

## Magnetic Spirals in the Molecular Field Approximation

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We consider a Bravais lattice of spins interacting via isotropic exchange with arbitrary interaction parameters. Villain has shown that the free energy, in the molecular field approximation (MFA), is a local minimum when the spin configuration is a simple spiral. It is possible to prove, however, by a method analogous to that of Luttinger and Tisza, that the simple spiral provides an absolute minimum to the free energy in the MFA. This result rules out the possibility of obtaining with the MFA any phase transition in such a system, except at the ordering temperature.

MUCH of our present understanding of cooperative magnetic phenomena in solids is based on the Heisenberg theory in which the spins at the various lattice sites interact with an energy

$$E = -\sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1)$$

Furthermore, the relatively simple molecular field treatment has provided much insight into the physical consequences of (1) at temperatures  $T > 0$ . An appealing derivation<sup>1</sup> of the equations of the molecular field theory can be based on a variational principle as follows: The exact canonical distribution  $p \propto \exp(-\beta E)$  being generally too complex to work with, one attempts to approximate it by a distribution describing independent spins, i.e., by a distribution of the form

$$p'(\mathbf{S}_1, \dots, \mathbf{S}_n) = p_1(\mathbf{S}_1) p_2(\mathbf{S}_2) \cdots p_n(\mathbf{S}_n). \quad (2)$$

Since the free energy  $A$  is minimized over all distributions by the canonical distribution<sup>2</sup>  $p$ , the "best"  $p'$  is defined to be the minimum free-energy-independent spin distribution. Variation of  $A$  with respect to  $p_i$  leads directly to the molecular field equations

$$p_i = Z_i^{-1} \exp[\mathbf{S}_i \cdot \boldsymbol{\sigma}_i \mathcal{L}^{-1}(\sigma_i)/\sigma_i], \quad (3)$$

with the spin averages  $\boldsymbol{\sigma}_i$  given by

$$\boldsymbol{\sigma}_i \mathcal{L}^{-1}(\sigma_i)/\sigma_i = 2\beta \sum_j J_{ij} \boldsymbol{\sigma}_j, \quad \text{all } i. \quad (4)$$

Here  $Z_i^{-1}$  is a normalizing factor independent of  $\mathbf{S}_i$ , and  $\mathcal{L}(x)$  is the Langevin function. (For simplicity, we have absorbed the spin lengths into the exchange parameters  $J_{ij}$ , so the spins are unit vectors.) We shall call a set of spin averages which satisfies (4), a "molecular field spin configuration" or MFSC. Each MFSC gives, via (3), an independent spin distribution for which  $A$  is stationary with respect to variations of the  $p_i$ . It remains to minimize  $A$  over all MFSC. Since this appears to be a somewhat formidable problem, it has been customary except at  $T=0$  and  $T \sim T_c$  to consider only a restricted class of solutions of (4), e.g.,

Néel or Yafet-Kittel configurations, or more generally, simple spirals.<sup>3</sup>

In the remaining discussion, unless explicitly stated otherwise, we shall consider only Bravais lattices of spins. However, the exchange parameters  $J_{ij}$  are not otherwise restricted in any way; for example, we do not restrict the range of interaction. Villian<sup>3</sup> has shown that in this case the lowest spiral MFSC, is locally stable. That is, any configuration close to the lowest spiral but otherwise arbitrary, has higher free energy. At  $T=0$ , (4) implies the usual "strong constraints" on the length of the spins. It is known<sup>4</sup> that in this case the classical energy is rigorously minimized by the lowest spiral. Also, near the ordering temperature, (4) becomes

$$3\boldsymbol{\sigma}_i = 2\beta \sum_j J_{ij} \boldsymbol{\sigma}_j. \quad (5)$$

In general, the only solutions of (5) have Fourier components belonging to a single star in  $\mathbf{k}$  space, so that near  $T_c$ , one can restrict consideration to this class (which contains all simple spirals). In view of all the above results, it seems probable that the lowest spiral gives an absolute minimum to the free energy in the molecular field approximation. This would rule out the possibility of obtaining with the molecular field theory any phase transition in the system except at the ordering temperature. At first glance, however, such a result appears difficult to prove in view of the complicated nature of the molecular field equations. It is the purpose of this note, nevertheless, to present a simple proof using a sort of generalized Luttinger-Tisza<sup>5</sup> method that the molecular field free energy as given below in (6) is rigorously minimized by some simple spiral configuration.

We obtain our result by adopting a somewhat different point of view than is usual. We first note that minimizing the free energy over all distribution of the form (3), where the set of spin averages or configuration is *not* constrained by (4), must, because of the way in which (3) was derived, lead to the lowest independent spin configuration (also perform lowest MFSC). In fact, (4) just defines the configurations for which  $A$  is sta-

<sup>1</sup> H. M. James and T. A. Keenan, *J. Chem. Phys.* **31**, 12 (1959).

<sup>2</sup> J. W. Gibbs, *Elementary Principles in Statistical Mechanics*, (Yale University Press, New Haven, 1902); J. von Neumann, *Göttinger Nachr.* 245 and 273 (1927).

<sup>3</sup> J. Villian, *J. Phys. Chem. Solids* **11**, 303 (1959).

<sup>4</sup> D. H. Lyons and T. A. Kaplan, *Phys. Rev.* **120**, 1580 (1960).

<sup>5</sup> J. M. Luttinger and L. Tisza, *Phys. Rev.* **70**, 954 (1946).

tionary.<sup>6</sup> Using (3) and not (4), the free energy  $A$  becomes, apart from an additive constant,

$$A = -\sum J_{ij}\sigma_i \cdot \sigma_j + kT \sum_i \int_0^{\sigma_i} \mathcal{L}^{-1}(x) dx = U + TN. \quad (6)$$

(Here  $N$  is the "negentropy.") As just stated, setting the variation of (6) equal to zero leads immediately to the complexities of (4). Hence, we must find another way to minimize  $A$ .

We begin by splitting the entire configuration space, bounded only by  $0 \leq \sigma_j \leq 1$ , all  $j$ , into mutually exclusive and exhaustive subsets  $\Omega_\alpha$ , where

$$\{\sigma_1 \cdots \sigma_n\} \in \Omega_\alpha \leftrightarrow \sum_i \sigma_i^2 = n\alpha^2, \quad (7)$$

i.e., a configuration belongs to  $\Omega_\alpha$  if and only if the equality on the right of (7) is satisfied. This condition is the analog of the weak constraint in the Luttinger-Tisza method.<sup>5</sup> We now show that a simple spiral configuration in  $\Omega_\alpha$  minimizes each term in (6), and, hence, their sum, which is  $A$  itself. This being true for all  $\alpha$ , the free energy (6) is minimized by a simple spiral, which is what we set out to prove.

It is easily shown, e.g., by using the calculus of variations, that the following spiral minimizes the internal energy  $U$  over  $\Omega_\alpha$ :

$$\sigma_i = \alpha[\hat{x} \sin(\mathbf{k}_0 \cdot \mathbf{R}_i) + \hat{y} \cos(\mathbf{k}_0 \cdot \mathbf{R}_i)], \quad (8)$$

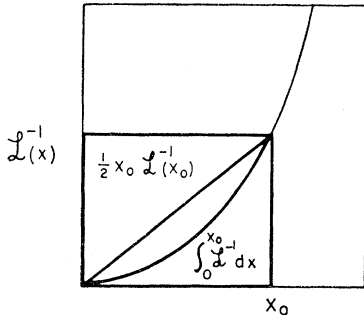
where  $\mathbf{k}_0$  maximizes the Fourier transform  $J(\mathbf{k})$  of  $J_{ij}$ . The unit vectors  $\hat{x}$  and  $\hat{y}$  are orthogonal but otherwise arbitrary. The internal energy becomes

$$\min_{\{\sigma_i\} \in \Omega_\alpha} U = -n\alpha^2 J(\mathbf{k}_0). \quad (9)$$

Turning now to the entropy term, variation with respect to  $\sigma_i$  immediately gives

$$2\lambda\sigma_i = k\mathcal{L}^{-1}(\sigma_i), \quad (10)$$

FIG. 1. Illustration in terms in Eq. (12).



<sup>6</sup> Since, in general, stationary points of a function are isolated, unless the function is constant over a continuum of stationary points, one may wonder how the simple spiral class of configurations (with properly adjusted amplitudes) can all be stationary since they apparently form a connected set. The answer is, of course, that for any finite lattice, the permissible propagation vectors are discrete (are just the  $\mathbf{k}$ 's in the Brillouin zone)—the connectedness is only apparent.

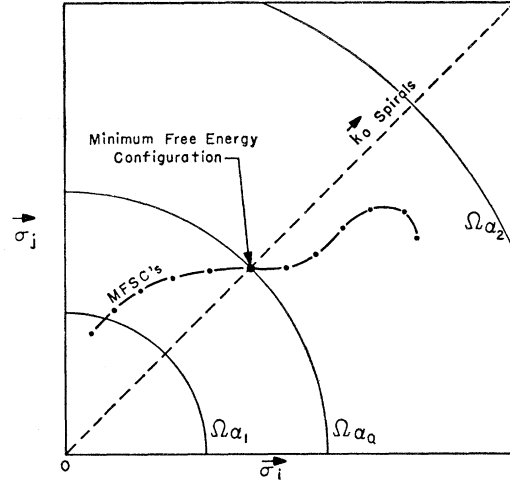


FIG. 2. Schematic representation of configuration space illustrating pertinent sets of configurations.

where  $\lambda$  must be chosen so that (7) is satisfied. Equation (10) has at most one nonzero solution, so that all nonzero spins must have the same length  $\sigma = \alpha n/m$ , where  $m$  is the number of nonzero spins. We have

$$\min_{\{\sigma_i\} \in \Omega_\alpha} N = \min_{m \leq n} mk \int_0^{\alpha(n/m)^{1/2}} \mathcal{L}^{-1}(x) dx \equiv \min_{m \leq n} N(m). \quad (11)$$

We show that  $N(m) \geq N(n)$  for  $m \leq n$ , by computing the derivative

$$\frac{1}{k} \frac{dN}{dm} = \int_0^{\alpha(n/m)^{1/2}} \mathcal{L}^{-1}(x) dx - \frac{1}{2} \alpha (n/m)^{1/2} \mathcal{L}^{-1}[\alpha(n/m)^{1/2}]. \quad (12)$$

It follows from (12) and the convexity of  $\mathcal{L}^{-1}(x)$  that the derivative is negative. This is shown in Fig. 1 in which both terms in (12) are illustrated. Therefore,

$$\min_{\{\sigma_i\} \in \Omega_\alpha} N = nk \int_0^\alpha \mathcal{L}^{-1}(x) dx, \quad (13)$$

and *all* spins have the same length  $\alpha$ . But this condition is satisfied also in the configuration (8) that minimizes the internal energy  $U$ . It follows that (8) gives the absolute minimum to the free energy  $A$  over  $\Omega_\alpha$ . We repeat that this then implies that the minimum free-energy configuration is a simple spiral, and, hence, the proof is now complete.

From the above, we have

$$\min_{\{\sigma_i\} \in \Omega_\alpha} A = -n\alpha^2 J(\mathbf{k}_0) + nkT \int_0^\alpha \mathcal{L}^{-1}(x) dx. \quad (14)$$

We may now complete the minimization of  $A$  over all configurations by minimizing (14) with respect to  $\alpha$ .

This gives

$$\alpha_0 = \mathcal{L}[2\alpha_0\beta J(\mathbf{k}_0)]. \quad (15)$$

It is easily seen that configuration (8) with  $\alpha = \alpha_0$  is a solution of (4). This is an explicit verification of the remarks above (6). Figure 2 is a schematic representation of the pertinent sets of configurations and is useful for visualizing the course of the proof.

Although we used the classical formulation, the quantum mechanical treatment using the density matrix is the same in all essentials. Of course, the Langevin function is then replaced by a Brillouin function, and the spin length appears explicitly. On the other hand, the theorem and proof can be modified and extended only to certain special cases<sup>7</sup> of anisotropic interaction and/or non-Bravais lattices. For example, we expect further results are obtainable when some form of generalized Luttinger-Tisza method<sup>4,8</sup> is successful in rigorously determining the ground state. However, it is clear that the technique is not adequate to deal with the general case. For it has been shown<sup>9</sup> that in at least some non-Bravais lattices, even with only Heisenberg interactions, the angles between spins in the classical ground state

<sup>7</sup> The hcp lattice is an example of a non-Bravais lattice to which the proof may easily be extended.

<sup>8</sup> M. J. Freiser, *Phys. Rev.* **123**, 2003 (1961).

<sup>9</sup> D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, *Phys. Rev.* **126**, 546 (1962)

fail to satisfy the very plausible translational invariance condition,

$$\mathbf{S}_{n\nu} \cdot \mathbf{S}_{m\mu} = f_{\nu\mu}(\mathbf{R}_m - \mathbf{R}_n).$$

Here  $\nu$  and  $\mu$  label the sublattices and  $m$  and  $n$  label the unit cells. The ground state is, therefore, probably very complex and no method is known for discovering it. This difficulty is compounded at temperatures higher than  $T=0$ .

Finally, a word about the use of the molecular field idea. As it stands, the theorem has precise meaning for  $T>0$  only in the context of the molecular field or independent spin approximation. One may wonder whether the theorem reflects a similar precise statement true for the exact canonical distribution. We feel this to be unlikely, if only for the reason that the concept of a spiral configuration for  $T>0$  loses its precision outside of the molecular field approximation. Rather, the molecular field results suggest a single high peak in the transform of the spin correlation function  $\langle \mathbf{S}(\mathbf{R}_n) \cdot \mathbf{S}(\mathbf{R}_n + \mathbf{R}) \rangle$ . Of course, this transform is essentially what is measured in neutron diffraction experiments on magnetic ordering.

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## Effect of Temperature and Pressure on the Resistance of Four Alkali Metals\*

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The electrical resistance of lithium, sodium, potassium, and rubidium has been measured as a function of pressure to over 500 kbar at 77°K and 296°K. Lithium exhibits an initial rise in resistance, a first-order phase transition at 70 kbar with a large resistance drop, and a very gradual rise in resistance at high pressure. Sodium has a rise in resistance with pressure at both 77 and 296°K. The high-temperature isotherm exhibits a very broad maximum at high pressure. For potassium, the 296°K isotherm shows a rise by a factor of 50 in 600 kbar. The 77°K isotherm shows a sluggish transition at 280 kbar and a very sharp transition at 360 kbar. The latter is almost certainly martensitic. Both isotherms for rubidium have qualitatively similar behavior: a rise in resistance which accelerates with increasing pressure, a discontinuous rise at 190 kbar (210 kbar at 77°K), and a broad maximum at high pressure. The discontinuous rise is probably due to a electronic transition.

**T**HE effect of pressure to over 500 kbar has been measured on the electrical resistance of lithium, sodium, potassium, and rubidium at 296 and 77°K. At appropriate pressures isobars were also measured. The experimental techniques have been previously de-

scribed.<sup>1,2</sup> The methods for preventing sample oxidation are mentioned in a previous paper on alkaline earth metals.<sup>3</sup> The metals used in this work are c.p. materials.

<sup>1</sup> A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* **32**, 308 (1961).

<sup>2</sup> H. G. Drickamer and A. S. Balchan, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths Scientific Publications, Ltd., London, 1962).

<sup>3</sup> R. A. Stager and H. G. Drickamer, *Phys. Rev.* **132**, 124 (1963).

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