Free Energy of the Antiferromagnetic Linear Chain*

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Rigorous upper and lower bounds for the free energy of the antiferromagnetic Heisenberg linear chain are obtained from general convexity properties of the free energy. The lower bound is here derived; the upper bound has been obtained previously by Bulaevskii. Both are compared with the calculations of Bonner and Fisher for finite chains.

FOR a linear chain of spin-$\frac{1}{2}$ atoms we define the Hermitian operators ($J>0$)

$$X=2J\sum_i S_i^x S_{i+1}^x,\quad Y=2J\sum_i S_i^y S_{i+1}^y,\tag{1}$$
$$Z=2J\sum_i S_i^z S_{i+1}^z,\quad M=\mu\sum_i S_i^z,$$

where $\mathbf{S}_i$ is the spin operator for the i'th atom with Cartesian components denoted by superscripts, and μ is the magnetic moment. Given a linear combination A of these operators, we are interested in the free energy

$$F(A,T)=-kT\ln\mathrm{Tr}[e^{-A/kT}],\tag{2}$$

(Tr stands for "trace") at a temperature T in the limit of an infinitely long chain.[1]

The free energy is known exactly for the Ising Hamiltonian[2]

$$\mathcal{H}_I=Z-HM,\tag{3}$$

where H is an external magnetic field, and for the transverse Hamiltonian[3]

$$\mathcal{H}_T=X+Y-HM,\tag{4}$$

but not for the Heisenberg Hamiltonian

$$\mathcal{H}_H=X+Y+Z-HM.\tag{5}$$

In this last case, however, the exact[4] ground-state energy[1] (in the limit of an infinite chain) has been computed for[5] $H=0$ and[6] $H\neq0$ (the latter yields the exact magnetization curve at zero temperature); also the exact[4] spectrum of the lowest lying excitations.[7] Numerical results for finite chains[8] of up to 11 spins provide good estimates of the thermodynamic quantities for $T>J/k$, and the extrapolations[8] of these results to low temperatures are fairly credible.

Bulaevskii[9] has calculated the free energy for (5) using a finite-temperature Hartree-Fock approximation. The result is a rigorous upper bound for the free energy. This may be seen as follows: Through a suitable transformation,[3] (4) may be expressed as the energy of a set of noninteracting fermions. In this representation define a density matrix ρ as the direct product of density matrices

$$\rho_k=\begin{pmatrix} n_k & 0\\ 0 & 1-n_k\end{pmatrix},\tag{6}$$

where n_k is the occupation number ($0\leq n_k\leq 1$) of the kth fermion mode. Bulaevskii minimizes

$$F_B(\rho)=\mathrm{Tr}[\rho\mathcal{H}_H]+T\,\mathrm{Tr}[\rho\ln\rho]\tag{7}$$

by varying the n_k. However, (7)[10] is a convex downwards function over the set of all density matrices ρ and achieves its minimum for the canonical density matrix[11] which yields the canonical free energy (2) with $\mathcal{H}_H$ in place of A. Therefore the free energy F_B obtained by Bulaevskii is never less than the exact result.

In fact (we shall not give the proof) F_B is just the free energy obtained by replacing Z in (5) by its diagonal part in the fermion representation in which (4) is diagonal. Peierls' theorem[12] then states that the result is greater than or equal to the exact free energy.

The theorems of Peierls[12] and Bogoliubov[13] are expressions of the following convexity[14] property of F as defined by (2): The inequality

$$F[\lambda A+(1-\lambda)B,\,T]\geq\lambda F(A,T)+(1-\lambda)F(B,T)\tag{8}$$

holds whenever A and B are Hermitian matrices of the same (finite) dimension and λ is a real number between 0 and 1. More generally, if for $i=1,2,\cdots,n$, A_i

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[1] Throughout this paper we use "energy" and "free energy" to denote the extensive thermodynamic quantities (see Ref. 14), that is, the portion of (2) which is proportional to the length of the chain for a very long chain.
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[4] There is no rigorous proof that these "exact" results are correct. See the discussion in Refs. 6 and 7.
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[11] This is an immediate consequence of the fact that the entropy $S(\rho)=-\mathrm{Tr}[\rho\ln\rho]$ is a convex-upwards function which achieves its maximum, subject to the constraint that the average energy, $\mathrm{Tr}[\rho\mathcal{H}_H]$, have a fixed value, for the canonical density matrix. See E. H. Wichmann, J. Math. Phys. **4**, 884 (1963).
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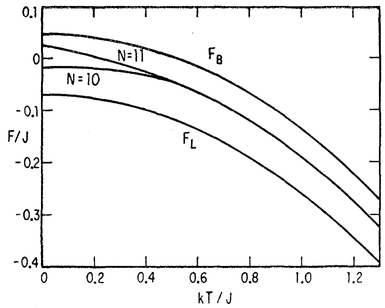

FIG. 1. Approximate values for the free energy of the antiferromagnetic linear chain. Energies are measured from the exact ground-state energy (Ref. 5).

are Hermitian matrices and α_i positive numbers with sum equal to 1, the result

$$F(\sum_i \alpha_i A_i,T)\geq\sum_i \alpha_i F(A_i,T) \quad (9)$$

follows from (8) by induction.

The Hamiltonian (5) with $H=0$ may be written in the form

$$X+Y+Z=\tfrac{1}{3}\{\tfrac{3}{2}X+\tfrac{3}{2}Y\} +\tfrac{1}{3}\{\tfrac{3}{2}Y+\tfrac{3}{2}Z\}+\tfrac{1}{3}\{\tfrac{3}{2}X+\tfrac{3}{2}Z\}. \quad (10)$$

By symmetry, the same free energy is associated with each term in curly brackets and hence we obtain by applying (9)

$$F(X+Y+Z,T)\geq F_L(T) =F(\tfrac{3}{2}X+\tfrac{3}{2}Y,\ T)=\tfrac{3}{2}F(X+Y,\ \tfrac{2}{3}T). \quad (11)$$

The right side involves only the transverse Hamiltonian for which the free energy is already known.[3]

Both F_B and F_L have been calculated as functions of temperature—the requisite integrals were evaluated numerically—and are plotted in Fig. 1 together with the values for closed chains containing $N=10$, 11 atoms.[8] There is evidence (but no proof) that the $N=10$, 11 results provide lower and upper bounds for the free energy of the infinite chain, and in this respect they are far superior to F_B and F_L at temperatures above $J/2k$.

Let S_B, S_L, and S_F be the entropies $(-dF/dT)$ per spin associated with F_B, F_L, and calculated by extrapolation[8] of the finite chain results, respectively. At low temperatures the asymptotic behavior is

$$S_B\sim 0.320k^2T/J,\quad S_L\sim 0.349k^2T/J,\quad S_F\sim 0.35k^2T/J. \quad (12)$$

The agreement among these results is quite remarkable: They all predict a linear behavior at low temperatures, and the numerical coefficients differ by only 10%. There is probably a certain similarity between the low-lying spectrum of $\mathcal{H}_H$ and $\mathcal{H}_T$, since the latter provides the starting point for calculations of both F_B and F_L. This may explain the relatively successful calculations[15] of the free energy of (5) treating Z as a perturbation.

At $T=0$, F_B and F_L provide, of course, upper and lower bounds for the ground-state energy of the infinite chain: $-0.839\,J$ and $-0.955\,J$, respectively. These may be compared with the rigorous upper and lower bounds given by Anderson[16]: $-0.500\,J$ and $-1.000\,J$; and with the exact[4,5] value: $-0.886\,J$.

A lower bound to $F(\mathcal{H}_H)$ with $H\neq 0$ is obtained by applying (8) to (5) written in the form

$$X+Y+Z-HM =\tfrac{1}{2}\{2X+2Y-HM\}+\tfrac{1}{2}\{2Z-HM\}. \quad (13)$$

[A better result might be obtained using a division analogous to (10); unfortunately, the free energy of the Hamiltonian $X+Z-HM$ is not yet known.] We have elsewhere[6] utilized this bound at zero temperature. It is not very useful for small magnetic fields, but becomes extremely good (at $T=0$) in large fields when the magnetization approaches saturation. Bulaevskii's estimate is also good[6] under the same conditions, and not unreasonable (though not as good) in small magnetic fields.

In conclusion we may emphasize that both the upper and lower bounds for the free energy are based upon the convexity property (8); the lower bound directly and the upper bound by way of Peierls' theorem. The convexity property is thus quite useful for approximate estimates as well as existence proofs.[14]

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