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Shape Dependence of the Thermodynamic Properties of Magnetic Systems*

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To investigate the dependence of the thermodynamic properties of a magnetic system in an applied field on the shape of the external boundary, we have studied the shape dependence of the free energy. Shape enters the thermodynamic properties through the dipolar sum, $\Phi=-(1/N)\Sigma_j(1-3\cos^2\theta_{ij})/r_{ij}^3$. The dependence of the free energy on shape has been ascertained for ellipsoids by using a linked-cluster diagrammatic expansion of the free energy. We have considered the full dipole-dipole interaction between the spins in materials for which the magnetization is parallel to the magnetic field, when applied along a principal axis for the sample, and have found that if we write a pseudo-free-energy in terms of the local field $L=H_0+\Phi M$, or the internal field $H_i=H_0-DM$, the resulting function is independent of the shape of the sample. Here H_0 represents the applied field, M the magnetization, and D is the demagnetization factor of the sample. Also, for a magnetic system in an applied field, the specific heat at constant local (internal) field is the same function of local (internal) field and temperature for all ellipsoidal shapes of the same material. The same is true of the susceptibility to within a demagnetization factor.

INTRODUCTION

A DIPOLE-DIPOLE coupling between spins exists in all magnetic materials; its presence causes the thermodynamic properties of the material to depend on the shape of the external boundary of the sample. For those materials in which this long-range interaction provides the dominant contribution to the magnetic ordering, we expect that their thermodynamic properties will strongly depend on the shape of the sample. Whereas it has long been recognized that the susceptibility of two samples of the same material will differ, the dependence on shape of the specific heat of a sample in a magnetic field has received relatively little attention.

Hiley and Joyce[1] have shown that the specific heat in zero field above T_c is independent of shape, and that the zero-field susceptibility of an Ising model with long-range dipole forces has a simple dependence on shape

$$\chi^{-1}(T)=\chi_0^{-1}(T)-\Phi, \qquad (1)$$

where χ_0 does not depend on the shape of the sample and Φ is the dipole sum defined by Eq. (2) below. We have extended their investigation by finding the shape dependence of the specific heat and susceptibility for finite magnetic fields. Furthermore, we consider the full dipole-dipole interaction, not only the longitudinal component of this coupling. As all the thermodynamic properties of a system are derivable from the free energy, we have chosen to study the shape dependence of this quantity in finite magnetic fields.

The origin of this dependence on shape lies in the long-range nature of dipolar forces. The shape of the external boundary of a sample explicitly enters the thermodynamic properties as the dipole sum

$$\Phi(i)=-(1/N)\textstyle\sum_j(1-3\cos^2\theta_{ij})/r_{ij}^3. \qquad (2)$$

This sum is conditionally convergent,[2] i.e., the sum depends on the shape of the external boundary. We shall only consider ellipsoidal shapes; for these the dipole sum Φ in a *large* specimen is independent of the position of the origin (i). With this restriction the dipole sum can be decomposed into a sum about the origin and a remainder which is accounted for by the classical demagnetization factor,[3] i.e.,

$$\Phi=\Phi_0+D_0-D, \qquad (3)$$

where

$$\Phi_0=-(1/N_0)\sum_{V_0}{}'_j(1-3\cos^2\theta_{ij})/r_{ij}^3$$

is the lattice sum over a volume V_0 close to the origin (i), D_0 is the demagnetization factor for the surface enclosing the volume V_0, and D is the demagnetization factor for the external boundary of the sample. The values of the demagnetization factors D and D_0 lie between zero for a cylinder and 4π for a flat disc perpendicular to the magnetization; for a sphere it is $4\pi/3$. The dipole sum Φ_0 depends on the structure of the magnetic sublattice and on the shape of the volume V_0; for a simple cubic lattice and a spherical boundary Φ_0 is zero. For other combinations Φ_0 can take on values of the same order of magnitude as D, and its sign can be positive or negative depending on the lattice structure and shape of the volume V_0. The dipole sums Φ for samples which differ only in shape will differ only in their demagnetization factors D; the first two terms in Eq. (3) depend only on the crystal structure of the sample.

To ascertain the shape dependence of the free energy

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[1] B. J. Hiley and G. S. Joyce, Proc. Phys. Soc. (London) **85**, 493 (1965).

[2] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937); J. A. Sauer, Phys. Rev. **57**, 142 (1940).

[3] See, for example, J. H. Van Vleck, Ref. 2.

of a magnetic system in a finite field we use the linked-cluster diagrammatic expansion of the free energy as developed by Brout,[4] Horwitz and Callen,[5] Englert,[6] and Stinchcombe *et al.*[7] This expansion is preferable to the low-field, high-temperature expansion introduced by Opechowski[8] and Van Vleck[9] because it allows us to obtain results that are valid for all temperatures and fields *provided* the series expansion is convergent. We consider our magnetic system to be represented by the Hamiltonian

$$\mathcal{H} = -g\mu_B H_0 \textstyle\sum_i S_i^z - \displaystyle\sum_{ij} \mathbf{S}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{S}_j, \tag{4}$$

where

$$\mathbf{J}_{ij} = -\tfrac{1}{2} g^2 \mu_B^2 \, \mathbf{T}_{ij},$$

$$\mathbf{T}_{ij} = \frac{1}{r_{ij}^3}\{\mathbf{u} - 3\hat{r}_{ij}\hat{r}_{ij}\}. \tag{5}$$

$\mathbf{u}$ is the unit tensor whose Cartesian components are $\delta_{\alpha\beta}$, and H_0 is an applied magnetic field. An arbitrary number of short-range exchange forces can also be included in the above Hamiltonian by redefining the coupling tensor $\mathbf{J}_{ij}$. The presence of short-range forces only alters the value of Φ_0, Eq. (3); the demagnetization factors D_0 and D are unchanged. As only the long-range dipole forces contribute to the shape dependence we will only talk about these forces, but all our results apply equally well when short-range exchange forces are also present.

We will first consider only the longitudinal part of the dipole-dipole coupling between spins. In this approximation the Hamiltonian representing the magnetic system is analogous to the one for the Ising model with arbitrary spin and a long-range coupling constant. All the operators commute and the free energy has been expanded in a series by considering the operators as c numbers.[4–6] When we include the diagonal transverse components of the dipolar coupling, the Hamiltonian is analogous to the anisotropic Heisenberg model, again with long-range coupling constants. The noncommutativity of the operators is dealt with by using time-ordered semi-invariants and averages.[7] To arrive at the shape dependence of the free energy for the full dipole-dipole interaction we have to restrict our analysis to those materials for which the magnetization is parallel to the field when applied along a principal axis of the sample; this ensures us that some off-diagonal dipole sums vanish. In each of the above cases, all the shape-dependent terms in the series expansion of the free energy are resummed by a special vertex renormalization known as $\bar{S}$ renormalization,[5] therefore, the shape-dependent terms are accounted for by an effective field. Finally, we derive the shape dependence of the specific heat and susceptibility for samples in finite fields.

SHAPE DEPENDENCE OF THE FREE ENERGY

A. Ising Model

If we neglect all components of the interaction tensor $\mathbf{J}_{ij}$, Eq. (5), other than the longitudinal, the Hamiltonian for the magnetic system reduces to that of the Ising model with arbitrary spin

$$\mathcal{H} = -g\mu_B H_0 \textstyle\sum_i S_i^z - \sum_{ij} J_{ij} S_i^z S_j^z,$$

where

$$J_{ij} = -\tfrac{1}{2} g^2 \mu_B^2 \{(1-3\cos^2\theta_{ij})/r_{ij}^3\}. \tag{4$'$}$$

We consider the single-ion term as the unperturbed Hamiltonian $\mathcal{H}_0$:

$$\mathcal{H}_0 = -g\mu_B H_0 \textstyle\sum_i S_i^z,$$

and the remaining term which couples the spins as a perturbation V:

$$V = -\textstyle\sum_{ij} J_{ij} S_i^z S_j^z.$$

The free energy is defined as

$$e^{-\beta F} = \mathrm{tr}\, e^{-\beta\mathcal{H}}$$

or

$$-\beta F = \ln \mathrm{tr}\, e^{-\beta\mathcal{H}}. \tag{6}$$

This can be written as

$$-\beta F = -\beta F_0 - \beta F', \tag{7}$$

where

$$-\beta F_0 = \ln \mathrm{tr}\, e^{-\beta\mathcal{H}_0}$$

and

$$-\beta F' = \ln \mathrm{tr}\, \rho_0 e^{-\beta V}.$$

The density matrix ρ_0 is defined as

$$\rho_0 = e^{-\beta\mathcal{H}_0} / \mathrm{tr}\, e^{-\beta\mathcal{H}_0}. \tag{8}$$

By using the linked-cluster diagrammatic expansion of Horwitz and Callen[5] (hereafter abbreviated as HC) or Englert[6] we expand the perturbed part of the free energy (7) as a series of semi-invariants

$$\ln \mathrm{tr}\, \rho_0 e^{-\beta V} = \sum_{n=1}^{\infty} \frac{\beta^n}{n!} M_n(-V), \tag{9}$$

where the semi-invariant of the nth order M_n is defined as

$$M_n(V) = (\partial/\partial\alpha)^n \,|_{\alpha=0} \ln \mathrm{tr}(e^{\alpha V}\rho_0). \tag{10}$$

These semi-invariants are related to the thermodynamic average of the perturbation V taken with respect to the density matrix ρ_0, Eq. (8). For example

$$M_0 = \ln \mathrm{tr}\, e^{-\beta\mathcal{H}_0},$$

$$M_1(V) = \mathrm{tr}\, e^{-\beta\mathcal{H}_0} V / \mathrm{tr}\, e^{-\beta\mathcal{H}_0} = \mathrm{tr}\, \rho_0 V = \langle V\rangle_0,$$

$$M_2(V) = \langle V^2\rangle_0 - \langle V\rangle_0^2. \tag{11}$$

By realizing that the perturbation V is a sum of terms,

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[4] R. Brout, Phys. Rev. **115**, 824 (1959); **118**, 1009 (1960).

[5] G. Horwitz and H. B. Callen, Phys. Rev. **124**, 1757 (1961).

[6] F. Englert, Phys. Rev. **129**, 567 (1963).

[7] R. B. Stinchcombe, G. Horwitz, F. Englert, and R. Brout, Phys. Rev. **130**, 155 (1963).

[8] W. Opechowski, Physica **4**, 181 (1937).

[9] See J. H. Van Vleck, Ref. 2.

each coupling a pair of spins, Brout[10] expanded the free energy F' as a series of linked clusters. After rearranging the terms in Brout's expansion HC[5] were able to write the free energy F' in the simple form

$$-\beta F'=\sum_{n,t}(2\beta)^n G_{n,t}{}^{-1}M_{(n,t)}\sum_{ijk\cdots}J_{ij}J_{kl}\cdots. \tag{12}$$

This form of the expansion has the simple graphical interpretation that each term $(n,\ t)$ corresponds to a topologically inequivalent diagram of n bonds between $m\leq n+1$ spins. Each vertex of the diagram with p bonds contributes a semi-invariant $M_p(S^z)$ where from Eqs. (10) and (8)

$$M_p(S^z)=(\partial/\partial\alpha)^p\,|_{\alpha=0}\ln\operatorname{tr}(e^{\alpha S^z}\rho_0) \tag{10'}$$

and $\alpha=\beta g\mu_B H_0$; each bond contributes the factor J_{ij}, and $G_{n,t}$ is related to the symmetry of the diagram. The major advantage of this form of the expansion over Brout's is the mathematical convenience of an *unrestricted* sum over the coupling constants J_{ij}. The only diagrams that contribute to the free energy are those that are entirely linked together, therefore the name *linked*-cluster expansion.

As examples of diagrams which contribute to the free energy we have the single bond $(n=1)$, see Fig. 1(a), which gives a contribution of

$$2\beta\tfrac{1}{2}M_1{}^2(S^z)\sum_{ij}J_{ij},$$

where the first-order semi-invariant is just the magnetization divided by $Ng\mu_B$. The triangle $(n=3)$, Fig. 1(b), contributes

$$(2\beta)^3(1/3!)M_2{}^3(S^z)\sum_{ijk}J_{ij}J_{jk}J_{ki}.$$

The main task in determining how shape enters the free energy is to find *all* terms in the series expansion (diagrams) containing the shape-dependent dipole sum Φ. Shape only enters when the unrestricted sum $\sum_{ijk\cdots}J_{ij}J_{kl}\cdots$ contains the sum[11]

$$\sum_j J_{ij}=J_0=\tfrac{1}{2}Ng^2\mu_B{}^2\Phi. \tag{13}$$

The diagrams which correspond to these shape-dependent terms contain pairs of spins which are *singly* bonded. The simplest shape-dependent contribution to the free energy comes from the diagram in Fig. 1(a). Only the sum Eq. (13) is shape-dependent.[12]

FIG. 1. Diagrams which give contributions to the free energy F'; (a) the single bond, (b) the triangle.

FIG. 2. Examples of how single bonds appear in diagrams; (a) with one free end, (b) with both ends attached to subdiagrams.

All other sums,[13] e.g., $\sum_j J_{ij}{}^n n>1$, and $\sum_{ijk}J_{ij}J_{jk}J_{ki}$, are absolutely convergent, and therefore independent of shape. There are two ways in which single bonds, or chains of single bonds, between spins appear in diagrams. Either with one end attached to a diagram and the other end free, see Fig. 2(a), or with diagrams attached at both ends, Fig. 2(b). The most general diagrams containing single bonds are hyper-Cayley trees, i.e., the $\bar{S}$-reducible diagrams of HC. These trees are open diagrams composed of single-bond chains where instead of simple vertices we have hypervertices which are, for our purpose, diagrams that do not contain any single bonds; this type of a cluster is called an $\bar{S}$-irreducible diagram.[5]

The contributions from all possible hyper-Cayley trees can be summed by using either the methods of HC of $\bar{S}$ renormalization and subtraction of hyperbond-rooted from hypervertex-rooted diagrams, or the similar approach of the irreducibly linked-cluster expansion of Englert.[14] With these methods we can sum an infinity of diagrams by renormalizing each hypervertex ($\bar{S}$-irreducible diagram) by alternately appending single bonds and other hypervertices in an infinite sequence. The contributions from the appended parts can be summarized as[6]

$$\bar{M}_n=\exp\left[\sum_k G_k(\partial^k/\partial\alpha^k)\right]_{\alpha=0}M_n(\alpha), \tag{14}$$

where $\bar{M}_n$ is the renormalized semi-invariant representing a vertex of the hypervertex and G_k is the self-energy[15] of the appended part, which is itself renormalized. Because of the structure of hyper-Cayley trees each vertex of a hypervertex can only be renormalized by single bonds, i.e., $G_k=0$ for $k\neq1$. By using Eq. (14) and the definition of the semi-invariant M_n [Eq. (10′)] we find

$$\begin{aligned}\bar{M}_n&=(\partial/\partial\alpha)^n e^{G_1(\partial/\partial\alpha)}\,|_{\alpha=0}\ln\operatorname{tr}(e^{\alpha S^z}\rho_0)\\&=(\partial/\partial\alpha)^n\,|_{\alpha=0}\ln\operatorname{tr}\{e^{(\alpha+G_1)S^z}\rho_0\},\end{aligned} \tag{15}$$

therefore, $\bar{M}_n=M_n(\alpha+G_1)$.
Each free end of the added single bond can remain free or be renormalized by either another single bond or any of the hypervertices γ; therefore, the renormalized semi-invariant representing the renormalized free end of an added bond is

$$\bar{M}_1=M_1(\alpha+G_1)-(\beta/N)\sum_\gamma D\bar{F}_\gamma, \tag{16}$$

where $(-\beta/N)D\bar{F}_\gamma=G_\gamma\bar{M}_{1+\gamma}$ represents the contribution of a hypervertex, and the sum runs over all hyper-

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[10] The original expansion of Brout contained restricted sums which lead to "excluded volume" diagrams. See R. Brout, Ref. 4.

[11] For temperatures below the Curie or Néel point we must furthermore stipulate that the sample is *uniformly* magnetized for the above to be true.

[12] For the full dipole-dipole interaction and the Heisenberg model, we will assume the sample *size* is large enough to neglect magnetostatic modes.

[13] These sums represent multiply bonded pairs of spins.

[14] See Ref. 6, Eq. (4.7).

[15] For a definition of the self-energy G_k, see Ref. 6, Sec. III.

vertices, and vertices thereof, that can be attached to the free end of a single bond.[16] From the definition of self-energy[15] we find

$$G_1 = 2\beta J_0 \bar{M}_1;$$

this can be rewritten as $\beta g \mu_B \Phi M$ by using Eq. (13) and the definition of the magnetization M:

$$M = N g \mu_B \langle S^z \rangle = N g \mu_B \bar{M}_1. \tag{17}$$

We conclude that the hyper-Cayley trees are accounted for by the vertex renormalization

$$\begin{aligned} \bar{M}_n &= M_n(\beta g \mu_B (H_0 + \Phi M)) \\ &= M_n(L), \end{aligned} \tag{18}$$

where the magnetization M is self-consistently calculated as

$$M = N g \mu_B \{ M_1(L) - (\beta/N) \sum\nolimits_\gamma D \bar{F}_\gamma \} \tag{19}$$

and the local field L is defined as

$$L = H_0 + \Phi M. \tag{20}$$

This renormalization is just what HC call $\bar{S}$ renormalization. Each hypervertex of the Cayley tree perceives the remainder of the tree through single bonds; therefore $\bar{S}$ renormalization is relatively simple.

The contribution to the free energy from all hyper-Cayley trees is given as the free energy of the renormalized hypervertices[17]

$$F = \tfrac{1}{2} \Phi M^2 + \bar{F}_0 + \sum_\gamma \bar{F}_\gamma, \tag{21}$$

where $\bar{F}_\gamma$ is the renormalized free energy of the γth hypervertex and $\bar{F}_0 = \ln \operatorname{tr} e^{\beta g \mu_B L S^z}$. Therefore, the subset of all diagrams containing shape-dependent terms are resummed by replacing the external field H_0 in F_0 and the density matrix ρ_0 Eq. (8) by the local field L.

$$\rho = e^{\beta g \mu_B L S^z} / \operatorname{tr} e^{\beta g \mu_B L S^z}. \tag{8$'$}$$

As the *bare* hypervertices by definition do not contain any shape-dependent contributions to the free energy, we conclude that shape only enters the terms $\sum_\gamma \bar{F}_\gamma$ through the renormalization of the semi-invariants M_n by using the density matrix ρ [Eq. (8′)] instead of ρ_0. The terms $\bar{F}_0 + \sum_\gamma \bar{F}_\gamma$ are only implicit functions of the shape through the local field:

$$\bar{F}_0 + \sum_\gamma \bar{F}_\gamma = f(L, T). \tag{22}$$

Instead of using the Helmholtz free energy

$$dF = -S dT - M dH_0, \tag{23}$$

we define a pseudo-free-energy F_A[18]:

$$dF_A = -S dT - M dL, \tag{24}$$

where

$$F_A = F - \tfrac{1}{2} \Phi M^2. \tag{25}$$

The "free energy" $F_A(L, T)$ is the same function of local field and temperature for all shapes; replacing the external field by the local field in F_0 and the density matrix Eq. (8′) accounts for *all* shape-dependent terms entering the free energy F_A.

B. Heisenberg Model

If we neglect only the off-diagonal components of the dipole-dipole interaction and make the simplifying assumption that the diagonal components are equal[19] the resulting Hamiltonian is that of the Heisenberg model

$$\mathcal{H} = -g \mu_B H_0 \sum\nolimits_i S_i^z - \sum\nolimits_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \tag{4$''$}$$

The thermodynamic behavior of this model has been studied by Stinchcombe *et al.*[7] using a linked-cluster expansion with time-ordered averages and semi-invariants. The perturbed part of the free energy, i.e.,

$$\beta F' = \ln \operatorname{tr} \rho_0 e^{\beta \mathcal{H}_0} e^{-\beta(\mathcal{H}_0 + V)}, \tag{26}$$

has been expanded as a linked-cluster series similar to Eq. (12), but with two notable differences. As the components of the perturbation V commute neither amongst themselves nor with the unperturbed Hamiltonian $\mathcal{H}_0$, the exponentials in Eq. (26) are expanded as

$$\begin{aligned} e^{\beta \mathcal{H}_0} e^{-\beta(\mathcal{H}_0 + V)} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \\ \times \int_0^\beta \cdots \int_0^\beta T[V(\beta_n) \cdots V(\beta_1)] d\beta_1 \cdots d\beta_n, \end{aligned} \tag{27}$$

where the operators $V(\beta_i)$ are in the interaction representation and the symbol T represents the Dyson time-ordering operator. The other notable difference is that there are transverse $(J_{ij} S_i^+ S_j^-)$ as well as longitudinal components of the interaction which couple the spins on sites i and j. Because of these differences the expansion of the free energy F' for the Heisenberg model is in terms of time-ordered semi-invariants of mixed arguments[20]

$$\begin{aligned} M_{\Sigma n_{\nu_i} > 0} \Big(T \prod_{\nu i} [S^{(\nu i)}(\beta_i)]^{n_{\nu i}} \Big) = \prod_{\nu i} (\partial / \partial t^{\nu i})^{n_{\nu i}} \Big|_{t^{\nu i} = 0} \\ \times \ln \Big\langle T \exp \Big(\sum_{\nu i} S^{(\nu i)}(\beta_i) t^{\nu i} \Big) \Big\rangle_0. \end{aligned} \tag{28}$$

The expansion of the free energy F' [Eq. (26)] in time-ordered semi-invariants has a graphical interpretation

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[16] We could also use

$$\bar{M}_1 = \exp\Big[\sum_{\{\gamma\}} G_\gamma (\partial / \partial \alpha)^{k_\gamma} \Big] M_1(\alpha).$$

[17] See Ref. 5, p. 1760, Eq. (15), and p. 1772, Eq. (149).

[18] Equation (24) does not define a *true* free energy because MdL does not represent the differential external work done on the system; the term MdL includes the mutual interaction of the spins. This definition of a *pseudo*-free-energy is the same as the free energy F_2 defined by A. H. Wilson, in *Thermodynamics and Statistical Mechanics* (Cambridge University Press, Cambridge, England, 1957), p. 286.

[19] This simplification in no way affects our conclusions about the shape dependence of the free energy, because the sums $\Sigma_j J_{ij}^{xx}$ and $\Sigma_j J_{ij}^{yy}$ do not enter the free energy.

[20] See Ref. 7, p. 157, Eq. (20).

in terms of time-ordered diagrams which parallels the diagrammatic expansion of the Ising model;[21] the new features are: (1) the transverse bonds with arrows pointing from the vertex containing S^+ to the vertex containing S^-, (2) the temperature labels β_i on the bonds, (3) that semi-invariants are integrated over all temperatures from 0 to β, and (4) the numerical changes in the symmetry factors $G_{(n,t)}$ [see Eq. (12)] because of the transverse bonds. As before, the shape-dependent terms only enter diagrams from which one can split off from the unrestricted sum in Eq. (12) sums of the type $\sum_j J_{ij}$. But now we must consider not only longitudinal but transverse bonds as well; these new bonds might conceivably contribute shape-dependent sums to the free energy. A transverse bond with one end attached to a diagram and the other free contributes to F' the term $2\beta\sum_j J_{ij}M_1(S^\pm)$; this multiplies the contribution to F' from the remainder of the diagram. The contribution from the entire diagram vanishes because the first-order semi-invariant of a raising or lowering operator is zero, therefore, no shape-dependent terms come from transverse bonds with free ends. A nonzero semi-invariant must have in its argument an equal number of raising and lowering operators (S^+, S^-). It is for this reason that a transverse bond cannot act as the sole connection (single bond) between two points in a diagram. The proof of this comes from realizing that when one or an odd number of transverse bonds are appended to a balanced hypervertex (nonvanishing contribution to the free energy), the hypervertex will be unbalanced because the number of raising and lowering operators will be unequal. To compensate for this imbalance another transverse bond must be added. When one appends hypervertices to the free ends of the single transverse bonds one is forced once more to add transverse bonds on the appended hypervertex to maintain the balance. Now let us consider trees with transverse bonds connecting hypervertices. If an end of the tree is a transverse bond the contribution of the tree to the free energy vanishes; if the end is a hypervertex by definition it has only one transverse bond attached to it and once again the contribution vanishes because the contribution of the end vertex (which multiplies the remainder) is zero. We are thereby lead to conclude that the only trees, i.e., diagrams with shape-dependent sums, that contribute to F' are those with longitudinal bonds joining the hypervertices. For this reason the transverse dipole sums

$$T^{\lambda\lambda}=\sum_j T_{ij}{}^{\lambda\lambda}\qquad \lambda=x,\,y$$

do not enter the free energy.

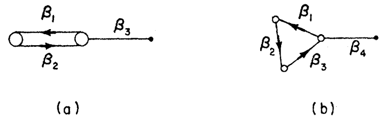

FIG. 3. Examples of longitudinal bonds which have a time-ordered diagram attached to one of their free ends.

To use $\tilde{S}$ renormalization on these time-ordered trees two necessary conditions must be fulfilled: (1) that the addition of longitudinal bonds to a vertex does nothing more than renormalize the vertex by replacing the applied field H_0 in the density matrix Eq. (8) by the local field L Eq. (20), and (2) that the renormalization of the free end of a longitudinal bond by time-ordered vertices does not depend on the temperature label attached to the longitudinal bond. As it has been proven by Stinchcombe *et al.*[22] that any time-ordered vertex can be simply renormalized by longitudinal (Cayley) trees, the first condition is satisfied. By explicitly evaluating the contribution to the free energy from diagrams in which a longitudinal bond is appended to a time-ordered diagram, see Figs. 3(a) and 3(b), we have shown that the contributions do not depend on the temperature labels on the longitudinal bonds. In other words we have shown[23] that the integrals

$$\int_0^\beta d\beta_1\int_0^\beta d\beta_2 M_2(TS^-(\beta_1)\,S^+(\beta_2))\times M_3(TS^+(\beta_1)\,S^-(\beta_2)\,S^z(\beta_3))$$

and

$$\int_0^\beta d\beta_1\int_0^\beta d\beta_2\int_0^\beta d\beta_3 M_3(TS^+(\beta_1)\,S^-(\beta_3)\,S^z(\beta_4))\times M_2(TS^+(\beta_2)\,S^-(\beta_1))M_2(TS^+(\beta_3)\,S^-(\beta_2))$$

corresponding to the free energy of the diagrams in Figs. 3(a) and 3(b) do not depend on the temperature labels, β_3 for the first integral and β_4 for the second. One can probably generalize this result to any vertex with one longitudinal bond that is renormalized by time-ordered diagrams.[23a] In the notation of Stinchcombe *et al.*[24] we write this as

$$M_1{}^T(S^z(\beta_1))=R_TM_1(S^z(\beta_1)),\tag{29}$$

where the renormalization R_T is *independent* of the label β_1. For vertices with transverse bonds the renormalization produced by transverse loops (time-ordered loops) depends on the temperature labels

$$M_{2k+l}{}^T(TS^+(\beta_1)\cdots S^z(\beta_{2k+l}))=R_T(\beta_1\cdots\beta_{2k+l})M_{2k+l}(TS^+(\beta_1)\cdots S^z(\beta_{2k+l})).\tag{30}$$

It is only for the special case of no transverse parts in the vertex ($k=0$, $l=1$) that the renormalization is simple.

As the necessary conditions for $\tilde{S}$ renormalization are fulfilled, the contributions from all time-ordered

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[21] An excellent discussion of the linked-cluster expansions for the Ising and Heisenberg models is given in an article by R. Brout, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. II A.

[22] See Ref. 7, pp. 161–162, Eqs. (38–42).

[23] We have confined our calculations to a spin value $s=\frac{1}{2}$. The effects of the noncommutativity of the operators are most pronounced for this value of the spin, therefore, the conclusions we draw are valid for all values of the spin.

[23a] P. M. Levy and R. B. Stinchcombe (to be published).

[24] See Ref. 7, Eqs. (93–94).

hyper-Cayley trees can be summed by using this renormalization. The results on the shape dependence of the free energy are identical to those for the Ising model, i.e., the "free energy" $F_A(L, T)$ is independent of shape where the local field is the same as before Eq. (20) and the free energy is a sum of contributions from $\bar{S}$-renormalized hypervertices. The ability to do this renormalization rests on the fact that the renormalization of the free ends of longitudinal bonds does not depend on the temperature labels; if it did the temperature labels would enter the renormalization in a manner that would require a separate evaluation of each term.

Only the longitudinal bonds give shape-dependent sums Φ because at least two transverse bonds must connect a pair of spins; transverse bonds only appear in hypervertices. For this reason the shape dependence of the free energy predicted on the basis of the Heisenberg and Ising models is identical.

C. Dipole-Dipole Interaction

The Hamiltonian for the full dipole-dipole interaction Eq. (4) contains in addition to the Heisenberg Hamiltonian, Eq. (4″), the off-diagonal terms

$$\sum_{ij} J_{ij}^{\alpha\beta} S_i^{\alpha} S_j^{\beta} \qquad \alpha \neq \beta.$$

These additional terms lead to diagrams where points are singly connected by off-diagonal terms as well as by diagonal transverse bonds. The renormalization of these diagrams is difficult and it is not clear if trees made up of these diagrams can be resummed by simple $\bar{S}$ renormalization. It is known that the shape dependence of the free energy is more complicated[25] than that discussed in the preceeding sections for materials where the off-diagonal sums

$$T^{\lambda z} = \sum_j T_{ij}^{\lambda z}, \qquad \lambda = x, y$$

do not vanish. Complications arise for these materials because the magnetization **M** is not parallel to the applied field $\mathbf{H}_0$. Even if we apply the field $\mathbf{H}_0$ along a symmetry axis of the crystal, the magnetization will not be parallel to the field when the principal axes of the sample's external shape do not coincide with the crystal's symmetry axes. If we confine ourselves to materials for which **M** is parallel to $\mathbf{H}_0$ (when applied along a principal axis of the sample), we are assured, as proven in the Appendix, that the dipole sums $T^{\lambda z} (\lambda = x, y)$ vanish (x, y, and z are the principal axes of the sample).

With this restriction the only new lattice sum that could appear in the free energy is the nondiagonal transverse term T^{xy}. By using arguments identical to those used for the diagonal transverse bonds, these new bonds cannot join two hypervertices in an open diagram (tree). Therefore, they never exist as single bonds between spins, and the dipole sum T^{xy} does not enter the free energy. As in the preceeding models, only the dipole sum Φ contributes a shape-dependent term to the free energy. Again the shape dependence of the free energy is contained in the local field, and the "free energy" $F_A(L, T)$ is the same function of local field and temperature for all shapes of the external boundary of a material.[26]

The rigorous proof of this result depends on the unproven assumption that the linked-cluster expansion is convergent.[27] This is a reasonable assumption for the paramagnetic phase of a magnetic system, and for the ferromagnetic phase in a finite field provided we perform the expansion in terms of the *Holstein-Primakoff* spin-wave-like deviations from the ground state at absolute zero as found by Holstein and Primakoff.[28] For other magnetically ordered phases, e.g., antiferromagnetic ordering, we must do an entirely new expansion with the ordered-state configuration as a basis. An alternate method of arriving at the shape dependence of the free energy involves the use of a phenomenological argument[29] which contains some unproven assertions.

Suppose we carve out from a uniformly magnetized sample a long thin cylinder parallel to the magnetiza-

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[25] Marquard points out that for materials for which the off-diagonal sums T^{xz} and T^{yz} do not vanish, the inverse susceptibility

$$1/\chi = (T/C) \{1 + \sum_{n=1}^{\infty} (B_n/T^n)\}$$

contains an unusual shape-dependent term in the coefficient B_3. Shape dependence enters the coefficient B_3 through terms like

$$T^{z\lambda} T^{\lambda\lambda} T^{\lambda z}, \qquad \lambda = x, y.$$

Whereas the off-diagonal sums $T^{z\lambda}$ are shape-independent, the diagonal dipole sums $T^{\lambda\lambda}$ which are similar to the sum T^{zz}, i.e., Φ, depend on shape. The usual shape dependence enters the inverse susceptibility in the second term B_1/C as the sum T^{zz} or Φ. If the sums $T^{z\lambda}$ do not vanish shape-dependent terms T^{xx} and T^{yy} enter the inverse susceptibility in such a way that they cannot be accounted for by an effective field, e.g., the local field L. [See C. D. Marquard, Proc. Phys. Soc. (London) **92**, 650 (1967), and Doctoral thesis, University of Oxford, 1966, Appendix III, pp. B86–88 (unpublished).] This unusual shape dependence is no longer present if one considers the inverse of the susceptibility tensor χ and finds $(\chi_{zz})^{-1}$ instead of only the inverse of the element χ_{zz}. See H. Horner (to be published).

[26] These remarks about the shape dependence should not lead one to infer that the free energies for the three cases are identical. This is not true because the hypervertices have entirely different structures. Only the single bonds between the hypervertices are the same and therefore the Ising, Heisenberg, and dipole-dipole interactions share a common shape dependence of their free energies.

[27] We have succeeded in resumming a subset of the infinity of diagrams entering the free energy. If the series does not converge, this summation is not valid.

[28] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940). For an excellent review of the behavior of magnetic systems with dipole-dipole coupling at low temperatures, see the article by F. Keffer, in *Handbuch der Physik* (Springer-Verlag, Berlin, Germany, 1966), Vol. 18/II, Secs. 12–17 and 27. Although transverse demagnetization factors D^x and D^y enter the $k=0$ spin-wave energy, they do not contribute to the ground-state (zero point energy) or finite-temperature free energy of a large specimen magnetized along the z axis; the volume of phase (k) space these contributions occupy is negligible. However, if our specimen is small enough so that we must consider magnetostatic modes, we should expect to find that the transverse demagnetization factors enter.

[29] This argument is fairly common. See, for example, C. D. Marquard, Doctoral thesis, Ref. 25, Appendix III, pp. B87–88 (unpublished).

tion. If we place this cylinder in an external field of strength equal to the field inside the cylindrical cavity, i.e., the internal field

$$H_i = H_0 - DM, \tag{31}$$

its free energy is identical to that of the cylinder in the cavity. This argument leads us to conclude that the pseudo-free-energy $\bar{F}_A(H_i, T)$ defined as

$$\bar{F}_A(H_i, T) = \bar{F}(H_i, T) + \tfrac{1}{2}DM^2 \tag{32}$$

is independent of the shape of the body. From their definitions the difference between the internal and local fields, Eqs. (20) and (31), i.e., $\Phi_0 + D_0$, is independent of the shape of the sample and depends only on the crystal structure of the material. Therefore the conclusion that the shape dependence of the free energy is accounted for by the local field also applies to the internal field.

As this argument, valid for any magnetic material, is substantiated by our analysis for paramagnetic and ferromagnetic materials it strongly suggests that the proper free-energy expansion for the antiferromagnetic and other magnetically ordered states would give us the result that $F_A(L, T)$ [Eq. (25)] or $\bar{F}_A(H_i, T)$ [Eq. (32)] is the same function for all shapes.

Finally it should be emphasized that we have assumed throughout that the dipole sum Φ [Eq. (2)] is independent of the origin (i); therefore, we must restrict ourselves to ellipsoidal samples that are *uniformly* magnetized. If there are domains, our preceeding proof only applies for fields greater than the demagnetization field, for only then will the magnetization be uniform.

SHAPE DEPENDENCE OF THERMODYNAMIC PROPERTIES

Having ascertained how the free energy depends on the shape of a sample we now discuss the shape dependence of some thermodynamic properties derivable from the free energy. The internal energy U_A is derived from the "free energy" F_A by using the relation

$$U_A = (\partial/\partial\beta)(\beta F_A)_L, \tag{33}$$

where the derivative is taken while holding the local field constant. The specific heat at constant local field is defined as

$$C_L = T(\partial S/\partial T)_L = (\partial U_A/\partial T)_L, \tag{34}$$

where S is the entropy of the system. When written as a function of L, this specific heat does not involve the sum Φ and, therefore, is the same function of field L and temperature for all shapes of the same material. The shape of the sample is accounted for in the local field Eq. (20).

As it is practically impossible to vary the external field in such a way as to keep the local field constant, it is necessary to relate the specific heat at constant L to that for constant applied field H_0. By means of the mathematical identities

$$(\partial S/\partial T)_{H_0}(\partial T/\partial H_0)_S(\partial H_0/\partial S)_T = -1$$

and

$$(\partial S/\partial H_0)_T = (\partial S/\partial L)_T(\partial L/\partial H_0)_T,$$

we find

$$\left(\frac{\partial S}{\partial T}\right)_L = \left(\frac{\partial S}{\partial T}\right)_{H_0}\frac{(\partial L/\partial H_0)_S}{(\partial L/\partial H_0)_T}.$$

By using this relation and the definitions of the local field [Eq. (20)] and specific heat [Eq. (34)] we can write

$$C_L/C_{H_0} = (1+\Phi\chi_S)/(1+\Phi\chi_T),$$

where χ_S is the differential adiabatic susceptibility $(\partial M/\partial H_0)_S$, and χ_T is the isothermal one. By using the two thermodynamic relations[30]

$$C_M = C_{H_0} - (T/\chi_T)(\partial M/\partial T)_{H_0}^2$$

and $C_M/C_{H_0} = \chi_S/\chi_T$, we find that

$$C_L(L, T) = C_{H_0}(L, T) - \frac{\Phi T(\partial M/\partial T)_{H_0}^2}{1+\Phi\chi_T}. \tag{35}$$

To relate the specific heat at constant applied field to that at constant local field it is necessery to know in addition to C_{H_0}, the differential isothermal susceptibility and the differential change of magnetization with temperature for a constant applied field H_0, i.e., the isoerstedic temperature coefficient. This relation enables us to reduce to a common specific heat $C_L(L, T)$ the specific-heat measurements in finite fields on samples of various shapes of the same material.[31] The importance of this relation and the experimental data necessary to apply Eq. (35) is discussed by Levy and Landau.[32] They have shown that the specific heat $C_{H_0}(H_0, T)$ for two sample shapes of the same material (dysprosium aluminum garnet) can differ by as much as 40%. Furthermore as the material used for their analysis was in an antiferromagnetically ordered state the good agreement between the specific heats C_L arrived at by using Eq. (35) lends experimental support to the hypothesis that the shape dependence of the free energy of an antiferromagnet is accounted for by the local field.

The specific heat at constant internal field is defined as

$$C_{H_i} = T(\partial S/\partial T)_{H_i} = (\partial \bar{U}_A/\partial T)_{H_i}. \tag{36}$$

The relation of this specific heat to the one for constant

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[30] A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, England, 1957).

[31] With results obtained by HC for the free energy, susceptibility, and specific heat C_{H_0}, we have calculated the specific heat C_L by using the two approaches Eqs. (34) and (35); we have found that the two results are in complete agreement.

[32] P. M. Levy and D. P. Landau, J. Appl. Phys. **39**, 1128 (1968).

external field is similar to Eq. (35):

$$C_{H_i}(H_i,\,T)=C_{H_0}(H_i,\,T)+\frac{DT(\partial M/\partial T)_{H_0}{}^2}{1-D\chi_T}. \tag{37}$$

By using the definition of the "free energy" F_A [Eq. (24)] the magnetization is given as

$$M=-(\partial F_A/\partial L)_T. \tag{38}$$

This magnetization $M(L,\,T)$ is independent of shape. It follows that the susceptibility given by

$$\chi_T=\left(\frac{\partial M}{\partial H_0}\right)_T=\left(\frac{\partial M}{\partial L}\right)_T\left(\frac{\partial L}{\partial H_0}\right)_T=\frac{g(L,\,T)}{1-\Phi g(L,\,T)} \tag{39}$$

or

$$\chi_T^{-1}(L,\,T)=g^{-1}(L,\,T)-\Phi$$

depends on shape *only* through the explicit term Φ and the implicit relation of the local field to Φ. The function $g(L,\,T)$ is just the "pseudosusceptibility" $(\partial M/\partial L)_T$ and is the same for all *uniformly* magnetized samples of a material.

As it is also true that the magnetization $M(H_i,\,T)$ is independent of shape, if follows that the susceptibility can be written as

$$\chi_T^{-1}(H_i,\,T)=\bar{g}^{-1}(H_i,\,T)+D, \tag{40}$$

where $\bar{g}(H_i,\,T)$ is the pseudosusceptibility $(\partial M/\partial H_i)_T$; this depends on shape only through the internal field. The relation amongst the pseudosusceptibilities is

$$\bar{g}^{-1}(H_i,\,T)=g^{-1}(L,\,T)-(\Phi_0+D_0). \tag{41}$$

Whereas the microscopic treatment favors the local field, the macroscopic and concomitantly empirical treatment favors the internal field.

To summarize we have found that the pseudo-free-energy $F_A(L,\,T)$ is the same function of local field and temperature for all *uniformly* magnetized samples of a material, and that the magnetization $M(L,\,T)$, specific heat $C_L(L,\,T)$ and "pseudosusceptibility" $g(L,\,T)$ are all independent of the shape of a sample. We have also demonstrated that the shape dependence of the magnetic susceptibility for finite fields, to within a demagnetization factor, is accounted for by the local or internal field. Whereas we have explicitly only considered dipolar forces all the above results hold equally well when short-range exchange forces are also present. Inclusion of these forces only alters the value of the dipole sum Φ_0 Eq. (3); it does not change the shape dependence of the dipole sum Φ.

From this study we can not make any statements about the shape dependence of the thermodynamic properties of a magnetic material in zero applied field, because the series expansions we have used may not converge for zero field. Griffiths[33] has developed an argument that the thermodynamic properties of a magnetic system in zero field are independent of the shape of the sample; for zero field domains will form in the material in such a way that the sample is demagnetized.

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APPENDIX

Marquard has shown[34] that the dipole sums T^{xz} and T^{yz} vanish, "if the lattice has at least twofold rotational symmetry about the z axis (defined as the direction of the magnetic field); or if the lattice has at least threefold symmetry about an axis perpendicular to the magnetic field."[35]

To ascertain the conditions under which components of the magnetization vanish we consider its transformation properties. The magnetization transforms under rotations as a vector, thus for rotations ϕ about an axis, the magnetization transforms as $e^{im\phi}$ where $m=0$, ± 1. If the crystal lattice has a twofold or higher axis of symmetry the transverse components $m=\pm 1$ are not allowed and the magnetization must lie parallel to the symmetry axis (collinear with the magnetic field). If the crystal has a symmetry axis perpendicular to the magnetic field, transverse components of the magnetization $m=\pm 1$ will always exist because when one refers the transverse components to an axis perpendicular to the field a component $m'=0$ is present; this component is invariant under any rotation.

We conclude that the dipole sums T^{xz} and T^{yz}, and the transverse components of the magnetization M_x and M_y vanish if the z axis is along a crystal axis with at least twofold symmetry. We note that if the transverse components of the magnetization vanish, then the dipole sums T^{xz} and T^{yz} also vanish, but the vanishing of the sums T^{xz} and T^{yz} does *not* necessarily imply $M_x=M_y=0$. As long as we magnetize our sample along directions for which $M_x=M_y=0$, we are assured that the dipole sums T^{xz} and T^{yz} vanish. Finally if a crystal has threefold and higher symmetry about an axis (the z axis) the dipole sum T^{xy} vanishes; for twofold symmetry it can exist. Also T^{xy} can exist for a crystal with any axis of rotational symmetry perpendicular to the z axis (direction of the field H_0).

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[33] R. B. Griffiths (private communication).

[34] See C. D. Marquard, Doctoral thesis, Ref. 25, Sec. B, Chap. 3.

[35] C. D. Marquard, Doctoral thesis, Ref. 25, pp. B34–35 (unpublished).