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Joint Density of States Calculation Employing Wang–Landau Algorithm

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Abstract Joint density of states (JDoS), which depends both on energy and another variable like order parameter provides more information than the conventional density of states (DoS) which depend only on energy. Calculation of JDoS requires huge computational time. In this paper we employ two level method to calculate JDoS which requires relatively much less computational time. We demonstrate this method on a two dimensional Ising spin system, lattice spin model of double strand DNA (dsDNA) and Heisenberg ferromagnet.

Keywords Monte Carlo methods · Wang–Landau algorithm · Joint density of states · Ising model · DNA · Heisenberg ferromagnet

1 Introduction

Wang–Landau (WL) algorithm [1] has emerged as a powerful Monte Carlo technique in statistical physics. It has been applied to variety of studies which include polymers and biopolymers [2,3], Potts spin model [4], Heisenberg ferromagnetic system [5], Ising Model [6], liquid crystals [7,8] etc. In this algorithm we perform a random walk in energy space and estimate density of states (DoS), $g(E)$. A major advantage of the WL algorithm is that it can be employed for calculating thermal properties like entropy and free energy. These properties are not accessible to conventional Markov chain Monte Carlo methods based on Metropolis algorithm. Often we need to calculate joint density of states (JDoS) $g(E, M)$, where M is order parameter, to calculate thermodynamic properties like Landau free energy [9]. In that case we perform random walk both in energy and order parameter spaces to estimate JDoS

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as described by Landau et al. [10]. We call this LTE method. This method requires large amount of computational time. The time required depends on the system size. Hence there is a limitation on such kind of calculations for large systems.

In this paper, we employ a simple two level method proposed by Gervais et al. [11] to calculate JDoS and show that this method requires much less computational time than that required by LTE method. The two level method essentially consists of calculating the JDoS in the production run of the WL algorithm by unweighting and reweighting of microstate from the entropic ensemble. See also [12] and [13] for other applications of this method. The paper is organized as follows. Section 2 describes briefly the estimation of JDoS through LTE method. In Sect. 3, we present the two level method to calculate JDoS and hence average thermodynamic properties and Landau free energy. In Sect. 4, we present the results obtained for Ising spin system, dsDNA and Heisenberg ferromagnet. We conclude the paper by summarizing the principal results in Sect. 5.

2 Calculation of Joint Density of States Using LTE Method

In this section we describe the method of calculating JDoS employing LTE method.

Let $g(E, M)$ denote the joint density of states. We start with $g(E, M) = 1 \ \forall E, M$. Let $h(E, M)$ denote the histogram and we set $h(E, M) = 0 \ \forall \ E, M$. We start with an arbitrary initial microstate C_0. Let $E_0 = E(C_0)$ be the energy of the microstate and $M_0 = M(C_0)$ be the value of the order parameter. We update $g(E_0, M_0) = g(E_0, M_0) \times f$ and $H(E_0, M_0) = H(E_0, M_0) + 1$, where f is the Wang-Landau factor set to $\exp(+1)$ in the first iteration run. We then generate a chain of microstates $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow \cdots C_i \rightarrow C_{i+1} \rightarrow \cdots$ as follows. Let C_i be the current microstate. Let $E_i = E(C_i)$ and $M_i = M(C_i)$ be the energy and order parameter of the current microstate. We make a local change in the current microstate C_i and construct a trial microstate C_t. For example flipping a randomly chosen spin gives a trial state in Ising spin system. Let $E_t = E(C_t)$ and $M_t = M(C_t)$ be the energy and order parameter of the trial microstate. We calculate the ratio

$$p = \min \left(\frac{g(E_i, M_i)}{g(E_t, M_t)}, 1 \right) \tag{1}$$

Generate a random number ξ uniformly distributed in the range 0 and 1. If $\xi \leq p$ accept the trial state and advance the chain to $C_{i+1} = C_t$. Otherwise reject the trial state and advance the chain to $C_{i+1} = C_i$. Update the density of states:

$$g[E(C_{i+1}), M(C_{i+1})] = g[E(C_{i+1}), M(C_{i+1})] \times f$$

and the histogram:

$$H[E(C_{i+1}), M(C_{i+1})] = H[E(C_{i+1}), M(C_{i+1})] + 1.$$

A single acceptance or rejection step is called a Monte Carlo step. L^d number of Monte Carlo steps constitutes one Monte Carlo sweep (MCS), where L is size of the system and d is dimensionality. We repeat the process till we get a flat histogram. Then we reduce modification factor $f \rightarrow \sqrt{f}$ and reset $H(E, M) = 0$ and repeat the above process. We repeat the whole process described above till $(f - 1) \simeq 10^{-8}$. As $f \rightarrow 1$, $g(E, M)$ converges to true joint density of states.

As discussed earlier, flattening the histogram in the two dimensional space (of energy and order parameter) takes more computational time than flattening the histogram in one

dimensional space of energy). Keeping in mind that the dynamics of the system depends on energy of the system but not on the order parameter (order parameter changes according to energy variations), we go for the alternate method given by Gervais et al. [11] which reduces computational time enormously. This method is described in the next section.

3 Two Level Method to Calculate the Joint Density of States

The two steps in this method are

1. Estimate DoS, $g(E)$ using W–L algorithm. We call this learning run.
2. Estimate JDoS in the production run. We treat $g(E_i, M_j)$ as a thermodynamic variable whose average over a microcanonical ensemble is to be obtained. From entropic ensemble, we construct a microcanonical ensemble by un-weighting and re-weighting, see below.

In the production run, we start with a microstate C_0 taken from the last W–L iteration of learning run and generate sequence of microstates

$$C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow \cdots C_i \rightarrow C_{i+1} \rightarrow \cdots \rightarrow C_N$$

employing W–L algorithm with the converged DoS, $g(E)$. In production run we do not update DoS. The above sequence of microstates correspond to the ones obtained after every Monte Carlo Sweep i.e., C_{i+1} is a microstate evolved from the microstate C_i after one Monte Carlo Sweep. The number of Monte Carlo sweeps is denoted by N.

Since entropic ensemble is collected with a probability proportional to $[g(E)]^{-1}$, to calculate average of any macroscopic observable O over a desired ensemble, we need to first un-weight it (by dividing by $[g(E)]^{-1}$) and then reweight it to the desired ensemble; for example we can reweight it to canonical ensemble by multiplying with Boltzmann weight, see below.

$$\langle O \rangle_T = \frac{\sum_C O(C) \, g(E(C)) \, \exp(-\beta E(C))}{\sum_C g(E(C)) \, \exp(-\beta E(C))} \tag{2}$$

where C denotes a microstate belonging to the entropic ensemble, $O(C)$ is the value of macroscopic property O when the system is in microstate C; $E(C)$ is the energy of the system when it is in microstate C and $\beta = \frac{1}{k_B T}$ with k_B Boltzmann constant and T the temperature. We set $k_B = 1$ in all the calculations reported here.

Similarly to calculate average of any macroscopic observable over a microcanonical ensemble, we need to unweight and reweight with suitable factors. Unweighting is carried out by dividing with $[g(E)]^{-1}$ and the reweighting factor is unity since the probabilities of microstates of a microcanonical ensemble are all equal for a given energy.

$$\langle O \rangle_E = \frac{\sum_C O(C) \, \delta(E(C) - E) \, g(E(C))}{\sum_C \delta(E(C) - E) \, g(E(C))} \tag{3}$$

Our aim is to calculate average of JDoS over a microcanonical ensemble. This can be done as follows.

From the microcanonical ensemble we compute the following

$$\langle g(E_i, M_j) \rangle = \frac{\sum_C \delta(E(C) - E_i)\, \delta(M(C) - M_j)\, g(E(C))}{\sum_C \delta(E(C) - E_i)\, g(E(C))} \qquad \forall\, i, j \qquad (4)$$

and get the microcanonical average of JDoS.

Once we get the microcanonical average of JDoS, we can calculate the average of any other macroscopic observable over a canonical ensemble as

$$\langle O \rangle_T = \frac{\sum_C O(C) \sum_j \langle g(E(C), M_j) \rangle\, \exp(-\beta E(C))}{\sum_C \sum_j \langle g(E(C), M_j) \rangle} \qquad (5)$$

Also we can calculate Landau free energy as

$$F_L(M_j, T) = -k_B T \ln \sum_i \langle g(E_i, M_j) \rangle \exp(-\beta E_i) \qquad (6)$$

where we take T to be very close to the transition temperature.

4 Results and Discussions

We have chosen Ising spin system [14] to demonstrate both LTE and the alternate two level method. We have also employed the two level method to a lattice model of double strand DNA and Heisenberg ferromagnet system.

4.1 Ising Spin System

Consider an $L \times L$ square lattice with each lattice site holding a spin. A spin takes a value of $+1$ if it points upwards and -1 if it points downwards. The interaction energy between two spins S_i and S_j which are located at nearest neighbour lattice sites i and j is given by $\epsilon_{ij} = -J S_i S_j$, where J is the strength of spin-spin interaction and we set it to unity in our simulations. We employ periodic boundary condition in both directions. For a two dimensional lattice, each spin interacts with four nearest neighbours.

The total energy of the system is given by

$$H = -J \sum_{\langle i, j \rangle} S_i S_j \qquad (7)$$

where $\langle i, j \rangle$ denotes that i and j are nearest neighbour sites and the summation runs over all the distinct nearest neighbour pairs with periodic boundary conditions. $M = \sum_i S_i$ is the order parameter of the system. JDoS is calculated as follows.

We have considered two dimensional Ising spin system on a square lattice of size $L = 10, 16, 32$. For system sizes of $L = 10$ and 16, we obtained JDoS from both LTE and the two level method. For system size of 32, we have calculated JDoS only with the two level method. The LTE method takes huge computational time.

Average energy can be calculated by substituting $E(C)$ in place of $O(C)$ in Eq. 5. In Fig. 1, we have plotted average energy per spin against temperature. It shows a transition from low
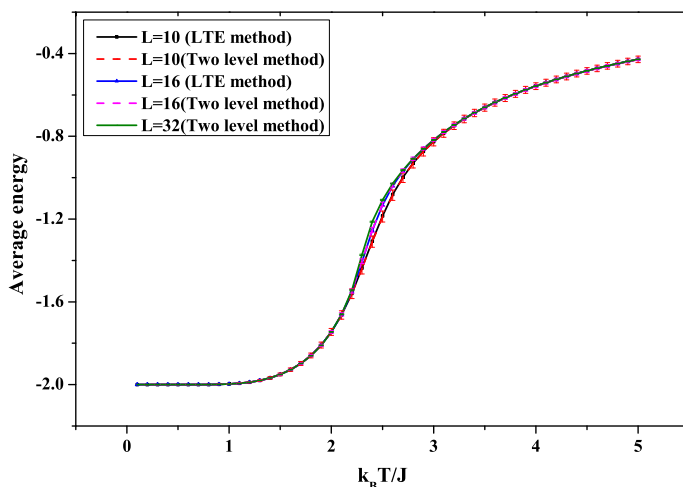
Fig. 1 Average energy per spin vs $\frac{k_B T}{J}$ for various system sizes of L calculated from LTE and two level methods
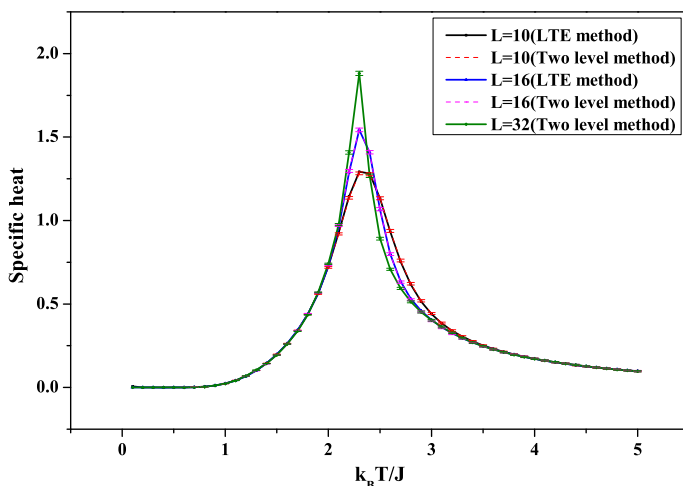

Fig. 2 Specific heat vs $\frac{k_B T}{J}$ for various system sizes of L calculated from LTE and two level methods

energy ferromagnetic state to a high energy paramagnetic state. For $L = 10$ and 16, we can observe that average energy profiles calculated from JDoS obtained from both the methods agree with each other within the error bars.

Specific heat calculated from JDoS obtained from both the methods match with each other for $L = 10$ and 16 at different temperatures as shown Fig. 2. The figure also shows specific heat for $L = 32$. The temperature at which specific heat is maximum is taken as transition temperature.

Landau free energy as a function of the order parameter is plotted in Figs. 3, 4 and 5 for system $L = 10$ at temperatures close to transition temperatures. We observe that the Landau free energy calculated from JDoS obtained from both the methods match with each other and the error bars are negligible.
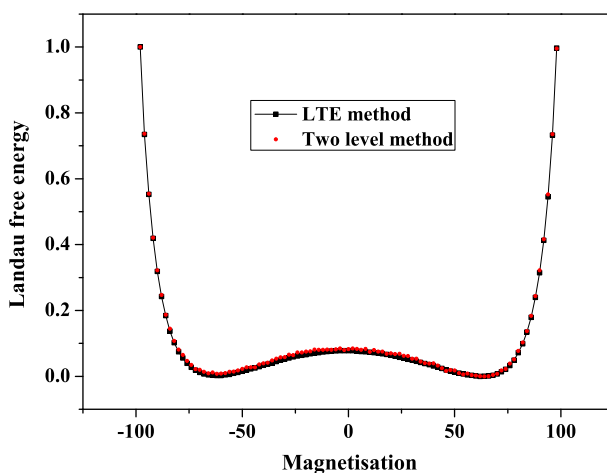
Fig. 3 Normalized Landau free energy at $T(= 2.6) < T_c$ for 10×10 Ising spin system
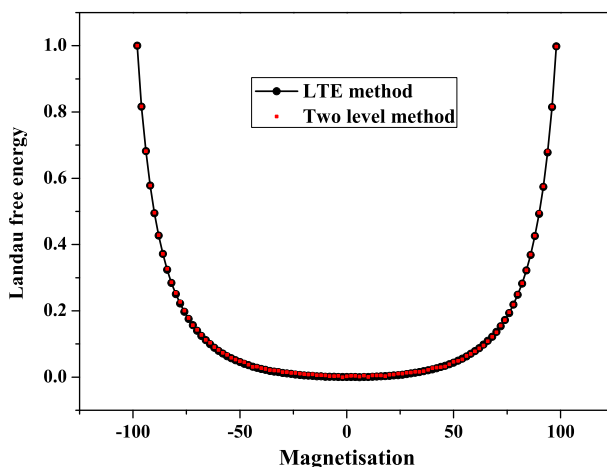

Fig. 4 Normalized Landau free energy profile at $T(= 2.7) = T_c$ for 10×10 Ising spin system

Figures 6 and 7 show Landau free energy profile calculated from JDoS obtained with the LTE and two level method for system of size $L = 16$.

Figure 8 shows Landau free energy profile calculated from JDoS calculated with the two level method for system of size $L = 32$.

4.2 Lattice Model of Double Strand DNA

We consider a double strand DNA on a two dimensional square lattice. It is observed that lattice models of polymers exhibit qualitatively similar behaviour as real polymers and give results qualitatively in good agreement with experiments. A major advantage of lattice models is that the excluded volume effect/hard core repulsion can be easily implemented. In this model, the base of one strand pairs with the corresponding base of the second strand when they are at the nearest neighbour distance; i.e, the first base of one strand pairs with first base
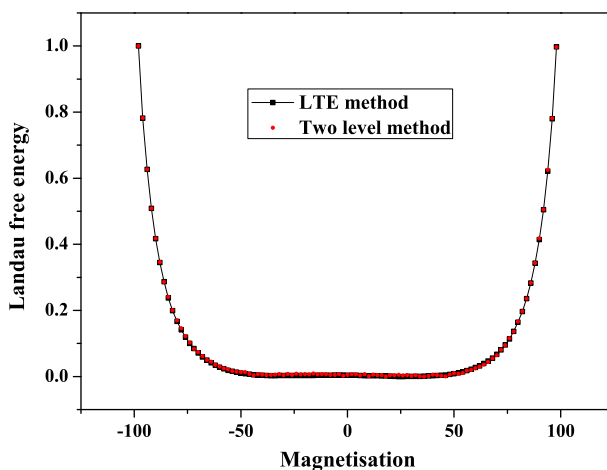
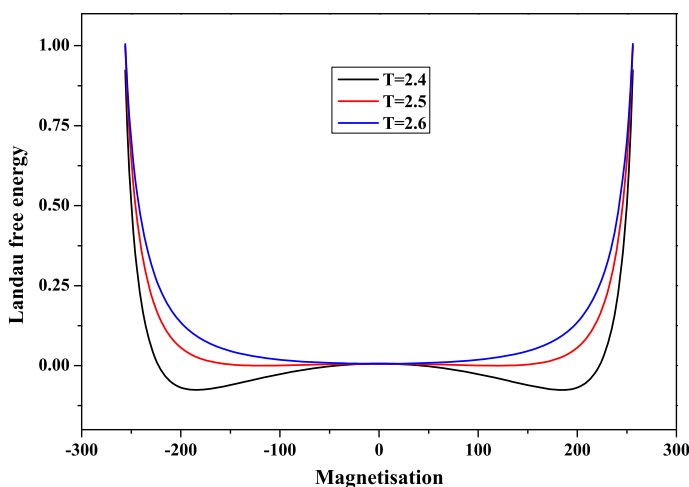**Fig. 5** Normalized Landau free energy at at $T(=2.8) > T_c$ for 10×10 Ising spin system

Fig. 6 Scaled Landau free energy calculated with JDoS obtained from LTE method as a function of magnetisation close to transition temperature T_c for 16×16 Ising spin system

of other strand; second base with second; and so on. We call these native contacts. We assign an interaction energy of $-\epsilon_b$ for each base pair [15,16]. Without loss of generality we set $\epsilon_b = 1$. We fix both the ends of one strand and one end of the second strand and we subject the free end of the second strand to a small external force (small compared to the critical force required for unzipping) in a direction perpendicular to the DNA. The energy due to this applied force is $\epsilon_f = -\mathbf{f} \cdot \boldsymbol{\xi}$, where $\boldsymbol{\xi}$ is distance between the base at the free end and its native contact. The total energy thus, is

$$E = -\gamma \epsilon_b - \mathbf{f} \cdot \boldsymbol{\xi} \tag{8}$$

where γ is the number of native contacts in a conformation and ξ is the order parameter of the system. In our simulation we have used strands of length 80 and $\mathbf{f} = 0.02$. We employed
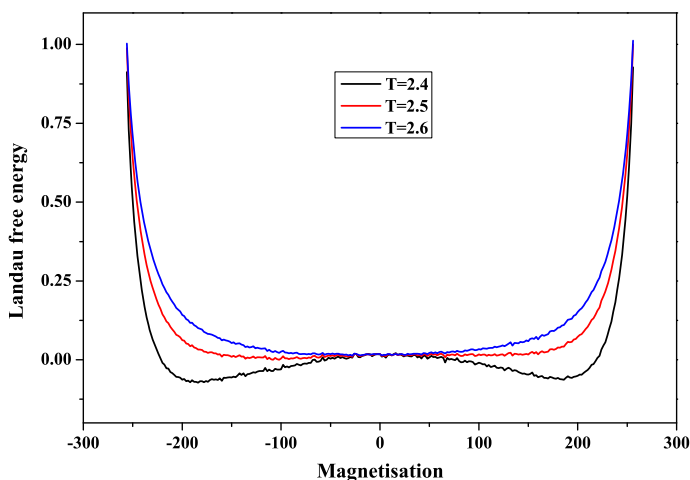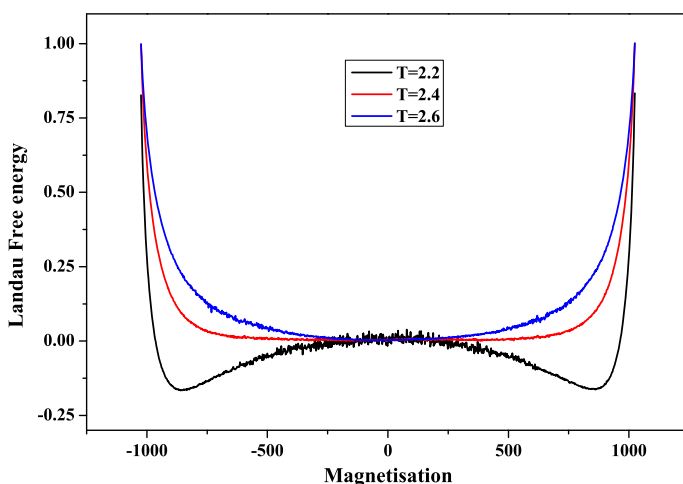
Fig. 7 Scaled Landau free energy calculated with JDoS obtained from the two level method as a function of magnetisation close to transition temperature T_c for 16×16 Ising spin system

Fig. 8 Scaled Landau free energy calculated with JDoS obtained from the two level method as a function of magnetisation close to transition temperature T_c for 32×32 Ising spin system

bond fluctuation model (BFM) [17] to generate different conformations of dsDNA. This is demonstrated in the next subsection.

4.2.1 Bond Fluctuation Model

Bond fluctuation model (BFM) provides an efficient algorithm to simulate an equilibrium ensemble of lattice polymer conformations. The algorithm helps generate different conformations in an easy manner. Recently it has been shown that bond fluctuation model can be employed in the study of thermodynamic properties of DNA molecules [3]. Implementation of BFM is explained below.
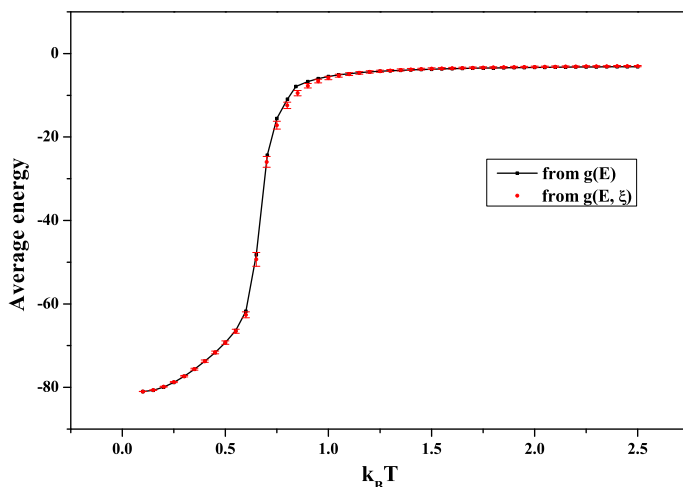
Fig. 9 Comparison of average energy of dsDNA as a function of $k_B T$ calculated from $g(E)$ (estimated from WL algorithm) and $g(E, \xi)$ (calculated from two level method)

In a single-site lattice model of BFM, a monomer occupies a lattice site. The minimum value allowed for bond-length is unity to ensure self avoidance. The maximum value allowed is taken as less than $\sqrt{4}$ to avoid bond cuts [17]. Hence the allowed values for bond length are 1, $\sqrt{2}$, $\sqrt{3}$. We start with a zipped state of ds-DNA with the bond length equal to 1 between the monomers. We move a randomly selected monomer by a lattice spacing along any one of the randomly chosen direction; in a two dimensional lattice model there are four possible directions. If either self avoidance or maximum bond length condition is not satisfied we move the monomer to its initial position and carry out the whole process again by selecting a monomer and its direction randomly. If both the conditions are satisfied we consider that conformation as a trial conformation and is accepted or rejected on the basis of WL sampling.

We have employed two level method for obtaining JDoS; from the JDoS, we have calculated average energy, heat capacity and Landau free energy.

Figure 9 compares average energy calculated from $g(E)$ and $g(E, \xi)$. These values are in good agreement with each other. The curves show that at low temperatures the system is in a low energy zipped state. As temperature increases the energy increases and system transits to an unzipped state.

In Fig. 10, we have plotted heat capacity calculated from $g(E)$ and $g(E, \xi)$. The temperature at which the heat capacity is maximum, is taken as the transition temperature T_c. The maximum relative difference between these values is 2 % at T_c.

Figure 11 shows Landau free energy as a function of order parameter ξ. We can observe that the melting transition is first order, in agreement with the earlier predictions [3,18].

4.3 Heisenberg Ferromagnetic System

We have considered a three dimensional Heisenberg ferromagnet spin system on a cubic lattice. The Hamiltonian for this model is

$$H = -J \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{9}$$
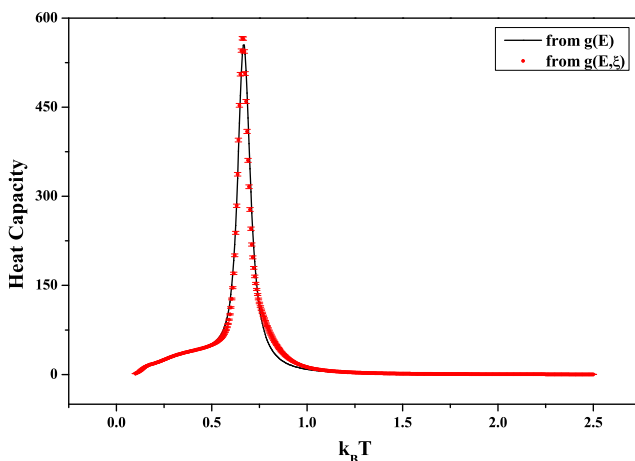
Fig. 10 Heat capacity of dsDNA as a function of $k_B T$ calculated from both $g(E)$ (estimated from WL algorithm) and $g(E, \xi)$ (calculated from two level method)
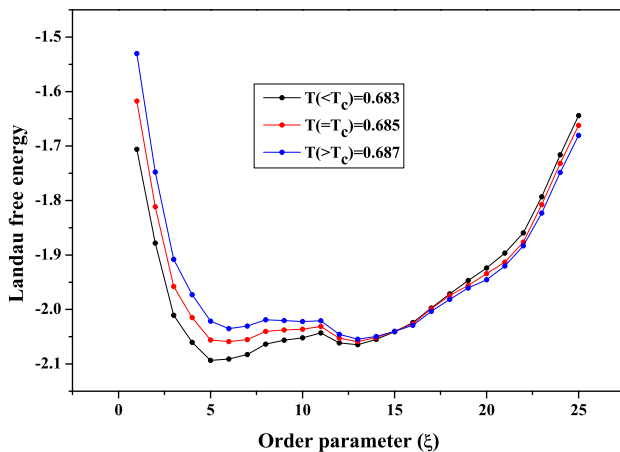

Fig. 11 Landau free energy of dsDNA as a function of order parameter ξ obtained from $g(E, \xi)$ (calculated from two level method)

where the summation goes over all the distinct nearest neighbours with periodic boundary conditions. Here J is the interaction strength which we set to unity in our simulations. The order parameter for this system is given by,

$$M = \sum_i S_i^z \tag{10}$$

We have employed the two level method to obtain the JDoS for $L = 5$ system. However, in the first step to estimate the DoS, we employed JSM method as described in [7] since the system has continuous degrees of freedom. $g(E)$ is calculated by dividing the total energy range into 1250 bins and JDoS is calculated by dividing the total magnetization range into 1000 bins.
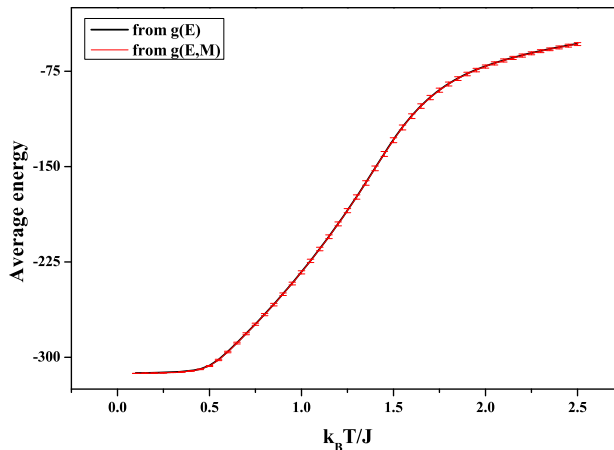
Fig. 12 Comparison of average energy of Heisenberg ferromagnet system as a function of $\frac{k_B T}{J}$ calculated from $g(E)$(estimated from JSM method) and $g(E, M)$(calculated from two level method)
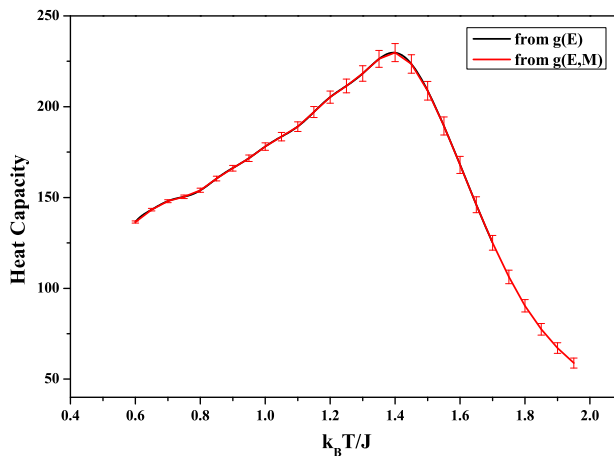

Fig. 13 Heat capacity of Heisenberg ferromagnet system as a function of $\frac{k_B T}{J}$ calculated from both $g(E)$(estimated from JSM method) and $g(E, M)$(calculated from two level method)

Figure 12 compares variation of average energy as a function of temperature calculated from $g(E)$ and $g(E, M)$. It shows a transition from a ferromagnetic to paramagnetic state. The values calculated from $g(E)$ and $g(E, M)$ are in good agreement with each other, within the error bars.

In Fig. 13, we compare the heat capacities obtained from $g(E)$ and $g(E, M)$ at different temperatures. Within the error bars, the values match with each other.

5 Conclusions

In summary, we have described an efficient and simple numerical method proposed in [11] to estimate joint density of states which takes much less computational time. We have suc-

cessfully employed this method to study a two dimensional Ising spin system on a square lattice, a lattice model of dsDNA, and an Heisenberg ferromagnet on a cubic lattice.

For Ising spin systems with $L = 10$ and 16 the average mechanical properties calculated from JDoS obtained with LTE and the two level method, match with each other. For a $L = 16$, the time taken to estimate $g(E, M)$ with LTE method is more by a factor $\zeta = 500$ compared to the time it takes to estimate $g(E)$. Whereas for the two level method the factor ζ is only 2.5.

In case of dsDNA, the Landau free energy profile calculated from the joint density of states shows that the transition is first order, in agreement with earlier reports.

The two systems discussed above have discrete energy and order parameters. When we go to systems with continuous energy and order parameter like Heisenberg ferromagnet, we could obtain good results on average quantities like energy and heat capacity. However, We could not get good results on those properties which rely solely on the joint density of states e.g. Landau free energy (with the same size of the entropic ensemble generated in production run). An ensemble size of one million (which is the ensemble size in our study) is adequate to estimate average energy and heat capacity, but not good enough for calculating Landau free energy. To obtain Landau free energy with the two level method we need to sample a very large number of microstates; in that case the two level method looses its advantage. Perhaps one would require additional numerical techniques for simulating continuous systems.

References

1. Wang, F., Landau, D.P.: Efficient, multiple-range random walk algorithm to calculate the density of states. Phys. Rev. Lett. **86**, 2050 (2001)
2. Rathore, N., de Pablo, J.J.: Monte Carlo simulation of proteins through a random walk in energy space. J. Chem. Phys. **116**, 7225–7230 (2002)
3. Suman Kalyan, M., Murthy, K.P.N.: Monte Carlo study of force induced melting of DNA hairpin. Physica A **428**, 38–45 (2015)
4. Yamaguchi, C., Okabe, Y.: Three-dimensional antiferromagnetic q-state Potts models: application of the Wang-Landau algorithm. J. Phys. A: Math. Gen. **34**, 8781 (2001)
5. Zhou, C., Schulthess, T.C., Torbrugge, S., Landau, D.P.: Wang-Landau algorithm for continuous models and joint density of states. Phys. Rev. Lett. **96**, 120201 (2006)
6. Okabe, Y., Tomita, Y., Yamaguchi, C.: Application of new Monte Carlo algorithms to random spin systems. Comput. Phys. Commun. **146**, 63–68 (2002)
7. Jayasri, D., Sastry, V.S.S., Murthy, K.P.N.: Wang-Landau Monte Carlo simulation of isotropic-nematic transition in liquid crystals. Phys. Rev. E **72**, 036702 (2005)
8. Mukhopadhyay, K., Ghoshal, N., Roy, S.K.: Monte Carlo simulation of joint density of states in one-dimensional Lebwohl–Lasher model using Wang–Landau algorithm. Phys. Lett. A **372**, 3369–3374 (2008)
9. Tolédano, J.C., Tolédano, P.: The Landau Theory of Phase Transitions. World Scientific publishing Co. Pte. Ltd., Singapore (1987)
10. Landau, D.P., Tsai, S-H., Exler, M.: A new approach to Monte Carlo simulations in statistical physics: Wang-Landau sampling. Am. J. Phys. **72**, 1294–1302 (2004)
11. Gervais, C., Wüst, T., Landau, D.P., Xu, Y.: Application of the Wang–Landau algorithm to the dimerization of glycophorin. J. Chem. Phys. **130**, 215106 (2009)
12. Kumar, Santosh: Random matrix ensembles: Wang-Landau algorithm for spectral densities. EPL **101**, 20002 (2013)
13. Maerzke, K.A., Gai, L., Cummings, P.T., McCabe, C.: Simulating phase equilibria using Wang-Landau-transition matrix Monte Carlo. J. Phys. **487**, 012002 (2014)
14. Brush, Stephen G.: History of the Lenz-Ising model. Rev. Mod. Phys. **39**, 883 (1967)

15. Li, M.S., Cieplak, M.: Folding in two-dimensional off-lattice models of proteins. Phys. Rev. E. **59**, 970 (1999)
16. Go, N., Abe, H.: Noninteracting local-structure model of folding and unfolding transition in globular proteins. I. Formulation. Biopolymers **20**, 991–1011 (1981)
17. Carmesin, I., Kremer, K.: The bond fluctuation method: a new effective algorithm for the dynamics of polymers in all spatial dimensions. Macromolecules **21**, 2819–2823 (1988)
18. Mishra, G., Giri, D., Li, M.S., Kumar, S.: Role of loop entropy in the force induced melting of DNA hairpin. J. Chem. Phys. **135**, 035102 (2011)