XXVII IUPAP **Conference on Computational Physics**
(CCP-2015)

Indian Institute of Technology

Guwahati, Assam

(2 - 5, December 2015)

Non-Boltzmann Ensembles and Monte Carlo Simulations

K. P. N. Murthy

Manipal Centre for Natural Sciences (MCNS),
Manipal University, Manipal 567104, Karnataka

3 December 2015

collaborator

M Suman Kalyan (Hyderabad)

R Bharath (Mumbai)

V S S Sastry (Hyderabad)

Acknowledgements

THANKS TO

- Santra, (IIT-G) and Purusattam (IMSC, Chennai) for the invitation
- Computations reported in this talk were carried out in
  - the Centre for Modelling Simulation and Design (CMSD), University of Hyderabad, Hyderabad
  - the Shakti cluster, Manipal Centre for Natural Sciencs (MCNS), Manipal University
  - the Boltzmann cluster, School of Physics, University of Hyderabad, Hyderabad

Thermodynamics and Statistical Mechanics

- For every thermodynamic property we have in statistical mechanics a random variable
- the average of the random variable over a suitable ensemble gives the corresponding thermodynamic property
- consider a thermodynamic property called internal energy usually denoted by the symbol U
- In statistical mechanics we have the corresponding random variable called energy denoted by the symbol E

- energy fluctuates as the macroscopic system moves from one microstate to another ... in equilibrium
- these fluctuations are an integral part of an equilibrium system
- in fact we relate these fluctuations to heat capacity - a well defined thermodynamic property of the system
- We carry out an average of this fluctuating energy over say a canonical ensemble and make correspondence with internal energy of a closed system in thermodynamics : $\langle E \rangle = U$.
- we employ suitable Monte Carlo method - *e.g.* Metropolis algorithm, to generate the canonical ensemble of microstates

Mechanical and thermal properties

- Such a computational scheme has possible because
- a numerical value for energy can be assigned to each microstate of a macroscopic system.
- Let us now look at computation of Entropy
- we notice that a numerical value of entropy can not be assigned to a single microstate
- entropy is something that belongs to a collection of microstates
- energy is a "private" property
- entropy is a "public" property
- entropy is a property that belongs to all the microstates
- How de we calculate entropy employing Monte Carlo simulations ?

Nature of Entropy

- Let $\{C_i \ : \ i = 1, 2, \cdots\}$ denote the microstates of a system
- Let $\{p(C_i) \ : \ i = 1, 2, \cdots\}$ denote their probabilities
- the entropy of the system is given by,

$$S = -k_B \sum_i p(C_i) \ln p(C_i).$$

- $p(C_i) = \dfrac{1}{\widehat{\Omega}(E, V, N)} \Rightarrow S = k_B \ln \widehat{\Omega}$: Isolated system : Microcanonical
- $p(C_i) = \dfrac{\exp(-E(C_i)/k_B T)}{Q(T, V, N)} \Rightarrow$ closed system : Canonical
- $p(C_i) = \dfrac{\exp[-(E(C_i) - \mu N(C_i))/k_B T]}{\mathcal{Q}(T, V, \mu)} \Rightarrow$ open : Grand canonical
- *etc.*

Monte Carlo Simulation based on Metropolis algorithm

- Consider an equilibrium system characterized by $\{p(C_i) \ : \ i = 1, 2, \cdots\}$.
- Aim : simulate the system employing Markov Chain Monte Carlo methods based on Metropolis rejection technique; *i.e.* generate a large number of microstates belonging to an ensemble defined by $\{p(C_i)\}$
- Start with an initial microstate C_0;
- Generate a Markov Chain

$$C_0 \rightarrow C_1 \rightarrow \cdots C_i \rightarrow C_{i+1} \rightarrow \cdots$$

following Metropolis rejection procedure :

Metropolis Rejection

- Let C_i be the current microstate in the Markov Chain;
- let $p_i = p(C_i)$ be its probability.
- Construct a trial microstate by making a local change in C_i.
- Call it C_t.
- Let $p_t = p(C_t)$ be its probability.
- Calculate $p = \min\left(1, \frac{p_t}{p_i}\right)$
- generate a random number r;
- if $r \leq p$, accept the trial microstate and advance the Markov Chain to $C_{i+1} = C_t$;
- if not, reject the trial state and advance the Markov Chain to $C_{i+1} = C_i$.
- iterate

Closed and Open systems

Note :

- since the algorithm requires only ratio of probabilities, we need to know $p(C)$ only upto a normalization constant.
- It is precisely because of this we can simulate
  - a closed system :
  - knowledge of Boltzmann weight $\exp[-\beta E(C)]$ is adequate
  - we need not know the partition function, $Q = \sum_i \exp[-\beta E(C_i)]$
  - an open system :
  - knowledge Boltzmann-Gibbs weight $\exp[-\beta\{E(C) - \mu N(C)\}]$ is adequate
  - we need not know the grand canonical partition function, $\mathcal{Q} = \sum_i \exp[-\beta\{E(C_i) - \mu N(C_i)\}]$

Strategy :

- Generate a long Markov Chain from an arbitrary initial microstate C_0 employing Metropolis algorithm
- Discard initial microstates : let the system equilibrate and lose its memory of C_0
- Consider a property ξ_i that is defined for a microstate *e.g.* energy
- calculate its average : $\langle \xi \rangle = (1/N) \sum_i \xi_i$ over a Monte Carlo sample of size N taken from the end segment of the Markov chain.
- what if the property can not be defined for a microstate *e.g.* entropy ?
- we need special techniques : Non - Boltzmann Monte Carlo
- Let $g_i = g(E_i)$ define density of states : number of microstates in an interval around E_i divided by the width of the interval ΔE_i.

Entropic Sampling

- We estimate $\{g_i : i = 1, 2, \cdots\}$ over the required range of energy, iteratively
- Several techniques have been proposed for the iteration; we describe below entropic sampling
- ENTROPIC SAMPLING:
- Set $g_i = 1 \ \forall \ i$ and $h_i = 0 \ \forall \ i$.
- Start with an initial microstate C_0.
- update $h(E(C_0)) = h(E(C_0)) + 1$
- make a local change in C_0 and construct a trial state C_t
- calculate $p = g(E(C_0))/g(E(C_t))$.
- Generate a random number r;

ENTROPIC ENSEMBLE

- if $r \leq p$ accept the trial state and set $C_1 = C_t$
- if not, reject the trial state and set $C_1 = C_0$.
- update the histogram of energy $h(E(C_1)) = h(E(C_1)) + 1$
- iterate After some 10,000 runs, we update the density of states as follows :

$$g_i = \begin{cases} g_i \times h_i & \text{if} \quad h_i \neq 0 \\ g_i & \text{if} \quad h_i = 0 \end{cases}$$

- this completes the first iteration.
- re-set the histogram to zero;
- employ the updated density of states $\{g_i : i = 1, 2, \cdots\}$ in the second iteration, collect histogram, and employing the histogram update the density of states for the next iteration

ENTROPIC ENSEMBLE

- and proceed to the next iteration and so on
- after a few iterations the histogram would become flat
- this signals that the the underlying density of states has converged to its true value
- from the converged density of states, we can calculate entropy and free energy as follows

$$\begin{aligned} S(E_i) &= -k_B \ln g(E_i) \\ F(E_i, T) &= E_i - k_B T \ln g(E_i) \end{aligned}$$

ENTROPIC ENSEMBLE

- We can employ the converged density of states in a production run and generate an entropic ensemble of microstates
- We first un-weight the entropic ensemble to a micro canonical ensemble :
  - Let C be a microstate belonging to the entropic ensemble; we attach a statistical weight and set it to unity to begin with. We divide the statistical weight by $g^{-1}(E(C))$; this ensures passage from entropic ensemble to a micro canonical ensemble
- we then re-weight to a canonical ensemble : multiply the statistical weight by Boltzmann weight $\exp[-\beta E(C)]$.
- canonical ensemble average of a mechanical property say E can be obtained as

$$\langle E \rangle = \frac{\sum_C E(C)\ g(E(C))\ \exp[-\beta E(C)]}{\sum_C g(E(C))\ \exp[-\beta E(C)]}$$

where the sum runs over the microstates of the entropic ensemble generated employing the converged density of states.

Wang-Landau Algorithm

- Start with an initial microstate C_0.
- update $g(E(C_0)) = \alpha \times g(E(C_0))$ where the Wang-Landau factor is taken as $\alpha = e$.
- $h(E(Ca_0)) = h(E(C_0)) + 1$
- construct a trial state C_t from C_0
- calculate the ratio $p = g(E(C_0))/g(E(c_t))$
- generate a random number r
- if $r \leq p$ accept the trial state : $C_1 = C_t$
- if not reject : $C_1 = C_0$
- update g and h : $g(E(C_1)) = \alpha \times g(E(C_1))$, and $h(E(C_1)) = h(E(C_1)) + 1$
- Proceed to the next step : generate C_2, and update g and h.
- Typically we carry out some ten thousand Monte Carlo steps
- This constitutes the first Wang-Landau iteration run

Wang-Landau Algorithm

- Reduce α to $\sqrt{\alpha}$, reset the histogram values to zero and start the second Wang-Landau iteration run.
- Iterate further until α is nearly unity when the simulation stops
- for example, after 25 iterations, the Wang-Landau factor α is $1 - 3 \times 10^{-8}$.
- $\{g_i\}$ at the end of the last run gives a good estimate of the density of states upto a multiplicative constant.
- $\ln g_i$ gives entropy upto an additive constant
- We can monitor the histogram $h(E)$ and check if it is flat
- Flatter the histogram, closer is $g(E)$ to the true density of states.
- we follow the criterion : If the maximum and minimum of the entries in the histogram do not differ more than 20% we take the histogram to be flat.

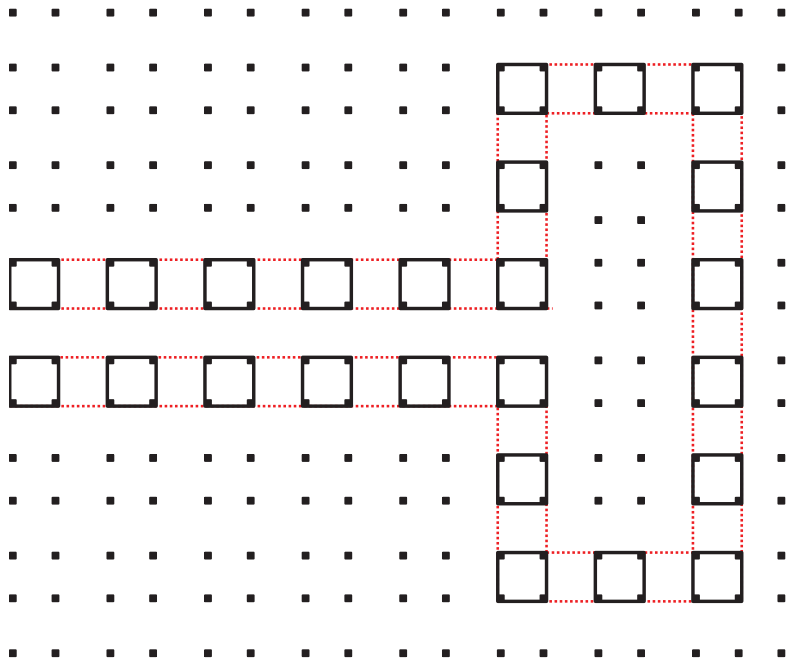
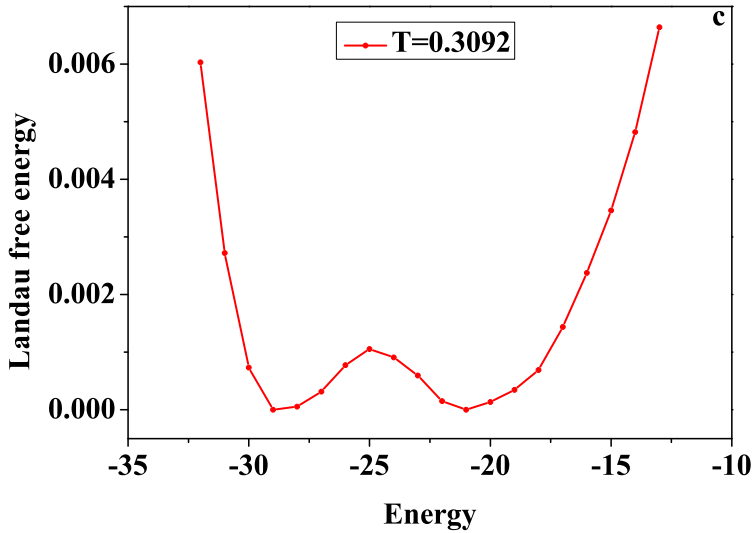
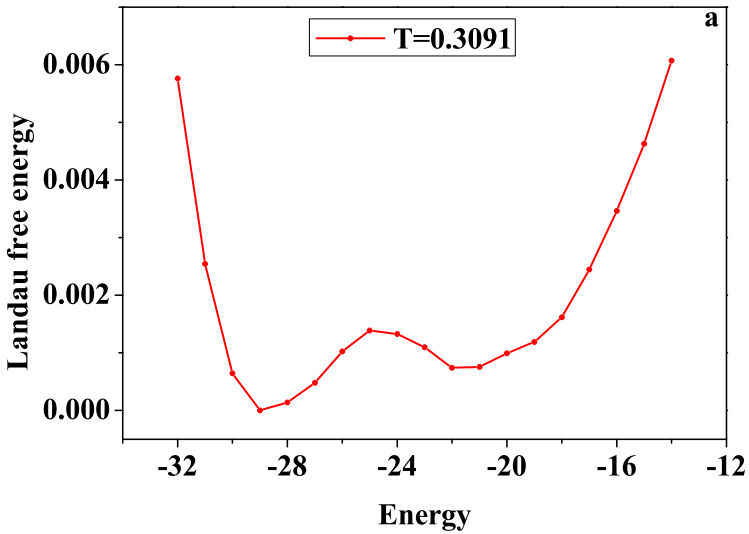


Figure : Two dimensional lattice model of an hairpin DNA : loop structure-Four-site occupation Bond FLuctuation Model





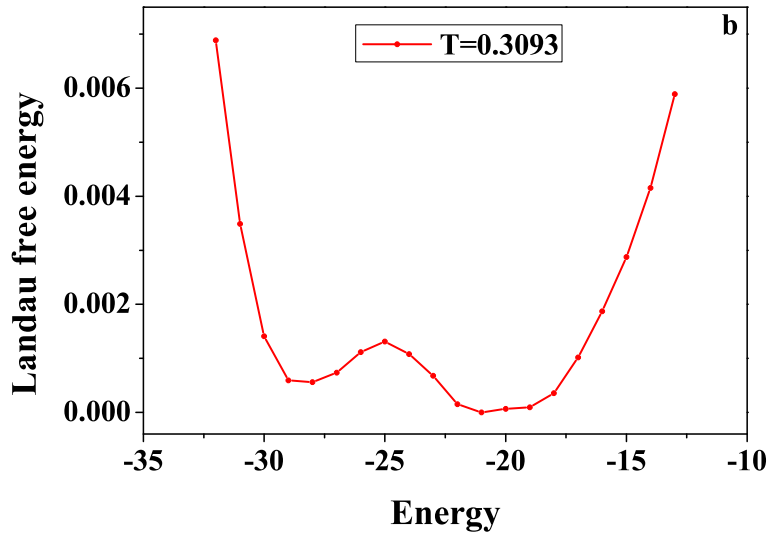


Figure : Free Energy as a function of energy : $N = 110$; $f = 0.06$; $T = T_C$ (TOP) $T < T_C$(LEFT) and $T > T_C$ (RIGHT)

- often we require free energy as a function of order parameter
- for the polymer the end - to - end distance x is good order parameter.
- We need $g(E, x)$ - density of states in both energy E and order parameter x space.
- An early strategy proposed consists of flattening the histogram in the $E - x$ space.
- however such a calculation is time consuming;

- we propose a technique in which we estimate $g(E,x)$ in the production run of the Wang-Landau method
- The operating equation is

$$\langle g(E_i,x_j)\rangle \quad = \quad \frac{\sum_C \delta(E(C)-E_i)\delta(x(C)-x_j)g(E(C))}{\sum_C \delta(E(C)-E_i)g(E(C))}$$

- the sum runs over the microstates generated during the production run.
- the Landau free energy is given by

$$F_L(x_j,T) \quad = \quad -k_B T \ln \sum_i \langle g(E_i,x_j)\rangle \exp(-\beta E_i)$$

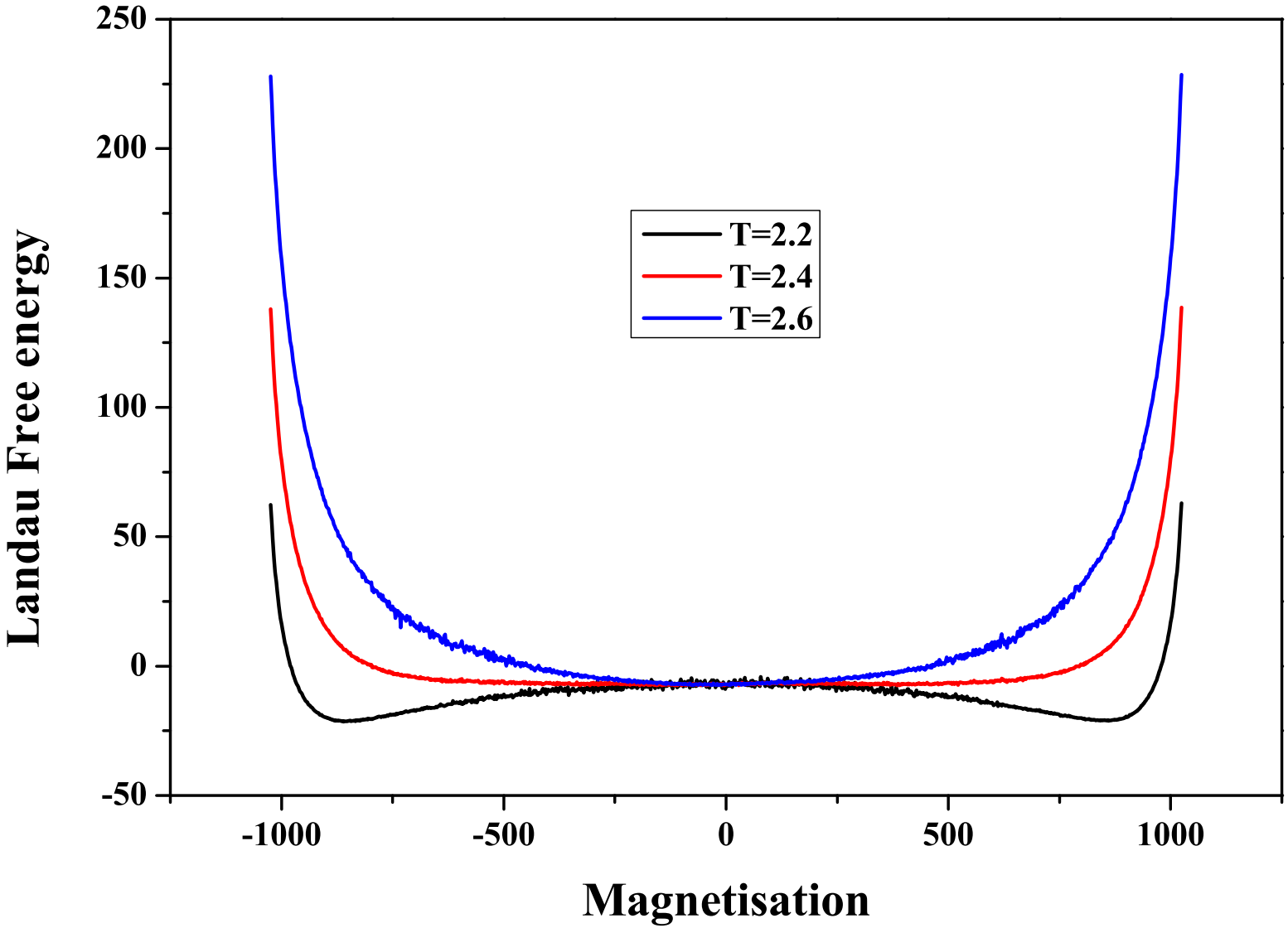


Figure : Free Energy as a function of magnetization in a 32×32 Ising spins on a square lattice

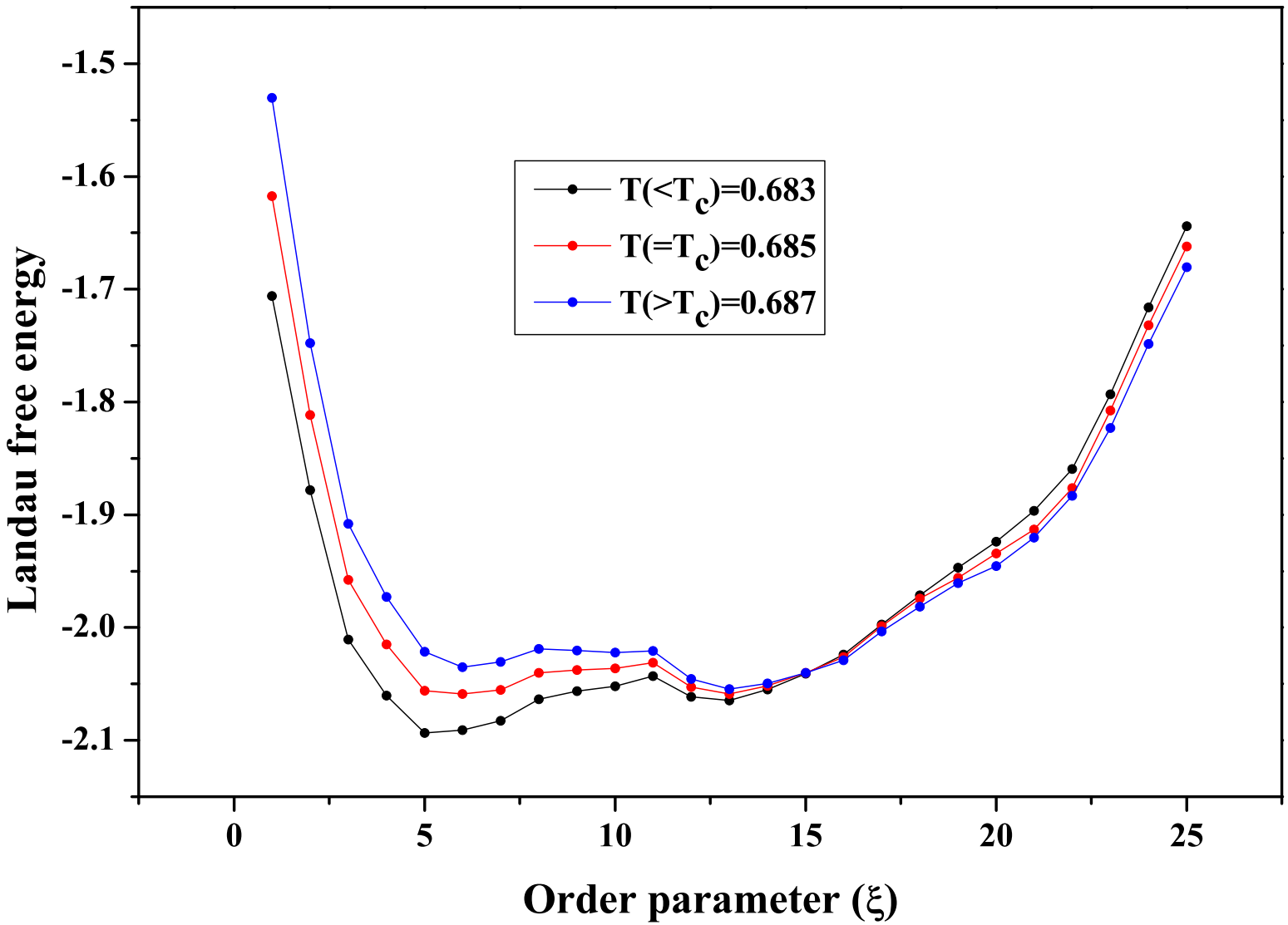


Figure : Free Energy as a function of end-to-end distance for a double stranded DNA in the preence of a force

Free Energy Difference

- Another important area of research in computational soft condensed matter physics is estimation of free energy between two equilibrium states of a system

$$\Delta F = F(B) - F(A)$$

- See C Chipot, and A Pohorille, *Free Energy Calculations : Theory and Applications in Chemistry and Biology*, Springer (2007)
- Several computational methods have been developed
  - thermodynamic integration
  - adaptive integration
  - perturbation
  - slow switching
  - fast switching
  - instantaneous switching
  - *etc.*

- perhaps the most recent of these is a method based on Jarzynski equality

$$\langle \exp(\beta W) \rangle = \exp(-\beta \Delta F)$$

- LHS : averaging over an ensemble of work done in switching experiments, all carried out with the same time protocol
- a parameter λ is switched from an initial value λ_I to a final value λ_F
- C Jarzynski, *Nonequilibrium equality for free energy differences*, Phys. Rev. lett. **78** 2690 (1997).

- A typical Monte Carlo simulation proceeds as follows :
- start with an initial microstate C_0 of the macroscopic closed system from an equilibrium ensemble at temperature $T = 1/k_B\beta$ and $\lambda = \lambda_I$.
- You can use Metropolis algorithm to equilibrate the system
- find the energy of the initial microstate
- change the value of λ by $\Delta\lambda$
- call it a work step
- calculate the resulting change of energy ΔE
- energy transacted by work is $w_1 = \Delta E$

- carry out a few heat steps employing Metropolis algorithm
- in a Metropolis step the system transacts energy with the surroundings by heat
- the system tries to equilibrate at the changed value of λ; but it does not
- find the energy of the system at the end of a few heat steps

- change λ by $\Delta\lambda$; work step
- calculate the change in energy; it equals w_2, the work done in the second work step
- proceed in the same way until $\lambda = \lambda_F$
- this constitutes a switching experiment
- $W_1 = \sum_i w_i$ is the energy transacted by work

- repeat the above starting with a new initial equilibrium microstate with λ_I and T
- the experimental protocol remains the same : number of work steps and the number of heat steps between two consecutive work steps are the same for all the experiments
- accumulate an ensemble of work values
- the free energy difference is given by

$$\Delta F = -k_B T \ln \left[\frac{1}{N} \sum_{i=1}^{N} \exp(-\beta W_i) \right]$$

Slow Switching :

- $\Delta\lambda$ is small
- quasi static limit obtains when $\Delta\lambda \to 0$
- the work distribution is Gaussian by virtue of central limit theorem
- work distribution is sharply peaked at ΔF
- the variance is extremely small
- the fluctuations of W are small
- the statistical error bar on the average work - given by one-sigma confidence interval - is small
- but the computational time required is large since the number of work steps is large

Fast switching

- $\Delta\lambda$ is large
- instantaneous switching obtains when $\Delta\lambda = \lambda_F - \lambda_I$
- the work distribution is not Gaussian
- the work distribution is very broad *i.e.*, the variance is large
- W fluctuates heavily from one experiment to the other
- the statistical error bar on the average work is large
- to reduce the statistical error bar we need to simulate the experiment a very large number of times
- this would require very large computer time

In this context Suman Kalyan proposed a new Method for computing free energy difference. It employs

- Jarzynski equality, in conjunction with
- instantaneous switching and
- entropic ensemble.

It employs Wang-Landau algorithm to obtain

- the density of states in the iteration run and
- an entropic ensemble in the production run

- initial microstate C is random sampled from an entropic ensemble;
- let the energy of the initial microstate be denoted by $E_I(C)$
- the switching is instantaneous : $\Delta\lambda = \lambda_F - \lambda_I$
- let the energy of the microstate after switching be denoted by $E_F(C)$;
- the work done is obtained as the difference of energy of the microstate before and after switching : $W = E_F(C) - E_I(C)$

- we first un-weight the microstate to a microcanonical ensemble
  - multiply by the density of states, $g(E_I(C))$
- we then re-weight it to the required canonical ensemble
  - multiply by Boltzmann weight, $\exp(-\beta E_I(C))$
- the free energy difference is given by

$$\Delta F = -k_B T \ln \left[\frac{\sum_C g(E_I(C)) \exp[-\beta E_F(C)]}{\sum_C g(E_I(C)) \exp[-\beta E_I(C)]} \right]$$

- in the above, the sum both in the numerator and the denominator runs over the microstates generated in the production run of the Wang-Landau algorithm driven by the density of states obtained in the previous iteration run.

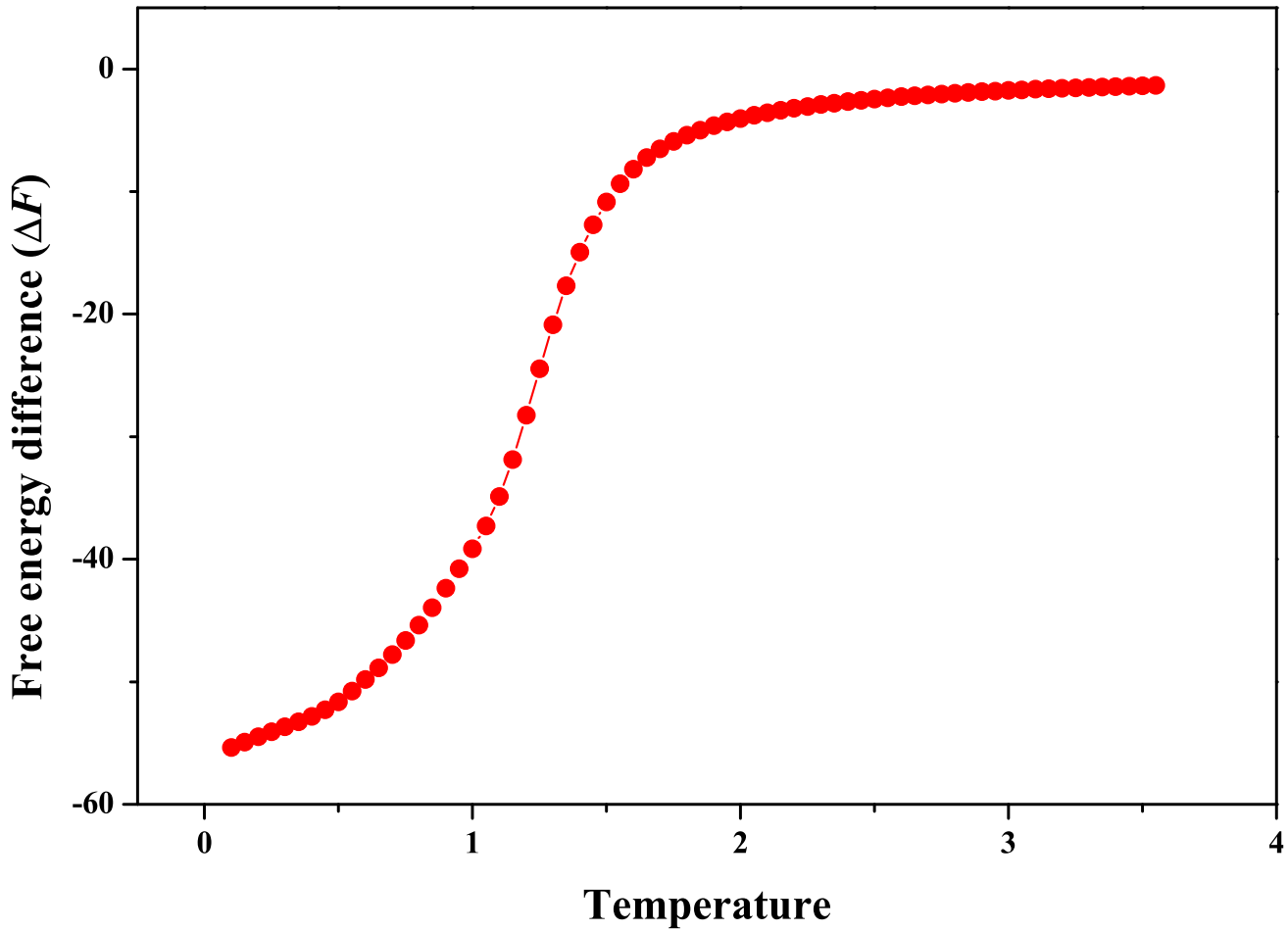


Figure : Free Energy difference as a function of temperature for a liquid crystalline system $5 \times 5 \times 5$ cubic lattice; Lebwohl - Lasher model; electric field is switched from 0 to 1.0

and

THANKS