A MONTE CARLO COMPUTATION OF THE ENTROPY AND THE FREE ENERGY OF A THREE-DIMENSIONAL ISING SPIN GLASS

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A new method to compute the entropy and the free energy using Monte Carlo simulations is applied to a three-dimensional Ising spin glass. The system shows a spin-glass phase transition and seems to obey the third law of thermodynamics.

1. Introduction

Recently Kimura and the present author proposed [1] a method to compute the entropy and the free energy of lattice systems using Monte Carlo (MC) simulations. The idea of the method, which originates from the "multistage sampling" method by Valleau and Card [2], can be summarized as follows. Let us start with a partition function

$$Z(T) = \mathrm{Tr}\, \mathrm{e}^{-H/T} = \sum_E W(E)\, \mathrm{e}^{-E/T} \tag{1}$$

$$= \mathrm{e}^{-F(T)/T}, \tag{2}$$

where $W(E)$ is the density of states and $F(T)$ is the free energy. The point is to consider the energy distribution function $P(E, T)$ at temperature T, which is defined by

$$P(E, T) = W(E)\, \mathrm{e}^{-E/T}/Z(T). \tag{3}$$

From eqs. (2) and (3), the difference in the F/T at two successive temperatures is given by

$$\Delta(F/T) = F(T)_2/T_2 - F(T_1)/T_1 = \ln[P(E, T_2)/P(E, T_1)] + E/T_2 - E/T_1. \tag{4}$$

Then from eq. (4) and the relation $S = (U - F)/T$, the entropy difference is given by

$$\Delta S = S(T_2) - S(T_1) = U(T_2)/T_2 - U(T_1)/T_1 - \Delta(F/T), \tag{5}$$

where the internal energy $U(T)$ is given by

$$U(T) = \sum_E EP(E, T). \tag{6}$$

Now since the computer simulation gives the energy distribution function $P(E, T)$ directly, we can utilize those MC data to compute the differences $\Delta(F/T)$ and ΔS according to eqs. (4)–(6). by taking account of the boundary condition at $T = 0$ or $T = \infty$, we can compute in this way the entropy and the free energy at any temperature. In ref. [1] this method was applied to the two-dimensional Ising model, and a good agreement with the exact solution was obtained for the values of the entropy and the free energy.

In this note we apply the same method to the three-dimensional Ising spin glass. There have already been several attempts [3,4] to compute the entropy of the Ising spin glass using simulations. These previous works have, however, some flaws in the algorithm or disadvantages in the computational accuracy. For instance, ordinary methods use the formula

$$S(T) = S(\infty) - \int_T^\infty \frac{\mathrm{d}U}{\mathrm{d}T}\frac{\mathrm{d}T}{T}, \tag{7}$$

which is an integral version of eq. (5). This method has two practical defects. First, the quantity $\mathrm{d}U/\mathrm{d}T$ contains non-negligible statistical errors as a usual consequence of MC simulations and second, it is necessary to sum up infinitely many

infinitesimal terms to reach the boundary $T = \infty$. On the contrary, our method avoids such difficulties, because first, it allows a finite step without spoiling computational accuracy as far as the overlap in the $P(E, T)$ exists, and second, the accuracy of the simulation can be assured by checking the E-independence of the r.h.s. of eq. (4).

For definiteness, in this note we concentrate our consideration on the thermodynamic properties of the Ising spin glass which has a special distribution of coupling constants, that is, a symmetric double-gaussian distribution function. The reason why we have chosen the symmetric double-gaussian model rather than the $\pm J$ bond mode [5] is that this model represents a more or less realistic situation in real materials. Although our method to compute the entropy and the free energy can be applied to spin glasses with any kind of distribution, this special case of distribution will be sufficient to investigate fundamental problems of spin glasses, such as the third law of thermodynamics.

2. Computation of entropy and free energy

2.1. Sample preparation in the computer

We consider a three-dimensional Ising spin glass on a cubic lattice, whose size is $N = 12^3$, with periodic boundary conditions,

$$H = -\Sigma J_{ij}\sigma_i\sigma_j. \tag{8}$$

The nearest neighbor coupling constants J_{ij} take random values according to the distribution function

$$P(J) = (1/2\sqrt{2\pi}\,\Delta)\left\{\exp\left[-(J-J_0)^2/2\Delta^2\right] + \exp\left[-(J+J_0)^2/2\Delta^2\right]\right\}, \tag{9}$$

i.e. a symmetric double-gaussian distribution.

First, let us explain how to prepare such a sample in the computer. The values of J_{ij} were determined by use of the built-in subroutine which generates random numbers with a normal distribution according to the Box–Müller method. Since these generated numbers are quasi-random (reproducible from the same seed), we can deal with exactly the same sample at each computer run, which is just the same situation as we encounter in real experiments. Although in theoretical works on the spin glass the configurational averaging is usually employed for technical reasons, real material experiments take only one sample (one configuration) at each measurement. And it is another problem to consider sample-to-sample variations.

In fig. 1 the actual distribution of coupling constants is shown, generated according to eq. (9) with $J_0 = 1.0$ and $\Delta = 0.2$. The realized values have moments $\langle J\rangle = 0.015$ and $\langle J^2\rangle = 1.038$ (to be compared with $J_0^2 + \Delta^2 = 1.04$).

Can we expect before making simulations that the prepared sample will really show spin glass properties? To see this we measured the distribution of "frustration". We define the frustration variable F by the product of four coupling constants on a fundamental plaquette. If F is negative, the four spins on the plaquette are frustrated; on the contrary, if F is positive, they are not frustrated. The realized sample has 49.3% of frustrated plaquettes, which is to be compared with 50% for the ideal case.

2.2. Computation of entropy and free energy

Now let us describe the results of the actual MC simulations. We made simulations at each temperature by the heat bath algorithm over 80000

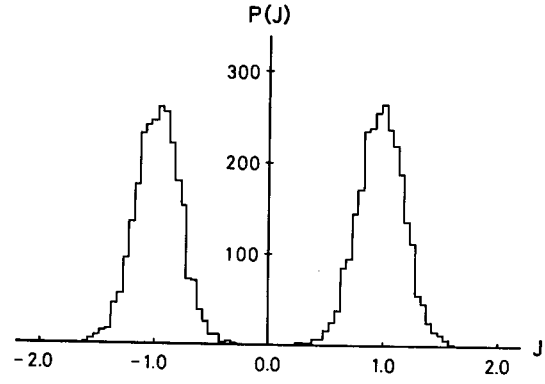

Fig. 1. Distribution of coupling constants. The moments are computed as $\langle J\rangle = 0.015$ and $\langle J^2\rangle = 1.038$.

MC sweeps after 10000—20000 thermalization sweeps. The initial spin configuration was set up randomly (hot start). Equilibriumness was checked by the (approximate) E-independence of eq. (4), which assures a Boltzmann distribution of the system.

In fig. 2 the internal energy is plotted against temperature, which seems to exhibit no critical behavior as is expected. It is believed that the spin-glass phase transition does not show criticality in thermodynamic quantities such as the internal energy and the specific heat, but shows a cusp-like singularity in the magnetic susceptibility. In fig. 3 the susceptibility per site is depicted against temperature. Although there are considerable statistical errors, we can recognize the expected cusp-like shape at $T_C = 1.75$. We have measured the magnetization and the Edwards–Anderson order parameters [5] as well. The absolute values of magnetization per site range from 10^{-2} to 10^{-3}, and the possibility of an antiferromagnetic transition could be excluded. The time dependence of the Edwards–Anderson order parameter

$$q(t) = \frac{1}{N}\sum_i \sigma_i(0)\sigma_i(t) \qquad (10)$$

is shown in fig. 4 at several temperatures. Although they were computed within a finite MC time (80000 MC sweeps), we can see an apparent difference between the cases $T > T_G$ and $T < T_G$

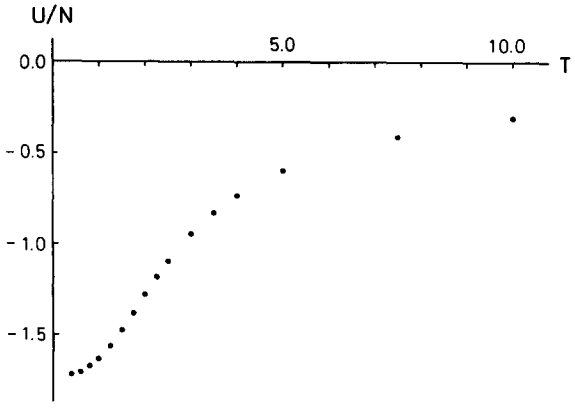

Fig. 2. Internal energy versus temperature. Errors are confined in the circles.

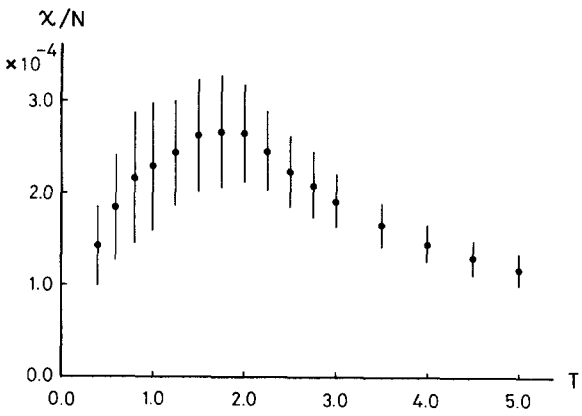

Fig. 3. Magnetic susceptibility versus temperature.

($T_G = 1.0$, the precise value could not be determined). These results are very similar to the results for the $\pm J$ model [5] ($T_C = 1.8$ and $T_G = 1.2$).

The free energy and the entropy were computed by the procedure explained before. The results are given in fig. 5 (free energy) and fig. 6

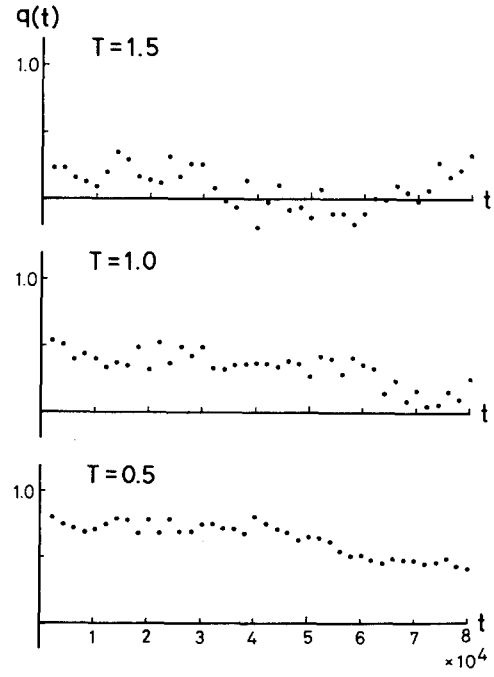

Fig. 4. Time dependence of the Edwards–Anderson order parameter.

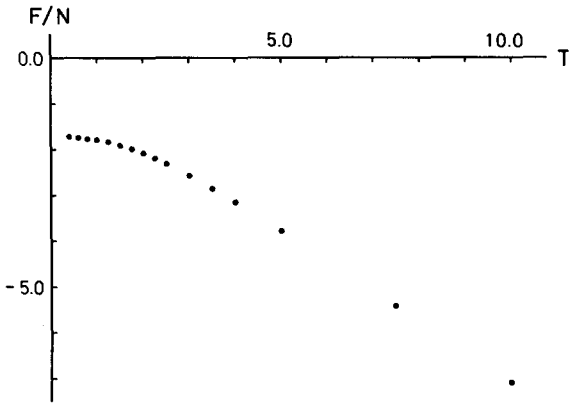

Fig. 5. Free energy versus temperature. Errors are estimated to be a few percent.

(entropy). The resultant behaviors are quite reasonable. Especially significant is the shape of the entropy (computed down to $T = 0.4$). It shows a power-law (probably linear) behavior at low temperature and definitely not an activation energy type behavior. Furthermore the computed entropy seems to be extrapolated to zero at $T = 0.0$ (the boundary condition is taken as $S(\infty) = N \ln 2$). In other words, the third law of thermodynamics (the Nernst–Planck theorem) seems to hold for the present sample of the spin glasses, although it is very difficult to ascertain it for $T = 0.0$ in MC simulations because of the reason explained later.

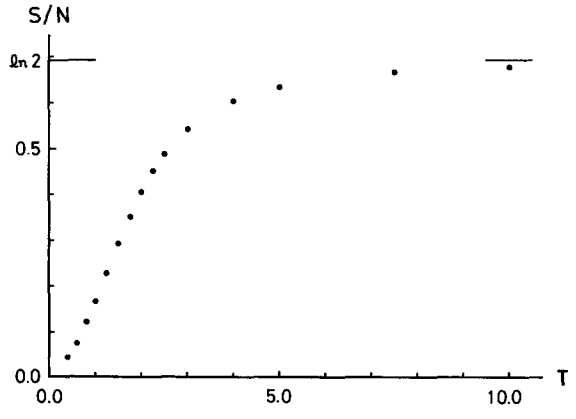

Fig. 6. Entropy versus temperature. Errors are estimated to be a few percent.

3. Conclusions and discussions

The new method to compute the entropy and the free energy using the Monte Carlo simulations is applied to the three-dimensional Ising spin glass. The sample prepared in the computer shows criticality at $T_C = 1.75$ (susceptibility) and $T_G = 1.0$ (Edwards–Anderson order parameter). The internal energy, the free energy and the entropy are computed using the procedure explained in the introduction. Especially the Nernst–Planck theorem seems to hold for our sample, that is, the entropy at zero temperature seems to vanish.

Some discussions on the results are in order. First, we have to mention a difficulty which was met at temperatures lower than 0.2. At such low temperatures, the system did not reach the equilibrium state, which can be checked by examining the E independence of eq. (4), even after 320000 MC sweeps (CPU time = 2 h). For the purpose to overcome this difficulty, it is desirable to improve the acceptance rate in updating, which might be achieved by changing the heat bath algorithm. This problem will be left for future work.

Second, we always have to be aware of the finiteness of the system size. As far as the present simulation is concerned, the spin glass transition at T_G is an equilibrium phase transition, which has recently been convinced in the tremendous simulations by Ogielski and Morgenstern [6]. On the other hand, validity of the Nernst–Planck theorem in bulk systems is related to the problem of degeneracy of the ground states in the thermodynamic limit. And it is very subtle process to extrapolate results from finite systems to that of an infinite (bulk) system. Although the finite-size scaling approach is employed usually, the spin glass problem adds a complexity due to the randomness. And some modification will be necessary to apply to the spin glass.

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