_i = \log(w(i))$ is updated with a Gaussian kernel function:

$$\xi(i) \to \xi(i) + \gamma \exp \left( \frac{|x - x_0|}{\delta} \right)^2.$$  

We have taken initial values of $(\gamma, \delta)$ as $(1.0, 100)$. After every 100 MCS, the value of $\gamma$ is reduced $\gamma \to 0.95\gamma$. This updation of $\gamma$ is continued until it reaches a preset minimum value (typically 0.001). We call this entire computation as one iteration. After every two successive iterations, we calculate the difference between the updated values of $\xi$ as a function of bin number. Initially, the cut-off bin number is chosen as that corresponding to 95% of the difference, $\xi^k(i) - \xi^{k-1}(i)$, where $k$ is the iteration index, and the bin index, $i$ corresponds to the highest energy of interest, typically zero with LL potential. Once a frontier is defined as the cut-off bin value so defined, the algorithm continues the process of iterations, each time looking for two successive iterations yielding for a lower cut off bin number (i.e., lower energy bin). If a cut-off value is found which is lower than the current one, a new frontier is defined at this latest value and the entire process in search of another new frontier continues. In terms of the algorithm the following steps are followed. We check if there is any other bin $j$ in the lower energy range at which the difference is greater than the
cut-off. If it is so, we reset the cut-off to 95% of $\xi^k(j) - \xi^{k-1}(j)$. This sets the frontier as the bin $j$ above which there is an uniform growth of $\xi_T(x) \forall x = j, N$. Now we boost the values of $\xi_T(x)$ which are present towards right side of $j$. This introduces a high entropic barrier for the random walker to enter the higher energy regions. So there is an accumulation of states near the frontier till the height becomes equal to the boosted area. Consequently, the area of the explored region extends towards lower energy region. We perform this simulation until $\xi_T(x)$ covers the entire energy range. After $\xi_T(x)$ covers the desired energy range, a long smoothening run is performed with initial values of ($\gamma, \delta$) set to (0.01, 0.0001). The value of $\gamma$ is progressively reduced during this part of the simulation until it reaches a low value of $\approx 10^{-4}$. This ensures that the discontinuities in DoS introduced artificially during the global updation are eventually minimized, and $\xi$ converges to its asymptotic value. The final $\xi$ is then used to generate a large non-Boltzmann ensemble from which the relevant thermodynamic observables are extracted using unweighting-reweighting techniques, as described earlier. As in our earlier modified version of WL algorithm discussed in section 3.3, we have performed the above simulation also on log-log scale to minimize computational errors. In between the neighbouring bins, linear interpolation is performed to calculate acceptance probabilities.

It is observed that the speed up in the computational time employing this algorithm is about ten times compared to the earlier versions of WL algorithm (without frontier sampling). We now apply the modified frontier sampling method to bulk liquid crystal systems and a more realistic liquid crystal system confined to porous medium, and present the results in the subsequent sections. The latter system serves as a benchmark to test the applicability of the modified version of frontier sampling method to simulate complex systems with possible rich free-energy landscapes. The subsequent Chapters present the application of this method to other complex systems
like liquid crystal elastomers, liquid crystals in contact with geometrical and chemical patterned substrates, etc.

### 3.5.4 Application to bulk liquid crystals

We have applied the modified version of *frontier sampling* method to study nematic-isotropic phase transition in bulk liquid crystals. Figure 3.11 shows the logarithm of entropy $\xi(x)$ as a function of energy per particle for a cubic lattice of size, $L = 20$. The figure on the right hand side depicts the energy histogram $H(E)$. We observe that the histogram is not as flat as is expected from simulations on discrete systems. But typically the minimum number of microstates in any of the bins is about $5 \times 10^5$ which ensures that any canonical ensemble extracted have at least these many microstates. is reasonably good for bulk liquid crystal systems. We stipulate that sampling of microstates is reasonably good if we obtain similar energy histograms when we repeat the same simulation with different random seeds. One can improve the accuracy of the results by concatenating the microstates obtained from two or more simulations with different random seeds and extracting the thermodynamic observables from this larger concatenated ensemble. Figure 3.12 shows the thermodynamic observables like energy, order parameter, nematic susceptibility, Binder’s cumulant and specific heat, in clock-wise order, obtained from the simulation. The transition temperature obtained from the position of specific heat peak is about $1.124 \pm 0.001$, which is in good agreement with the earlier results.

### 3.5.5 Application to liquid crystals confined to porous media

Liquid crystals confined to porous media make a very interesting study due to its technological as well as academic importance [54, 55]. A porous medium with a
random network of interconnected pores of random sizes and shapes provides a simple confining medium. The size of the pores, the geometry and connectivity of the pores influence the nature of the phase transition. Many attempts were made earlier to understand the effect of pore size on the phase transitions of liquid crystals both experimentally and using computer simulations [54–57]. Confinement of any system in a porous matrix can be modelled in one of the following ways:

- construction of an independent pore with different rigid boundary conditions and director configurations [58],
- Potts spin models with the porous medium approximated by the diffusion-limited cluster-cluster aggregate [59],
- random field Ising models [60],
- random anisotropy nematic models [61]
- introduction of quenched random disorder into the system (also called dilution) [62]
Figure 3.12 Energy, Orientational order parameter, Specific heat, Orientational susceptibility and Binder’s fourth cumulant profiles versus temperature for a liquid crystal system of linear size, $L = 20$. 

3.5 Frontier Sampling based WL algorithm

Figure 3.13 Orientational order parameter (left) and Specific heat (right) obtained from frontier sampling method (red lines) and canonical simulations (black squares) respectively versus temperature for a liquid crystal system of linear size $L = 20$. Results from frontier sampling method tally well with the canonical results.

In the present study, we attempt to investigate the effect of porous medium as modelled by the introduction of quenched random disorder (QRD) on the nature of phase transition using our modified frontier sampling method.

Recently a phenomenological model has been proposed to describe the number of quenched random disorders, $N_d$ to be introduced in the liquid crystal system to mimick effectively a system confined in a porous medium. This value $N_d$ is expressed in terms of actual pore size ($d$), the system size ($L$) and volume occupied by each liquid crystal molecule ($v$) [53]. The relation between the pore size and the number of quenched disorders is proposed as:

$$N_d(L, d, v) = \frac{L^3}{d} \left( \frac{v}{36\pi} \right)^\frac{1}{2}.$$  \hspace{1cm} (3.8)

Based on this prescription, canonical simulations were performed to study the effect of the pore size on the nature of NI transition by introducing appropriate amount of QRD and a lattice model based on Lebwohl-Lasher potential is used. It was observed that the transition temperature, $T_{NI}$ decreases as the pore size is
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reduced and the shift in the $T_{NI}$ agrees well with the experimental findings proving the validity of the model. But it is to be appreciated that QRD introduces several minima in the free energy surface of the system, thereby making it in principle difficult for canonical sampling methods to sample the energy landscape comprehensively, more so, when a first order transition occurs in the system. In the present study we have applied the modified *frontier sampling* method to systematically study the effect of QRD on the nematic-isotropic phase transition. We considered a range of pore sizes from 1200 Å to 25 Å, and chose a cubic lattice of size, $L = 20$. The variation of orientational order parameter $S$, orientational susceptibility $\chi$ and average energy $E$ with the increasing amount of disorder is shown in the figure 3.14. The figures confirm the earlier observations of the shift in $T_{NI}$ towards lower temperatures with the increase in disorder as observed from the canonical simulations. The transition temperatures $T_{NI}$ obtained from the location of the peaks of $C_V$ and $\chi$ profiles are plotted against the pore size $d$ in the figure 3.15. The variation of $T_{NI}$ as obtained from the two response functions are comparable, and agrees well with the predictions from the earlier work [53]. It may be noted in this context that the computational effort needed in the WL procedure is significantly small when compared to canonical methods with similar temperature resolution. The common feature between these two methods in the context of this system is that, as QRD is increased, both the procedures demand correspondingly more effort, owing to the complexity introduced in the free energy profile. This, in entropic sampling procedure translates to a very long learning time for the DoS to converge.

Based on the comparison of results of canonical and entropic sampling methods as shown in figure 3.13, as well as on the satisfactory results obtained on progressively introducing QRD into the system, application of the entropic method to LC system, based on the WL algorithm (aided by frontier sampling technique) thus appears
to stand validated. While being able to handle moderately large sizes, it scores over the canonical sampling procedure, as was noted earlier. We take advantage of these features to investigate LC systems, and report these results in the subsequent chapters.

Figure 3.14 Variation of orientational order parameter, susceptibility and energy with temperature for pore sizes $d = 0, 10, 20, 100$ and $160$ respectively, for a liquid crystal system of linear size, $L = 20$. 
Figure 3.15 Variation of normalized $T_{NI}$ with respect to (inverse) pore size obtained from specific heat peaks (left) and orientational susceptibility peaks (right) respectively, for a liquid crystal system of linear size, $L = 20$. The solid lines are best fit straight lines.
Bibliography


