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A Class of Energy Levels for the Heisenberg Linear Chain. II. Levels near the Antiferromagnetic Ground State.

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Abstract

The distribution of "unbound" states in the Bethe formalism for the linear chain of spin $\frac{1}{2}$ atoms with a Heisenberg exchange interaction between nearest neighbors is investigated in the vicinity of the antiferromagnetic ground state, utilizing the spin wave states discovered by des Cloizeaux and Pearson. An upper bound is obtained for the free energy of the antiferromagnetic chain at very low temperatures. Plausible arguments are presented to show that the "unbound" states actually make a negligible contribution to the partition function of an infinite chain, at least in the absence of a magnetic field.

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I. Introduction.

The Hamiltonian

$$\mathcal{H} = 2J \sum_{i=1}^{N} \underset{\sim}{S}_i \cdot \underset{\sim}{S}_{i+1} \qquad (1)$$

$$\underset{\sim}{S}_{N+1} \equiv \underset{\sim}{S}_1$$

for a linear chain of spin $\frac{1}{2}$ atoms closed upon itself ($\underset{\sim}{S}_1$ is the spin operator for the i'th atom and J the "exchange integral") has been the subject of several investigations. The entire spectrum for a few fairly short chains (up to N=10 or 11) has been calculated by Orbach[1], Bonner and Fisher[2], and the author[3]. For the infinite chain very little is known about the distribution of levels lying between the ferromagnetic ($J < 0$) ground state and the antiferromagnetic ($J > 0$) ground state. The energy of the latter was calculated by Hulthén[4] using a formalism due to Bethe[5].

In a previous report[6], hereafter referred to as CELI, we derived the maximum and minimum energies as a function of the total spin of the state, S, for levels belonging to the class C of "unbound states" in the Bethe formalism. (For a brief summary of Bethe's procedure and a precise definition of class C, see CELI, Sec. II.) Recently, des Cloizeaux and Pearson[7] have calculated the energies of the lowest lying states in the antiferromagnetic chain as a function of wave vector q. These "spin wave" states, as well as the ground state, belong to class C. The present report is an extension of des Cloizeaux and Pearson's work to a detailed study of the distribution of levels in class C near the antiferromagnetic ground state.

When we began the calculation, we hoped to derive the low temperature properties of the chain using only states in class C. This category contains

a small fraction[8] of all the states ($2^{0.694N}$ vs a total of 2^N), but a sufficient number to yield a free energy proportional to N. Furthermore, some of the lowest levels of the antiferromagnetic chain belong to C. However, our calculations lead to the conclusion that, in the absence of a magnetic field (and in the limit of an infinite chain), the thermal properties are determined entirely by the levels in class B, the complement of C, at all temperatures.

This essentially negative conclusion is reached via two routes. Section VII contains the direct route: a very plausible argument based upon magnetic susceptibility. The more leisurely route begins in Section II with an "educated guess" for the energy of the chain at low temperatures, which is compared with the usual spin-wave theory. Section III begins the discussion of class C with an extension of des Cloizeaux and Pearson's results to states containing several spin waves. The free energy for the modified spin-wave theory thus obtained is calculated in Section IV and shows fair (though spurious!) agreement with the results of Section II.

An unsatisfactory feature of spin waves--the introduction of spurious states--is remedied in Section V. Several independent checks indicate that the "balls in pockets" model there introduced provides a very good approximation to the lowest levels in class C. By means of the model, the contribution of states in class C to the total partition function at low temperatures is estimated in Section VI. The resulting upper bound on the free energy (lower bound on its absolute value) is definitely in excess of the estimate in Section II, but may still be useful for some purposes. Section VIII contains a summary of our conclusions.

II. Low Temperature Properties from Finite Chains

For short chains the various thermal properties may be obtained by inserting the eigenvalues of the Hamiltonian (1) (obtained by use of a high speed computer) into a partition function

$$Z = Trace\left(e^{-\mathcal{H}/kT}\right) \tag{2}$$

Bonner and Fisher[2] calculated the energy and magnetic susceptibility for N=2, 3, . . ., 11; the results for N=2, 3, . . ., 10 were also obtained by the author.[3] We are much indebted to Dr. Fisher for sending us his results for the case N=11 prior to publication, and we have made use of these in Figs. 1, 2, and 5.

The calculated thermodynamic quantities for finite chains show a very regular behavior as a function of N. If the regularities present for $N \leq 11$ persist for $N > 11$, the calculations provide: 1. Very good estimates for energy, entropy, and magnetic susceptibility at temperatures above J/k. 2. Upper and lower bounds for the same quantities at all temperatures.

The energy U of the linear antiferromagnetic chain varies as T^2 at low temperatures according to the usual spin-wave theory.[9] Let us assume, more generally, the behavior:

$$U = \alpha T^n \tag{3}$$

with α and n to be determined by calculations on finite chains.

The corresponding entropy is:

$$S/k = n\alpha T^{n-1}/(n-1) \tag{4}$$

We shall henceforth assume that all extensive thermodynamic variables have been normalized by dividing them by the number of spins in the chain.

In Fig. 1, energy (measured from the exact ground state of the infinite chain) is plotted as a function of entropy for chains containing 10 and 11 atoms. Note that for N odd the ground state is degenerate and hence the entropy is not zero at zero temperature. The energy vs. entropy curve for N=8 (not shown in Fig. 1) lies below the curve for N=10, that for N=6 below that for N=8, etc. The curve for N=9 lies above the curve for N=11, that for N=7 above that for N=9, etc. These regularities suggest that the energy vs. entropy curve for an infinite chain lies between the curves for N=10 and 11.

The dotted curve in Fig. 1 represents the function

$$U/J = 1.19\,(S/k)^{1.9} \tag{5}$$

Curves with the exponent in (5) equal to 1.8 or 2.0 which pass midway between the N=10 and 11 curves at S/k=.20 in Fig. 1 are definitely low and high, respectively, at S/k=.30. Let T, the normalized temperature, be equal to kT/J. The estimates

$$\begin{aligned} U/J &= .21\,T^{2.1} \\ S/k &= .40\,T^{1.1} \end{aligned} \tag{6}$$

follow immediately from (3), (4), (5) and provide an "educated guess" for

the low temperature behavior of these quantities.

Fig. 2 shows the energy as a function of temperature for chains containing 10 and 11 spins. The dotted curve is a plot of Eq. (6). The curve for N=8 (not shown) lies below that for N=10; the curve for N=9 above that for N=11, etc. This suggests that the energy for an infinite chain should lie between the curves N=10 and 11.

Eq. (6) shows surprisingly good agreement with the T^2 dependence for the energy predicted by spin-wave theory. We do not regard the difference in exponents--2.1 instead of 2--as very significant, since (6) has been obtained by extrapolating results which are less precise as the temperature decreases. The calculations in Section VI below indicate that if (3) is the correct asymptotic form for the energy, the exponent n must be less than or equal to 2. Hence it seems likely that the $T^{2.1}$ behavior predicted by (6) is gradually replaced by a T^2 behavior for very low temperatures. The following values for energy, entropy, and free energy are then not unreasonable

$$U/J \approx .18\,\tau^2$$

$$S/k \approx .36\,\tau$$

$$F/J \approx -.18\,\tau^2 \qquad (7)$$

The coefficients have been chosen to make the energy predicted by (6) and (7) approximately equal in the vicinity of $\tau = .2$ or .3. It should be emphasized that (7) represents an educated guess, and the values must be used with caution. Nevertheless, it appears that the prediction of spin-wave

theory[9] for the coefficient of τ^2 in the expression for the energy at low temperatures, $\pi/6 = .52$, is definitely too large by a factor of 2 or 3. This is borne out by Figs. 1 and 2 which show the spin-wave predictions for energy as a function of entropy and temperature.

III. Spin-Wave Model for Class C.

In Bethe's[5] formalism, an eigenstate of the Hamiltonian (1) with total spin S and wave number q is associated with a set of $\frac{1}{2}N-S$ integers λ_j satisfying

$$0 < \lambda_j < N \tag{8}$$

$$q = 2\pi m / N \tag{9}$$

where

$$m = \sum_j \lambda_j \pmod N \tag{10}$$

The class C contains "unbound" states which correspond to sets of integers, no two of which differ by less than 2; all other states are in class B. (For a more detailed discussion, see CELI, Section II.) The ground state[4] (S=0) corresponds to the set of integers

1, 3, 5, . . ., N-1.

Recently des Cloizeaux and Pearson[7] have shown that the lowest excited state (S=1) of wave number q corresponds to the set:

$$\begin{aligned} &1,3,5,\ldots,(N-2m-1),\ (N-2m+2),\ (N-2m+4),\ldots,\ (N-2) \quad \text{for } q > 0 \\ &2,4,6,\ldots,(2|m|-2),\ (2|m|+1),\ (2|m|+3),\ldots,\ (N-1) \quad \text{for } q < 0 \end{aligned} \tag{11}$$

where q and m are related by (9). The energy of the state (11) minus

the energy of the ground state is:[10]

$$E_q = \pi J |\sin q| \qquad (12)$$

provided N is large.

Fig. 3 illustrates the nature of the sets $\{\lambda_j\}$ for N=16. Each row corresponds to one eigenstate of the chain. When some λ is equal to an integer k, a box is placed in the k'th column. Columns in which no box appears contain dots or "spacers." Each pair of boxes is separated by at least one spacer for states belonging to class C. State A is the ground state. State B, the lowest excited state for m=3 (or q=3(2π/16)), may be produced from A by inserting a spacer in column 11 and displacing the pattern in columns 11 to 15 one step to the right, discarding the portion displaced to the right of column 15. An anlogous procedure results in state D, the lowest excited state for m=-3.

If one inserts an additional spacer in column 7 of state D and shifts the pattern in columns 1 to 7 one step to the left, the resulting state E corresponds to two "spin waves" with m=-3. The second spin wave also corresponds to m=-3 (and not, for example, m=-4) because <u>three</u> boxes were shifted to the left when the spacer was added in column 7. See Eq. (10). States with several spin waves are obtained by repeating the procedure just described.

The energy of a state containing two spin waves is equal to the sum of the energies of the corresponding single spin-wave states (given by (12)), plus a correction term of order 1/N. An analogous result holds for

a state containing several spin waves, provided the total number is small compared to N. Consider, for example, a state with two spin waves and assume the wave numbers q_1 and q_2 are both negative. Eq. (19) of reference 7 is replaced by:

$$\lambda(x) = x + \frac{1}{N}\left[\Theta\left(\frac{2}{N} - x\right) - \Theta\left(\frac{|q_1|}{\pi} - x\right) - \Theta\left(\frac{|q_1|}{\pi} + \frac{2}{N} - x\right)\right] \qquad (13)$$

The reader may verify that des Cloizeaux and Pearson's procedure applied to the modified $\lambda(x)$ in (13) yields the result stated above.

States produced from different combinations of spin waves are not necessarily independent. With reference to Fig. 3 suppose that, starting from the ground state we add one spin wave with m=8 (state F) and another with m=5. The end result, state G, is identical to state D, which contains a single spin wave with m=-3. A little reflection shows that, in fact, all states in class C may be produced by superimposing only spin waves of positive (or, if one prefers, negative) q. Roughly speaking, we can produce a state with q negative by superimposing two states of positive q, one of which has wave number nearly equal to π.

From this point on we shall restrict our considerations to spin waves with positive q. Even such states need not be independent. State H in Fig. 3, for example, may be thought of as composed of either two spin waves with m=1 and one with m=2, or four spin waves with m=1. However, if there are only a few spin waves present, there is an approximate agreement between the number of spin-wave states and the number of states in class C, as we now show.

The number of states in class C with a given total spin S, corresponding to $\frac{1}{2}N$-S non-zero λ values, is given by:[8]

$$n(S) = (2S+1)\binom{\frac{1}{2}N+S}{2S} \tag{14}$$

States with one or two spin waves present are specified by $\frac{1}{2}N$-1 non-zero λ's and hence correspond to S=1; states with three or four spin waves to S=2, etc. For a given S the number of spin-wave states is thus:

$$\bar{n}(S) = f(2S) + f(2S-1) \tag{15}$$

where

$$f(b) = \binom{\frac{1}{2}N+b-1}{b} \tag{16}$$

is the number of states containing b spin waves, assuming the spin waves obey Bose statistics.

Let $S=\frac{1}{2}\rho N$. One obtains by use of Stirling's approximation:

$$\begin{aligned} \log n(S) &= \rho N\left[1 - \log 2\rho + O(\rho^2)\right] + O(\log N) \\ \log \bar{n}(S) &= \rho N\left[1 - \log 2\rho + \rho + O(\rho^2)\right] + O(\log N) \end{aligned} \tag{17}$$

Eq. (17) shows in what sense n(S) and $\bar{n}$(S) are "approximately equal" for small values of S.[11]

IV. Partition Function for Class C: Spin-Wave Model

One can estimate the contribution of states in class C to the total partition function using the spin-wave approximation developed in Section III. Before doing so we make a slight digression to discuss the significance of such a calculation. The partition function for the antiferromagnetic chain,

$$Z = \sum_n e^{-\beta E_n} \tag{18}$$

where $\beta = 1/kT$ and the E_n are the energy levels of the chain, may be written as

$$Z = Z_B + Z_C \tag{19}$$

where Z_B is that part of Z which comes from a sum over states in class B, and Z_C that part coming from a sum over states in class C. The total number of states in class C[8] is very much less than the total number of states for the chain. On the other hand, as noted above, certain states in class C are lower in energy than the corresponding states in class B, and hence it is not immediately evident whether or not Z_C makes a significant contribution to the total partition function Z.

The free energy (per spin) for the chain is given by:

$$F = -(N\beta)^{-1} \log Z \tag{20}$$

Define:

$$F_c = -(N\beta)^{-1} \log Z_c \tag{21}$$

Clearly,

$$F_c \geq F \tag{22}$$

or, in other words, F_C provides an upper bound on the free energy. Under certain circumstances, F_C might be equal to F in the limit of large N; for example, if there were a constant μ independent of N such that

$$Z_c / Z \geq \mu > 0$$

as N becomes infinite. In the remainder of this report we shall occasionally use F_C as a convenient measure for the magnitude of Z_C, and refer to it loosely as the "free energy."

Let us calculate F_C using the spin-wave approximation. The problem is merely that of obtaining the free energy for a set of N/2 uncoupled harmonic oscillators with energies given by Eq. (12);[12] hence

$$F_c = (\pi\beta)^{-1} \int_0^{\pi/2} \log\left[1 - \exp(-\pi\beta J \sin q)\right] dq \tag{23}$$

Let the normalized temperature τ be equal to $(\beta J)^{-1}$. Then for small τ the asymptotic value of (23) is:

$$F_c / J \sim -\tau^2/6 \tag{24}$$

At $\tau = .6$, Eq. (24) gives $F_C/J = -.06$, whereas numerical integration of (23) yields $-.062$. At lower temperatures the asymptotic estimate is even better.

The coefficient of T^2 in (24) is somewhat less, in absolute magnitude, than the coefficient in (7). However, as we shall show in Section VI, the spin-wave approximation actually leads to a significant overestimate of the contribution of states in class C to the partition function, and hence even the approximate agreement between (24) and (7) is spurious.

V. "Balls in Pockets" Model for Class C

The spin-wave approximation to the states in class C, discussed in Sections III and IV, suffers from at least one serious defect: the introduction of spurious states. It is true that if the number of spin waves is small the "overcounting" is not large; this is shown by Eq. (17). Nevertheless, one suspects that the most serious overcounting occurs for states in which the spin waves all have low energies, and these states, of course, make an important contribution to the partition function at low temperatures. We introduce the following model to avoid overcounting.

Consider a potential

$$V(x) = -2\pi J \sin x \tag{25}$$

for x between 0 and π. Let the interval from $\pi/2N$ to $\pi(1-1/2N)$ be divided into N-1 equal subintervals or "pockets," as shown in Fig. 4 for the case N=16. Some of the pockets contain balls, which correspond to the boxes of Section III and Fig. 3. Each set of m λ's for a state in class C corresponds in an obvious manner to a distribution of m balls in pockets satisfying the two rules: 1. Each pocket is empty or contains one ball. 2. Two adjacent pockets cannot both contain balls.

A ball in a pocket centered at x shall have a potential energy $V(x)$, and we define the energy of a state to be the total potential energy of the corresponding distribution of balls in pockets. The ground state of the system (illustrated in Fig. 4 for N=16), for which N/2 pockets are filled, has the energy

$$E_0 = -2JN \tag{26}$$

if N is large.

A state in class C characterized by $r = \frac{1}{2}N - S$ λ values has a degeneracy 2S+1, whereas it corresponds to a single state in our model. However, the factor 2S+1 is of no consequence in computing the partition function in zero magnetic field (see the appendix for further remarks) and hence, for this purpose, the model provides essentially exact counting of states.

The separation between the highest and lowest energy states in our "balls in pockets" model is 2JN, whereas in class C (which contains both the highest and the lowest levels of the linear chain) it is 1.386 JN. Thus the spectrum of the model cannot coincide exactly with the spectrum of class C. Nevertheless, the model appears to give a good approximation for the low-lying levels in class C, as we shall now show.

In the first place, as the reader may verify, the model correctly reproduces the energies (see Eq. (12)) of the single spin-wave states discussed by des Cloizeaux and Pearson;[7] in fact, the potential (25) was chosen for just this reason. Similarly, for a state where only a few spin waves are present, the model shows the approximate additivity of spin-wave energies discussed in Section III.

In addition, certain other energy levels in our model can be compared with exact calculations for the corresponding states in class C. For this purpose it is convenient to introduce the abbreviation

$$\rho_1 = S/N \tag{26a}$$

We shall be interested in states near the antiferromagnetic ground state; i.e., those for which ρ_1 is small.

Consider the state with the lowest energy for a given ρ_1: the pockets are empty for $0 \le x \le \pi\rho_1$ and $\pi(1-\rho_1) \le x \le \pi$, whereas in the interval $\pi\rho_1 \le x \le \pi(1-\rho_1)$ every other pocket contains a ball. (Compare this with CELI, (16)). Our model predicts an energy:

$$E = 2NJ\left[1 - \cos(\pi\rho_1)\right] + E_0 \tag{27}$$

or, for small values of ρ_1,

$$E - E_0 \sim NJ\pi^2\rho_1^2 \tag{28}$$

The exact energy for the corresponding state in class C (see CELI, Fig. 1) lies below the prediction (27) for finite ρ_1; the asymptotic formula (28) is, however, correct, at least to within .5 per cent. See CELI, Eq. (51).[13]

For a given ρ_1, the state with maximum energy in the model corresponds to empty pockets in the interval $\pi(\frac{1}{2}-\rho_1) \le x \le \pi(\frac{1}{2}+\rho_1)$, whereas in the rest of the interval every other pocket contains a ball. (Compare this with CELI (18).) The model predicts an energy:

$$E = 2NJ\sin(\pi\rho_1) + E_0 \tag{29}$$

and for small ρ_1:

$$E - E_0 \sim 2\pi NJ\rho_1 \tag{30}$$

Again, the exact energy for the corresponding state in class C (see CELI, Fig. 1) lies below the prediction (29); but the asymptotic formula (30)

is correct. See CELI, Eq. (58).

A "uniform density" state shall be one in which for every interval $b \leq x \leq d$ such that $d-b \gg 1/N$, a total of $(d-b)\rho N/\pi$ pockets contain balls. The "density" ρ is equal to $\frac{1}{2}$ for the ground state (in which every other pocket is filled) and the quantity ρ_1 is equal to $\frac{1}{2}-\rho$. For such states our model predicts an energy:

$$E = 4NJ\rho_1 + E_0 \tag{31}$$

The exact energy for the corresponding state in class C is easily obtained by a straightforward modification of the Hulthén integral equation, (III.35) in reference 2, with the result:

$$E - E_0 = 2NJ \log(1+2\rho_1) \tag{32}$$

Clearly (31) is larger than (32) for finite ρ_1, and asymptotically equal to (32) as ρ_1 goes to zero.

On the basis of the three categories of states discussed above--minimum energy, maximum energy, and "uniform density"--it is tempting to speculate that for any given state the balls-in-pockets model always yields an energy higher than the exact energy. Of this we have no proof. In any case, the fact that the model gives the correct asymptotic form for the energy when ρ_1 is small, for all three categories, as well as for the des Cloizeaux and Pearson spin waves, gives one confidence that it provides a good description of the energy level structure of class C near the antiferromagnetic ground state.

VI. Partition Function for Class C: Balls-in-Pockets Model

The balls-in-pockets model discussed in Section V appears to provide a good approximation to the low-lying energy levels of class C. In this section we shall use the model to estimate the contribution of the levels in class C to the total partition function of the antiferromagnetic chain. The problem becomes that of computing the partition function for a system of balls in pockets, as shown in Fig. 4, subject to rules 1 and 2 of Section V and with a potential energy given by Eq. (25).

One approach, motivated by a procedure used with the Ising linear chain,[14] is as follows. Let the pockets be numbered consecutively from 1 to N-1 and denote the state of the i'th pocket by an index:

$$p_i = \begin{cases} 0 \text{ if the pocket is empty.} \\ 1 \text{ if the pocket contains a ball.} \end{cases}$$

The energy of a state shall be set equal to:

$$E = \sum_{i=1}^{N-2} E(p_i, p_{i+1}) + p_{N-1} V(x_{N-1}) \tag{33}$$

where

$$E(p_i, p_{i+1}) = p_i V(x_i) + f(p_i, p_{i+1})$$
$$f(0,0) = f(0,1) = f(1,0) = 0$$
$$f(1,1) = +\infty$$
$$x_i = \tilde{\pi} i / N \tag{34}$$

A state for which two adjacent pockets both contain balls will have an

infinite energy due to the function f and therefore will not contribute to the partition function. The partition function for the model, Z_M, is given by:

$$Z_M = \sum_{P_1=0}^{1} \sum_{P_2} \cdots \sum_{P_{N-1}} \exp\left\{-\beta\left[\sum_{i=1}^{N-2} E(P_i, P_{i+1}) + P_{N-1} V(x_{N-1})\right]\right\} \quad (35)$$

where $\beta = 1/kT$.

Let $Q^{(i)}$ be a 2 x 2 matrix with rows and columns labeled by the indices p_i and p_{i+1}, respectively:

$$Q^{(i)} = \begin{pmatrix} 1 & 1 \\ \mu_i & 0 \end{pmatrix} \quad (36)$$

where

$$\mu_i = \exp\left[-\beta V(x_i)\right] . \quad (37)$$

Let T be the column vector

$$T = \begin{pmatrix} 1 \\ \exp\left[-\beta V(x_{N-1})\right] \end{pmatrix} . \quad (38)$$

Eq. (35) may now be rewritten as:

$$Z_M = \sum Q^{(1)} \cdot Q^{(2)} \cdots Q^{(N-2)} \cdot T \quad (39)$$

where the products are to be understood as matrix products and Σ denotes the sum of the two elements in the resulting column vector.

If the matrices $Q^{(i)}$ were all equal to the same matrix Q with eigenvalues of unequal magnitude, the evaluation of (39) would be straightforward. One could diagonalize Q by means of a similarity transformation:

$$Q = S D S^{-1}$$

$$D = \begin{pmatrix} \lambda & 0 \\ 0 & \nu \end{pmatrix} \qquad (40)$$

$$|\lambda| > |\nu|$$

The product of the $Q^{(i)}$ would be Q raised to the (N-2)nd power:

$$Q^{N-2} = S D^{N-2} S^{-1} \qquad (41)$$

But for large N, $|\lambda|^{N-2} \gg |\nu|^{N-2}$, and the partition function would be equal to the (N-2)nd power of the largest eigenvalue of Q, times a constant independent of N.

In our case, unfortunately, the matrices $Q^{(i)}$ depend on the index i. Nevertheless, the $Q^{(i)}$ are <u>nearly</u> constant for i restricted to a range $m \leq i \leq n$ where $n-m \ll N$. If N is very large we can also have $n-m \gg 1$. The considerations of the preceding paragraph then make it reasonable to assume that in the limit of large N the partition function (39) is equal to:

$$Z_M = B \prod_{i=1}^{N-2} \lambda_i \qquad (42)$$

where B is a constant independent of N and λ_i is the larger (in magnitude) of the two eigenvalues of $Q^{(i)}$.

We have given an intuitive justification for (42); in fact, it is not difficult to prove the result rigorously under certain restrictions (which the $Q^{(i)}$ satisfy) on the class of matrices involved. Since the proof is a bit detailed and adds no further insight into the problem, we shall not reproduce it here.

The largest eigenvalue of (36) is:

$$\lambda_i = \tfrac{1}{2} + \tfrac{1}{2}(1 + 4\mu_i)^{\frac{1}{2}} \tag{43}$$

whence

$$\log Z_M = \sum_{i=1}^{N-2} \log \tfrac{1}{2}\left[1 + (1 + 4\mu_i)^{\frac{1}{2}}\right]$$

$$\simeq \frac{2N}{\pi}\int_0^{\pi/2} \log \tfrac{1}{2}\left\{1 + \left[1 + 4\exp(2\pi\beta J \sin x)\right]^{\frac{1}{2}}\right\} dx \tag{44}$$

At this point it is convenient to introduce the renormalized partition function Z_m which differs from Z_M in that all energies are measured from the ground state of the model. Thus Z_m should provide, at low temperatures, a good approximation to Z_C, the contribution of states in class C to the partition function of the linear chain when energies are measured from the exact ground state. Using (26) we obtain immediately:

$$-N\beta F_c = \log Z_m = \log Z_M - 2\beta J N \tag{45}$$

which becomes for low temperatures (large β):[15]

$$\log Z_m \sim \frac{N}{2\pi^2 \beta J} \int_0^\infty \frac{y\,dy}{(1+4e^y)^{\frac{1}{2}}} = \frac{N}{10\,\beta J} \tag{46}$$

The normalized temperature τ is equal to $(\beta J)^{-1}$. For small τ the free energy (per spin) corresponding to (46) is:

$$F_c/J \sim -\tau^2/10 \tag{47}$$

The coefficient of τ^2 in (47) is significantly smaller (in magnitude) than the coefficient in (24). In our opinion the disagreement indicates that the overcounting of states in the spin-wave model used in Section IV leads to a significant error.

The quantity F_C, determined by numerical integration of (44), is plotted in Fig. 5 together with the free energies for short chains containing 10 and 11 spins. This figure together with the observation that the coefficient of τ^2 in (47) is only half the coefficient in (7) lends support to the conclusion that even at low temperatures the actual free energy of the antiferromagnetic linear chain, F, is strictly less than (in absolute magnitude strictly greater than) F_C. If this last inference is correct, the discussion at the beginning of Section IV allows us to conclude that Z_C makes a negligible contribution to the partition function as N becomes infinite. Further evidence for this result is found in Section VII.

VII. Class C and the Magnetic Susceptibility

In CELI, Section IV, we computed the magnetic susceptibility of the antiferromagnetic chain at T=0 utilizing only states in class C, and only a small fraction of such states. The method there employed cannot be extended to finite temperatures. In fact, by considering the contribution of the states in class C to the susceptibility at finite temperatures, one obtains rather conclusive evidence that Z_C is a negligible fraction of the total partition function for long chains.

The number of states in class C with total spin S is:[8]

$$n(S) = (2S+1)\binom{\frac{1}{2}N+S}{2S} \tag{48}$$

including the degeneracy factor 2S+1. Define:

$$\langle S\rangle_C = \left(\Sigma_C e^{-\beta E_n} S_n\right) / \left(\Sigma_C e^{-\beta E_n}\right) \tag{49}$$

where S_n is the total spin and E_n the energy of the n'th state, and the summation goes over all states in class C. The fact that n(S) is very sharply peaked around S=N/(2/5) leads one to suspect that

$$\langle S\rangle_C \propto N \tag{50}$$

On the other hand, the magnetic susceptibility (per spin) of the chain in the limit of zero magnetic field is given by

$$\chi = A\langle S^2\rangle / N \tag{51}$$

where A is a constant independent of N, and the angular brackets denote an average as in (49), but with summation extending over all energy levels of the chain. If $\langle S^2 \rangle$ in (51) were replaced by $\langle S^2 \rangle_C$, one would expect, on the basis of (50), to find $\chi \propto N$; i.e., an infinite susceptibility for a chain of infinite length.

The foregoing considerations may be made more precise as follows. The calculations in CELI, Section III (compare with Section V above) indicate that the energies of all states in class C with total spin S lie within the bounds:[13]

$$0 \leq E \leq 2\pi J S \tag{52}$$

For the considerations which follow, the weaker condition

$$0 \leq E \leq N f(S/N) \tag{53}$$

is sufficient, where f denotes any positive, continuous, monotone function of x such that f(0)=0.

Let us assume that in some temperature region there is a constant μ (independent of N) such that

$$Z_C / Z \geq \mu > 0 \tag{54}$$

where Z_C is the contribution of states in class C to the total partition function. Further assume that the susceptibility is finite in the same temperature region where (54) holds:

$$\chi \leq A_1 \tag{55}$$

where A_1 is a constant independent of N. We shall now show that the inequalities (53), (54), and (55) lead to the result that the free energy of the chain is constant, and therefore the entropy is equal to zero, in the temperature region for which (54) and (55) hold. Since this result is highly unlikely, we conclude that one of the three inequalities from which it is derived must be invalid. Of these three, the most likely to be at fault is (54). That is, it appears highly probable that the contribution of states in class C to the total partition function is negligible as N becomes infinite.

The proof of the result claimed in the preceding paragraph is obtained as follows. Since both the quantities

$$\sum_C S_n e^{-\beta E_n} \qquad \text{and} \qquad \sum_B S_n e^{-\beta E_n}$$

(where the second sum extends over all states in class B) are positive, the inequality (54) implies that

$$\langle S \rangle \geq \mu \langle S \rangle_C / (1+\mu) \tag{56}$$

From (51), (55), (56) and the fact that $\langle S^2 \rangle \geq \langle S \rangle^2$ it follows that

$$\langle S \rangle_C \leq A_2 N^{\frac{1}{2}} \tag{57}$$

where A_2 is independent of N. Define

$$T = 2 A_2 N^{\frac{1}{2}} \tag{58}$$

and let $\sum_C'$ and $\sum_C''$ denote sums over states for which S is less than T or

greater than T, respectively.

A consequence of these definitions and Eq. (49) is the inequality:

$$\langle S \rangle_c \geq T \left(\sum_c'' e^{-\beta E_n} \right) / \left(\sum_c' e^{-\beta E_n} + \sum_c'' e^{-\beta E_n} \right) \tag{59}$$

Then (57), (58), and (59) imply that

$$\sum_c' e^{-\beta E_n} \geq \sum_c'' e^{-\beta E_n} \tag{60}$$

or

$$\sum_c' e^{-\beta E_n} \leq Z_c \leq 2 \sum_c' e^{-\beta E_n} \tag{61}$$

Define n_o by:

$$n_o = \sum_{S=1}^{T} n(S) \tag{62}$$

Combining (53), (54), and (61) one obtains (note that Z_c has been replaced by Z):

$$-\beta f\left(\frac{T}{N}\right) + \frac{1}{N} \log n_o \leq \frac{1}{N} \log Z \leq \frac{1}{N} \log \frac{2}{\mu} + \frac{1}{N} \log n_o \tag{63}$$

We may make a crude estimate:

$$1 \leq n_o \leq N\, n(T) \tag{64}$$

By use of Stirling's approximation for n(T) and the inequalities (64), one may easily verify that (1/N) log n_o goes to zero as N becomes infinite. The inequalities (63) then imply that the free energy is identically zero in the limit of infinite N. This completes the proof.

VIII. Conclusion

The balls-in-pockets model introduced in Section IV appears to provide a very good description of the energy level structure in class C near the antiferromagnetic ground state. Unfortunately, this does not enable one to conclude very much about the low temperature thermal properties of the chain, because the partition function is dominated by the contributions from levels in class B. The upper bound on the free energy, (47), may not be entirely useless. For example, it rules out the possibility that

$$-F \propto T^{2.1} \tag{65}$$

at very low temperatures, a form suggested by Eq. (6).

Equations (47) and (7), taken together, indicate that

$$\lim_{N\to\infty} \frac{\log Z_c}{N} < \lim_{N\to\infty} \frac{\log Z}{N} \tag{66}$$

for $T > 0$. The calculations in Section VII, on the other hand, show that

$$\lim_{N\to\infty} \frac{Z_c}{Z} = 0 \tag{67}$$

for $T > 0$, on the basis of very plausible assumptions. Strictly speaking, the result (66) is stronger than (67). But the arguments leading to (66) are much more tenuous; in particular (7) is based on an extrapolation of results for short chains at temperatures on the order of $\frac{1}{2}J/k$ and above. In any case, the conclusion is the same: namely, an adequate discussion

of the thermal properties of the antiferromagnetic chain at low temperatures, if based upon the Bethe formalism, must take into account the "bound" states in class B.

Acknowledgments

Professor W. Kohn brought to my attention the work of des Cloizeaux and Pearson; I am also indebted to him for several helpful discussions. I wish to thank Dr. M. E. Fisher for sending me the results of calculations for a chain of 11 atoms prior to publication.

Appendix

In Sections V and VI we disregarded a certain difference in the counting between class C and the "balls-in-pockets" model. Associated with a single state in the model is a set of 2S+1 states in class C forming a single multiplet with total spin S. It is easy to show that this "counting error" has no effect upon the thermal properties in zero magnetic field.

Let Z_S be the contribution of states with a given total spin S to the partition function of the model. Thus the model partition function Z_m is given by:

$$Z_m = \sum_{S=0}^{N/2} Z_S \tag{A1}$$

If, on the other hand, we used the "correct" counting of levels, the partition function would be

$$Z_m' = \sum_{S=0}^{N/2} (2S+1)\, Z_S \tag{A2}$$

Clearly,

$$Z_m \leq Z_m' \leq (N+1)\, Z_m \tag{A3}$$

and hence

$$\lim_{N\to\infty} \frac{\log Z_m}{N} = \lim_{N\to\infty} \frac{\log Z_m'}{N} \tag{A4}$$

That is, in the limit of large N the free energy corresponding to Z_m' is identical with that corresponding to Z_m.

Figure Captions

Fig. 1. Energy vs. entropy for the antiferromagnetic chain. The solid curves are from calculations on finite chains; the dotted curve represents Eq. (5). The dot-dash curve is the prediction of spin-wave theory (reference 9).

Fig. 2. Energy vs. temperature for the antiferromagnetic chain. The solid curves are from calculations on finite chains; the dotted curve represents Eq. (6). The dot-dash curve is the spin-wave prediction (reference 9).

Fig. 3. Some sets of integers $\{\lambda_j\}$ for the case N=16 (see text).

Fig. 4. Balls-in-pockets model for N=16 (see text).

Fig. 5. Free energy vs. temperature for the antiferromagnetic chain. The dotted curve is F_C, determined by Eq. (44).

Footnotes

1. R. Orbach, Phys. Rev. 115, 1181 (1959).
2. J. C. Bonner and M. E. Fisher (to be published).
3. R. B. Griffiths (unpublished).
4. L. Hulthén, Arkiv Mat. Astron. Fysik 26A, No. 11 (1938).
5. H. Bethe, Z. Physik 71, 205 (1931).
6. R. B. Griffiths, "A Class of Energy Levels for the Heisenberg Linear Chain. I." (unpublished).
7. J. des Cloizeaux and J. J. Pearson, Phys. Rev. 128, 2131 (1962).
8. Reference 4, p. 46.
9. R. Kubo, Phys. Rev. 87, 568 (1952); J. Van Kranendonk and J. H. Van Vleck, Rev. Mod. Phys. 30, 1 (1958).
10. Note that the convention $J=\frac{1}{2}$ is employed in reference 7.
11. The excess of spin-wave states compared to true states in the theory of ferromagnetism is of the same order of magnitude.
12. As usual, we exclude from consideration the oscillators corresponding to $q=0$ or π, for which the energy is zero.
13. Note that the quantity ϵ_1 in CELI must be multiplied by $2JN$ to yield an actual energy. See CELI, Eq. (9).
14. G. F. Newell and E. W. Montroll, Rev. Mod. Phys. 25, 353 (1953).
15. Numerical evaluation of the integral in (46) shows that it is very close to $\pi^2/5$, but we have been unable to prove this result.

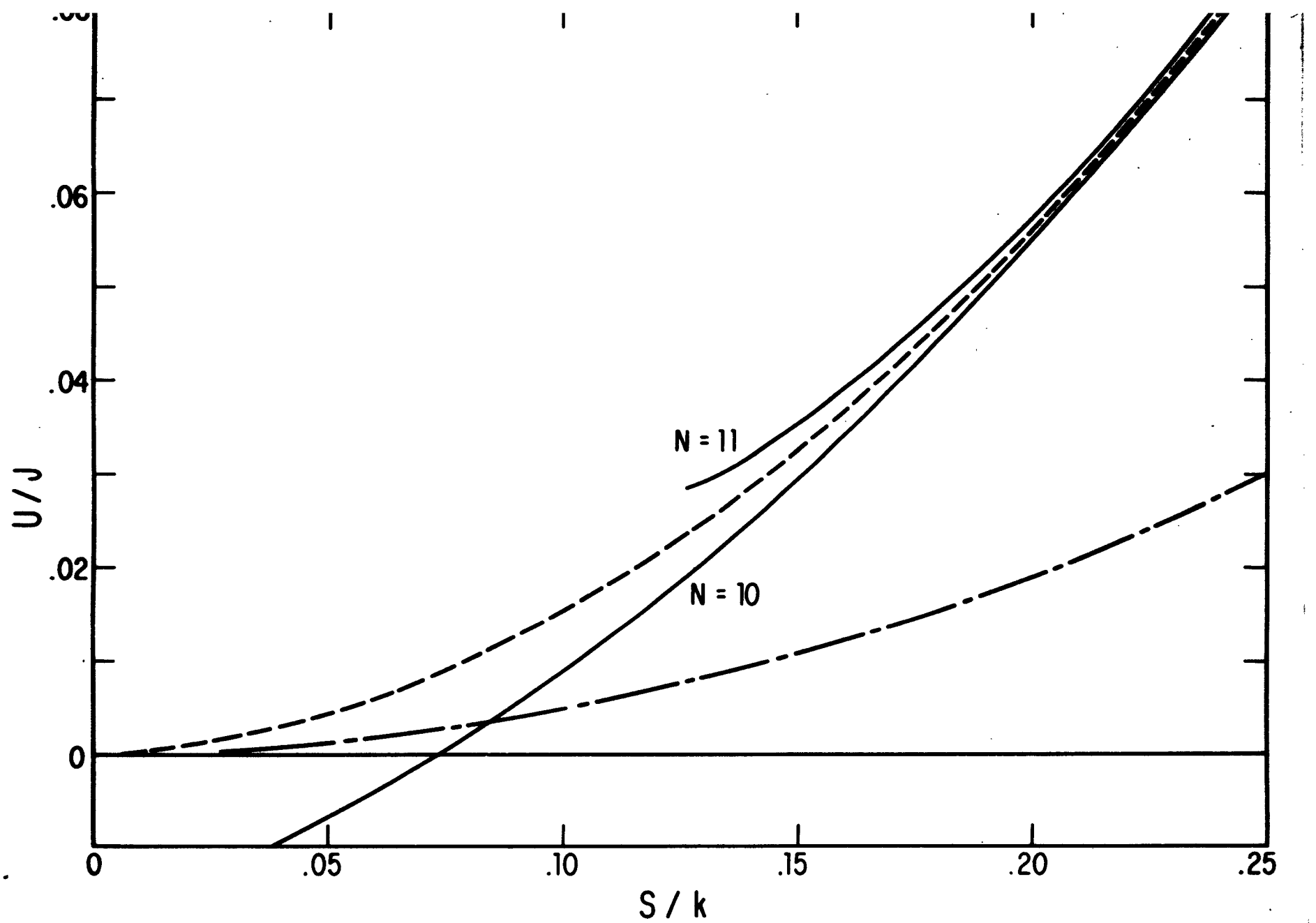

FIG. 1

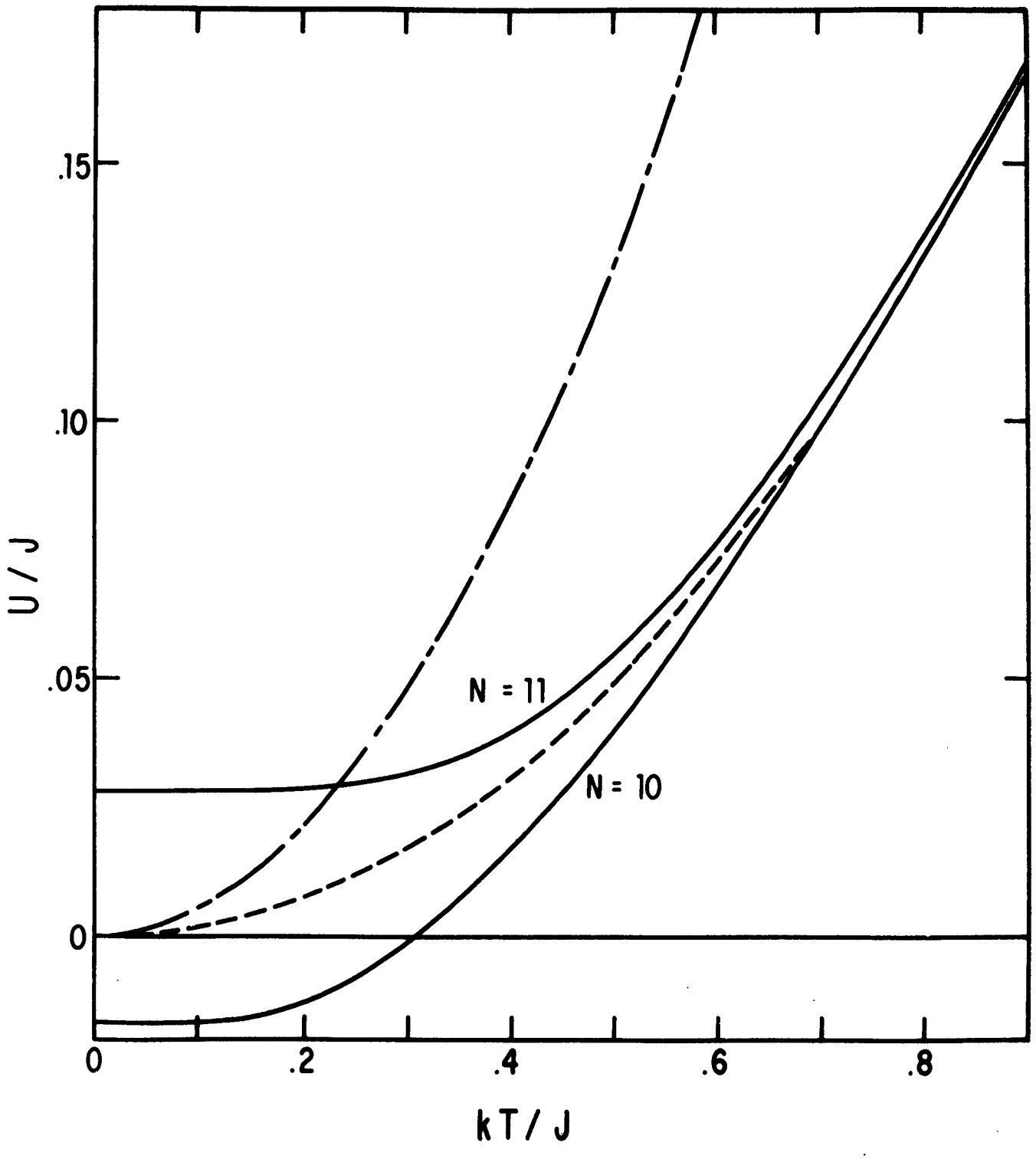

FIG. 2

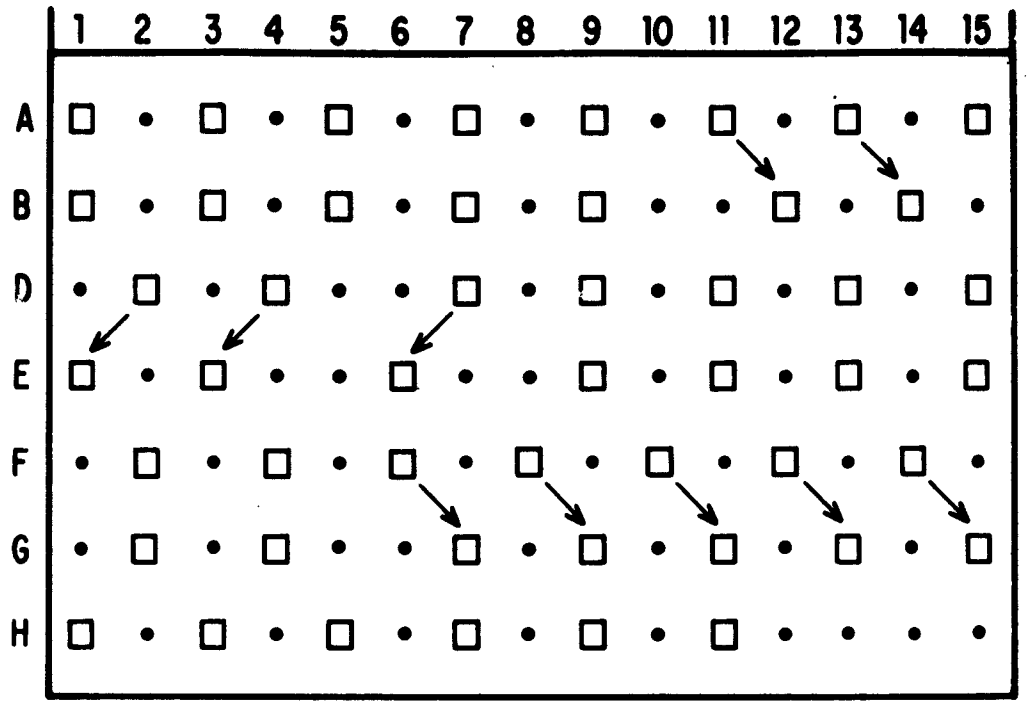

FIG. 3

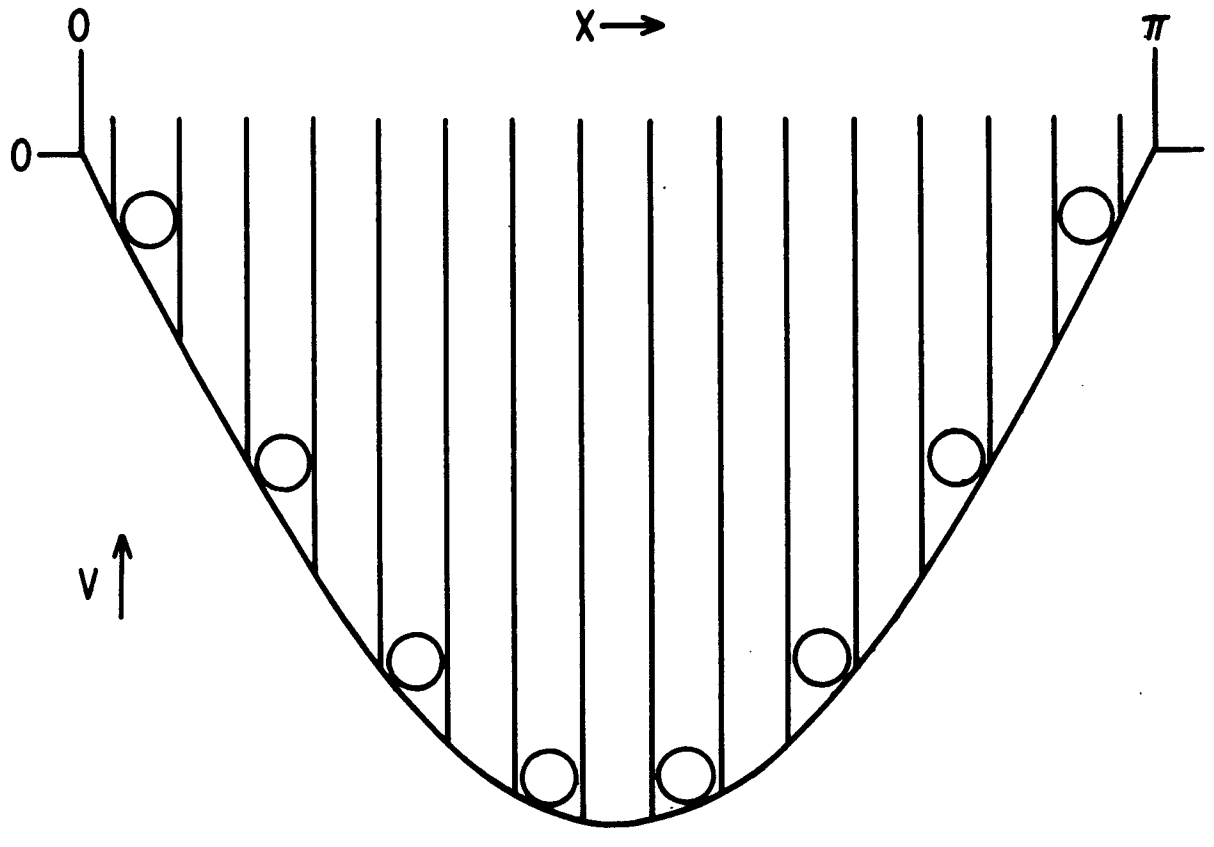

FIG. 4

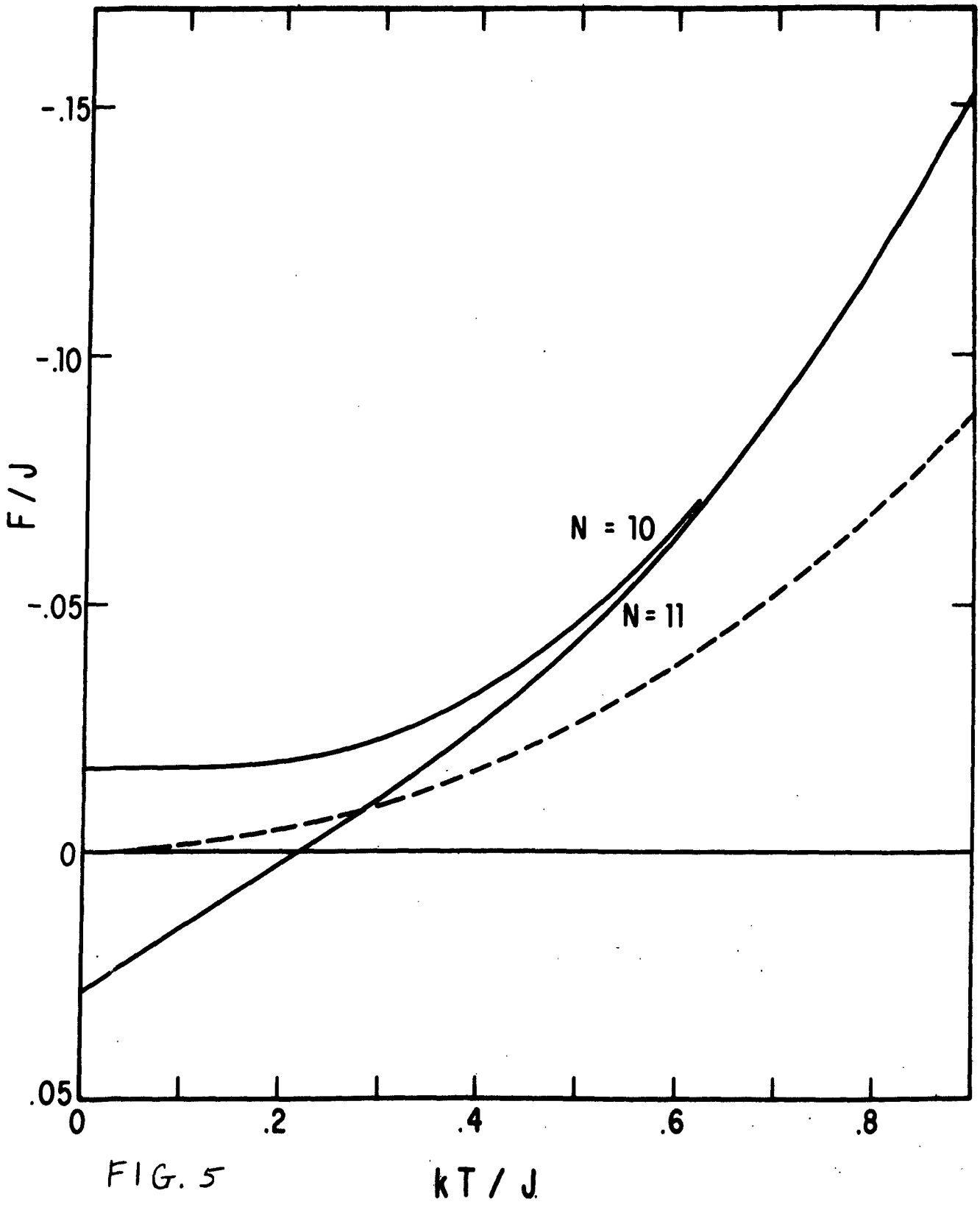

FIG. 5