then

$$I_1(\mathbf{q},\omega_\nu)=I_{-+++}(\mathbf{q},\omega_\nu),$$
$$I_2(\mathbf{q},\omega_\nu)=I_{-+-+}(\mathbf{q},\omega_\nu),$$
$$I_3(\mathbf{q},\omega_\nu)=I_{+++-}(\mathbf{q},\omega_\nu),$$
$$I_4(\mathbf{q},\omega_\nu)=I_{--++}(\mathbf{q}+\mathbf{Q},\omega_\nu). \quad \text{(A13)}$$

In deriving these equations, the facts that

$$G_{--}(-k,-K)=G_{++}(k,K)$$

and

$$G_{-+}(k,K)=G_{+-}(-k,-K)$$
$$=G_{+-}(k+Q+K,-K)$$

have been used.

In the text, the notations

$$D(\omega)=\beta D(\omega_\nu\to\omega+i\delta),$$
$$A(q,\omega)=\mathrm{Im}D(q,\omega)/\langle S\rangle \quad \text{(A14)}$$

are used where δ approaches zero from above. As in Ref. 1, the value of the lattice magnetization may be obtained by the formulas

$$\langle S\rangle=\frac{(S-\phi)(1+\phi)^{2S+1}+(S+1+\phi)\phi^{2S+1}}{(1+\phi)^{2S+1}-\phi^{2S+1}},$$

$$\phi=N_i^{-1}\sum_q\int\frac{d\omega}{2\pi}A(q,\omega)[e^{\beta\omega}-1]^{-1}. \quad \text{(A15)}$$

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Shape-Dependent Thermodynamic Quantities in Magnetic Systems with Dipole Interaction*

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If dipolar forces in magnetic materials are comparable to the exchange interactions, the thermodynamic properties in an external applied field are, in general, dependent on the shape of the sample. Recently, Levy has shown that shape-independent thermodynamic properties can be defined from a free energy at given internal field, rather than at given external field. This result is generalized to include anisotropic exchange interaction and arbitrarily oriented ellipsoidal samples. Functional-derivative techniques allow a more condensed notation for the problem. The results given here hold in any order of perturbation theory.

IF the dipole-dipole interaction in magnetic materials is of the same order of magnitude as the exchange interaction, the thermodynamic properties will depend on the shape of the sample. Levy[1] has shown that in this case a free energy can be introduced which is shape-independent. This free energy depends on the internal or local magnetic field instead of the external field. The thermodynamic quantities derived from this free energy, e.g., the specific heat at constant local field, are also shape-independent.

Levy gave a proof of this result, valid if the internal field is parallel to the external field, i.e., if off-diagonal contributions to the dipole sum can be neglected. He used a linked-cluster diagrammatic expansion and a resummation procedure. In the present paper, we give a more general proof of this result, using functional-derivative techniques[2] and all orders of perturbation theory.

I. FREE ENERGY

The Hamiltonian of a system of localized spins in an external field is assumed to be

$$\mathcal{H}=-\sum_{i\alpha}H_{i\alpha}S_{i\alpha}-\tfrac{1}{2}\sum_{ij}\sum_{\alpha\beta}I_{ij,\alpha\beta}S_{i\alpha}S_{j\beta}. \quad (1)$$

$H_{i\alpha}$ is the external-field component in the α direction ($\alpha=x, y, z$) and at the lattice point i. $S_{i\alpha}$ is the α component of the spin vector for lattice site i. $I_{ij,\alpha\beta}$ is the matrix element of the spin-spin interaction, containing the exchange interaction and the dipole-dipole interaction

$$I_{ij,\alpha\beta}=I^e{}_{ij,\alpha\beta}+I^d{}_{ij,\alpha\beta},$$
$$I_{ij,\alpha\beta}=|\,r_{ij}\,|^{-3}\{\delta_{\alpha\beta}-3r_{ij,\alpha}r_{ij,\beta}/|\,r_{ij}\,|^2\}. \quad (2)$$

We use units such that $g\mu_\beta=1$.

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[1] P. M. Levy, Phys. Rev. **170**, 595 (1968); P. M. Levy and D. P. Landau, J. Appl. Phys. **39**, 1128 (1968).

[2] See, e.g., L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

To apply functional-derivative techniques we have to treat the more general case where $H_{i\alpha}(t)$ and $I_{ij,\alpha\beta}(tt')$ are time-dependent. It is convenient to use imaginary time variables.[2] The starting point is a generalized free energy

$$F=-\beta^{-1}\ln \mathrm{Tr}\left\{T\exp\left[i\int_0^{-i\beta}dt\sum_{i\alpha}H_{i\alpha}(t)S_{i\alpha}(t)+\frac{1}{2}\int_0^{-i\beta}dtdt'\sum_{ij}\sum_{\alpha\beta}I_{ij,\alpha\beta}(tt')S_{i\alpha}(t)S_{j\beta}(t')\right]\right\}. \quad (3)$$

T is the usual time-ordering operator, ordering the spin operators so that those with the greater time argument ($it>it'$) stand to the left of those with the smaller arguments. The operators are time-independent Schrödinger operators, and the time argument is to be considered only as a label on which the time-ordering operator can act. In the special case of an Ising-model Hamiltonian, one can drop the time ordering, since this contains only the z components of the spin operators, and one does not have to worry about the commutator relations.

If $H_{i\alpha}(t)$ is time-independent and

$$I_{ij,\alpha\beta}(tt')=i\delta(t-t')I_{ij,\alpha\beta},$$

the generalized free energy (3) becomes the usual free energy

$$F=-(1/\beta)\ln \mathrm{Tr}e^{-\beta\mathcal{H}}, \quad (4)$$

where $\mathcal{H}$ is given by (1).

It is convenient to introduce a short notation: $1=\{i,\alpha,t\}$, $2=\{j',\beta',t'\}$, and a sum convention so that double indices are summed and double time arguments are integrated from 0 to $-i\beta$. In this notation, the generalized free energy reads

$$F=-(1/\beta)\ln \mathrm{Tr}\{T\exp[iH(1)S(1)+\tfrac{1}{2}I(12)S(1)S(2)]\}. \quad (3')$$

The functional derivatives of F are

$$-\beta[\delta^\nu F/\delta H(1)\cdots\delta H(\nu)]_I=M_\nu(1\cdots\nu). \quad (5)$$

In the limit $I\to 0$, these quantities are usually called semi-invariants. The first M_ν are in terms of expectation values of spin operators:

$$M_1(1)=i\langle S(1)\rangle,$$
$$M_2(12)=-[\langle TS(1)S(2)\rangle-\langle S(1)\rangle\langle S(2)\rangle]. \quad (6)$$

It should be pointed out again that the expectation values of spin operators in (6) are in terms of the full Hamiltonian. $M_1(1)$ is the true expectation value of the spin at point 1, and $M_2(12)$ is the true spin-spin correlation function. Since in $M_2(12)$ the factorizable part $\langle S(1)\rangle\langle S(2)\rangle$ of the two-spin expectation value $\langle TS(1)S(2)\rangle$ is subtracted, $M_2(12)$ vanishes for large space (or time) variables. This is shown in any order of perturbation theory in the Appendix.

Also of interest is the first derivative with respect to $I(12)$:

$$-\beta[\delta F/\delta I(12)]_H=\tfrac{1}{2}\langle TS(1)S(2)\rangle=-\tfrac{1}{2}\{M_2(12)+M_1(1)M_1(2)\}. \quad (7)$$

The subscripts H and I in (5) indicate that the derivatives have to be taken at constant H and I, respectively.

The fact that (7) contains a term $M_1(1)M_1(2)$ indicates that F contains a term $A(1)I(12)A'(2)$, where $A(1)$ and $A'(1)$ are certain functionals of I and H. They depend explicitly on the set of variables $1=\{i\alpha t\}$.

For a homogeneous and time-independent external field $H_{i\alpha}(t)=H_\alpha$ and an ellipsoidal-shaped sample, one expects that any quantity of the form $A(1)$ is actually independent of i and t, at least far from the surface. In this case, the contribution $A(1)I(12)A'(2)$ to the free energy reduces to

$$A(1)I(12)A'(2)=\beta\sum_{\alpha\beta}A_\alpha A'_\beta\sum_{ij}I_{ij,\alpha\beta}=N\sum_{\alpha\beta}A_\alpha A'_\beta\phi_{\alpha\beta}. \quad (8)$$

$\phi_{\alpha\beta}$ contains a sum over the exchange interaction and over the dipole-dipole interaction. The first sum is harmless, but the latter sum, the so-called dipole sum, depends on the shape of the sample. This sum again can be split into a shape-independent part and a shape-dependent part, which is the classical demagnetization factor D.[3] For general orientations of the ellipsoid to the external field, D is a tensor with the eigenvalues D_a, D_b, D_c equal to the demagnetization factors for the principal directions a, b, c of the ellipsoid. Concluding, we can write

$$\phi_{\alpha\beta}=\hat{\phi}_{\alpha\beta}-D_{\alpha\beta}, \quad (9)$$

where $\hat{\phi}_{\alpha\beta}$ is shape-independent. For nonellipsoidal-shaped samples in general, a quantity like $A(1)$ is not homogeneous; thus (8) becomes more complicated, and we will not consider this case. The same is true if the sample forms domains with different orientations; thus we will restrict our considerations to a single-domain sample or a strong enough external field, if the temperature is below the transition temperature.

From $M_2(12)$ in (7) we conclude that there exists also a term of the form $B(12)I(12)$ in F. Since its derivative $M_2(12)$ vanishes at large distances, $B(12)$ has also to vanish at large distances, and this contribution to F cannot be shape-dependent. Thus, shape dependence enters only via (8). If we can find a new free energy $\mathfrak{F}$ depending on another field $L(1)$ instead of $H(1)$, which contains no term of the form $A(1)I(12)A'(2)$, then we have found a shape-independent "free energy." This means we have to find an $\mathfrak{F}$ where $[\delta\mathfrak{F}/\delta I(12)]_L$ contains no factorizing term like $M_1(1)M_1(2)$. The "natural variables" of $\mathfrak{F}$ are L and

[3] See, e.g., I. H. Van Vleck, J. Chem. Phys. 5, 320 (1937).

I, instead of H and I, which were the "natural variables" of F.

To find this new free energy we make a Legendre transformation of the old free energy, where L is to be determined later.

$$-\beta\mathfrak{F}=-\beta\mathfrak{F}(L, I)$$
$$=-\beta F-\tfrac{1}{2}M(1)\{H(1)-L(1)\}. \quad (10)$$

The derivative with respect to $I(12)$ at constant L is

$$-\beta\left(\frac{\delta\mathfrak{F}}{\delta I(12)}\right)_L=-\beta\left(\frac{\delta F}{\delta I(12)}\right)_H-\beta\left(\frac{\delta F}{\delta H(3)}\right)_I\left(\frac{\delta H(3)}{\delta I(12)}\right)_L$$
$$-\tfrac{1}{2}\{H(3)-L(3)\}\left(\frac{\delta M_1(3)}{\delta I(12)}\right)_L-\tfrac{1}{2}M_1(3)\left(\frac{\delta H(3)}{\delta I(12)}\right)_L$$
$$=-\tfrac{1}{2}M_2(12)-\tfrac{1}{2}M_1(1)M_1(2)$$
$$+\tfrac{1}{2}M_1(3)[\delta H(3)/\delta I(12)]_L$$
$$-\tfrac{1}{2}\{H(3)-L(3)\}[\delta M_1(3)/\delta I(12)]_L. \quad (11)$$

Now one has to determine L in such a way that all factorizing parts in (11) vanish. If we follow Levy[1] and choose

$$L(1)=H(1)-I(12)M_1(2), \quad (12)$$

we find

$$[\delta H(3)/\delta I(12)]_L$$
$$=\delta(13)M_1(2)+I(34)[\delta M_1(4)/\delta I(12)]_L,$$

so that

$$-\beta[\delta\mathfrak{F}/\delta I(12)]_L=-\tfrac{1}{2}M_2(12). \quad (11')$$

Since here the term $M(1)M(2)$ no longer occurs, we have found the shape-independent free energy.

Similar to (11), one gets

$$-\beta[\delta\mathfrak{F}/\delta L(1)]_I=M_1(1). \quad (11'')$$

From Eq. (6) we see that $M(1)$ is related to the magnetization $\mathfrak{y}$ per unit volume:

$$\mu_\alpha=N\langle S_\alpha\rangle/V=-iNM_\alpha/V \qquad (g\mu_\beta=1). \quad (13)$$

With the definition of $\phi_{\alpha\beta}$, Eq. (8), we find

$$L_\alpha=H_\alpha+\sum_\beta\phi_{\alpha\beta}\mu_\beta; \quad (14)$$

thus, the new shape-independent free energy becomes

$$\mathfrak{F}=F-\tfrac{1}{2}V\sum_{\alpha\beta}\mu_\alpha\phi_{\alpha\beta}\mu_\beta. \quad (15)$$

In the case that the magnetization is parallel to the external field, $\mathfrak{F}$ reduces to the result found earlier by Levy.[1] L is the local field, and (14) reduces again to the local field defined by Levy in the case of $\mathfrak{y}$ parallel to $\mathbf{H}$.

Adding a shape-independent term to $\mathfrak{F}$, of course, does not destroy its shape independence. Thus, one can go from the free energy at given local field to the free energy at given internal field:

$$\hat{F}=F+\tfrac{1}{2}\sum_{\alpha\beta}\mu_\alpha D_{\alpha\beta}\mu_\beta, \quad (16)$$

since the shape dependence enters $\phi_{\alpha\beta}$ only via the demagnetization factor (9). The internal field is

$$H^i_\alpha=H_\alpha-\sum_\beta D_{\alpha\beta}\mu_\beta. \quad (17)$$

II. SUSCEPTIBILITY AND SPECIFIC HEAT

We give now a brief discussion of the shape dependence of the specific heat and of the susceptibility, where we have generalized Levy's discussion to treat the tensor properties of $\phi_{\alpha\beta}$ and $D_{\alpha\beta}$. Since only the microscopic treatment favors the free energy at given local field, we consider now only the thermodynamic quantities derivable from the free energy at given internal field.

The magnetization is usually given by $\mu_\alpha=-(\partial F/\partial H_\alpha)_T$. Using (16) and (17) we find that it is also

$$\mu_\alpha=-(\partial\hat{F}/\partial H^i_\alpha)_T. \quad (18)$$

The isothermal susceptibility is, in general, a tensor given by $\chi_{T\alpha\beta}=(\partial\mu_\alpha/\partial H_\beta)_T$. Considering $\mathfrak{y}$ as a function of $\mathbf{H}^i$ according to (18) leads to

$$\chi_{T\alpha\beta}=\sum_\gamma(\partial\mu_\alpha/\partial H^i{}_\gamma)_T(\partial H^i{}_\gamma/\partial H_\beta)$$
$$=\hat{g}_{\alpha\beta}-\sum_{\alpha\beta}\hat{g}_{\alpha\gamma}D_{\gamma\delta}\chi_{T\delta\beta}$$

or[4]

$$(\chi_T^{-1})_{\alpha\beta}=(\hat{g}^{-1})_{\alpha\beta}+D_{\alpha\beta}. \quad (19)$$

$\hat{g}_{\alpha\beta}=(\partial\mu_\alpha/\partial H^i_\alpha)$ is the isothermal "pseudosusceptibility," introduced by Levy, which is the same for all uniformly magnetized samples of a material. The shape independence of $\hat{g}$ follows from the fact that it is the second derivative of the shape-independent free energy $\hat{F}$.

The entropy can be found differentiating F or $\hat{F}$

$$S=-(\partial F/\partial T)_H=-(\partial\hat{F}/\partial T)_{H^i}. \quad (20)$$

The specific heat at constant external field is

$$C_H=T(\partial S/\partial T)_H; \quad (21)$$

the specific heat at constant internal field is

$$C_{H^i}=T(\partial S/\partial T)_{H^i}. \quad (21')$$

Using Eqs. (16), (17), and (20), one finds

$$C_H=C_{H^i}-T\sum_{\alpha\beta}(\partial\mu_\alpha/\partial T)_{H^i}D_{\alpha\beta}(\partial\mu_\beta/\partial T)_H. \quad (21'')$$

[4] This simple form, even in the case of $\mathfrak{y}$ nonparallel to $\mathbf{H}$, has been questioned by C. D. Marquard [Proc. Phys. Soc. (London) **92**, 650 (1967)]; see, also, footnote 25 of Ref. 1. This arises from the fact that in the interesting case, $\chi_{\alpha\beta}$ is nondiagonal, thus $(\chi^{-1}{}_{zz})\neq 1/\chi_{zz}$. The expression given by Marquard is a series expansion of $1/\chi_{zz}$.

The change of the magnetization with temperature at a given internal or external field, respectively, is found to be

$$\left(\frac{\partial\mu_\alpha}{\partial T}\right)_H=\left(\frac{\partial\mu_\alpha}{\partial T}\right)_{H^i}+\sum_\beta\left(\frac{\partial\mu_\alpha}{\partial H^i{}_\beta}\right)_T\left(\frac{\partial H^i{}_\beta}{\partial T}\right)_H \quad (22)$$
$$=(\partial\mu_\alpha/\partial T)_{H^i}-\sum_{\beta\gamma}\hat{g}_{\alpha\beta}D_{\beta\gamma}(\partial\mu_\gamma/\partial T)_H$$

or

$$(\partial\mu_\alpha/\partial T)_{H^i}=\sum_\beta(\partial\mu_\beta/\partial T)_H\{\delta_{\alpha\beta}+\sum_\gamma D_{\beta\gamma}\hat{g}_{\gamma\alpha}\}. \quad (22')$$

Using Eq. (19) it can also be written as

$$(\partial\mu_\alpha/\partial T)_{H^i}=\sum_\beta(\partial\mu_\beta/\partial T)_H(1-D\chi_T)^{-1}{}_{\beta\alpha}. \quad (22'')$$

Finally, the specific heat at constant internal field becomes

$$C_{H^i}=C_H-T\sum_{\alpha\beta\gamma}(\partial\mu_\alpha/\partial T)_H(1-D\chi_T)^{-1}{}_{\alpha\beta}D_{\beta\gamma}(\partial\mu_\gamma/\partial T)_H, \quad (21''')$$

which is essentially the generalization of the specific heat at constant internal field found by Levy.

Since C_{H^i} and $(\partial\mu_\alpha/\partial T)_{H^i}$ as well as $\hat{g}_{\alpha\beta}$ are second derivatives of the shape-independent free energy $\hat{F}$, these quantities are the same for all uniformly magnetized samples of the same material.

III. SUMMARY

We have found that for all homogeneously magnetized samples of a material, a free energy can be defined which is independent of the shape of the sample. The second derivatives with respect to temperature and internal field define thermodynamic quantities which are the same for all homogeneously magnetized samples of a particular material. These are not new results; they are only generalizations of the results found by Levy[1] to the case where the external field and the magnetization are not necessarily parallel. The proof given here is valid if the system is homogeneous and if the spin-spin interaction is quadratic in the spin operators which allows an anisotropic exchange interaction. The proof can be generalized to antiferromagnetic materials, if each sublattice magnetization is separately taken into account. The final results are unchanged. The proof of the cluster property of the correlated part of the spin-spin correlation function, given in the Appendix, depends on the convergence of a perturbation series.

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APPENDIX

It has to be shown that $M_2(12)$ has a cluster property, i.e., that $M_2(12)$ vanishes if the spins, denoted as 1 and 2, are far apart. This property can be shown to hold in each order of perturbation theory, where $I(12)$ is replaced by $\lambda I(12)$ and an expansion is made in powers of λ.[5]

To do this, we look at

$$\delta M_2(34)/\delta I(12)=-\beta\delta^3F/\delta I(12)\delta H(3)\delta H(4)$$
$$=M_4(1234)+M_3(134)M_1(2)$$
$$+M_3(234)M_1(1)+M_2(13)M_2(24)+M_2(14)M_2 \quad (23)$$

and

$$\delta M_3(345)/\delta I(12)=M_5(12345)+M_4(1345)M_1(2)+\cdots$$
$$+M_3(135)M_2(24)+\cdots,$$

and so on.

Assuming the cluster property is true in nth order for M_2 and all higher M_μ, Eq. (23) shows that all terms on the right-hand side of Eq. (23) vanish for large separations (1, 2) except the last two terms. The behavior of the derivatives of the higher M_μ functionals is corresponding. Formal integration of (23) shows that the $(n+1)$st order $M_2{}^{(n+1)}(12)$ contains a term $M_2{}^{(m)}(13)I(34)M_2{}^{(m')}(42)$, where $m+m'=n$ or m, $m'\leq n$. Thus, if this term vanishes for large distances, the cluster property holds in $(n+1)$st order, corresponding for higher M_μ. In zeroth order, the cluster property is fulfilled since $M\mu^{(0)}(1\cdots\mu)\neq 0$ only if all spatial indices $1\cdots\mu$ are the same.

In first order, $M_2{}^{(1)}(12)$ behaves asymptotically like $I(12)$, i.e., $|M_2{}^{(1)}(12)|\leq R_{12}{}^{-3}\times$const, which is easily seen from (23). We assume the same asymptotic behavior for all $M_2{}^{(m)}$ up to order n and estimate $M(13)I(34)M(42)$, where we have to sum over 3 and 4. These sums are split up into a sum over a subvolume around 1 and 2, and the remaining sums, which can be replaced by integrals, if the dimensions of the subvolumes are large compared to the lattice constants. The sums over these subvolumes give again an asymptotic behavior like $R_{12}{}^{-3}$; the rest becomes

$$|\tilde{M}_2{}^{(n+1)}(12)|\leq\text{const}\times\int_{v'}d^3\rho d^3\rho'$$
$$\times\{(R_{12}{}^2+\rho^2-2\mathbf{R}_{12}\boldsymbol{\rho})(\rho^2+\rho'^2-2\boldsymbol{\rho}\boldsymbol{\rho}')\rho'^2\}^{-3/2}, \quad (24)$$

where $\tilde{M}_2{}^{(n+1)}$ is the contribution to the $(n+1)$st order due to this critical term. The integrals over ρ and ρ' run over the volume V' remaining if the subvolumes are excluded. The integration of (24) shows that also $|M_2{}^{(n+1)}(12)|\leq\text{const}\times R_{12}{}^{-3}$. The considerations for the higher M_μ are analogous. Thus, our assumption about the asymptotic behavior of the nth order is justified and in each order of the perturbation theory $|M_2(12)|\leq\text{const}\times R_{12}{}^{-3}$.

[5] The method used here is analogous to an all-order linked-cluster diagrammatic expansion.