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Comments and Addenda

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Comment on compressible spin systems*

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The zero-temperature phase diagram for the linear compressible chain of classical Heisenberg spins is obtained. In the space of appropriate coupling constants, the spin-flop phase is separated from the aligned phase by a surface along which runs a line of tricritical points. Also, the molecular-field approximation for coupled spin-lattice systems is examined. With classical variables, there are two ways of proceeding, and both have been used previously. The procedures are discussed on a variational basis, and it is pointed out that one gives a lower upper bound on the free energy than the other.

I. INTRODUCTION

The compressible chain of classical Heisenberg spins was studied by Lee[1] and the present author.[2,3] The coupling of the spins to phonons through exchange striction gave rise to effective biquadratic interactions between spins, and thermodynamic functions at finite temperature and zero field were studied.[1,2] Further, in Ref. 2 it was shown that antiferromagnetically coupled spins in an external field H at $T=0\,^\circ\mathrm{K}$ underwent a first-order phase transition of the type studied by Kittel[4] who used a mean-field theory for a system characterized by just one elastic coordinate—the volume. The free energy derived by Bean and Rodbell[5] would presumably also yield the transition.

Two points are discussed in this paper. First, the $T=0\,^\circ\mathrm{K}$ phase diagram is discussed for the chain, allowing for the application of a force λ on its ends. In $\lambda\gamma$-H-γ^2 space (γ is the spin-phonon coupling), the spin-flop phase is separated from the aligned phase by a surface along which runs a line of tricritical points (Fig. 1). Second, mean-field theories for coupled spin-lattice systems are discussed for classical spin and lattice variables. There are two distinct ways (methods 1 and 2 in Sec. III) of proceeding, and both have been used in the literature.[4-7] Whereas method 2 has been derived[7] on the basis of a variational principle for the free energy F, it seems that method 1 has not. A variational derivation is given here, and it is pointed out that, in general, method 1 does not give as low an upper bound on F as method 2.

II. $T=0\,^\circ\mathrm{K}$: PHASE DIAGRAM FOR COMPRESSIBLE CLASSICAL HEISENBERG CHAIN

If a force λ is applied inwards at either end of the chain, the Hamiltonian is

$$\mathcal{H}=J\sum_i \hat{S}_i\cdot\hat{S}_{i+1}-H\sum_i S_i^z-\gamma\sum_i(x_{i+1}-x_i)\hat{S}_i\cdot\hat{S}_{i+1}+\frac{1}{2m}\sum_i p_i^2+\frac{k}{2}\sum_i(x_{i+1}-x_i)^2+\lambda\sum_i(x_{i+1}-x_i). \tag{1}$$

Except for the last term, this is the Hamiltonian studied in Ref. 2. Application of the unitary transformation (2.2) [i.e., Eq. (2) of Ref. 2] yields

$$U\mathcal{H}U^{-1}=\tilde{\mathcal{H}}_s+\mathcal{H}_{\mathrm{ph}}, \tag{2}$$

where

$$\tilde{\mathcal{H}}_s=\frac{\lambda^2}{2k}+J(\lambda)\sum_i\hat{S}_i\cdot\hat{S}_{i+1}-H\sum_i S_i^z-A\sum_i(\hat{S}_i\cdot\hat{S}_{i+1})^2. \tag{3}$$

Here A is $\gamma^2/2k$, $J(\lambda)=J+\gamma\lambda/k$, and $\mathcal{H}_{\mathrm{ph}}$ is defined in (2.6).

At $T=0\,^\circ\mathrm{K}$ and $H=0$ there is a first-order transition when $J(\lambda)$ changes sign on varying λ. This is an example of exchange inversion discussed by Kittel.[4] Depending on the relative signs of J and γ, one needs to pull or squeeze the chain to reach $J(\lambda)=0$. The analogous transition in the Ising chain has been studied by Salinas.[8]

Now consider $H \neq 0$ and assume $J > 0$ (antiferromagnetic). From Eq. (2.21), the energy per spin is, except for an additive constant,

$$E(\theta) = A \sin^2 2\theta - J(\lambda)(1+\cos 2\theta) + H(1-\sin\theta). \tag{4}$$

Defining M_s to be $\cos\theta$, the component of the sublattice magnetization normal to H, and expanding E to order M_s^6, we find

$$E(M_s) = aM_s^2 + bM_s^4 + cM_s^6, \tag{5}$$

with $a = 4A - 2J(\lambda) + \frac{1}{2}H$, $b = -4A + \frac{1}{8}H$, $c = \frac{1}{16}H$. Equation (5) is of the Landau form, and since b can be negative, the transition can be first order. There is a tricritical point[9] at $A = \frac{1}{10}J(\lambda)$ and $h = \frac{16}{5}J(\lambda)$. Since $J(\lambda)$ depends linearly on $\lambda\gamma/k$ there is a line of tricritical points in $\lambda\gamma/k$-H-A space (Fig. 1). Below the surface shown, the spins are in the flopped phase. Above it, they are aligned along H. The transition is second order to the left of the line of TCP's and first order on its right. As $A \rightarrow \infty$, the surface of first-order transitions approaches the plane $H/2J - \lambda\gamma/kJ = 1$.

The phase transitions discussed here occur only at $T = 0$ °K. They are ruled out in the chain at $T \neq 0$ °K by a generalization of the Perron-Froebinius theorem[10] as the kernel of the transfer-matrix integral equation[11] has only positive elements.

On a general harmonic three-dimensional lattice, separation into phonon and spin Hamiltonians H_{ph} and $\tilde{H}_s$ goes through, but $\tilde{H}_s$ contains longer-range four-spin interactions.[7,12] An exception is the Baker-Essam lattice.[13,14] This is composed of interpenetrating chains, with no spring communication between chains in different directions, and no transverse restoring forces in a given chain. This leads to nearest-neighbor bilinear and biquadratic terms [Eq. (3)] on every chain. Thus Fig. 1 is also the phase diagram for this system at $T = 0$ °K provided we replace H by $2H/z$, where z is the number of nearest neighbors. Since we have a three-dimensional lattice of interacting spins on the Baker-Essam lattice we expect the phase transitions to occur at finite T.

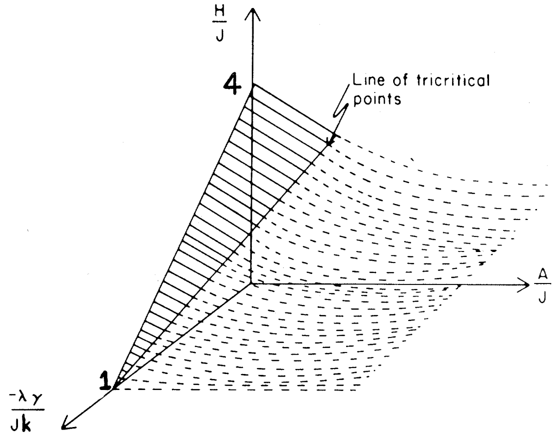

FIG. 1. $T = 0$ °K phase diagram is shown for positive A and J. Below the surface, the spins are flopped, and above it they are in the aligned phase. The transition is second order across the surface marked with solid lines and first order across the dashed surface.

III. VARIATIONAL APPROXIMATIONS FOR COUPLED SPIN-LATTICE SYSTEMS

Consider a system described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_1(\mathcal{U}, \mathcal{P}) + \mathcal{H}_2(\mathcal{U}, \mathcal{S}) + \mathcal{H}_3(\mathcal{S}), \tag{6}$$

where $\mathcal{U}$, $\mathcal{P}$, and $\mathcal{S}$ stand for the set of all the deviations from equilibrium, momenta, and spin variables, respectively, all taken to be classical. $\mathcal{H}_1$ describes a harmonic lattice, and $\mathcal{H}_3$ includes field-spin and spin-spin couplings. $\mathcal{H}_2$ is the spin-lattice interaction, assumed to be linear in the lattice variables.

In method 1, one performs the mean-field approximation directly on $\mathcal{H}$. Let us proceed variationally[15]:

$$\begin{aligned} Z &= \mathrm{Tr}_{\mathcal{U},\mathcal{P}}\, e^{-\beta\mathcal{H}_1(\mathcal{U},\mathcal{P})} \mathrm{Tr}_{\mathcal{S}}\, e^{-\beta\mathcal{H}_2(\mathcal{U},\mathcal{S}) - \beta\mathcal{H}_3(\mathcal{S})} \\ &\geqslant \mathrm{Tr}_{\mathcal{U},\mathcal{P}}\, e^{-\beta\mathcal{H}_1(\mathcal{U},\mathcal{P})} e^{-\beta\Phi(\mathcal{U},\rho)}, \end{aligned} \tag{7}$$

where $\mathrm{Tr}_{\mathcal{U},\mathcal{P}}$ and $\mathrm{Tr}_{\mathcal{S}}$ denote lattice and spin traces, respectively, and

$$\Phi(\mathcal{U},\rho) = (1/\beta)\, \mathrm{Tr}_{\mathcal{S}}\, \rho \ln\rho + \langle \mathcal{H}_2(\mathcal{U},\mathcal{S}) \rangle + \langle \mathcal{H}_3(\mathcal{S}) \rangle. \tag{8}$$

$\langle \cdots \rangle$ stands for $\mathrm{Tr}_{\mathcal{S}}(\rho \cdots)$ and ρ is a trial density matrix of the form $\Pi_i \rho_i$. The mean-field approximation is obtained on maximizing $\exp[-\beta\Phi(\mathcal{U},\rho)]$ by varying ρ. Such a maximization is impossibly complicated for arbitrary $\mathcal{U}$, but one may proceed by noting that

$$\begin{aligned} &\mathrm{Tr}_{\mathcal{U},\mathcal{P}} [e^{-\beta\mathcal{H}_1(\mathcal{U},\mathcal{P})} (\max_\rho e^{-\beta\Phi(\mathcal{U},\rho)})] \\ &\qquad = \max_\rho (\mathrm{Tr}_{\mathcal{U},\mathcal{P}}\, e^{-\beta\mathcal{H}_1(\mathcal{U},\mathcal{P}) - \beta\Phi(\mathcal{U},\rho)}). \end{aligned} \tag{9}$$

The lattice trace on the right-hand side can now be done. The only $\mathcal{U}$ dependence in Φ is in $\langle \mathcal{H}_2 \rangle$. Since $\mathcal{H}_1$ was assumed to be harmonic and $\mathcal{H}_2$ linear in $\mathcal{U}$, we can write

$$\mathcal{H}_1(\mathcal{U},\mathcal{P}) = \sum_q E_q (p_q^2 + u_q^2) \tag{10}$$

and

$$\mathcal{H}_2(\mathcal{U},\mathcal{S}) = \sum_q u_q \psi_q(\mathcal{S}). \tag{11}$$

Here u_q and p_q are the (dimensionless) coordinate and momentum of normal mode q, $E_q (\geqslant 0)$ is the corresponding energy, and ψ_q is some function of

$\hat{S}_1, \hat{S}_2, \ldots, \hat{S}_N$. Performing a displaced oscillator transformation for each q and doing the lattice trace, we find

$$Z \geq Z_{1\mathrm{att}}\, \max_\rho e^{-\beta\Phi_1(\rho)}, \tag{12}$$

where Z_{latt} is $\mathrm{Tr}_{\mathcal{U},\mathcal{P}}\{\exp[-\beta\mathcal{H}_1(\mathcal{U},\mathcal{P})]\}$ and

$$\Phi_1(\rho) = \frac{1}{\beta}\mathrm{Tr}_{\mathcal{S}}\,\rho\ln\rho + \langle\mathcal{H}_3\rangle - \sum_q \frac{\langle\psi_q(\mathcal{S})\rangle^2}{4E_q}. \tag{13}$$

Method 2 proceeds by separating $\mathcal{H}$ [Eq. (6)] into lattice and spin parts by means of a displaced oscillator transformation, and performing mean-field theory on the resulting spin Hamiltonian. We have, thus,

$$\begin{aligned} Z &= Z_{1\mathrm{att}}\,\mathrm{Tr}_{\mathcal{S}}\, \exp\left[-\beta\left(\mathcal{H}_3(\mathcal{S}) - \sum_q \frac{\psi_q^2(\mathcal{S})}{4E_q}\right)\right] \\ &\geq Z_{1\mathrm{att}}\, \max_\rho e^{-\beta\Phi_2(\rho)}, \end{aligned} \tag{14}$$

where

$$\Phi_2(\rho) = \frac{1}{\beta}\mathrm{Tr}_{\mathcal{S}}\,\rho\ln\rho + \mathrm{Tr}_{\mathcal{S}}\,\rho\left(\mathcal{H}_3(\mathcal{S}) - \sum_q \frac{\psi_q^2(\mathcal{S})}{4E_q}\right). \tag{15}$$

From Eqs. (13) and (15) we have

$$\Phi_2(\rho) - \Phi_1(\rho) = -\sum_q \frac{1}{4E_q}\left[\langle\psi_q^2(\mathcal{S})\rangle - \langle\psi_q(\mathcal{S})\rangle^2\right] \leq 0.$$

Thus

$$\min_\rho \Phi_2(\rho) \leq \min_\rho \Phi_1(\rho),$$

and so method 2 gives a better bound on the free energy than method 1. If $\mathcal{H}_2$ and $\mathcal{H}_3$ contain terms bilinear in the spins, method 1 yields only a vector order parameter $\langle\hat{S}\rangle$. Method 2 allows for the existence of an independent quadrupolar order parameter, which may be nonzero even when $\langle\vec{\mathcal{S}}\rangle = 0$.[16]

Method 1 is applicable without difficulty to a quantum spin system, whereas 2 is predicated on the separability of $\mathcal{H}$ into $\tilde{\mathcal{H}}_S$ and $\mathcal{H}_{\mathrm{latt}}$ by means of a unitary transformation. In general, such a separation is not possible for quantum spin systems, though there are exceptions.

Both methods 1 and 2 have been used in the past. For instance, Lee and Bolton[7] have used the procedure 2 to discuss Ising systems. The results of method 1 were used (though without the variational derivation) by Kittel,[4] Bean and Rodbell,[5] and Rodbell and Owen.[6] (Moreover these treatments did not allow for fluctuations of individual ions from their mean position.) Rodbell and Owen state[17] that it is strictly correct that exchange striction leads to contributions like $\langle S^z\rangle^4$ in the free energy within the molecular-field approximation. As our discussion above shows, this is true (with bilinear spin terms in $\mathcal{H}_2$ and $\mathcal{H}_3$) only if method 1 is used. If method 2 is used, contributions of the form $\langle(S^z)^2\rangle^2$ (not $\langle S^z\rangle^4$) appear in Φ_2, which for classical spin systems is a better approximation to the free energy than Φ_1.

To summarize, method 2 is, for classical spin systems, a better approximation than method 1. For quantum spin systems, however, method 2 is not always applicable, whereas method 1 still is.

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