Spin Correlation and Entropy

H. FALK
Department of Physics, The City College of the City University of New York, New York, New York 10031

AND

MASUO SUZUKI*
Baker Laboratory, Cornell University, Ithaca, New York 14850

(Received 2 December 1969; revised manuscript received 29 December 1969)

A cumulant-like expansion for the entropy of an N-spin system is presented. The successive terms in the expansion relate to successively higher orders of statistical association among spins. It is proved that for any Ising system of general dimensionality with ferromagnetic interactions of arbitrary range, the first two terms in the entropy expansion provide a lower bound for the exact entropy. A corollary of the theorem is that the lower-bound property is also valid for any two-sublattice Ising system with antiferromagnetic interactions between sublattices. An example is given which illustrates the fact that the vanishing of the two-spin cumulant (correlation) does not necessarily imply that the spins are statistically independent. The sum of the first two terms in the expansion is compared numerically with the exact entropy of an N-spin chain (and also a ring) with nearest-neighbor ferromagnetic or antiferromagnetic Ising interactions. The comparison, which measures the validity of a Kirkwood-type truncation in this context, is favorable only at sufficiently high temperatures.

INTRODUCTION

THE existence of a connection between entropy and correlation in statistical mechanics is indicated by an inequality of Gibbs.[1] In brief, the inequality states that if the coordinates of a system are separated into two disjoint subsets, then the entropy of the system is less than or equal to the sum of the two "reduced" entropies associated with the subsets. The inequality becomes an equation if and only if the two disjoint subsets are statistically independent with respect to the ensemble characterizing the system. Since the statistical independence of two variables, x and y, implies[2] that the covariance, $\langle xy\rangle-\langle x\rangle\langle y\rangle$, equals zero (although the converse is not true in general), the Gibbs inequality thus provides evidence for a connection between entropy and correlation.

If one approaches these matters from the point of view of information theory,[3] one finds that the Gibbs inequality expresses the fact that the "conditional" entropy, i.e., the entropy associated with *a priori* relevant knowledge, is less than or equal to the entropy corresponding to a lack of the *a priori* knowledge.

Furthermore, it is well known that for a system of N noninteracting spins (a paramagnetic gas) in a nonzero magnetic field, the canonical ensemble entropy decreases monotonically with decreasing temperature for fixed field. This decrease in entropy is identified with an increase in magnetic order (induced magnetization). Of course, there is no correlation here, since the spins are noninteracting and are statistically independent in the canonical ensemble.

The connections between entropy, order, correlation, *a priori* knowledge, and mathematical information provide valuable insights into the behavior of physical systems and contribute directly to the foundations[4] of statistical mechanics. In particular, the equilibrium statistical mechanics of systems of interacting objects (spins, particles) and the related phenomena of magnetic,[5] superfluid, and superconducting order, critical point behavior,[6] and descriptions of coherent radiation[7] make fruitful use of the concepts of correlation, order, and entropy. There is abundant motivation for attempting to examine carefully the interlacing of these concepts.

It is the purpose of this paper to study specifically an aspect of the relation between entropy and spin correlation. To do this an exact cumulant-like expansion[8] for the entropy S is given in terms of the reduced entropies for N-spin systems. Higher-order terms in the expansion represent successively higher degrees of spin correlation. We prove analytically that for an Ising system of any dimensionality with ferromagnetic interactions of arbitrary range, the first two terms in the entropy expansion provide a lower bound for the exact entropy. A corollary of the theorem is that the lower-bound property is also valid for any two-sublattice Ising system with antiferromagnetic interactions between

* On leave of absence from Institute for Solid State Physics, University of Tokyo, Tokyo, Japan.

[1] For a discussion and quantum generalization of this inequality see H. Falk and E. Adler, Phys. Rev. **168**, 185 (1968), and H. Falk, Am. J. Phys. (to be published).

[2] See, e.g., H. W. Alexander, *Elements of Mathematical Statistics* (Wiley-Interscience, New York, 1961), p. 166.

[3] See, e.g., A. I. Khinchin, *Mathematical Foundations of Information Theory* (Dover Publishing Co., New York, 1957), Eq. (1.2).

[4] D. ter Haar, *Elements of Thermostatistics* (Holt, Rinehart, and Winston, New York, 1966), Sec. 6.4.

[5] See, e.g., W. Marshall and R. D. Lowde, Rept. Progr. Phys. **31**, 705 (1968).

[6] See, e.g., M. E. Fisher, J. Math. Phys. **5**, 944 (1964).

[7] See, e.g., L. Mandel and E. Wolf, Rev. Mod. Phys. **37**, 231 (1965).

[8] A detailed discussion of the analogous expansion for classcial fluids is given by J. Yvon, *Correlations and Entropy in Classical Statistical Mechanics* (Pergamon Press, Inc., New York, 1969), Secs. 2.5 and 3.8; references to the earlier work of R. L. Stranovich and of R. E. Nettleton and M. S. Green are also given.

sublattices. The exact entropy S is compared with the sum of the first two terms in the expansion. The sum denotes the entropy contributions from one-spin probabilities and from pair correlations, and corresponds to what would be obtained from a Kirkwood[9]-type truncation. In that sense the difference [S-(first two terms)] is the entropy contribution from higher correlations.

A conclusion from numerical results for the one-dimensional N-spin Ising model is that the above Kirkwood truncation (more conventionally, approximation) generally leads one to underestimate the entropy, and the error is substantial for low temperatures and large N. All of these results are for zero external magnetic field.

1. REDUCED ENTROPY EXPANSIONS

Kubo[10] has discussed the important role of cumulants in statistical physics, and has stressed the fact that cumulants appear as connected-diagram contributions in the usual perturbation expansions. The hierarchy of cumulants for spin variables s_i, where $s_i \equiv 2s_i^z$ $i=1,\ldots,N$, may be written

$$\langle s_i \rangle_c = \langle s_i \rangle , \tag{1.1}$$

$$\langle s_i s_j \rangle_c = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle , \tag{1.2}$$

$$\langle s_i s_j s_k \rangle_c = \langle s_i s_j s_k \rangle - \langle s_i \rangle \langle s_j s_k \rangle - \langle s_j \rangle \langle s_i s_k \rangle - \langle s_k \rangle \langle s_i s_j \rangle + 2 \langle s_i \rangle \langle s_j \rangle \langle s_k \rangle , \tag{1.3}$$

$$\begin{aligned} \langle s_i s_j s_k s_l \rangle_c = {} & \langle s_i s_j s_k s_l \rangle - \langle s_i s_j s_k \rangle \langle s_l \rangle - \langle s_i s_j s_l \rangle \langle s_k \rangle \\ & - \langle s_i s_k s_l \rangle \langle s_j \rangle - \langle s_k s_j s_l \rangle \langle s_i \rangle - \langle s_i s_j \rangle \langle s_k s_l \rangle \\ & - \langle s_i s_k \rangle \langle s_j s_l \rangle - \langle s_i s_l \rangle \langle s_k s_j \rangle + 2 \langle s_i s_j \rangle \langle s_k \rangle \langle s_l \rangle \\ & + 2 \langle s_i s_k \rangle \langle s_j \rangle \langle s_l \rangle + 2 \langle s_i s_l \rangle \langle s_j \rangle \langle s_k \rangle \\ & + 2 \langle s_j s_k \rangle \langle s_i \rangle \langle s_l \rangle + 2 \langle s_j s_l \rangle \langle s_i \rangle \langle s_k \rangle \\ & + 2 \langle s_k s_l \rangle \langle s_i \rangle \langle s_j \rangle - 6 \langle s_i \rangle \langle s_j \rangle \langle s_k \rangle \langle s_l \rangle , \end{aligned} \tag{1.4}$$

where the subscripts i,j,k,l are distinct integers in each cumulant and take on values, $1,\ldots,N$. It is readily proved[10] that a cumulant is zero if its elements may be divided into two or more sets which are statistically independent; however, the vanishing of a cumulant, say $\langle xy \rangle - \langle x \rangle \langle y \rangle$, does not[11] in general imply that x and y are statistically independent. Although cumulants $\langle s_i s_j \rangle_c$, $\langle s_i s_j s_k \rangle_c$, etc., do not in general maintain a definite sign, Griffiths[12] has been able to prove that for Ising systems with ferromagnetic interaction, $\langle s_i s_j \rangle_c \geq 0$ and $\langle s_i s_j s_k \rangle_c \leq 0$, for positive magnetic fields. Definitive results[13] about some important thermodynamic properties of the above systems in the critical region have followed from the latter inequalities.

In what sense do the above spin cumulants, which are often taken to be a measure of successively higher orders of spin correlation, contribute to the entropy of the system? Can the entropy be resolved into a sum of contributions which correspond to the higher correlations, and do the successive terms all contribute to a decrease in disorder?

To study these questions consider the quantities

$$\hat{S}_i \equiv -\ln p_i(s_i;N) \ln p_i(s_i;N) , \tag{1.5}$$

$$\hat{S}_{ij} \equiv -\ln p_{ij}(s_i,s_j;N) \ln p_{ij}(s_i,s_j;N) , \tag{1.6}$$

$$\hat{S}_{ijk} \equiv -\ln p_{ijk}(s_i,s_j,s_k;N) \ln p_{ijk}(s_i,s_j,s_k;N) , \tag{1.7}$$

where $p_i, p_{ij}, \ldots,$ are the one-, two-, etc., spin reduced probabilities to be defined in the next section. The corresponding reduced entropies are defined as follows:

$$\langle \hat{S}_i \rangle \equiv -\sum_{s_i} p_i(s_i;N) \ln p_i(s_i;N) , \tag{1.8}$$

$$\langle \hat{S}_{ij} \rangle \equiv -\sum_{s_i,s_j} p_{ij}(s_i,s_j;N) \ln p_{ij}(s_i,s_j;N) , \tag{1.9}$$

where the sums are over all realizations of the spin variables, e.g., for spin $\frac{1}{2}$, s_i may realize the values ± 1.

Consider the cumulant-like quantities

$$\langle \hat{S}_i \rangle_c \equiv - \langle \ln p_i(s_i;N) \rangle , \tag{1.10}$$

$$\langle \hat{S}_{ij} \rangle_c \equiv - \langle \ln p_{ij}(s_i,s_j;N) - \ln p_i(s_i;N) p_j(s_j;N) \rangle , \tag{1.11}$$

$$\begin{aligned} \langle \hat{S}_{ijk} \rangle_c \equiv - \langle & \ln p_{ijk}(s_i,s_j,s_k;N) \\ & - \ln p_{ij}(s_i,s_j;N) p_k(s_k;N) \\ & - \ln p_{ik}(s_i,s_k;N) p_j(s_j;N) \\ & - \ln p_{jk}(s_j,s_k;N) p_i(s_i;N) \\ & + 2 \ln p_i(s_i;N) p_j(s_j;N) p_k(s_k;N) \rangle , \end{aligned} \tag{1.12}$$

which may be directly written in terms of the reduced entropies:

$$\langle \hat{S}_i \rangle_c = \langle \hat{S}_i \rangle , \tag{1.13}$$

$$\langle \hat{S}_{ij} \rangle_c = \langle \hat{S}_{ij} \rangle - \langle \hat{S}_i \rangle - \langle \hat{S}_j \rangle , \tag{1.14}$$

$$\langle \hat{S}_{ijk} \rangle_c = \langle \hat{S}_{ijk} \rangle - \langle \hat{S}_{ij} \rangle - \langle \hat{S}_{ik} \rangle - \langle \hat{S}_{jk} \rangle + \langle \hat{S}_i \rangle + \langle \hat{S}_j \rangle + \langle \hat{S}_k \rangle . \tag{1.15}$$

The symbol N has been suppressed, but it must be kept in mind that the quantities depend on the number of spins in the system.

To relate the cumulant-like quantities to the entropy S, it is sufficient to note[14] that one may define h functions according to the scheme

$$p_i(s_i;N) \equiv e^{h_i} , \tag{1.16}$$

$$p_{ij}(s_i,s_j;N) \equiv e^{h_i+h_j+h_{ij}} , \tag{1.17}$$

$$p_{ijk}(s_i,s_j,s_k;N) \equiv e^{h_i+h_j+h_k+h_{ij}+h_{ik}+h_{jk}+h_{ijk}} . \tag{1.18}$$

[9] See, e.g., T. I. Hill, *Statistical Mechanics* (McGraw-Hill Book Co., New York, 1956), p. 196.

[10] R. Kubo, J. Phys. Soc. Japan **17**, 1100 (1962).

[11] See Ref. 2.

[12] R. B. Griffiths [J. Math. Phys. **8**, 478 (1967); **8**, 484 (1967)] proved the first inequality which follows, and R. B. Griffiths, C. A. Hurst, and S. Sherman, J. Math. Phys. (to be published) proved the second inequality.

[13] For a referenced discussion of the applications of the first inequality and an alternative proof see J. Ginibre, Phys. Rev. Letters **23**, 828 (1969).

[14] Reference 8, Sec. 2.5.

Expressing h_i and h_j in terms of p_i and p_j leads, for example, to

$$p_{ij}=(p_ip_j)(p_{ij}/p_ip_j) \quad (1.19)$$

and ultimately to

$$p_{1\ldots N}(s_1,\ldots,s_N;N)=(\prod_{i=1}^{N}p_i)(\prod_{1\leq j<k\leq N}(p_{jk}/p_jp_k))$$
$$\times(\prod_{1\leq l<m<n\leq N}(p_{lmn}p_lp_mp_n/p_{lm}p_{ln}p_{mn}))$$
$$\times\cdots\times(\prod_{1\leq l_1<l_2<\cdots<l_N\leq N}\cdots), \quad (1.20)$$

from which it follows immediately that (with $k_B=1$) the total entropy

$$S=\sum_{i=1}^{N}\langle\hat{S}_i\rangle+\sum_{1\leq i<j\leq N}\langle\hat{S}_{ij}\rangle_c$$
$$+\sum_{1\leq i<j<k\leq N}\langle\hat{S}_{ijk}\rangle_c+\cdots$$
$$+\sum_{1\leq l_1<l_2<\cdots<l_N\leq N}\langle\hat{S}_{l_1\ldots l_N}\rangle_c. \quad (1.21)$$

Now an inequality of Gibbs[15] implies that

$$\langle\hat{S}_{ij}\rangle_c\leq 0 \quad (1.22)$$

with equality if and only if $p_{ij}=p_ip_j$. On the other hand, the corresponding spin cumulant $\langle s_is_j\rangle_c$ does not in general maintain a definite sign and it vanishes if, but not necessarily[16] only if $p_{ij}=p_ip_j$. The statistical association between spins i and j is therefore more reliably monitored by $\langle\hat{S}_{ij}\rangle_c$ than by $\langle s_is_j\rangle_c$. Furthermore, the fact that the sum over $\langle\hat{S}_{ij}\rangle_c$ contributes negatively to the entropy expansion, may be interpreted as a reduction in disorder due to the presence of pair correlations. This suggests that in the entropy expansion the additional cumulant-like terms, which relate to higher orders of statistical association, may also contribute to a reduction of disorder.

In the next section, however, it is proved analytically that the difference

$$\Delta_2\equiv S-[\sum_{i=1}^{N}\langle\hat{S}_i\rangle+\sum_{1\leq i<j\leq N}\langle\hat{S}_{ij}\rangle_c] \quad (1.23)$$

is positive for a large class of Ising systems of arbitrary dimensionality with either ferromagnetic of antiferromagnetic interactions.

[15] See Ref. 1.

[16] For the models under consideration the if and only if actually does obtain for zero magnetic field; however, in the Appendix we give a simple example which shows that the vanishing of the linear correlation may occur even though the spins are *not* statistically independent.

2. THEOREM AND COROLLARY

For spins of magnitude $\frac{1}{2}$ we have:

Theorem: For an Ising system of any dimensionality with ferromagnetic interactions of arbitrary range, in zero field Δ_2 is non-negative.

Corollary: For any two-sublattice Ising system with nearest-neighbor antiferromagnetic interaction, in zero magnetic field Δ_2 is non-negative.

The theorem and corollary, show that the first two terms in the entropy expansion provide a lower bound for the entropy of the Ising systems described. The lower bound is relevant only when it is positive, since $S\geq 0$. Of course, the first term in the entropy expansion provides a general (but in this case, trivial) upper bound for S.

To prove the above assertions, it is useful to employ the following representation[17] of the reduced spin probabilities for spin $\frac{1}{2}$.

$$p_{i_1\cdots i_n}(s_{i_1},\ldots,s_{i_n};N)$$
$$=(\tfrac{1}{2})^n(1+\langle s_{i_1}\rangle s_{i_1}+\cdots+\langle s_{i_n}\rangle s_{i_n}$$
$$+\langle s_{i_1}s_{i_2}\rangle s_{i_1}s_{i_2}+\cdots+\langle s_{i_1}\cdots s_{i_n}\rangle s_{i_1}\cdots s_{i_n}), \quad (2.1)$$

which is implicit in the sense that the quantities $\langle s_{i_1}\rangle,\ldots,\langle s_{i_1}\cdots s_{i_n}\rangle$ are defined in terms of the reduced spin probabilities. Equations (1.10) and (1.11) can now be written

$$\langle\hat{S}_i\rangle_c=-\langle\ln\tfrac{1}{2}(1+\langle s_i\rangle s_i)\rangle, \quad (2.2)$$

$$\langle\hat{S}_{ij}\rangle_c=-\left\langle\ln\frac{1+\langle s_i\rangle s_i+\langle s_j\rangle s_j+\langle s_is_j\rangle s_is_j}{(1+\langle s_i\rangle s_i)(1+\langle s_j\rangle s_j)}\right\rangle, \quad (2.3)$$

which, for zero field, reduce to

$$\langle\hat{S}_i\rangle_c=\ln 2, \quad (2.4)$$

$$\langle\hat{S}_{ij}\rangle_c=-\tfrac{1}{2}g_{ij}(x), \quad (2.5)$$

where

$$g_{ij}(x)\equiv(1+a_{ij}(x))\ln(1+a_{ij}(x))$$
$$+(1-a_{ij}(x))\ln(1-a_{ij}(x)), \quad (2.6)$$

$$a_{ij}(x)\equiv\langle s_is_j\rangle\leqslant 1, \quad (2.7)$$

and

$$x\equiv 1/T. \quad (2.8)$$

Now for a Hamiltonian

$$H=-\sum_{i<j}J_{ij}s_is_j, \quad J_{ij}\geqslant 0 \quad (2.9)$$

[17] R. J. Glauber, J. Math. Phys. 4, 294 (1963).

the partition function Z satisfies the relation

$$\ln Z=\int_{\infty}^{T} dT\frac{E(T)}{T^2}+N\ln 2 \quad (2.10)$$

$$=-\int_{0}^{x} dx'\bar{E}(x')+N\ln 2, \quad (2.11)$$

where

$$\bar{E}(x)\equiv\langle H\rangle=-\sum_{i<j} J_{ij}a_{ij}(x). \quad (2.12)$$

It follows immediately that the entropy is given by

$$S=\sum_{i<j} J_{ij}\int_{0}^{x} dx'a_{ij}(x')+N\ln 2-x\sum_{i<j} J_{ij}a_{ij}(x), \quad (2.13)$$

so that from (1.23), (2.4), and (2.5) we find

$$\Delta_2=\sum_{i<j} J_{ij}\int_{0}^{x} dx'a_{ij}(x') -x\sum_{i<j} J_{ij}a_{ij}(x)+\tfrac{1}{2}\sum_{i<j} g_{ij}(x). \quad (2.14)$$

Write

$$f(x)=\Delta_2, \quad (2.15)$$

so that one has

$$\frac{df(x)}{dx}=\sum_{i<j}\left\{\tfrac{1}{2}\ln\left(\frac{1+a_{ij}(x)}{1-a_{ij}(x)}\right)-xJ_{ij}\right\}\frac{da_{ij}(x)}{dx}. \quad (2.16)$$

From the work of Griffiths[12] it follows that

$$\frac{da_{ij}(x)}{dx}=\frac{d\langle s_is_j\rangle}{dx}\geq 0 \quad (2.17)$$

and[18] that

$$a_{ij}(x)\geq\tanh(\beta J_{ij}). \quad (2.18)$$

Consequently (we put $k_B=1$), we obtain

$$\tfrac{1}{2}\ln\left(\frac{1+a_{ij}}{1-a_{ij}}\right)\geq xJ_{ij}. \quad (2.19)$$

Thus, we have proved that df/dx is positive; and it is found by inspection that $f(0)=0$; therefore, we have established

$$\Delta_2>0. \quad (2.20)$$

The vanishing of Δ_2 is excluded for the system defined by (2.9) provided that at least two interaction bonds J_{ij} are nonvanishing and that the temperature is finite.

The proof of the corollary is accomplished by simply performing a unitary transformation which takes the two-sublattice antiferromagnet into a ferromagnet. It is only necessary to notice that *each* term in Δ_2 is invariant with respect to that transformation.

The proof for the case of the presence of the magnetic field seems to be difficult, because in (2.2) and (2.3), cumulants of odd order appear, and consequently it is rather hard to establish the positivity of the derivative df/dx. The extension of the theorem to higher-spin[19] and other classical systems such as the classical Heisenberg model will be reported in a separate paper.

[18] R. B. Griffiths, Commun. Math. Phys. **6**, 121 (1967).

[19] R. B. Griffiths, J. Math. Phys. **10**, 1555 (1969).

3. EXAMPLE: N-SPIN RING AND CHAIN

In this section, the linear Ising model is investigated in order to evaluate the value of the quantity Δ_2 and to discuss the validity of a Kirkwood-type approximation.[9] That is, the higher-order contribution Δ_2 has been calculated for the one-dimensional, N-spin Ising system with either ferromagnetic or antiferromagnetic interaction, free ends or periodic boundary conditions, and arbitrary N. It should be noted that if a Kirkwood-type truncation were used, all factors except the first two in (1.20) would be set equal to unity. This truncation would, in effect, approximate Δ_2 by zero; thus, the magnitude of Δ_2 provides a measure of the validity (or lack of validity) of the Kirkwood-type approximation in the context of the model being considered. The numerical behavior of the difference for either ferromagnetic or antiferromagnetic interaction, for either choice of boundary condition, and for certain values of N in the range 2, 3, . . ., 53, is displayed as a function of the temperature.

For the Ising *ring* of N spins (each of magnitude $\frac{1}{2}$) with nearest-neighbor interactions, the Hamiltonian, including the Zeeman energy, is

$$H=\sum_{i=1}^{N} H(s_i,s_{i+1}), \quad (3.1)$$

where

$$H(s_i,s_{i+1})=-\tfrac{1}{2}J[s_is_{i+1}+(s_i+s_{i+1})h], \quad s_{N+1}\equiv s_1. \quad (3.2)$$

The spin projection $s_i^z\equiv\frac{1}{2}s_i$ with ± 1 being the possible realizations of s_i, $i=1,\ldots,N$. The interaction energy J is a positive number for ferromagnetic interaction and a negative number for antiferromagnetic interaction, and h denotes the dimensionless product of the g factor, the Bohr magneton, the magnetic field, and $1/(2J)$.

The one-spin, reduced probability functions $p_i(s_i;N)$, for $i=1,\ldots,N$ are defined by

$$p_i(s_i;N)=\sum_{s_1}\cdots\sum_{s_{i-1}}\sum_{s_{i+1}}\cdots\sum_{s_N}[e^{-\beta H}]/Z \quad (3.3)$$

and the two-spin, reduced probability functions $p_{ij}(s_i,s_j;N)$, for $i,j=1,\ldots,N;\, i\neq j$ are defined by

$$p_{ij}(s_i,s_j;N) =\sum_{s_1}\cdots\sum_{s_{i-1}}\sum_{s_{i+1}}\cdots\sum_{s_{j-1}}\sum_{s_{j+1}}\cdots\sum_{s_N}[e^{-\beta H}]/Z, \quad (3.4)$$

where the partition function

$$Z=\sum_{s1}\cdots\sum_{sN}[e^{-\beta H}] \tag{3.5}$$

and ($1/\beta$ is the product of the Boltzmann constant and the absolute temperature).

From expression (2.1) of the reduced spin probabilities and also directly with the transfer-matrix approach of Ashkin and Lamb,[20] one obtains easily

$$p_i(s_i;N)=[\cos^2 d+(w_2/w_1)^N\sin^2 d]/[1+(w_2/w_1)^N],\quad s_i=-1 \tag{3.6}$$

$$=[\sin^2 d+(w_2/w_1)^N\cos^2 d]/[1+(w_2/w_1)^N],\quad s_i=+1, \tag{3.7}$$

and

$$p_{ij}(s_i,s_j;N)=[\cos^4 d+f(|i-j|)\sin^2 d\cos^2 d+(w_2/w_1)^N\sin^4 d]/[1+(w_2/w_1)^N],\quad s_i=s_j=-1 \tag{3.8}$$

$$=[\sin^4 d+f(|i-j|)\sin^2 d\cos^2 d+(w_2/w_1)^N\cos^4 d]/[1+(w_2/w_1)^N],\quad s_i=s_j=+1 \tag{3.9}$$

$$=[1-f(|i-j|)+(w_2/w_1)^N]\sin^2 d\cos^2 d,\quad s_i=-s_j=\pm1, \tag{3.10}$$

where

$$\cos d=-a/(1+a^2)^{1/2},\quad \sin d=1/(1+a^2)^{1/2}, \tag{3.11}$$

$$a=-[\exp(2K)]\{\sinh(2Kh)+([\sinh(2Kh)]^2+\exp(-4K))^{1/2}\}, \tag{3.12}$$

$$K=\tfrac{1}{2}\beta J, \tag{3.13}$$

$$w_r=[\exp(K)]([\cosh(2Kh)]+(-1)^{r+1}\{[\sinh(2Kh)]^2+\exp(-4K)\}^{1/2}) \tag{3.14}$$

and

$$f(|i-j|)=(w_2/w_1)^{|i-j|}+(w_2/w_1)^{N-|i-j|}=f(N-|i-j|),\quad i,j=1,\ldots,N;\, i\neq j. \tag{3.15}$$

It is worthwhile to notice at this point that for strictly positive absolute temperatures, the eigenvalues of the transfer matrix satisfy the inequality $|w_2/w_1|<1$; so that the double limit ($N\to\infty$ followed by $|i-j|\to\infty$) of $f(|i-j|)$ is zero. In that limit

$$p_{ij}(s_i,s_j;N)\to p_i(s_i;N)p_j(s_j;N);$$

i.e., any two spins at infinite separation are statistically independent for this infinite-spin Ising ring. In general the statistical independence implies the absence of infinite-range linear correlation. In fact, it is simple to show from the above reduced probabilities that the covariance

$$\tfrac{1}{4}[\langle s_is_j\rangle-\langle s_i\rangle\langle s_j\rangle]=\frac{f(|i-j|)\cos^2 d\sin^2 d}{1+(w_2/w_1)^N}+\frac{(\cos^2 d-\sin^2 d)(w_2/w_1)^N}{[1+(w_2/w_1)^N]^2} \tag{3.16}$$

vanishes in the above defined limit.

Subsequent discussion will be simplified by considering $h=0$:

$$w_1=\cosh K, \tag{3.17}$$

$$w_2=\sinh K, \tag{3.18}$$

$$w=w_2/w_1=\tanh K, \tag{3.19}$$

$$\sin d=\cos d=1/\sqrt{2}, \tag{3.20}$$

$$p_i(s_i;N)=\tfrac{1}{2},\qquad s_i=\pm1, \tag{3.21}$$

$$p_{ij}(s_i,s_j;N)=\tfrac{1}{4}[1+f(|i-j|)+w^N]/[1+w^N],\quad s_i=s_j=\pm1 \tag{3.22}$$

$$=\tfrac{1}{4}[1-f(|i-j|)+w^N]/[1+w^N],\quad s_i=-s_j=\pm1 \tag{3.23}$$

$$Z=w_1^N+w_2^N. \tag{3.24}$$

From Z, the entropy S is computed in the usual manner (put the Boltzmann constant$=1$):

$$S=N\ln 2+N\ln\cosh K-N[(1+w^{N-2})/(1+w^N)]K\tanh K+\ln(1+w^N). \tag{3.25}$$

The last term exhibits, at low temperatures, and for even N, the contribution[21] to the entropy from the twofold degeneracy of the ground state. For small N, the contribution to S/N is significant. It is also noteworthy that for N an *odd* integer, w^N and w^{N-2} are negative for the antiferromagnetic case and there is significant difference[22] between the antiferromagnetic and the ferromagnetic entropy per spin for small N and low temperature. The corollary proved in the previous section does not always hold *for the ring of odd N*, which cannot be divided into two sublattices. The "misfit spin"[22] appearing in the reduced probabilities plays the role of an impurity[23] in an antiferromagnetic host.

For the N-spin Ising chain with nearest-neighbor interactions and *free ends*, the Hamiltonian is

$$\tilde{H}=\sum_{i=1}^{N-1}\tilde{H}(s_i,s_{i+1}), \tag{3.26}$$

where

$$\tilde{H}(s_i,s_{i+1})=-\tfrac{1}{2}Js_is_{i+1}. \tag{3.27}$$

[20] J. Ashkin and W. E. Lamb, Jr., Phys. Rev. **64**, 159 (1943).

[21] J. C. Bonner and M. E. Fisher, Proc. Phys. Soc. (London) **80**, 508 (1962).

[22] C. Domb, Advan. Phys. **9**, 165 (1960), pp. 168–169.

[23] H. Falk, Phys. Rev. **151**, 304 (1966).

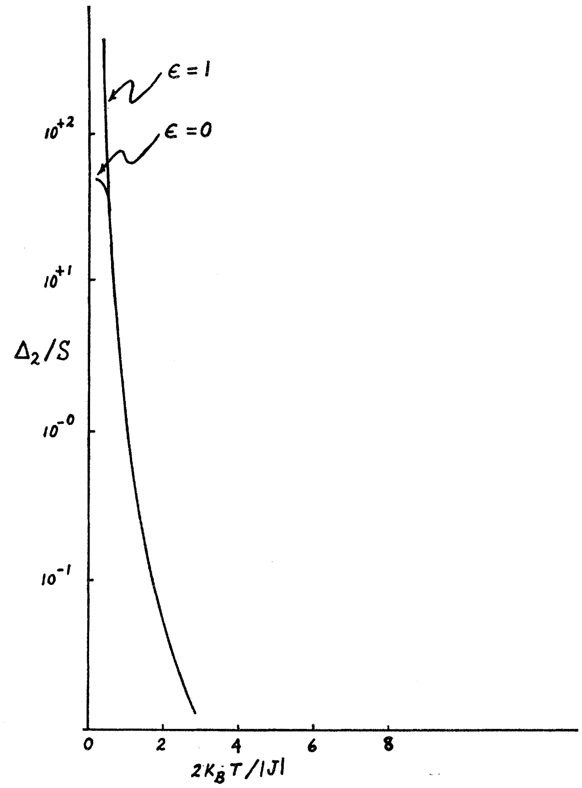

FIG. 1. Δ_2/S for a 53-spin antiferromagnetic ring ($\epsilon=0$) and chain ($\epsilon=1$). When the statistical association (g_l) is of sufficiently long range, the two boundary conditions become distinguishable.

The one- and two-spin reduced probability functions $\tilde{p}_i$, $\tilde{p}_{ij}$ are defined as for the N-spin ring; the only change being that of replacing H by $\tilde{H}$. By completely analogous methods one finds

$$\tilde{p}_i(s_i;N)=\tfrac{1}{2}, \qquad s_i=\pm 1, \tag{3.28}$$

$$\tilde{p}_{ij}(s_i,s_j;N)=\tfrac{1}{4}[1+w^{|i-j|}], \qquad s_i=s_j=\pm 1 \tag{3.29}$$

$$=\tfrac{1}{4}[1-w^{|i-j|}], \qquad -s_i=s_j=\pm 1 \tag{3.30}$$

where the partition function $\tilde{Z}$ is for this case, easily found[24] to be the solution of a first-order linear difference equation; explicitly

$$\tilde{Z}=2^N(\cosh K)^{N-1}. \tag{3.31}$$

The entropy (with the Boltzmann constant$=1$) is then found to be

$$\tilde{S}=N\ln 2+(N-1)\ln\cosh K-(N-1)K\tanh K. \tag{3.32}$$

Recall that the computation of the difference between the entropy S and the first two terms in the expansion of S was denoted by

$$\Delta_2=S-\Big[\sum_{i=1}^{N}\langle\hat{S}_i\rangle+\sum_{1\le i<j\le N}\langle\hat{S}_{ij}\rangle_c\Big]. \tag{3.33}$$

For the Ising ring in zero magnetic field, S is given by (3.25) and for the Ising chain, S is given by (3.32). Furthermore, the selection of $h=0$ led to

$$p_i(s_i;N)=\tfrac{1}{2} \quad \text{for } s_i=\pm 1,\ i=1,\ldots,N \tag{3.34}$$

which is consistent with the symmetry and independent of boundary conditions and the sign of J. Equations (1.8) and (3.34) imply that

$$\langle\hat{S}_i\rangle=\ln 2. \tag{3.35}$$

Now the definition (1.11) of $\langle\hat{S}_{ij}\rangle_c$ may be written

$$\langle\hat{S}_{ij}\rangle_c=-\langle\ln[p_{ij}(s_i,s_j;N)/(\tfrac{1}{2})^2]\rangle, \tag{3.36}$$

and with (3.22), (3.23), and (3.30),

$$\langle\hat{S}_{ij}\rangle_c=-\tfrac{1}{2}g_{|i-j|}(K), \tag{3.37}$$

TABLE I. Δ_2/S for antiferromagnetic ($J<0$) rings ($\epsilon=0$).

$2k_BT/\lvert J\rvert$	0.5	1	2	4	10
N					
3	$-6.52\ 10^{-2}$	$-5.25\ 10^{-2}$	$-2.17\ 10^{-2}$	$-4.77\ 10^{-3}$	$-4.08\ 10^{-4}$
5	$-4.11\ 10^{-2}$	$-1.20\ 10^{-2}$	$+5.84\ 10^{-3}$	$+1.29\ 10^{-3}$	$+5.53\ 10^{-5}$
7	$+1.92\ 10^{-1}$	$+1.57\ 10^{-1}$	$+3.35\ 10^{-2}$	$+2.72\ 10^{-3}$	$+7.21\ 10^{-5}$

[24] G. F. Newell and E. W. Montroll, Rev. Mod. Phys. **25**, 353 (1953), Appendix 2.

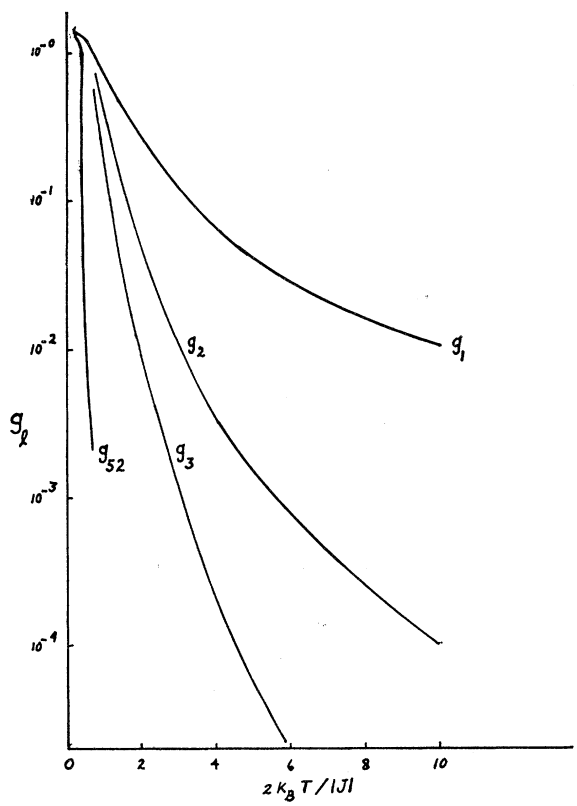

FIG. 2. g_l, the measure of statistical association between pairs, for a 53-spin antiferromagnetic chain ($\epsilon=1$; i.e., free ends). For $k_BT/|J|<\frac{1}{16}$, the statistical association is essentially a maximum and the same for all pairs.

where

$$g_l(K)=[1+\rho_l(K)]\ln[1+\rho_l(K)]+[1-\rho_l(K)]\ln[1-\rho_l(K)], \quad (3.38)$$

$$\rho_l(K)=[w^l+(1-\epsilon)w^{N-l}]/[1+(1-\epsilon)w^N]=\langle s_is_j\rangle-\langle s_i\rangle\langle s_j\rangle, \quad |i-j|=l, \quad (3.39)$$

$$\epsilon=0 \text{ (ring)}, \quad 1 \text{ (chain)}, \quad (3.40)$$

$$w=\tanh K, \quad (3.41)$$

and

$$K=\tfrac{1}{2}\beta J. \quad (3.42)$$

By combining (3.25), (3.32), (3.35), and (3.37) one arrives at the joint result

$$\frac{\Delta_2}{N}=\left(1-\frac{\epsilon}{N}\right)\ln\cosh K-\left(1-\frac{\epsilon}{N}\right)K\tanh K+\frac{1}{2N}\sum_{l=1}^{N-1}(N-l)g_l(K)+(1-\epsilon)[(1/N)\ln(1+w^N)-(K\tanh K)w^{N-2}(1-w^2)/(1+w^N)]. \quad (3.43)$$

The quantities $\Delta_2/N, S/N, \Delta_2/S, N^{-1}\sum_{1\leq i<j\leq N}\langle\hat{S}_{ij}\rangle_c$, and $-2\langle\hat{S}_{ij}\rangle_c$ (for $|i-j|=1,2,3,N-1$) have been computed for $N=3,\ldots,53$, for positive and negative values of K, where $0.05\leq|K|\leq5.00$, and for $\epsilon=0,1$. Selected results are displayed in Figs. 1 and 2 and Table I. It can be seen from the equations that Δ_2 is an even function of K for $\epsilon=1$ (chain), arbitrary N and for $\epsilon=0$ (ring), N even, yielding nice examples of the general properties derived by a unitary transformation which takes the two-sublattice antiferromagnet into a ferromagnet as was discussed in the previous section.

It is clear that: (1) Δ_2 is negative for antiferromagnetic *rings* with N odd and less than 6, but Δ_2 becomes positive for larger rings; whereas, Δ_2 is positive for all chains (with free ends) irrespective of whether they are ferromagnetic or antiferromagnetic, which is consistent with the theorem and corollary proved in the previous section; (2) $|\Delta_2/S|$ is small for temperatures greater than $5J/2k_B$ but becomes large for large N and for temperatures less than $J/8k_B$; (3) $-2\langle\hat{S}_{ij}\rangle_c$, which is a measure of the statistical association of spins i and j, is essentially a maximum and uniform for all pairs in a 53-spin chain at temperatures less than $J/16k_B$.

It is concluded that for the model studied, the sum of the first two terms in the entropy expansion provides a close approximation to the exactly computed entropy only for sufficiently high temperatures. Furthermore, for systems of 6 or more spins the additional terms in the expansion make a net *positive* contribution for all temperatures irrespective of whether the interaction is ferromagnetic or antiferromagnetic. In that sense the inclusion of pair correlations from all pairs, and the neglect of triplet,..., correlations leads to an *underestimate* of the entropy which in conventional language would imply an *overestimate of order* in this system. Thus, in this context, the Kirkwood truncation generally leads to an underestimate of the entropy, and the error is substantial for low temperatures and large N.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. C. T. Falk for performing the computer programming and for calling attention to Ref. 2. We would also like to thank Professor M. E. Fisher and Professor R. B. Griffiths for helpful comments. One of us (H.F.) thanks the City College Physics Department for a 1969 Summer Research Fellowship which was funded by the National Science Foundation; the other (M.S.) gratefully acknowledges the support of the National Science Foundation.

APPENDIX

Consider a pair of spins, each of magnitude 1, and take the Hamiltonian for the system to be

$$H=-J(S_1^zS_2^z)^2-A[2-(S_1^z)^2-(S_2^z)^2], \quad (A1)$$

where

$$S_i^z=-1,0,+1, \quad i=1,2. \quad (A2)$$

It is readily verified that in the canonical ensemble the two-spin probabilities satisfy

$$p(1,1)=p(1,-1)=p(-1,1)=p(-1,-1)=Z^{-1}\exp(\beta J), \quad (A3)$$

$$p(1,0)=p(-1,0)=p(0,1)=p(0,-1)=Z^{-1}\exp(\beta A), \quad (A4)$$

$$p(0,0)=Z^{-1}\exp(2\beta A), \quad (A5)$$

and the one-spin probabilities satisfy

$$p(1)=p(-1)=Z^{-1}[2\exp(\beta J)+\exp(\beta A)], \quad (A6)$$

$$p(0)=Z^{-1}[2\exp(\beta A)+\exp(2\beta A)], \quad (A7)$$

and Z may be obtained from the normalization equation

$$p(1)+p(0)+p(-1)=1. \quad (A8)$$

Consequently, $p(S_1^zS_2^z)$ is *not* in general equal to $p(S_1^z)p(S_2^z)$ although the cumulant vanishes:

$$\langle S_1^zS_2^z\rangle-\langle S_1^z\rangle\langle S_2^z\rangle=0. \quad (A9)$$

The latter result follows easily from the symmetry.

This counterexample, serves to illustrate the fact that the vanishing of the covariance does not, in general, imply that the variables are statistically independent.