Residual entropy and validity of the third law of thermodynamics in discrete spin systems

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We study the validity of the third law of thermodynamics and the occurrence of a nonzero residual entropy in discrete spin systems. For a general classical spin system on a d-dimensional hypercubic lattice with isotropic, translationally invariant, nearest-neighbor interactions, we establish the following. (i) The necessary and sufficient condition for the third law to hold. (ii) A lower bound on the residual entropy when the third law is not valid. It is also established that the residual entropy is nonzero for all d, if it is nonzero in any dimension $d > 1$.

The third law of thermodynamics states that the entropy of a physical system vanishes as the temperature approaches absolute zero. One important problem in statistical physics has been the consideration of the validity of the third law and its relation with the ground-state degeneracy.[1–3] While progress has been made in affirming the third law in specific systems such as ferromagnets,[3–5] it is also known that there exist notable exceptions, mostly in spin systems, where the residual entropy does not vanish.[6–10] It is therefore natural to inquire whether one can determine *a priori* the validity of the third law, given the Hamiltonian of a physical system, and, in case the third law does not hold, whether there exist *a priori* bounds on the residual entropy. These are difficult questions that are of fundamental importance.

In this paper we provide some answer to these questions. We consider a very general class of classical discrete spin systems and, using a graph-theoretical approach, obtain the necessary and sufficient condition for the third law of thermodynamics to hold; we also establish a lower bound for the residual entropy when the third law is not valid.

Consider a system of N classical spins on a hypercubic lattice in d dimensions. The spins can be in one of $q \geq 2$ distinct states, and interact with a nearest-neighbor interaction, which depends on the spin states as well as on the direction along which the two spins are placed, i.e., the interaction is asymmetric with respect to the spin states. Considerations of systems with such state-dependent and asymmetric interactions are not without physical interest. Models with interactions of this type have been used, e.g., in discussions of commensurate-incommensurate transitions occurring on surfaces,[11,12] and in descriptions of domain walls in adsorbed layers of krypton on graphite.[13,14] A polychromatic Potts model with state-dependent interactions, which encompasses the correlated polychromatic bond percolation and the dilute branched polymer problems as special cases, has also been proposed.[15] To properly describe this asymmetry, we associate Cartesian coordinate $\mathbf{n}=(n_1,n_2,\ldots,n_d)$, $n_i=1,2,3,\ldots,$ to lattice sites, and write the interaction energy between two neighboring spins, one at site $\mathbf{m}$ in state α and the other at site $\mathbf{n}$ in state β, as

$$E(\mathbf{m},\mathbf{n})=J_{\alpha\beta} ,$$

where

$$m_i \leq n_i \ \text{for}\ i=1,2,\ldots,d . \tag{1}$$

The asymmetry in spin states is then reflected by the fact that $J_{\alpha\beta}\neq J_{\beta\alpha}$. Note that the interaction (1) is translationally invariant, and isotropic in the d positive (or negative) spatial directions. We shall further restrict our considerations to systems whose ground states are attained, as in antiferromagnetic Potts models,[6–10] when *all* neighboring pairs interact with the same energy $J_{\min}$. This restriction effectively excludes the consideration of frustrated systems. However, it makes possible to relate the zero-temperature entropy S to the degeneracy of the ground state configurations W_N by taking the limit[3]:

$$S=\lim_{N\to\infty} N^{-1}\ln W_N , \tag{2}$$

where

$$W_N=\sum\prod_{nn} A_{\alpha\beta} , \tag{3}$$

$$A_{\alpha\beta}=1, \quad \text{if } J_{\alpha\beta}=J_{\min} ,$$
$$=0, \ \text{otherwise} . \tag{4}$$

Here, the summation in (3) extends over *all* q^N spin configurations and the product is taken over all nearest-neighboring pairs. Our goal is to determine, for a given spin system and the associated $A_{\alpha\beta}$, whether S vanishes, and to determine a bound on its numerical value if S does not vanish.

The $q \times q$ matrix $\underline{A}$, whose elements are $A_{\alpha\beta}=0$ or 1, can be considered as the adjacency matrix[16] of a directed graph G consisting of q vertices numbered from 1 to q. The directed graph G can be constructed from the matrix $\underline{A}$ by drawing, for each $A_{\alpha\beta}=1$, an arc pointing from the vertex α to the vertex β. For example, the graph G for the adjacency matrices

$$\underline{A}=\begin{bmatrix}1 & 1\\ 1 & 0\end{bmatrix},\quad \begin{bmatrix}0 & 1 & 1\\ 1 & 0 & 0\\ 1 & 0 & 0\end{bmatrix},\quad \begin{bmatrix}0 & 1 & 1 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{bmatrix}, \tag{5}$$

are shown, respectively, in Figs. 1(a), 1(b), and 1(c).[17]

It is convenient at this point to adopt the graph-theoretical language and consider W_N as the number of distinct q colorings[18] of the d-dimensional hypercubic lattice under the coloring rule specified by the adjacency matrix $\underline{A}$. That is, if a site at $\mathbf{m}$ bears a color α, then the neighboring site at $\mathbf{n}$, $m_i \le n_i$ for all i, can be colored β only if $A_{\alpha\beta}=1$.

We now state our results as a theorem.

Theorem. In a q-component spin system, $q \ge 2$, on a d-dimensional hypercubic lattice with nearest-neighbor interactions described in the above, there exists a nonzero residual entropy, i.e., the third law of thermodynamics does *not* hold, if, and only if, the graph G constructed from its adjacency matrix $\underline{A}$ contains, (i) for $d=1$, a subgraph consisting of two circuits[19] having at least one vertex in common, (ii) for $d \ge 2$, a subgraph isomorphic[20] to Fig. 2 (Ref. 21).

Corollary 1. The nonzero residual entropy has the lower bound:

$$S \ge \frac{1}{q}\ln 2, \quad \text{for } d=1\ , \tag{6}$$

$$S \ge \frac{1}{q+1}\ln 2, \quad \text{for } d \ge 2\ . \tag{7}$$

Corollary 2. If the residual entropy is nonzero in any dimension other than $d=1$, then it is nonzero in *all* dimensions.

Note the following remarks.

(1) For symmetric interactions, $J_{\alpha\beta}=J_{\beta\alpha}$, the adjacency matrix is also symmetric, and there is a circuit between any pair of vertices whose corresponding $A_{\alpha\beta}$ is 1. Then the condition of the Theorem is satisfied for $q>2$ and all d and, consequently, $S>0$ for all G except when G consists of disjoint subgraphs of one or two vertices, for which we have $S=0$.[22]

(2) For $d=1$, S is given by the logarithm of the largest eigenvalue of $\underline{A}$.[23]

(3) At first sight, it might appear puzzling that the bounds in corollary 1 decrease with increasing q. While the residual entropy for a given type of interaction, such as that in the antiferromagnetic Potts model, is expected to increase with q,[10] corollary 1 bounds the lowest possible residual entropy among *all* types of interactions and, as more types of interactions become accessible when q increases, this bound is actually lowered.

(4) Corollary 2 is a quite remarkable result. While a simple argument[24] establishes the fact that if $S>0$ in a given dimension, then it is nonzero in all *lower* dimensions, it is not intuitively clear why this should also hold for any *higher* dimension.

Now we prove the theorem.

(i) $d=1$. It can be seen that for a one-dimensional lattice we have, for $N>q$,

$$W_N \begin{cases} =0 & \text{if } G \text{ contains no circuits,}\\ <q^2 & \text{if } G \text{ consists of isolated circuits,}\\ <N^q & \text{if } G \text{ consists of simply-connected}\\ & \quad \text{circuits without common vertices}\ . \end{cases} \tag{8}$$

It follows that, if $S>0$, G must contain at least two circuits having at least one vertex in common.

Conversely, if G contains two circuits of lengths r and s each and having at least one vertex in common, then, by regarding the $r+s-1$ vertex colors as being all distinct, we obtain a lower bound to S by evaluating the largest eigenvalue of its adjacency matrix [Cf. remark (2)]. Straightforward algebra leads to the characteristic equation

$$\lambda^{r-1}+\lambda^{s-1}=\lambda^{r+s-1}\ . \tag{9}$$

Using the Perron-Fröbenius theorem, the largest eigenval-

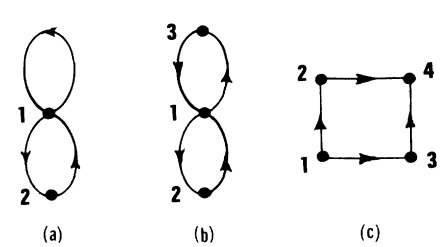

FIG. 1. Directed graphs associated with the adjacency matrices given by (5).

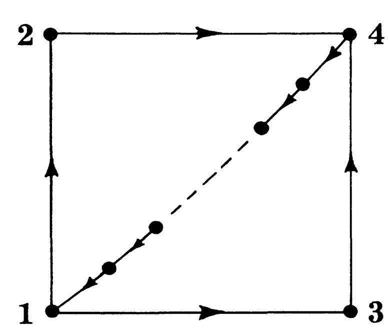

FIG. 2. A directed graph in which colors may be repeated (Ref. 21). Colors 2 and 3 are always distinct and colors 4 and 1 are connected by a directed path running through a sequence of p distinct colors (which may include colors 2 and 3) that are different from 1 and 4 ($p \le q-2$).

ue of the adjacency matrix (whose elements are nonnegative) is positive. Now the magnitude of the positive solution of (9) decreases with increasing r and s; a lower bound of this positive solution is therefore obtained by considering the case $r=s=q$. This leads to (6), thus completing the proofs of the converse and the $d=1$ part of corollary 1.

(ii) $d \geq 2$. We first establish that the existence of the subgraph Fig. 2 in G leads to $S>0$.[21]

Divide the N lattice points of the d-dimensional hypercubic lattice into parallel (hyper)planes such that the coordinates of all sites on a given plane P_μ satisfy

$$\sum_{i=1}^{d} n_i = d+\mu \;, \quad \mu=0,1,2,\ldots \;. \tag{10}$$

Thus these planes are perpendicular to the main diagonal of the lattice. We now proceed to color the d-dimensional hypercubic lattice by following the rule specified by Fig. 2.

Color the lattice site at $(1,1,\ldots,1)$ on the plane P_0 with the color 1. Then, proceeding in a diagonal direction and following the rule imposed by Fig. 2, *each* of the neighboring sites on the next plane P_1 can be colored with the color 2 or 3 independently.[25] However, *all* sites on *each* of the succeeding $p+2$ planes, $P_2, P_3, \ldots, P_{p+3}$, can be colored by the respective colors $4,\ldots,1$ by simply following the rule specified by the path running from color 4 to 1 in Fig. 2. After the plane P_{p+3} is colored by the color 1, we can repeat the above process by coloring *each* point of the next plane, P_{p+4}, independently with the color 2 or 3, *et al.* In this fashion we eventually succeed in coloring the whole lattice with colors fixed at all sites except those sites on one of every $p+3$ hyperplanes, which can be colored independently with either the color 2 or color 3. It follows that, for large N, we have bounded W_N by

$$W_N \geq 2^{N/(p+3)} \;, \tag{11}$$

leading to, after using $p \leq q-2$,

$$S \geq \frac{1}{p+3}\ln 2 \geq \frac{1}{q+1}\ln 2 > 0 \;. \tag{12}$$

Since the proof in the above depends solely on the fact that colors 2 and 3 in Fig. 2 are distinct, and, furthermore, the proof can be carried out in an obviously similar fashion if G contains any subgraph isomorphic to Fig. 2, we have proved the *if* part of the theorem. The inequality (12) also establishes the $d \geq 2$ part of Corollary 1.

The proof of the converse of above, that $S>0$ for $d \geq 2$ necessarily implies the existence of a subgraph isomorphic to Fig. 2 in G, is more delicate, and is outlined in the following.[26] First, subgraph isomorphic to Fig. 1(c), with colors 2 and 3 distinct and residing in the same hyperplane P_μ, must appear in some coloring of the lattice, for, otherwise, all sites in P_μ bear the same color,[25] and, as a result, the lattice is colored in a one-dimensional fashion along the main diagonal direction. Using the fact that there are $dN^{1/d}$ hyperplanes perpendicular to the main diagonal, we obtain the bound $W_N \leq q^{dN^{1/d}}$, which implies $S=0$ for $d \geq 2$, thus contradicting the assumption of $S>0$.

Next, divide the lattice into r^d cells of equal size and consider the r cells along the main diagonal direction. For r, large but finite, and provided that N is sufficiently large, one such subgraph, say, Fig. 1(c), will appear in two different cells along the diagonal in some coloring of the lattice.[27] It follows that there exists a route, tracing in directions of increasing coordinates from the vertex colored 4 in one subgraph Fig. 1(c), to the vertex colored 1 in the other. This route can be contracted by deleting all steps between any two identically colored sites along the route, resulting in a contracted route going from color 4 to color 1 and containing at most $q-2$ distinct colors in between. This establishes the converse we seek to prove, after identifiying this contracted route as the path illustrated in Fig. 2.

Finally, corollary 1 has already been proven; corollary 2 follows directly from Ref. 24 for $d=1$, and the fact that if the condition (ii) of the theorem holds for any $d \geq 2$, then it holds for *all* $d \geq 2$.

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[16] For definitions of graph-theoretical terms, see, e.g., J. W. Essam and M. E. Fisher, Rev. Mod. Phys. **42**, 271 (1970).
[17] For $\underline{A}$ given by the first expression in (5), W_N counts the configurations of hypercubes subject to nearest-neighbor exclusion, such as hard squares in $d=2$.
[18] A q-coloring of a lattice (graph) is the assignment of a color, chosen from a collection of q distinct colors, to each site (vertex) of the lattice (graph).
[19] Throughout this paper we use the word *circuit* to mean a directed closed path containing at least one arc, with *no* arc and *no* vertex occurring more than once. This is often called an elementary circuit (cf., e.g., Ref. 16).

[20]Two graphs are isomorphic to each other if they are identical topologically, except colorings.

[21]To facilitate discussions, we adopt in Fig. 2 a slightly expanded graphical notation by permitting repeated colors, except that colors 2 and 3 are always distinct, a key fact used in the proof. We can reduce Fig. 2 to graphs containing only distinct colors by coalescing repeated colors into a single vertex. For example, if colors 1 and 4 are identical, by coalescing vertices 1 and 4, Fig. 2 is seen to contain the subgraph Fig. 1(b).

[22]One example of $S=0$ with symmetric interactions is the ferromagnetic Potts model for which $A_{\alpha\beta}=\delta_{\alpha,\beta}$ and G consists of disjoint circuits, each containing a single vertex.

[23]This can be seen by considering $\underline{A}$ as a transfer matrix and formulate (3) as $W_N=\mathrm{Tr}[\underline{A}^N]$, assuming a periodic boundary condition.

[24]The value of W_N must increase if we remove coloring restrictions between nearest neighbors in a given spatial direction, a process which effectively reduces the dimensionality by 1. It follows that S cannot decrease in value in lower dimensions.

[25]Here, use has been made of the property of low connectivity of hypercubic lattices: Any two neighboring sites lie on adjacent hyperplanes and sites within a given hyperplane cannot be nearest neighbors.

[26]For a proof with complete mathematical rigor and further related results, see Y. Chow, Disc. Math. (to be published).

[27]This follows from the fact that the number of graphs isomorphic to Fig. 1(c), $q(q-1)(q-2)(q-3)$, is finite.