Variational Approaches to the Antiferromagnetic Linear Chain*

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Within the framework of a somewhat general free-energy variational calculation we find that a solution with an energy gap and spontaneous long-range order is favored. However, if on the basis of recent results one disallows the gap, then Bulaevskii's solution, without spontaneous long-range order, obtains. From Bulaevskii's coupled integral equations and the condition for maximum entropy with respect to variation of the external field h at fixed temperature θ, we obtain a pseudophase boundary in the h, θ plane. The analysis indicates that asymptotically along the boundary, $(2-h)/\theta \to$ positive constant as $\theta \to 0$, and $h/(\theta_0-\theta)^{1/2} \to$ positive constant as $\theta \to \theta_0$, where $(h=0, \theta=\theta_0)$ is the intersection of the boundary with the θ axis. Qualitatively similar behavior is displayed by the exactly soluble X-Y model for which the pseudophase boundary is also given here. The boundary curves are compared with one obtained for a finite chain by Bonner and Fisher.

1. INTRODUCTION

THE hope of gaining some insight into the illusive nature of approximations used to study many-spin models has, in part, motivated a significant amount of work on a linear chain of spins ($S=\frac{1}{2}$) with nearest-neighbor antiferromagnetic Heisenberg exchange interaction. Since the Hamiltonian for this system can be simply expressed[1] in terms quadratic and quartic in Fermi operators, without auxiliary conditions required in conventional Bose-operator formulations of the exchange Hamiltonian, the linear chain may be regarded formally as a many-fermion system with two-particle interactions.

The resulting literature contains a number of carefully derived properties of this model, viewed as a spin system, and these known properties make the model an interesting proving ground for certain conventional approximation techniques. From among the known investigations we refer in particular to: the ground-state energy determination[2]; the extension[3] of Marshall's theorem to show the nondegeneracy of the ground state; a theorem[3] showing the existence of a low-lying excited state and suggesting the absence of an energy gap in the excitation spectrum; the behavior[4] of certain ground-state properties as a function of an anisotropy parameter; a study[5] of the excitation spectrum arising from a subset of solutions to the secular equations; a study[6] of the zero-temperature limit of the magnetization for an infinite chain; numerical[7] calculations of the thermodynamic behavior of finite chains; the exact zero-field determination[8] of the free energy, correlation functions, and other aspects of the model in the limiting case of infinite spin per site.

In spite of these and other significant contributions during the last thirty-five years, tractable descriptions of either the ground state or the thermodynamic functions are not apparent. On the other hand, variational[9] and perturbation techniques[10] appear to be moving closer to a consistent thermodynamic description, although the lack of an exactly known ground state is at least an embarrassing situation.

It is our present purpose to describe an approximate calculation based on a free-energy variational technique which reflects the ideas in the Valatin and Bogoliubov formulations of superconductivity theory. The method was recently applied[11] to the simple cubic antiferromagnet in a magnetic field. In essence we have found that by starting with a somewhat general trial Hamiltonian, quadratic in Fermi operators, the variational method leads to the nonzero-temperature extension of the Ruijgrok and Rodriguez paper.[12] However, that description, which is to be compared with the instability of a plane-wave ground state to an Overhauser-type state,[13] allows an energy gap and an associated long-range order. If on the basis of indications given by the

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[1] See, for example, D. Frank, Z. Physik **146**, 615 (1956).

[2] L. Hulthén, Arkiv Mat. Astron. Fysik **26A**, No. 1 (1938).

[3] E. Lieb, T. Schultz, and D. Mattis, Ann. Phys. (N.Y.) **16**, 407 (1961). A more general theorem on the ordering of energy levels is given by E. Lieb and D. Mattis, J. Math. Phys. **3**, 749 (1962).

[4] R. Orbach, Phys. Rev. **112**, 309 (1958); L. R. Walker, *ibid.* **116**, 1089 (1959).

[5] J. des Cloizeaux and J. J. Pearson, Phys. Rev. **128**, 2131 (1962).

[6] R. B. Griffiths, Phys. Rev. **133**, A768 (1964).

[7] J. C. Bonner and M. E. Fisher, Proc. Phys. Soc. (London) **80**, 508 (1962); Phys. Rev. **135**, A640 (1964).

[8] M. E. Fisher, Am. J. Phys. **32**, 343 (1964).

[9] L. N. Bulaevskii, Zh. Eksperim. i Teor. Fiz. **43**, 968 (1962) [English transl.: Soviet Phys.—JETP **16**, 685 (1963)]; R. B. Griffiths, Phys. Rev. **136**, A751 (1964).

[10] S. Inawashiro and S. Katsura (to be published).

[11] H. Falk, Phys. Rev. **133**, A1382 (1964).

[12] T. W. Ruijgrok and S. Rodriguez, Phys. Rev. **119**, 596 (1960); H. Falk and T. W. Ruijgrok, Physica **27**, 710 (1961).

[13] E. M. Henley and T. W. Ruijgrok, Ann. Phys. (N. Y.) **12**, 409 (1961).

exact results, we disallow the gap, then, in this context, the "next best" solution is Bulaevskii's,[9] which has a higher ground-state energy but no spontaneous long-range order.

From Bulaevskii's coupled integral equations and the condition for maximum entropy with respect to variation of the external field h at fixed temperature θ, we obtain in the h, θ plane a pseudophase boundary which roughly separates a region of predominantly antiferromagnetic order from a region of predominantly ferromagnetic order. For $\theta>0$, there is *no* thermodynamic discontinuity as the boundary is crossed, and at $\theta=0$ the susceptibility is discontinuous[6] in accord with Jacobsohn's theorem.[14] Also given here is the pseudophase boundary for the exactly soluble X-Y model of Lieb, Schultz, and Mattis.[3,15] Comparison is made with a pseudophase boundary curve given by Bonner and Fisher[7] for a finite antiferromagnetic chain.

2. FREE-ENERGY EXTREMUM EQUATIONS

For N spins ($S=\frac{1}{2}$) the Hamiltonian for an antiferromagnetic chain with periodic boundary conditions is

$$\mathcal{H}=2J\sum_{f=1}^{N}(\mathbf{S}_f\cdot\mathbf{S}_{f+1}+hS_f^z),\quad(\mathbf{S}_{N+1}=\mathbf{S}_1),$$

where here $h=g\mu H/(2J)$ and the remaining notation is consistent with Ref. 11. It is convenient to express the spin operators with reference to the rotated sublattice coordinates described[11] in detail previously; then

$$\mathcal{H}=2J\sum_{f=1}^{N}[\tfrac{1}{2}(1-\gamma^2)(S_f^+S_{f+1}^++S_{f+1}^-S_f^-)-\tfrac{1}{2}\gamma^2(S_f^+S_{f+1}^-+S_{f+1}^+S_f^-)+(2\gamma^2-1)S_f^zS_{f+1}^z+\gamma hS_f^z]+O(0),$$

where $O(0)$ denotes terms which give no contribution for all ensembles here considered. For $\gamma=0$ the transformed sublattice coordinate systems have antiparallel z axes; whereas for $\gamma=1$ the z axes are parallel. Application of the well-known[1,3] canonical transformation

$$S_f^+=C_f^\dagger\exp[i\pi\sum_{j=1}^{f-1}C_j^\dagger C_j],\qquad S_f^-=(S_f^+)^\dagger,$$

which relates the spin operators associated with site f to Fermi operators C_r and $C_r^\dagger$ associated with sites $r=1, 2, \cdots, f-1, f$ [Note: $\exp(i\pi C_f^\dagger C_f)=1-2C_f^\dagger C_f=-2S_f^z$], enables one to write

$$\mathcal{H}=2J\sum_{f=1}^{N}[\tfrac{1}{2}(1-\gamma^2)(C_f^\dagger C_{f+1}^\dagger+C_{f+1}C_f)-\tfrac{1}{2}\gamma^2(C_f^\dagger C_{f+1}+C_{f+1}^\dagger C_f)+(2\gamma^2-1)(C_f^\dagger C_f-\tfrac{1}{2})\times(C_{f+1}^\dagger C_{f+1}-\tfrac{1}{2})+\gamma h(C_f^\dagger C_f-\tfrac{1}{2})]+O(0).$$

[14] B. A. Jacobsohn (private communication).
[15] S. Katsura, Phys. Rev. **127**, 1508 (1962).

Upon introducing an arbitrary trial Hamiltonian $\mathcal{H}_0$, where $\mathcal{H}=\mathcal{H}_0+(\mathcal{H}-\mathcal{H}_0)$, one can perform variations of the trial free energy

$$F=F_0+\langle\mathcal{H}-\mathcal{H}_0\rangle_0=\langle\mathcal{H}\rangle_0-TS_0,$$

which is known to be an upper bound to the exact free energy. As in Ref. 11, F_0, S_0, and $\langle\ \rangle_0$ are, respectively, the free energy, entropy, and thermal average identified with the canonical density

$$\exp(-\mathcal{H}_0/k_BT)/\mathrm{Tr}\exp(-\mathcal{H}_0/k_BT).$$

In this calculation we take for $\mathcal{H}_0$ the quadratic-Fermi-operator form

$$\mathcal{H}_0=\sum_{s,t}[C_s^\dagger A_{st}C_t+\tfrac{1}{2}(C_s^\dagger B_{st}C_t^\dagger+\text{Hermitian conjugate})],$$

where the real matrices A and B are, respectively, symmetric and antisymmetric. The choice of the above form was partly determined by the fact that it may be simply diagonalized and expressed as a free-fermion Hamiltonian for which F_0, S_0, and $\langle\ \rangle_0$ are relatively easy to calculate. For a clear exposition of the diagonalization of $\mathcal{H}_0$ we refer the reader to Appendix A of the cited paper[3] by Lieb, Schultz, and Mattis; here we give only the essentials.

The diagonalization is accomplished with the canonical transformation to Fermi operators $a_k^\dagger$ and a_k:

$$C_t^\dagger=\sum_k(\phi_{kt}a_k^\dagger+\psi_{kt}a_k),\qquad C_t=\sum_k(\phi_{kt}a_k+\psi_{kt}a_k^\dagger),$$

where ϕ_{kt} and ψ_{kt} are real and satisfy the orthonormality conditions

$$\sum_k(\phi_{ks}\phi_{kt}+\psi_{ks}\psi_{kt})=\delta_{st},\qquad\sum_k(\psi_{ks}\phi_{kt}+\phi_{ks}\psi_{kt})=0.$$

One further introduces the real quantities τ_{ks} and η_{ks} defined by

$$\phi_{ks}=\tfrac{1}{2}(\tau_{ks}+\eta_{ks}),\qquad\psi_{ks}=\tfrac{1}{2}(\tau_{ks}-\eta_{ks}),$$

so that the orthonormality conditions become

$$\tfrac{1}{2}\sum_k(\tau_{kt}\tau_{ks}+\eta_{kt}\eta_{ks})=\delta_{ts},\qquad\tfrac{1}{2}\sum_k(\tau_{kt}\tau_{ks}-\eta_{kt}\eta_{ks})=0,$$

which imply that

$$\sum_k\tau_{kt}\tau_{ks}=\sum_k\eta_{kt}\eta_{ks}=\delta_{ts}.$$

In terms of these quantities the diagonalization of $\mathcal{H}_0$ is found to be equivalent to solving the system

$$(A-B)(A+B)\boldsymbol{\tau}(k)=\epsilon_k^2\boldsymbol{\tau}(k),\qquad(A+B)\boldsymbol{\tau}(k)=\epsilon_k\boldsymbol{\eta}(k),\tag{1}$$

where the column vectors $\boldsymbol{\tau}(k)$ and $\boldsymbol{\eta}(k)$ are the kth columns of the τ and η matrices, respectively; and ϵ_k is the spectrum of the diagonalized $\mathcal{H}_0$. Although $\boldsymbol{\tau}(k)$ and $\boldsymbol{\eta}(k)$ are still arbitrary, since A and B are yet

unspecified, we can now write

$$\begin{aligned}\langle C_t^\dagger C_s\rangle_0 &= \langle C_s^\dagger C_t\rangle_0 = \delta_{st} - \langle C_s C_t^\dagger\rangle_0 \\ &= \tfrac{1}{2}\delta_{st} - \tfrac{1}{4}\textstyle\sum_k (\tau_{kt}\eta_{ks} + \eta_{kt}\tau_{ks})(1-2n_k)\,, \\ \langle C_t^\dagger C_s^\dagger\rangle_0 &= \langle C_s C_t\rangle_0 = -\langle C_s^\dagger C_t^\dagger\rangle_0 \\ &= +\tfrac{1}{4}\textstyle\sum_k (\tau_{kt}\eta_{ks} - \eta_{kt}\tau_{ks})(1-2n_k)\,,\end{aligned} \tag{2}$$

where

$$1-2n_k = \tanh(\epsilon_k/2k_BT)\,. \tag{3}$$

With the thermodynamic form of Wick's theorem,[16] the ensemble average of $\mathfrak{H}$ is

$$\langle \mathfrak{H}\rangle_0/2NJ = (1-\gamma^2)\chi_1 - \gamma^2 h_1 + (2\gamma^2-1)(\tfrac{1}{4}\sigma^2 - h_1^2 + \chi_1^2) - \tfrac{1}{2}h\gamma\sigma\,,$$

where

$$\begin{aligned}\sigma &\equiv 2(\tfrac{1}{2} - \langle C_f^\dagger C_f\rangle_0)\,, \\ h_1 &\equiv \langle C_f^\dagger C_{f+1}\rangle_0\,, \\ \chi_1 &\equiv \langle C_f^\dagger C_{f+1}^\dagger\rangle_0\,.\end{aligned}$$

Now the matrices A and B will be chosen to be translationally invariant, i.e., the commutator

$$[A,P]_- = [B,P]_- = 0\,,$$

where

$$P = \begin{pmatrix} 0 & 1 & & & & & & \\ & 0 & 1 & & & & & \\ \cdot & & \cdot & \cdot & & & & \\ \cdot & & & \cdot & \cdot & & & \\ \cdot & & & & \cdot & \cdot & & \\ & & & & & \cdot & 1 & \\ & & & & & & 0 & 1 \\ 1 & & & & & & & 0 \end{pmatrix}$$

is the $N\times N$ permutation matrix satisfying

$$P^N = I; \quad P^{N-r} = P^{-r}; \quad \tilde{P}^r = P^{-r}.$$

The symbol $\tilde{P}$ denotes the transpose of P. The above choice of A and B enables one to write

$$A = \sum_{l=1}^{N} A_l P^l\,,$$

and

$$B = \sum_{l=1}^{N} B_l P^l\,,$$

where the real coefficients A_l and B_l satisfy $A_{N-l} = A_l$; $B_{N-l} = -B_l$; and $B_0 = 0$. The diagonalization of $\mathfrak{H}_0$ is greatly simplified since

$$P\mathbf{v}(k) = e^{ik}\mathbf{v}(k)\,,$$

and

$$P^{-1}\mathbf{v}(k) = e^{-ik}\mathbf{v}(k)$$

with

$$\mathbf{v}(k) = \frac{1}{\sqrt{N}}\cdot\begin{pmatrix} e^0 \\ e^{ik} \\ e^{2ik} \\ \vdots \\ e^{(N-1)ik} \end{pmatrix},$$

for $k = 2\pi m/N$, $m = 0, \pm 1, \cdots, \pm(\frac{1}{2}N-1), \frac{1}{2}N$; N even; and a lattice spacing implicitly unity. It is now easy to verify that the solutions to (1) are

$$\tau_{tk} = (2/N)^{1/2}\cos[tk - \tfrac{1}{2}(\phi(k)) - \tfrac{1}{4}\pi]\,,$$

and

$$\eta_{tk} = (2/N)^{1/2}\cos[tk + \tfrac{1}{2}(\phi(k)) - \tfrac{1}{4}\pi]$$

with the relative phase $\phi(k)$ determined from

$$\begin{aligned}\sin\phi(k) &= (\textstyle\sum_l B_l \sin kl)/\epsilon_k \\ \text{or} \qquad \cos\phi(k) &= (\textstyle\sum_l A_l \cos kl)/\epsilon_k\,.\end{aligned} \tag{4}$$

Substitution into (2) gives

$$\begin{aligned}\langle C_t^\dagger C_s\rangle_0 &= \tfrac{1}{2}\delta_{st} - (1/2N)\textstyle\sum_k \cos[(t-s)k] \times \cos\phi(k)(1-2n_k)\,, \\ \langle C_t^\dagger C_s^\dagger\rangle_0 &= +(1/2N)\textstyle\sum_k \sin[(t-s)k]\sin\phi(k)(1-2n_k)\,,\end{aligned}$$

from which follow immediately the relations

$$\begin{aligned}\sigma &= N^{-1}\textstyle\sum_k \cos\phi(k)(1-2n_k)\,, \\ h_1 &= -(2N)^{-1}\textstyle\sum_k \cos k\,\cos\phi(k)(1-2n_k)\,, \\ \chi_1 &= -(2N)^{-1}\textstyle\sum_k \sin k\,\sin\phi(k)(1-2n_k)\,,\end{aligned} \tag{5}$$

where n_k is defined by (3).

We want to vary the trial free energy F with respect to γ, n_k, A_l, and B_l. Conveniently (3), (4), and the free-fermion entropy S_0 (expressed in terms of the average occupation numbers n_k) enable one to perform the equivalent variation of F with respect to γ, n_k, and $\phi(k)$. This leads to the extremum equations

$$\gamma = \tfrac{1}{2}h\sigma/[\sigma^2 - 2h_1(1+2h_1) - 2\chi_1(1-2\chi_1)], \tag{6}$$

$$\begin{aligned}\cos\phi(k) &= \xi_k/\omega_k\,, \quad \sin\phi(k) = \Delta_k/\omega_k\,, \\ \epsilon_k &= \partial(\langle\mathfrak{H}\rangle_0/N)/\partial n_k = 2J\omega_k\,,\end{aligned} \tag{7}$$

where we have introduced

$$\begin{aligned}\xi_k &= -[\gamma^2 + (2\gamma^2-1)2h_1]\cos k - (2\gamma^2-1)\sigma + h\gamma\,, \\ \Delta_k &= [(1-\gamma^2) + (2\gamma^2-1)2\chi_1]\sin k\,,\end{aligned}$$

and

$$\omega_k = (\xi_k/|\xi_k|)(\xi_k^2 + \Delta_k^2)^{1/2}.$$

Comparing (4) with (7) we see that the latter are satisfied for

$$\begin{aligned}A_0 &= -2J[(2\gamma^2-1)\sigma - h\gamma]\,, \\ A_1 &= -2J[\gamma^2 + (2\gamma^2-1)2h_1]\,, \\ B_1 &= 2J[(1-\gamma^2) + (2\gamma^2-1)2\chi_1]\,, \\ A_l &= B_l = 0\,, \quad \text{for} \quad l>1\,; \\ \epsilon_k &= 2J\omega_k\,.\end{aligned}$$

[16] A. Alekseev, Usp. Fiz. Nauk 73, 41 (1961) [English transl.: Soviet Phys.—Usp. 4, 23 (1961)].

For computational convenience we now take the thermodynamic limit of $N\to\infty$; so that Eqs. (5) become

$$\sigma=\frac{1}{2\pi}\int_{-\pi}^{\pi}dk\frac{\xi_k}{\omega_k}\tanh(\omega_k/2\theta),$$

$$2h_1=-\frac{1}{2\pi}\int_{-\pi}^{\pi}dk\,\cos k\frac{\xi_k}{\omega_k}\tanh(\omega_k/2\theta), \tag{8}$$

$$2\chi_1=-\frac{1}{2\pi}\int_{-\pi}^{\pi}dk\,\sin k\frac{\Delta_k}{\omega_k}\tanh(\omega_k/2\theta),$$

where $\theta=\frac{1}{2}k_BT/J$.

The problem confronting us at this point may be summarized as follows: with ξ_k and Δ_k given in terms of γ, σ, h_1, χ_1, and h, solve the coupled equation (6) and (8) to obtain $\gamma(h,\theta)$, $\sigma(h,\theta)$, $h_1(h,\theta)$, and $\chi_1(h,\theta)$. Then $\langle\mathcal{H}\rangle_0$, F, and other thermodynamic quantities may be expressed as functions of h and θ.

3. SOLUTIONS FOR $h=\theta=0$

When $h=0$ (zero external field), we can find a solution with

$$\gamma=0,$$

and

$$h_1=0.$$

The spectrum becomes

$$\omega_k=[\sigma^2+(1-2\chi_1)^2\sin^2k]^{1/2}$$

with σ and χ_1 determined from

$$\sigma=\frac{\sigma}{2\pi}\int_{-\pi}^{\pi}dk\frac{1}{\omega_k}\tanh(\omega_k/2\theta);$$

$$2\chi_1=\frac{-(1-2\chi_1)}{2\pi}\int_{-\pi}^{\pi}dk\frac{\sin^2k}{\omega_k}\tanh(\omega_k/2\theta).$$

At zero temperature the integrals reduce to linear combinations of complete elliptic integrals $K(\kappa)$ and $E(\kappa)$ with

$$(1-\kappa^2)/\kappa^2\equiv\sigma^2/(1-2\chi_1)^2.$$

Explicitly

$$\sigma=\frac{2}{\pi}(1-\kappa^2)^{1/2}K(\kappa)$$

and

$$2\chi_1=\frac{2}{\pi}[((1-\kappa^2)/\kappa)K(\kappa)-(E(\kappa)/\kappa)],$$

with the value of κ which minimizes the energy determined from

$$(2/\pi)[K(\kappa)-E(\kappa)]/\kappa=1. \tag{9}$$

But these are just the equations previously obtained and solved by Ruijgrok and Rodriguez[12] who were working in the unrotated system. They found $\bar{\kappa}=0.951$ for the solution of (9) from which

$$\langle\mathcal{H}\rangle_0/2NJ+\tfrac{1}{4}=K^2(\bar{\kappa})/\pi^2\cong-0.68$$

compared to the exact value $\cong-0.69$. Note that $\sigma>0$; consequently the solution displays an energy gap and a corresponding long-range order. As formerly discussed by the present authors,[12] the gap and the order persist for nonzero $\theta<\theta_{\text{critical}}$ above which they both vanish. Now there are indications from recent work[3,5] that the gap may not be present in an exact solution for $h=0$. If on that basis one disallows the nontrivial solution $\sigma>0$, then there remains the trivial solution with $\sigma=0$ at $h=0$ for all $\theta\geq0$. The spectrum becomes

$$\omega_k=|(1-2\chi_1)\sin k|$$

with

$$2\chi_1=-\frac{2}{\pi}\int_0^{\pi/2}dk(\sin k)\tanh\left[\frac{(1-2\chi_1)\sin k}{2\theta}\right].$$

At $\theta=0$, $\chi_1=-1/\pi$ and

$$\omega_k=(1+2/\pi)|\sin k|,\quad(\theta=0),$$

which is similar to the spectrum obtained by des Cloizeaux and Pearson.[5] The corresponding ground-state energy is

$$\langle\mathcal{H}\rangle_0/2NJ+\tfrac{1}{4}\cong-0.66.$$

Now the latter energy corresponds to the value found by Bulaevskii[9] who was working with the unrotated coordinates and so obtained a $\theta=0$ spectrum $=(1+2/\pi)\cos k$. Both forms lead to the same free energy and thermodynamic behavior for $h=0$. [In this respect it is interesting to note that $H'=-\frac{1}{2}\sum_{f=1}^{N}(C_f^\dagger C_{f+1}+C_{f+1}^\dagger C_f)$ and $H''=+\frac{1}{2}\sum_{f=1}^{N}(C_f^\dagger C_{f+1}^\dagger+C_{f+1}C_f)$, with $C_{N+1}=C_1$, lead to the same free energy in the thermodynamic limit even though they have single-particle spectra $\epsilon_k'=-\cos k$ and $\epsilon_k''=|\sin k|$, respectively.]

An alternative way of viewing the above result is found by noting that we may select a trial Hamiltonian[17]

$$\mathcal{H}_0=A_0\sum_{f=1}^{N}a_f^\dagger a_f+A_1\sum_{f=1}^{N}(a_f^\dagger a_{f+1}+a_{f+1}^\dagger a_f)$$
$$+D_0\sum_{f=1}^{N}(-1)^f a_f^\dagger a_f,$$

by replacing A by $A+D$ in Sec. 2, where

$$D=D_0\cdot\begin{bmatrix}1&&&&&\\&-1&&&&\\&&1&&&\\&&&\pm&&\\&&&&\ddots&\\&&&&&-1\end{bmatrix}$$

[17] This Hamiltonian is diagonalized in k space by the canonical transformation given by Ruijgrok and Rodriguez (Ref. 12).

and $B\equiv 0$; $A_l\equiv 0$, $l>1$. Now A commutes with P^2 rather than P, and for $D_0\neq 0$, $\mathcal{H}_0$ "tempts" the system with long-range antiferromagnetic order which is "accepted" by the system in the variational approximation. However, the variational method is merely a method for suggesting how to split $\mathcal{H}$ for perturbation purposes. That spurious results are possible is not surprising nor a reason to abandon these Hartree-Fock techniques which may be viewed as motivation for a careful analysis.

4. PSEUDOPHASE BOUNDARY

We noted that Bulaevskii's solution (for $h=0$ and $\gamma=1$) is equivalent to the above trivial solution for $h=0$ and $\gamma=0$. In the following we will not consider γ a variational parameter but will take $\gamma=1$ for $h\geq 0$, so that our coupled Eqs. (8), for the trivial case ($\Delta_k=\chi_1=0$; $\omega_k=\xi_k$), reduce to Bulaevskii's Eqs. (13) and (14). In terms of a convenient notation these equations are written

$$1-h+\theta w=S_0(w,l)\,,\quad \theta l=1+S_1(w,l)\,, \tag{10}$$

where

$$S_m(w,l)=\frac{1}{2}-\int_0^{\pi} dk(\cos k)^m n_k(w,l)\,,$$

and

$$w=(h-\sigma)/\theta\,,\quad l=(1+2h_1)/\theta\,,\quad n_k(w,l)=(e^{w-l\cos k}+1)^{-1}.$$

On the basis of the physical argument[18] that increasing the field h from zero to ≈ 2 should gradually reduce antiferromagnetic short-range order and produce ferromagnetic order for $\theta\ll 1$ and $h\approx 2$, we expect the locus of entropy maxima to roughly indicate the separation, in the h,θ plane, of regions of predominantly antiferromagnetic order from regions of predominantly ferromagnetic order.

We will refer to the maximum entropy locus as a *pseudo*phase boundary, since there is *no* discontinuity in the thermodynamic quantities as the boundary is crossed for $\theta>0$. Recall that we are taking the

$$\text{entropy}=-k_B\textstyle\sum_k [n_k \ln n_k+(1-n_k)\ln(1-n_k)];$$

so that by implicit differentiation we obtain, with the coupled Eqs. (10), the condition for maximum entropy:

$$w/l=T_1/[T_0-(T_2T_0-T_1^2)], \tag{11}$$

where the function T_m of w and l is defined by

$$\theta T_m(w,l)=\frac{1}{2}-\int_0^{\pi} dk(\cos k)^m n_k(w,l)[1-n_k(w,l)].$$

We have solved the three coupled Eqs. (10) and (11) with the IBM-7090 computer. The resulting pseudophase boundary is shown in Fig. 1 [which also includes the corresponding boundary for the X-Y model in a magnetic field (see our Appendix A)]. We note that both curves[19] fall off linearly in θ for $\theta\ll 1$; i.e., $2-h\sim(1.25\pm 0.10)\theta$ for the Heisenberg chain, and $1-h\sim(1.31\pm 0.10)\theta$ for the X-Y model.

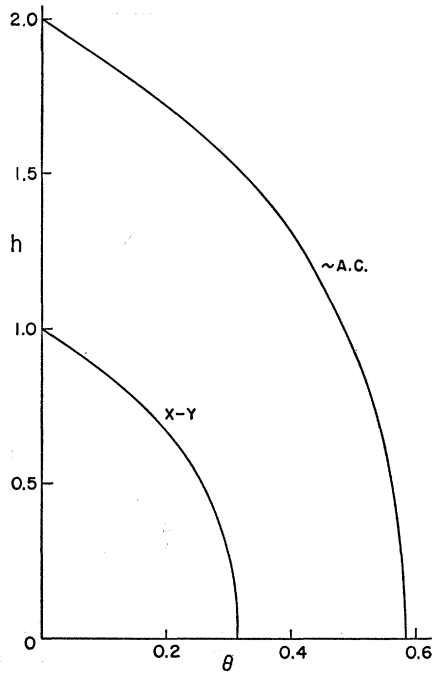

FIG. 1. Loci of entropy maxima for the X-Y model and for the Bulaevskii variational approximant ("~A.C.") to the antiferromagnetic linear chain; ($h=g\mu H/2J$; $\theta=kT/2J$).

Perturbation analysis shows that for $h\ll 1$ the curves satisfy $h\cong\text{const}(\theta_0-\theta)^{1/2}$ for θ slightly less than θ_0, where $\theta_0\cong 0.584$ for the Heisenberg chain, and $\theta_0\cong 0.316$ for the X-Y model. The $h=0$ end point of the pseudophase boundary is determined from (11) which yields

$$1/l_0=\frac{(N_1-N_3)+\frac{1}{2}[(1-M_2)^2/(1+N_1)]}{(1-M_2)[1+N_1/(1+N_1)]}+O(h^2),$$

where

$$M_r(l_0)=\frac{2}{\pi}\int_0^{\pi/2} dk\left[\tanh\left(\frac{l_0}{2}\cos k\right)\right]^r,$$

$$N_r(l_0)=\frac{2}{\pi}\int_0^{\pi/2} dk(\cos k)\left[\tanh\left(\frac{l_0}{2}\cos k\right)\right]^r.$$

Figure 2 shows a copy of Bonner and Fisher's locus of maximum entropy for an 8-spin isotropic antiferromagnetic chain. They claim that the solid portion of their curve should differ by no more than a few percent from the exact limiting curve (for $N\to\infty$). If that is

[18] C. Domb, Advan. Phys. 9, 149 (1960); in particular see pp. 166–168.

[19] Dr. R. B. Griffiths pointed out that each curve also corresponds to the locus of magnetization maxima for $h\geq 0$ and that the intersection with the θ axis locates the $h=0$ susceptibility maxima at $\theta=\theta_0$.

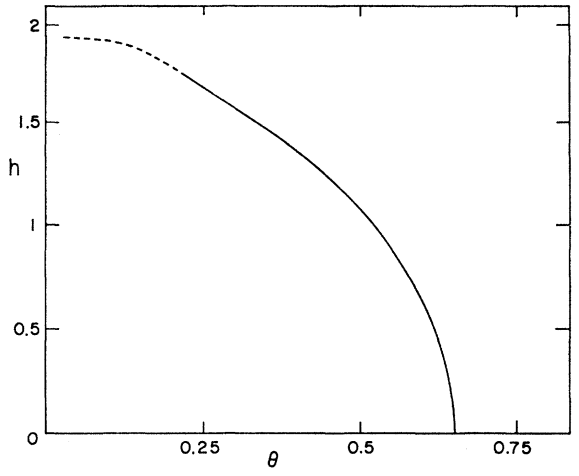

FIG. 2. Locus of entropy maxima for an 8-spin antiferromagnetic chain [from Fig. 8 of J. C. Bonner and M. E. Fisher, Proc. Phys. Soc. (London) **80**, 508 (1962); the axes have been relabeled to coincide with the present notation].

correct, then for intermediate and small h the comparison is encouraging; however, it is difficult to draw conclusions for $h\approx 2$. The difficulty is enhanced by the existence of multiple entropy maxima at $\theta=0$ for finite chains which, as Bonner and Fisher note, violate the third law of thermodynamics; whereas the free-particle form of the entropy used in the present approximation manifestly satisfies the third law.

It is easy to verify that the susceptibility

$$\partial\sigma/\partial h=[1-(1-T_2)/((1+T_0)(1-T_2)+T_1^2)]$$

reduces, for $h=0$, to Bulaevskii's 2χ [his Eq. (29)], since for $h=0$, $T_1=0$. The X-Y model susceptibility is given in Appendix A. For $h=0$, $(\partial\sigma/\partial h)_{\theta_0}\cong 0.326$ for the Heisenberg chain and $\cong 0.723$ for the X-Y model.

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Just prior to submitting this paper we were most kindly informed by Dr. Jill Bonner of her unpublished results for a 10-spin chain. On the basis of her estimates we expect the exact limiting ($N\to\infty$) pseudophase boundary to be remarkably similar to the present variational result for all h and θ.

APPENDIX A

For the X-Y model,[3,15] which results from discarding the Ising term in the Heisenberg Hamiltonian, one has

$$\mathcal{H}=2J\sum_{f=1}^{N}[h(C_f^\dagger C_f-\tfrac{1}{2})-\tfrac{1}{2}(C_f^\dagger C_{f+1}+C_{f+1}^\dagger C_f)].$$

Diagonalization is simply accomplished by Fourier transforming $C_f^\dagger$ and C_f to obtain

$$\mathcal{H}/2NJ=(1/N)\textstyle\sum_k[(h-\cos k)C_k^\dagger C_k-\tfrac{1}{2}h].$$

In the thermodynamic limit $N\to\infty$, the maximum entropy is achieved when

$$w/l=T_1/T_0, \tag{A1}$$

where $T_m(w,l)$ are given in Sec. 4; however we now have

$$w\equiv h/\theta,$$

and

$$l\equiv 1/\theta.$$

As $h\to 0$ the limiting form of (A1) is

$$1/l_0=[(N_1-N_3)/(1-M_2)]+O(h^2),$$

where $N_r(l_0)$ and $M_r(l_0)$ are also the same as in Sec. 4.

For this model the susceptibility is[20]

$$\partial\sigma/\partial h=T_0. \tag{A2}$$

[20] For $h=0$ Eq. (A2) reduces to the zero-field susceptibility shown in Fig. 13 of S. Katsura and S. Inawashiro, J. Math. Phys. **5**, 1091 (1964).