

Global Thermodynamic Properties of Complex Spin Systems Calculated from Density of States and Indirectly by Thermodynamic Integration Method

Marek Semjan^{1,*} and Milan Žukovič^{1,**}

¹*Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Park Angelinum 9, 040 01 Košice, Slovakia*

Abstract. Evaluation of global thermodynamic properties such as the entropy or the free energy of complex systems featuring a high degree of frustration or disorder is often desirable. Nevertheless, they cannot be measured directly in standard Monte Carlo simulation. Therefore, they are either evaluated indirectly from the directly measured quantities, for example by the thermodynamic integration method (TIM), or by applying more sophisticated simulation methods, such as the Wang-Landau (WL) algorithm, which can directly sample density of states. In the present investigation we compare the performance of the WL and TIM methods for the calculation of the entropy of an Ising antiferromagnetic system on a Kagome lattice – a typical example of a complex spin system with high geometrical frustration resulting in a non-zero residual entropy the value of which is exactly known. It is found that the easier to implement TIM can yield results of comparable accuracy with that of the more involved WL method.

1 Introduction

Calculation of global thermodynamic properties, which cannot be measured in Monte Carlo (MC) simulation directly, such as the free energy and the entropy, is generally a difficult task. A brute force approach of scanning the entire configuration space to obtain density of states is feasible only for sufficiently small systems. The exponential increase of the configurational space with the system size N makes this approach intractable even for moderate sizes and small number of degrees of freedom, such as the Ising model with the configuration space increasing as 2^N .

In statistical physics, the commonly used standard MC methods, such as the Metropolis algorithm (MA) [1], allow direct evaluation of several thermodynamic quantities, such as the internal energy or magnetization, but not global ones, such as the free energy and the entropy. One possible approach that allows a direct evaluation of density of states (DOS) and consequently the entire thermodynamics is the Wang-Landau (WL) algorithm [2], which has been successfully applied to a variety of problems, e.g., in efficient studies of first-order and second-order phase transitions. It is a powerful tool for the investigation of systems with rough energy landscapes with large energy barriers separating local minima, which make the use of other standard methods infeasible. An alternative indirect approach

*e-mail: marek.semjan@student.upjs.sk

**e-mail: milan.zukovic@upjs.sk

to the calculation of the global thermodynamic quantities which avoids the calculation of the DOS is the so-called thermodynamic integration method (TIM) [3]. Since its introduction in 1977, it has been sparingly used, even though several studies pointed to its competitiveness [4, 5], for example in calculation of the ground-state entropy of some typical disordered/frustrated spin systems, such as the $\pm J$ Ising model and the spin- s triangular lattice Ising antiferromagnet.

In the present study, we compare the performance of the WL and TIM methods for the calculation of the global thermodynamic quantities of a highly frustrated Ising antiferromagnet on a Kagome lattice (IAKL) [6] with the focus on the entropy, the ground-state value of which is exactly known [7].

2 Model and methods

2.1 IAKL model

The Hamiltonian of the studied spin $s = 1/2$ IAKL system is given by

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j, \quad (1)$$

where the summation goes over the nearest neighbors and $\sigma_i = \pm 1$ is the spin at the i th site. To introduce frustration, the interactions between neighboring spins were chosen to be antiferromagnetic ($J < 0$). A schematic illustration of the Kagome lattice is shown in the inset of Fig. 1(a). IAKL is a typical example of a complex spin system with high geometrical frustration resulting in a massive ground-state degeneracy with a finite residual entropy and no long-range ordering at any temperature.

2.2 MA and TIM

MA is a well-known, general, easy to implement and therefore widely used MC method [1]. The algorithm performs a random walk in the energy space. In every MC step a new state with the energy \mathcal{H} is proposed and accepted with the probability $p(s_{\text{old}} \rightarrow s_{\text{new}}) = \min(1, e^{-\beta\Delta\mathcal{H}})$, where $\Delta\mathcal{H}$ is the energy difference between the new state and the old state, $\beta = 1/(k_B T)$ is the inverse temperature, and k_B is the Boltzmann constant (hereafter set to $k_B = 1$). MA can be used for direct calculation and investigation of several quantities, such as the internal energy $e = \langle \mathcal{H} \rangle / N$ and magnetization $m = \langle M \rangle / N$, where $M = \sum_{i=1}^N \sigma_i$, N is the number of spins and $\langle \dots \rangle$ denotes the thermal average.

The entropy of the magnetic system with a discrete spin number s can be obtained as a function of the inverse temperature by TIM [3] as:

$$S(\beta) = N \ln(2s + 1) + \beta E(\beta) - \int_0^\beta E(\beta') d\beta', \quad (2)$$

where $E = \langle \mathcal{H} \rangle$. Assuming equilibrium conditions and thermal averages calculated based on a fixed number of MC sweeps N_{sweeps} for a given temperature range $[T_1, T_{N_T}]$ and a fixed lattice size L , the only relevant parameter that can influence the accuracy of the entropy estimation is the temperature mesh density, characterized by the number of temperature points N_T and their distribution. Generally, a denser mesh (large N_T) leads to a smaller quadrature error and thus a more accurate estimation.

2.3 WL algorithm

The WL method is a relatively new MC method producing accurate results, including the global thermodynamic functions [2]. A random walk is performed in the energy space to extract an estimate

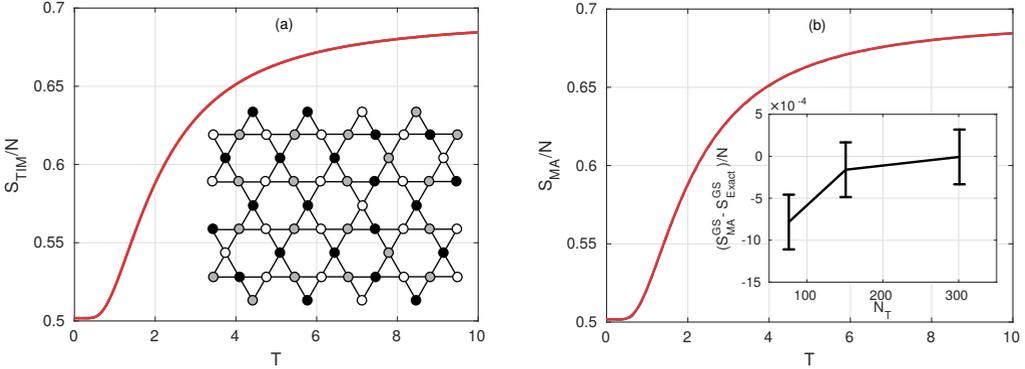


Figure 1. (a) Entropy density obtained by the TIM method, for $L = 16, 32, 68, 76, 84$ with $N_T = 301$. The lines for different L coincide (the error bars are not shown because they are smaller than the line widths). The inset shows the Kagome lattice composed of three interpenetrating sublattices (different shades). (b) Entropy density for $L = 32$ and $N_T = 76, 151, 301$. Lines for different N_T are almost identical. The inset shows the difference between the ground state entropy density calculated using TIM and the exact value.

of the DOS, $g(E)$, from which one can calculate the partition function at any temperature and consequently all other thermodynamic quantities. In particular, the partition function can be obtained as:

$$Z(\beta) = \sum_E g(E) \exp(-\beta E), \quad (3)$$

where the summation goes over all possible energy values E . Consequently, a mean value of any thermodynamic quantity, including the entropy, can be evaluated by using the standard statistical physics relations. For a given lattice size, the user-defined parameters in the WL method are the flatness criterion $F_C < 1$ and the modification factor $f_{\text{final}} > 1$ [2]. Generally, the closer the values of F_C and f_{final} to 1, the more precise results can be expected. Typically chosen values include $F_C = 0.8$ or 0.9 and $f_{\text{final}} = 1 + 10^{-k}$, with $k = 8, 9$, and 10 .

3 Results and discussion

We performed several simulations using both MA (in Matlab) and WL (using C++) to calculate the entropy per spin (entropy density) and the free energy. Below, we only present the former quantity, as the latter one is just a simple function of the former. The presented results were calculated as averages obtained from 10 independent runs.

First, we present results obtained by MA, with the following parameters: $N_{\text{sweeps}} = 5 \times 10^5$ and $[T_1, T_{N_T}] = [0.0064, \infty]$ (or $[\beta_1, \beta_{N_T}] = [156.3731, 0]$). The temperature mesh was chosen non-uniformly with the largest density of points in the region of the largest variation of the energy $E(\beta)$ in order to increase the precision of the numerical quadrature in Eq. (2). In Figure 1(a) we examine the lattice size dependence of TIM with $N_T = 301$, for $L = 16, \dots, 84$. All the curves are found to collapse on a single curve within the error bars and, hence, we can conclude that the finite-size effects are very small. In Figure 1(b) we study the influence of the parameter N_T , for a fixed value of $L = 32$. $N_T = 151$ and 76 case were obtained from the initial $N_T = 301$ cases by repeatedly removing every second node from the previous denser grid. Again, all the curves appear to coincide within statistical errors. Nevertheless, as shown in the inset, by comparing the ground-state value estimate $S_{\text{MA}}^{\text{GS}}/N$ with

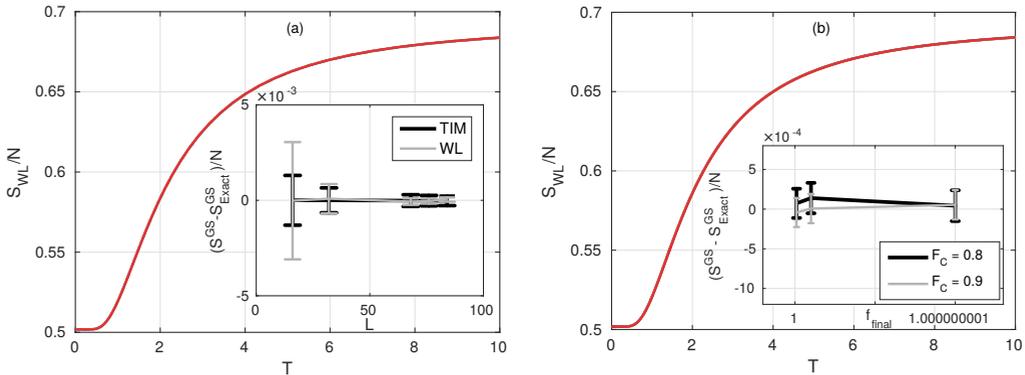


Figure 2. (a) Entropy density obtained by the WL method, for $L = 16, 32, 68, 76, 84$ with $F_C = 0.8$ and $f_{\text{final}} = 1 + 10^{-8}$. The lines for different L coincide and the errorbars (not shown) are smaller than the line widths. The inset shows differences of the residual values by the respective methods from the exact value. (b) Entropy density curves for all combination of values of the WL parameters $F_C = 0.8, 0.9$ and $f_{\text{final}} = 1 + 10^{-8}, 1 + 10^{-9}, 1 + 10^{-10}$ (the lines are almost identical) and their difference from the exact value in the ground state (inset).

the exact value $S_{\text{exact}}^{\text{GS}}/N = 0.5018$ [7] one can notice a gradual improvement with the increasing N_T , even though the accuracy is fairly high for all values of N_T .

In Figure 2(a) we present the WL results for different $L = 16, \dots, 84$ and the simulation parameters set to $F_C = 0.8$ and $f_{\text{final}} = 1 + 10^{-8}$. Like for the TIM results in Figure 1(a), all the curves coincide within the error bars. There is also a good coincidence between the WL and TIM results, as evidenced in the inset of Figure 2(a) that shows the deviation of the residual entropies obtained by the WL method and TIM (for $N_T = 301$) from the exact value. Finally, in Figure 2(b) we demonstrate the effect of the choice of the WL method parameters F_C and f_{final} . Again, for the standard values the differences are within the error bars.

To conclude, when standard values of the parameters are chosen, both the TIM and WL methods yield sufficiently accurate results which are mutually indistinguishable. The advantage of the TIM is its simplicity but the simulation has to be run at all desired temperatures. On the other hand, the WL simulation enables straightforward calculation of any thermodynamic quantity at all temperatures.

Acknowledgement

This work was supported by the Scientific Grant Agency VEGA (Grant No. 1/0531/19).

References

- [1] N. Metropolis, *et. al.*, J. Chem. Phys. **21**, 1087–1091 (1953)
- [2] F. Wang, D. P. Landau, Phys. Rev. Lett. **86**, 2050–2053 (2001)
- [3] S. Kirkpatrick, Phys.Rev. B **16**, 4630–4641 (1977)
- [4] F. Romá, F. Nieto, E.E. Vogel, A.J. Ramirez-Pastor, J. Stat. Phys. **114**, 1325–1341 (2004)
- [5] M. Žukovič, Eur. Phys. J. B **86**, 283-1–6 (2013)
- [6] I. Syozi, Progress of Theoretical Physics **6**, 306–308 (1951)
- [7] K. Kano, S. Naya, Progress of Theoretical Physics **10**, 158–172 (1953)