Entropy of spin models by the Monte Carlo method

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We introduce a method to calculate the entropy and the free energy of spin systems by the Monte Carlo method. The method is used to determine the entropy of the antiferromagnetic Ising model subject to an external field on triangular and face-centered-cubic lattices.

I. INTRODUCTION

The Monte Carlo method is an algorithm capable of numerical estimation of any quantity which can be written as the average of a state function. The estimation of the entropy, however, is a difficult task since there is no state function whose average is the entropy. The same can be said about the free energy. To overcome this difficulty, direct and indirect methods were introduced to calculate the entropy of lattice spin systems by Monte Carlo. Direct methods[1–6] use a quantity related to entropy or free energy, which can be estimated from Monte Carlo. In indirect methods,[7,8] the entropy or the free energy is obtained by integrating numerically a quantity which can be obtained from Monte Carlo.

Here we introduce a direct method of evaluating the free energy of spin systems. The method uses a relationship between the largest eigenvalue of the transfer matrix and the averages of certain state functions. The free energy is then obtained by taking the logarithm of the largest eigenvalue. The method is here applied to the cases of two frustrated Ising spin systems defined on a triangular and on a face-centered-cubic (fcc) lattice with nearest-neighbor antiferromagnetic interactions and subject to an external field.

The triangular Ising antiferromagnetic in zero field is known to be disordered at all temperatures and to have a residual entropy.[9,10] In the presence of a field H, there is an ordered ferrimagnetic state at low temperature as long as the field is smaller than the critical field H_c.[11–13] The low-temperature ordered state is separated from the paramagnetic state by a line of second-order phase transition. At the critical field and zero temperature, the state is highly degenerate with a nonzero entropy.[14]

The fcc Ising antiferromagnetic in a field has been intensively studied[15–18,7,3,19,20,8,5,21] because, in the lattice-gas language, it describes the ordering of binary alloys such as copper gold. At zero field, a first-order transition occurs at a nonzero temperature T_1. In the presence of a field H, the model exhibits three first-order transition lines that meet at a triple point. One line terminates at $H = 0$ and temperature T_1, whereas the other two lines terminate at zero temperature at the critical fields H_1 and H_2. At these two terminal points there is a residual entropy.

II. LARGEST TRANSFER MATRIX EIGENVALUE

Let us consider an Ising system whose partition function can be written as the trace of a product of transfer matrices. Consider a lattice composed of K layers of N sites each. The probability $P(\tau_1, \tau_2, ..., \tau_K)$ of the state $\tau_1, \tau_2, ..., \tau_K$ of the system, where τ_ℓ is the configuration of the ℓth layer, is given by

$$P(\tau_1, \tau_2, ..., \tau_K) = \frac{1}{Z} T(\tau_1, \tau_2) T(\tau_2, \tau_3) ... T(\tau_K, \tau_1), \quad (1)$$

where $T(\tau_i, \tau_j)$ is the element of the transfer matrix T and

$$Z = \mathrm{Tr}(T^K) \quad (2)$$

is the partition function. The marginal probability distributions $P(\tau_1)$ and $P(\tau_1, \tau_2)$ are given by

$$P(\tau_1) = \frac{1}{Z} T^K(\tau_1, \tau_1) \quad (3)$$

and

$$P(\tau_1, \tau_2) = \frac{1}{Z} T(\tau_1, \tau_2) T^{K-1}(\tau_2, \tau_1). \quad (4)$$

Next we use the spectral development of the matrix T given by

$$T(\tau_1, \tau_2) = \sum_k \phi_k(\tau_1) \lambda_k \phi_k^*(\tau_2), \quad (5)$$

where $\phi_k(\tau_1)$ is the normalized eigenvector and λ_k is the corresponding eigenvalue of T, to write

$$P(\tau_1) = \frac{1}{Z} \sum_k \phi_k(\tau_1) \lambda_k^K \phi_k^*(\tau_1) \quad (6)$$

and

$$P(\tau_1, \tau_2) = \frac{1}{Z} T(\tau_1, \tau_2) \sum_k \phi_k(\tau_2) \lambda_k^{K-1} \phi_k^*(\tau_1). \quad (7)$$

Taking into account that

$$Z = \sum_k \lambda_k^K \tag{8}$$

we obtain, in the limit $K \to \infty$,

$$P(\tau_1) = \phi_0(\tau_1)\phi_0^*(\tau_1) \tag{9}$$

and

$$P(\tau_1, \tau_2) = T(\tau_1, \tau_2)\phi_0(\tau_2)\lambda_0^{-1}\phi_0^*(\tau_1), \tag{10}$$

where λ_0 is the largest eigenvalue of T and ϕ_0 the leading eigenvector.

For $\tau_2 = \tau_1$ this equation can be written in the form

$$P(\tau_1, \tau_1) = T(\tau_1, \tau_1)P(\tau_1)\lambda_0^{-1} \tag{11}$$

from which we get

$$\langle \delta(\tau_1, \tau_2) \rangle = \lambda_0^{-1} \langle T(\tau_1, \tau_1) \rangle. \tag{12}$$

This formula allows the calculation of the largest eigenvalue of T from the Monte Carlo estimation of the averages $\langle \delta(\tau_1, \tau_2) \rangle$ and $\langle T(\tau_1, \tau_1) \rangle$. In actual calculations, where K is finite but large, the errors will be of the order $(\lambda_1/\lambda_0)^K$ where λ_1 is the second largest eigenvalue of T. The free energy per site f can then be calculated by using the relation $-\beta f = (\ln \lambda_0)/N$.

Suppose that there is a transformation $\tau_1 \to \tau_2 = \zeta(\tau_1)$ which leaves $\phi_0(\tau_1)$, or equivalently $P(\tau_1)$, invariant. In this case, from Eq. (10), we get

$$P[\tau_1, \zeta(\tau_1)] = T[\tau_1, \zeta(\tau_1)]\lambda_0^{-1}P(\tau_1) \tag{13}$$

from which we obtain

$$\langle \delta[\zeta(\tau_1), \tau_2] \rangle = \lambda_0^{-1} \langle T[\tau_1, \zeta(\tau_1)] \rangle \tag{14}$$

which is an alternative to formula (12).

III. TRIANGULAR ISING ANTIFERROMAGNET

We have simulated the triangular Ising antiferromagnetic in a square lattice with $L \times K$ sites by using the Metropolis algorithm. The Hamiltonian reads

$$\mathcal{H} = \sum_{j=1}^{L} \sum_{k=1}^{K} \{ J\sigma_{jk}(\sigma_{j,k+1} + \sigma_{j+1,k} + \sigma_{j+1,k+1}) - H\sigma_{jk} \}, \tag{15}$$

where $\sigma_{jk} = \pm 1$, $J > 0$, and periodic boundary conditions are used. The transfer matrix T is given by

$$T(\{\sigma_{jk}\}, \{\sigma_{j,k+1}\}) = \exp\left\{ \sum_{j=1}^{L} [-\beta J\sigma_{jk}(\sigma_{j,k+1} + \sigma_{j+1,k} + \sigma_{j+1,k+1}) + \beta H\sigma_{jk}] \right\}, \tag{16}$$

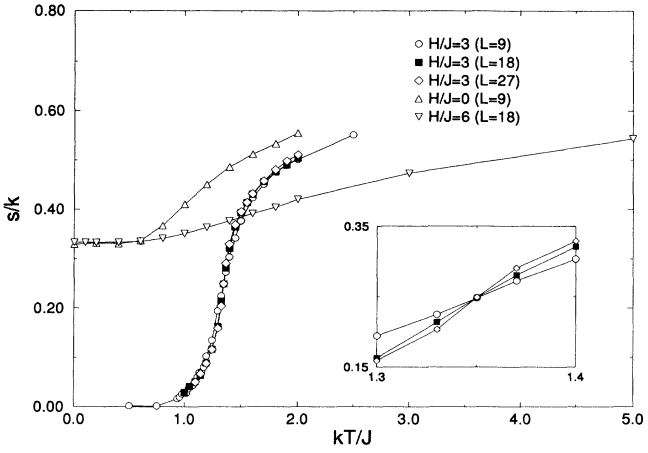

FIG. 1. Entropy per site s versus temperature T for the antiferromagnetic Ising model on a triangular lattice for several values of the external field H. The inset shows the entropy versus temperature for the case $H = 3J$ around the transition point.

where $\beta = 1/kT$. From the largest eingenvalue λ_0 of T estimated from Monte Carlo by using formula (14) we determined the free energy per site f by

$$f = -\frac{1}{\beta L} \ln \lambda_0. \tag{17}$$

From the estimate of the energy per site u and the free energy f we get the entropy per site s by

$$\frac{s}{k} = \beta u - \beta f. \tag{18}$$

Figure 1 shows the entropy as a function of temperature for three values of the field. We used lattices of sizes 9×81, 18×81, and 27×81. Along $H = 0$ and $H = H_c = 6J$ there is no phase transition and the system is disordered for all temperatures. For these two cases there is a residual entropy at zero temperature. Our estimates of the residual entropies are $s/k = 0.3229(4)$ for $H = 0$ and $s/k = 0.3333(1)$ for $H = 6J$. In these cases the exact values are known as value 0.323 0659... (Ref. 9) and 0.333 27... (Ref. 14), respectively.

In contrast to the two cases above the system orders when $0 < H < 6J$ for sufficient low temperatures. Along $H = 3J$, there is a continuous transition around $kT/J = 1.4$ and the entropy vanishes at zero temperature. The inflection point of the entropy indicates the critical temperature.

IV. fcc ISING ANTIFERROMAGNET

The fcc Ising antiferromagnet was simulated in a cubic lattice with $L \times L \times K$ sites. The Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^{L}\sum_{j=1}^{L}\sum_{k=1}^{K}\mathcal{H}_{ijk}, \tag{19}$$

where

$$\mathcal{H}_{ijk} = -H\sigma_{ijk} + J\sigma_{ijk}(\sigma_{ij,k+1} + \sigma_{i,j+1,k} + \sigma_{i+1,jk} + \sigma_{i+1,j+1,k} + \sigma_{i,j+1,k+1} + \sigma_{i+1,j+1,k+1}), \tag{20}$$

where periodic boundary conditions are used. The transfer matrix T is given by

$$T(\{\sigma_{ijk}\},\{\sigma_{ij,k+1}\}) = \exp\left\{-\beta\sum_{i=1}^{L}\sum_{j=1}^{L}\mathcal{H}_{ijk}\right\}. \tag{21}$$

From the estimate of the largest eigenvalue λ_0 of T we determined the free energy per site by

$$f = -\frac{1}{\beta N}\ln\lambda_0, \tag{22}$$

where $N = L^2$ and the entropy by Eq. (18).

Figure 2 shows the entropy versus temperature for three values of the field for a lattice with $4 \times 4 \times 16$ spins. At $H = H_2 = 12J$ the system displays a paramagnetic phase at all temperatures. At zero temperature there is a residual entropy which we estimated to be $s/k = 0.2498(3)$. This value should be compared to other Monte Carlo estimation such as $s/k = 0.249\,89(2)$.[3] For $H < 12J$ the system is ordered if the temperature is small enough. The phase transition from the disordered to ordered state is of the first order. At $H = H_1 = 4J$, there is a residual entropy estimated to be $s/k = 0.235(1)$ which we compare to another Monte Carlo estimation $s/k = 0.239(1)$.[3] At $H = 0$, the entropy vanishes at zero temperature and there is a first-order phase transition around $kT/J = 1.7$.

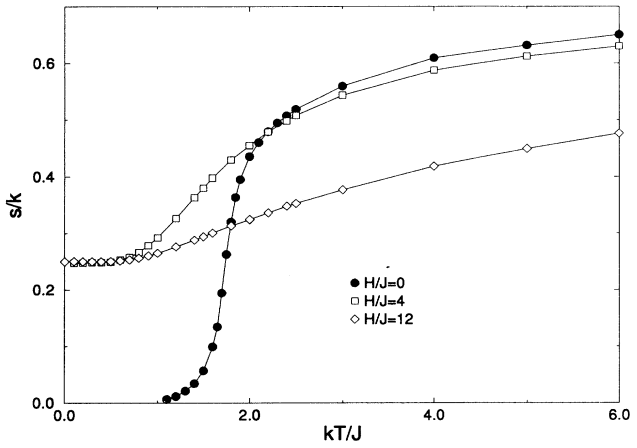

FIG. 2. Entropy per site s versus temperature T for the antiferromagnetic Ising model on a face-centered-cubic lattice for several values of the external field H.

V. CONCLUSION

We introduce a direct method to estimate the entropy of spin models from Monte Carlo simulation. The method was applied to the antiferromagnetic Ising model on triangular and fcc lattices. The results are in agreement with the exact results and results coming from other Monte Carlo simulations.

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