a slight qualitative difference in the nature of the collision-broadening process between the stimulated- and spontaneous-emission experiments. This difference may become exaggerated above the transition region. The existence of comparably large exchange cross sections for resonant collisions between identical atoms suggests that the real case in the oscillating laser falls between the two limits of statistical independence and statistical correlation considered by Rautian and Sobel'man.[6]

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EXACT SOLUTION OF THE PROBLEM OF THE ENTROPY OF TWO-DIMENSIONAL ICE

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The entropy of two-dimensional ice has been found by the transfer-matrix method. Entropy $=Mk\ln W$, with $M=$ No. of molecules and $W=(\frac{4}{3})^{3/2}$.

At low temperatures ice has a residual entropy caused, presumably, by an indeterminacy of the crystal structure. The oxygen atoms constitute a periodic crystal lattice that is hydrogen bonded. The hydrogen atoms are not at the centers of the bonds, however, so that there are two possible states for each bond corresponding to the two positions of the hydrogen atom relative to the bond midpoint. Nevertheless, not all bond configurations are allowed, for there is a constraint called the "ice condition" such that for the four bonds emanating from each oxygen atom, exactly two of the bonds must have the hydrogen atoms close to the oxygen atom.

This problem has received a good deal of theoretical and numerical attention,[1-6] and the best numerical estimates of the entropy are in excellent agreement with experiment.[6] While the problem has also attracted the attention of mathematicians, no exact analytic solution of the problem has heretofore been obtained.

We have succeeded in solving the two-dimensional version of the problem which may be formulated as follows: Let the vertices of a square $N \times N$ net (as in the Ising model) represent the oxygen atoms, and on each bond draw an arrow (up or down for vertical bonds and left or right for horizontal bonds). The "ice condition" is that there must be precisely two arrows into each vertex. If $M = N^2$, then for large M the number of arrangements will be W^M, where W is to be calculated. The entropy is $Mk \ln W$. If we ignore the "ice condition," then obviously $W = 4$.

The best numerical estimate[6] for W in two dimensions was $W = 1.540 \pm 0.001$. Our exact result is

$$W = (\tfrac{4}{3})^{3/2} = 1.539\,600\,7.$$

The calculation uses the well-known transfer-matrix formalism which we briefly outline here. A configuration of the lattice consists of N rows of N vertical arrows alternating with N rows of N horizontal arrows. Let φ^1 represent a definite configuration of the first "vertical" row. There are obviously 2^N choices for φ^1. Likewise, let φ^j be the configuration of the jth "vertical" row. If φ and φ' are the configurations of two successive "vertical" rows, let $A(\varphi, \varphi')$ be the number of ways of placing arrows on the intervening "horizontal" row such that the ice condition is satisfied at every vertex of that "horizontal" row. Thus, A is a 2^N square matrix whose entries are integers, and Z, the total number of ways of correctly placing arrows on the lattice, is then $Z = \mathrm{Tr} A^N$ (assuming the lattice to be wrapped on a torus). As usual, $Z = \lambda^N$, where λ is the largest eigenvalue of A.

In general, a state φ' differs from φ by the replacement of certain "up" arrows by "down" arrows, namely, a +− exchange, or the reverse, which is a −+ exchange. A little reflection yields the following matrix elements for $A(\varphi, \varphi')$: (i) $A(\varphi, \varphi) = 2$; (ii) for $\varphi \neq \varphi'$, $A(\varphi, \varphi') = 1$ if there is a +− exchange between every pair of −+ exchanges, and vice versa; and (iii) $A(\varphi, \varphi') = 0$, otherwise. If we regard a state φ as a state of N spin-$\frac{1}{2}$ particles on a line, then the above rule is equivalent to $A = A_L + A_R$, where

$$A_L = 1 + \sum_{i<j} S_i^- S_j^+ + \sum_{i<j<k<l} S_i^- S_j^+ S_k^- S_l^+ + \cdots + (S_1^- S_2^+ \cdots S_{N-1}^- S_N^+)$$

(assuming N is even) and $A_R = A_L^+$. Since $S^z = \sum_1^N S_i^z$ is a constant, we must decide which S^z subspace has the largest eigenvalue. It can be shown, as expected, that $S^z = 0$ has the largest.

If ψ is an eigenvector of A, let $f(x_1, \cdots, x_n)$ be the amplitude in ψ of the state with up arrows (spins) at the sites $x_1 < x_2 < \cdots < x_n$ (we are interested in $n = \frac{1}{2}N$). Further reflection shows that f satisfies

$$\lambda f(x_1, \cdots, x_n) = \sum_{y_1=1}^{x_1} \sum_{y_2=x_1}^{x_2} \cdots \sum_{y_n=x_{n-1}}^{x_n} f(y_1, \cdots, y_n) + \sum_{y_1=x_1}^{x_2} \sum_{y_2=x_2}^{x_3} \cdots \sum_{y_n=x_n}^{N} f(y_1, \cdots, y_n). \tag{1}$$

On the right-hand side of (1) it is to be understood that f is replaced by zero if any $y_i = y_{i+1}$ (e.g., $y_2 = y_1 = x_1$).

We make the following <u>Ansatz</u> for f: Let $\{k\} = k_1, \cdots, k_n$ be a set of distinct numbers and let

$$f(x_1, \cdots, x_n) = \sum_P ! A(P) \exp\{i \sum_{i=1}^n k_{P(i)} x_i\}, \tag{2}$$

where the sum is on $n!$ permutations and $A(P)$ is some set of $n!$ coefficients. Now, if we insert a given plane wave $\exp\{i \sum k_i x_i\}$ into the first sum in (1), we get (assuming no $k_i = 0$)

$$\{\Pi_j [1 - \exp(ik_j)]^{-1}\} [e^{ik_1} - e^{ik_1(x_1+1)}] [e^{ik_2 x_1} - e^{ik_2(x_2+1)}] \cdots \{\exp[ik_n x_{n-1}] - \exp[ik_n(x_n+1)]\}. \tag{3}$$

Expanding the above product gives 2^n terms. One of these is proportional to the same plane wave we started with and is desirable. All the others are unwanted because one or more x_i's fail to appear.

The situation is saved, however, because we are obliged to subtract from (3) those terms in (1) for which $y_i = y_{i+1} = x_i$, and these have the same character as the unwanted terms. A similar situation obtains for the second sum in (1).

By choosing the $A(P)$ correctly we can eliminate all the unwanted terms. The rule (which can be proved by induction) is this: If P and Q are two permutations which differ only in the jth and $(j+1)$th position, then

$$A(P) = A(Q)B(k,q), \tag{4}$$

where $k_{P(j)} = k_{Q(j+1)} = k$ and $k_{P(j+1)} = k_{Q(j)} = q$, and where

$$B(k,q) = -[1 + T(k)T(q) - T(k)][1 + T(k)T(q) - T(q)]^{-1}$$

with $T(k) = \exp(ik)$. Finally, periodicity comes in through the n conditions

$$\exp(ik_i n) = \prod_{j \neq i} B(k_i, k_j). \tag{5}$$

The eigenvalue, λ, is the coefficient of the wanted term from A_L and A_R, namely,

$$\lambda = \{\prod_{j=1}^{n} (1 - \exp ik_j)^{-1}\}\{1 + \exp(i \sum_1^n k_j)\}. \tag{6}$$

It will be recognized that our wave function as defined by (4) and (5) is exactly the same as that for the anisotropic one-dimensional Heisenberg model[7]:

$$H = -\sum_{i=1}^{N} S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \tfrac{1}{2} S_i^z S_{i+1}^z. \tag{7}$$

Our eigenvalue (6) is different, however. For n even, the solution to (5) is such that no $k = 0$ and thus our previous analysis is correct. Furthermore, the maximum eigenstate of the transfer matrix and the ground state of (7) are identical because both are characterized by the fact that $f(x_1, \cdots, x_n) > 0$. For this state,

$$\sum_{j=1}^{n} k_j = 0.$$

As $N \to \infty$ one introduces a density function $\rho(k)$ for the k's. This function satisfies an integral equation which, fortunately, can be solved exactly for $S^z = 0$. All the details are in Ref. 7 where it is shown that in terms of a new variable α defined by $e^{ik} = (e^{i\mu} - e^{\alpha})(e^{i\mu+\alpha} - 1)^{-1}$ (with $\cos\mu = -\frac{1}{2}$), the density function is given by $R(\alpha) = [4\mu \cosh(\pi\alpha/2\mu)]^{-1}$.

Thus, we have

$$\begin{aligned} N^{-1} 2 \ln\lambda &= -\int dk\, \rho(k) \ln(2 - 2\cos k), \\ &= -\frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{3\,d\alpha}{4\cosh(3\alpha/4)} \ln\left(1 - \frac{3}{1 + 2\cosh\alpha}\right), \\ &= 3\ln(\tfrac{4}{3}). \end{aligned}$$

Therefore, $W = \lambda^{1/N} = (\frac{4}{3})^{3/2}$.

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