PHYSICAL REVIEW VOLUME 152, NUMBER 1 2 DECEMBER 1966

Spontaneous Magnetization in Idealized Ferromagnets*

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(Received 27 June 1966)

An attempt is made to clarify the concept of "spontaneous magnetization" in idealized ferromagnets such as the Ising and Heisenberg models. Some definitions in common use are discussed; their equivalence is not obvious. It is shown that a value based upon the probability distribution of the total magnetization cannot exceed the spontaneous magnetization based on bulk thermodynamic properties when the magnetization and exchange operators commute. A convexity argument shows that a definition of spontaneous magnetization based on minima in the (bulk) free energy is not applicable to systems with short-range interactions. Reference is made to difficulties arising when magnetization and exchange operators do not commute.

I. INTRODUCTION

SIMPLIFIED models of physical systems play a major role in the effort to understand the microscopic basis of phase transitions. Among these models certain idealized ferromagnets have an important place. For many years the Ising and Heisenberg models, in particular, have been investigated both because of their (presumed) relevance to real ferro- and antiferromagnets and also, because of their (relative) mathematical simplicity, in the hope that they might provide insight into liquid-vapor phase transitions, order-disorder transitions in solids, the λ transition in liquid helium, etc.

In such models the occurence of a phase transition is closely connected with the existence of spontaneous magnetization, a state in which the elementary magnetic moments line up parallel to each other without assistance from an external magnetic field. Although the concept is relatively simple, a precise statistical definition thereof (not to mention an exact calculation) poses several difficulties. As a matter of fact, more than one definition of spontaneous magnetization is in current use, and it is far from clear that different definitions are equivalent. Our purpose in this paper is to state as precisely as possible some of these definitions and, in certain cases, point out relationships among them.

We shall focus our attention on a model system consisting of a regular lattice of N atoms, each with angular momentum $\mathbf{S}$ (in units of $\hbar$) located in a constant external magnetic field H directed along the Z axis and described by a Hamiltonian

$$\mathcal{H}=\mathcal{H}_0-H\mathfrak{M}, \tag{1}$$

with

$$\mathcal{H}_0=-2\sum_{i<j} J_{ij}[S_i^zS_j^z+\gamma(S_i^xS_j^x+\delta S_i^yS_j^y)], \tag{2}$$

$$\mathfrak{M}=g\mu\sum_i S_i^z. \tag{3}$$

In these expressions γ, δ, and g are numerical constants, μ is the Bohr magneton, and the "exchange" constants J_{ij} depend only on the relative locations of atoms i and j. If r_{ij} is the distance from atom i to atom j, we shall assume that J_{ij} is bounded by $D/(r_{ij})^{d+\epsilon}$, where d is the dimensionality of the lattice and D and ϵ are positive constants. The case where J_{ij} is a constant J if atoms i and j are nearest neighbors and zero otherwise is often used in actual calculations. For $\gamma=0$ one has the so-called Ising interaction, whereas $\delta=\gamma=1$ gives the Heisenberg or vector coupling.

Spontaneous magnetization is present if, with $H=0$, $\mathfrak{M}$ in some sense attains a nonzero value proportional to the size of the system under consideration. It is clear that simply taking the average $\langle\mathfrak{M}\rangle$ in zero magnetic field will not do. The symmetry of $\mathcal{H}_0$ insures that positive and negative values of $\mathfrak{M}$ are equally likely, and hence the average is identically zero at any temperature. This fact has been used to argue that equilibrium statistical mechanics is incapable of predicting spontaneous magnetization. We are of the opinion that other ways of looking at the problem, some of which are introduced in Sec. II below, nevertheless allow a sensible definition of spontaneous magnetization for the idealized system described in (1)–(3).

The Hamiltonian (1) as a model of a "real" magnetic system is oversimplified in several ways. In the first place we have assumed that the electrons responsible for magnetic properties are localized on particular lattice sites and that a spin Hamiltonian gives an adequate description of the relevant energy states. Within this framework we have omitted the magnetic dipole-dipole interaction between different atoms—a simplification of considerable importance, as it presumably allows us to discuss spontaneous magnetization without concern for domain structure. On the other hand, single-atom anisotropy terms, in particular if they commute with $\mathfrak{M}$, could be added to $\mathcal{H}_0$ without substantially altering our discussion. Finally we shall pay particular attention to the case $\delta=1$, for then the exchange $\mathcal{H}_0$ and magnetization $\mathfrak{M}$ *commute*. This is not necessary for the definitions in Sec. II, but plays an essential part in the discussions in Secs. III and IV.

The system (1)–(3) in the case $S=\frac{1}{2}$ and $\gamma=0$ provides a model for certain order-disorder transitions as well as a lattice model for a classical gas.[1] With $\gamma\neq0$

* Research supported in part by the National Science Foundation and the U. S. Office of Naval Research.

[1] G. F. Newell and E. W. Montroll, Rev. Mod. Phys. 25, 353 (1953).

one has a quantum lattice gas of Bose particles.[2] Spontaneous magnetization in the ferromagnet is connected with a phase transition (usually identified as liquid-vapor) in the corresponding "gas," whereas the requirement that $\mathcal{M}$ and $\mathcal{H}_0$ commute corresponds to particle conservation.[3]

In Sec. II we discuss, with no attempt at completeness, some definitions of spontaneous magnetization which are in use at present, both from the point of view of formal rigor and "intuitive" appeal. An inequality relating the first two definitions is derived in Sec. III. The implications for the second and third definitions of a convexity theorem (an abbreviated proof of which occupies Appendix A) for the free energy are discussed in Sec. IV. Finally, Sec. V contains applications to the Ising ($\gamma=0$) and Heisenberg ($\gamma=\delta=1$) models.

II. DEFINITIONS OF SPONTANEOUS MAGNETIZATION

A. External Magnetic Field

Let us consider the average magnetization per atom,

$$m_N(H)=N^{-1}\langle\mathcal{M}\rangle_H=N^{-1}\,\mathrm{Tr}[\mathcal{M}e^{-\beta\mathcal{H}}]/\mathrm{Tr}[e^{-\beta\mathcal{H}}], \quad (4)$$

for a crystal containing N atoms, with $\mathcal{H}$ defined in (1) and $\beta=(kT)^{-1}$ the inverse temperature. The spontaneous magnetization m_0 shall be the limit as H goes to zero through positive values of the average magnetization per atom in the limit of an infinite system:

$$m_0=\lim_{H\to 0+}\lim_{N\to\infty} m_N(H), \quad (5)$$

where by $\lim(N\to\infty)$ we shall always mean the limit of a sequence of crystals of suitable shape (e.g., cubes) for which "surface" energies are negligible compared with "volume" energies.[4] This limit is necessary since for finite N (see Appendix B), $m_N(H)$ is a smooth (in fact analytic) function for $-\infty<H<\infty$ which vanishes at $H=0$.

The definition (5) has several advantages from a formal point of view when applied to systems here considered. For instance, the limit always exists and is independent of the usual type of boundary condition. To see this, we note that the free energy per atom,

$$f_N(H)=N^{-1}\beta^{-1}\ln\mathrm{Tr}[e^{-\beta(\mathcal{H}_0-H\mathcal{M})}], \quad (6)$$

related to the magnetization through

$$m_N(H)=-(\partial f_N/\partial H)_T, \quad (7)$$

is convex upwards in H. Further,

$$f(H)=\lim_{N\to\infty} f_N(H), \quad (8)$$

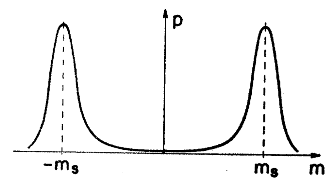

FIG. 1. Possible probability distribution for the magnetization.

which is known to exist under fairly general conditions on interactions and boundary conditions, is also convex upwards.[4] Thus

$$\lim_{N\to\infty} m_N(H)=m(H)=-(\partial f/\partial H)_T \quad (9)$$

holds at all points where the right side is continuous.[5] The fact that $m(H)$ has a left (and right) hand limit at every point guarantees the existence of (5).

The arguments of the preceding paragraph are valid whether or not $\mathcal{M}$ and $\mathcal{H}_0$ commute. For example, with a suitable change in the definition of $\mathcal{M}$, (5) serves to define the sublattice magnetization of a Heisenberg antiferromagnet.

The objection is sometimes made that the $N\to\infty$ limit is "unphysical" since experiments are always performed on finite systems. We have discussed this objection elsewhere[6] and believe the $N\to\infty$ limit is justified as a method of calculating bulk (as opposed to surface) thermodynamic quantities. Nonetheless, one must concede that the cost of formal rigor is some loss of physical insight, since (5) is obtained by taking two limits, the order of which cannot in general be interchanged.

B. Probability Distribution for $\mathcal{M}$ in Zero Field

Let $P_M(=P_M^\dagger)$ be the projection operator onto the subspace spanned by all eigenfunctions of $\mathcal{M}$ with eigenvalue M. The probability p_M of finding the system with total magnetic moment M in a field H is given by

$$p_M(H)=\langle P_M\rangle_H, \quad (10)$$

where $\langle\ \rangle_H$ is defined as in (4). For $H=0$ and a sufficiently low temperature one might suppose the probability distribution for $m=N^{-1}M$ would have the form shown schematically in Fig. 1: two sharp peaks at $m=\pm m_s$, each with a width going to zero as $N\to\infty$. Were this the case, the spontaneous magnetization could be defined as m_s or as

$$m_j=\lim_{N\to\infty} N^{-1}[\langle|\mathcal{M}|^j\rangle_0]^{1/j}, \quad (11)$$

where j is some number greater than 0 (typically, $j=1$ or 2) and $\langle\ \rangle_0$ denotes a thermal average, as in (4), with $H=0$.

The definition (11) has disadvantages from the viewpoint of formal rigor. There is no guarantee that for

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[2] T. Matsubara and H. Matsuda, Progr. Theoret. Phys. (Kyoto) **16**, 416 (1956); **16**, 569 (1956).
[3] T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).
[4] R. B. Griffiths, J. Math. Phys. **5**, 1215 (1964).
[5] Ref. 4, Appendix A.
[6] R. B. Griffiths, J. Math. Phys. **6**, 1447 (1965).

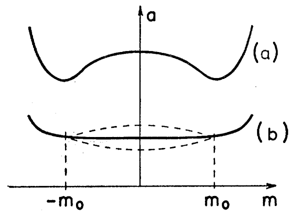

FIG. 2. Bulk free energy $a(m)$ for (a) mean-field model Hamiltonian (14) and (b) Heisenberg-Ising Hamiltonian (2), with possible behavior of $a_N(m)$ for finite N shown by dotted curves.

large N the probability distribution has the form we have suggested—for the Heisenberg interaction, $\gamma=\delta=1$, it certainly does not (see Sec. V). We have not been able to show that the limit (11) exists, or that it is independent of boundary conditions and insensitive to sample shape in the same sense as (5).

On the other hand, this definition (when it works) has a simple intuitive significance: If one were at some time to perform a "measurement" of the average magnetization for a large system, one would, with high probability, find a value near $+m_s$ or $-m_s$; other values (including zero) would be much less likely. "Measurement" must be understood in the idealized sense used in textbook expositions of quantum mechanics [that is, corresponding to the probability distribution $p_M(0)$] and not necessarily in the sense of ordinary laboratory procedures.

A relation between $p_M(0)$ and m_0 defined in (5) is proved in Sec. III under the assumption that $\mathfrak{M}$ and $\mathcal{H}_0$ commute. It would be valuable to know what relationship exists, if any, in cases where $\mathfrak{M}$ and $\mathcal{H}_0$ do not commute.

C. Long-Range Correlation

Consider a system of N atoms in a cube with periodic[7] boundary conditions. The relation

$$\begin{aligned} N^{-2}\langle\mathfrak{M}^2\rangle_0 &= g^2\mu^2N^{-2}\sum_i\sum_j\langle S_i^zS_j^z\rangle_0 \\ &= g^2\mu^2N^{-1}\sum_j\langle S_1^zS_j^z\rangle_0, \end{aligned} \tag{12}$$

where we have used periodicity to eliminate one of the sums in the last term, suggests a close connection between spontaneous magnetization as defined in (11) for $j=2$ and "long-range order" as determined by correlation functions. The right side of (12) as N goes to infinity is determined by correlation functions $\langle S_1^zS_j^z\rangle_0$ for atoms separated by distances which go to infinity with N. This suggests an alternative definition of spontaneous magnetization m_c in which distances go to infinity *after* N goes to infinity:

$$m_c^2=g^2\mu^2\lim(r_{1j}\to\infty)\lim(N\to\infty)\langle S_1^zS_j^z\rangle_0. \tag{13}$$

Periodic boundary conditions are not essential, though with other boundary conditions it is helpful to average the correlation functions over the finite lattice in analogy with Fisher's procedure for gases.[8] It has not been shown (as far as we are aware) that either of the limits in (13) exist, in general. And if the limits do exist, this is not sufficient to show that m_2 in (11) and m_c are identical, though (12) suggests they might be. The reader is referred to Ref. 9 for a careful discussion of the relationship between m_c and m_2 in the two-dimensional rectangular Ising model.

These formal problems should not obscure the importance of (13) as a possible definition of spontaneous magnetization. Correlation functions are in themselves of considerable interest in statistical mechanics. They are also accessible to experimental measurement by neutron diffraction in magnetic materials.[10]

D. Minima in the Free Energy

The mean-field model of a ferromagnet may be considered the solution to a Hamiltonian of the form

$$\mathcal{H}_1=-2N^{-1}J\sum_{i<j}S_i^zS_j^z, \tag{14}$$

in which each atom interacts equally with every other atom through an Ising type of exchange. If one calculates the free energy[11] per atom as a function of magnetization through

$$a_N(N^{-1}M)=-N^{-1}\beta^{-1}\ln\mathrm{Tr}[P_Me^{-\beta\mathcal{H}_1}] \tag{15}$$

(P_M is defined in part B, above), and its limit

$$a(m)=\lim_{N\to\infty}a_N(m), \tag{16}$$

the resulting function possesses for $T<T_c$ two minima at values of m, the average magnetization per atom, different from zero [see Fig. 2 (a)]. By defining spontaneous magnetization as the value of $m>0$ where the free energy is a minimum, one obtains a result identical in this instance with (5).

A generalization of this definition has been used by Landau in his theory of second-order phase transitions.[12] Unfortunately, its utility seems restricted to systems which, like (14), have potentials with range increasing with the size of the system. We discuss in Sec. IV below why it is inapplicable to systems of the form (2) and how it differs from the definition in part B above.

We should remark, however, that the notion of a trough in the free energy, in some sense, is probably an important feature of the spontaneously magnetized state in both idealized and "real" ferromagnets. The

[7] With periodic boundary conditions it is convenient to restrict the J_{ij} in (2) to a finite-range interaction in order to avoid complications of an atom interacting with itself.

[8] M. E. Fisher, J. Math. Phys. **6**, 1643 (1965).

[9] T. D. Schultz, D. C. Mattis, and E. H. Lieb, Rev. Mod. Phys. **36**, 856 (1964).

[10] P. G. de Gennes, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963) Vol. III, p. 115.

[11] Unfortunately, there seems to be no uniform terminology or notation for various "free energies" for magnetic systems. We shall use the symbol a for a free energy whose natural variables are m and T, and f for the free energy with natural variables H and T.

[12] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1958), pp. 434 ff.

"droplet" model of condensation[13] as applied to ferromagnets suggests that a trough corresponding to the stability of the system against the formation of regions of reversed magnetization smaller than a certain critical size may have an important influence on kinetic properties,[14] though it does not show up in the bulk free energy.

III. A RELATION BETWEEN DEFINITIONS A AND B

In the case where $\mathfrak{M}$ and $\mathcal{H}_0$ commute, one can show that the probability of finding a value of average magnetization per atom outside the interval $[-m_0, m_0]$, with m_0 defined in (5), is vanishingly small for a large crystal. A precise statement is found in the theorem and corollary 1 below. The theorem, unfortunately, places no restrictions on the probability distribution inside the interval $[-m_0, m_0]$. This distribution might have sharp peaks, as suggested in IIB, with m_s equal to or less than m_0, or it might have a single sharp peak at $m=0$, or any of a large number of other possibilities. The reason why it is difficult to relate a "thermodynamic" definition of the form (5) to the detailed probability distribution will become clearer upon examining Sec. IV below. In essence, the bulk thermodynamic properties provide a rather coarse description of the physical situation at a phase transition. The principle result of the present section is, thus, an inequality between the definitions (5) and (11):

$$m_j \leq m_0; \tag{17}$$

for a more precise statement, see corollary 2 below. Perhaps it is well to emphasize that even (17) is not known to hold in the case where $\mathfrak{M}$ and $\mathcal{H}_0$ do not commute.

Let $m=M/N$ denote the average magnetization per spin and $\epsilon_N(m^*,H)$ the probability of finding $m \geq m^*$, that is, the sum of the $p_M(H)$ defined in (10) for $M \geq Nm^*$.

Theorem. For any $m^* > m_0$ defined by (5), and provided $\mathfrak{M}$ and $\mathcal{H}_0$ commute, the probability with $H=0$ that m exceeds m^* goes to zero exponentially as N goes to infinity. That is, there is a $\delta > 0$ depending on m^* such that

$$\epsilon_N(m^*,0) \leq e^{-\beta N\delta} \tag{18}$$

for a sufficiently large system.

In the proof we use the following lemma: Given $m^* > m_0$, there is an m' in the interval $m_0 \leq m' < m^*$ and an $H' > 0$ such that

$$f(H') \geq f(0) - m'H', \tag{19}$$

where f is the function defined in (8). From (5) and (9) we see there is a sequence $H_k > 0$ tending to zero as $k \to \infty$ such that

$$m_k = -f'(H_k) \tag{20}$$

exists and tends to m_0 as $k \to \infty$. For m' choose some $m_k < m^*$ and let H' be the corresponding H_k. Then (19) merely expresses the fact that since $f(H)$ is convex upwards, $f(0)$ lies on or below a line drawn tangent to $f(H)$ at H'.[15]

To prove the theorem we note that (10) implies

$$p_M(H) = p_M(0) e^{\beta HM} e^{\beta N[f_N(H) - f_N(0)]}, \tag{21}$$

in the case where $\mathcal{H}_0$ and $\mathfrak{M}$ commute. Upon summing (21) over values of $M \geq Nm^*$, with $H > 0$, we have

$$1 \geq \epsilon_N(m^*,H) \geq \epsilon_N(m^*,0) e^{\beta HNm^*} e^{\beta N[f_N(H) - f_N(0)]}, \tag{22}$$

the first inequality reflecting, of course, the fact that ϵ is a probability. With H' and m' chosen as in the foregoing lemma, define

$$\delta = \tfrac{1}{2} H'(m^* - m') > 0. \tag{23}$$

Now since $f_N(H)$ converges to $f(H)$, we can choose N large enough so that the absolute difference is less than $\frac{1}{2}\delta$ both at $H=0$ and $H=H'$. It follows from (19) that

$$f_N(H') - f_N(0) \geq -m'H' - \delta, \tag{24}$$

which, inserted in (22), yields (18) for $H=H'$.

As $\mathcal{H}_0$ defined in (2) is invariant under time reversal ($\mathbf{S}_i$ replaced by $-\mathbf{S}_i$ for all i) while $\mathfrak{M}$ changes sign, it is evident that $f_N(H)$ and $f(H)$ are even functions of H. In certain circumstances it is convenient to use boundary conditions which are not invariant under time reversal, in which case the symmetry of $f_N(H)$ no longer holds. As long as $f_N(H)$ still converges to the same symmetric function $f(H)$ obtained previously, we have the following corollary 1: The above theorem remains valid with m replaced by $|m|$.

Another obvious consequence of the theorem is corollary 2: For any $j > 0$

$$\limsup(N \to \infty) N^{-1} [\langle |\mathfrak{M}|^j \rangle_0]^{1/j} \leq m_0. \tag{25}$$

We may remark that although the limit superior always exists for a given sequence of crystals with size going to infinity, the result may well depend on the particular sequence employed (we always assume it to be one for which $f_N(H)$ converges to $f(H)$) and in this sense the left side of (25) remains a trifle ill defined.

IV. CONVEXITY OF THE FREE ENERGY

Consider the free energy $a_N(m)$ defined as in (15) but with $\mathcal{H}_0$ from (2) in place of $\mathcal{H}_1$. In the case where $\mathcal{H}_0$ and $\mathfrak{M}$ commute one can show (Appendix A) that the limiting function $a(m)$ defined in (16) exists (with reasonable restrictions on crystal shape) and is a sym-

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[13] J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955), Chap. VII.

[14] R. B. Griffiths, C.-Y. Weng, and J. S. Langer, Phys. Rev. **149**, 301 (1966).

[15] G. H. Hardy, J. E. Littlewood, and G. Pólya, *Inequalities* (Cambridge University Press, London, 1964), p. 94.

metrical, convex-downwards function of m related to $f(H)$ by a (generalized) Legendre transformation.[16] In particular one can find the magnetic field associated with some magnetization m through

$$H=(\partial a/\partial m)_T. \qquad (26)$$

In the case of a spontaneous magnetization m_0 given by (5), the curve $a(m)$ has a "flat bottom," as in Fig. 2 (b), and is equal to its minimum value for all m in the interval $[-m_0, m_0]$. In fact, the extent of the "flat bottom" gives a definition of spontaneous magnetization fully equivalent to (5) in the case where $\mathfrak{M}$ and $\mathcal{H}_0$ commute. A double minimum in the free energy of the form exhibited by the mean-field model and shown in Fig. 2 (a) is not possible and thus definition D of Sec. II is inapplicable.

However, the free energy $a_N(m)$ for a finite system is not in general convex downwards.[17] In fact, since the probability distribution with $H=0$ is related to $a_N(m)$ through

$$p_{Nm}(0)=e^{-\beta N a_N(m)}/e^{-\beta N f_N(0)}, \qquad (27)$$

it is evident that a situation such as that envisaged in definition B of Sec. II—two peaks in the probability distribution—could only occur if $a_N(m)$ had two minima. A possible situation is shown by the upper dotted line in Fig. 2 (b). As $N\rightarrow\infty$, the height of the maximum separating the minima must, of course, decrease. Were it to decrease as, for example, $1/\sqrt{N}$, the factor N in the first exponent on the right side of (27) would still insure a rapid decrease with increasing N of $p_{Nm}(0)$ near $m=0$. Of course another possibility is represented by the lower dotted line in Fig. 2 (b). Although the valley between $-m_0$ and m_0 would have to disappear in the limit $N\rightarrow\infty$, this could still lead to a probability sharply peaked at $m=0$.

To see how the former situation might come about, consider for simplicity a two-dimensional square Ising lattice with nearest-neighbor interaction at low temperatures. The lowest energy states correspond to all the moments pointed "up" or "down," in our notation to $m/g\mu=+\frac{1}{2}$ or $-\frac{1}{2}$. A state with $m=0$ can, however, be produced by having half the spins pointed up and half down. This raises the energy by an amount on the order of $N^{1/2}$, the minimum energy required to insert a border between the "up" and "down" spins. Such a "surface" energy is negligible compared with the bulk energy as $N\rightarrow\infty$, and so has no influence on bulk thermodynamic properties. Such surface energies are, however, of importance in calculating the probability $p_{Nm}(0)$. It is hard to say how much validity this simple-minded picture retains at finite temperatures where considerations of entropy cannot be neglected.

V. APPLICATIONS TO THE ISING AND HEISENBERG MODELS

A major problem in discussing spontaneous magnetization in idealized ferromagnets is that the number of instances where exact solutions or even good approximations exist is quite limited. Most progress has been made in one-dimensional systems, where one knows from fairly general arguments that Ising models with finite range interaction exhibit no phase transitions[18] and it is suspected (though by no means proved) that the same is true for more complicated cases as, for example, the Heisenberg ferromagnet.[18a]

Ising models in two dimensions have received considerable attention, and a great deal is now known about their properties in zero magnetic field. Of particular interest is a calculation by Yang[19] of the spontaneous magnetization as a function of temperature for the square Ising model with nearest-neighbor interactions. This result has been discussed critically by Schultz, Mattis, and Lieb,[9] who show that Yang's procedure is not really equivalent to (5), but his result is equal to m_2 in (11) and m_c in (13). From the discussion in Sec. III above it is evident that m_0 in (5) certainly cannot be smaller than the value Yang has calculated, a fact also evident from the discussion in Ref. 9. Calculations on small systems by Katsura[20] give support to the suggestion in Sec. IIB that the probability becomes sharply peaked around values of $\pm m_s$ different from zero. Further investigations of this point would certainly be of interest.

Nothing is known with certainty about Ising models in three dimensions, though a fairly simple argument by Peierls[21]—rigorous versions of which have been published independently by the author[22] and by Dobrushin[23]— is easily extended to a simple cubic lattice. It shows that m_1 in (11) is greater than zero at low temperatures, and gives a lower bound on m_0.

The Heisenberg coupling ($\gamma=\delta=1$) is presumed to lead to a spontaneous magnetization in three-dimensional crystals, though this has never been proved. The use of a vector coupling means that the Hamil-

[16] For a convex function there is no particular difficulty in defining a Legendre transformation even when the second derivative vanishes or the first derivative is discontinuous. See Ref. 6, Appendix C.

[17] Our observations in this and the following paragraph are not original. See T. Hill, J. Chem. Phys. **23**, 812 (1955); S. Katsura, Advan. Phys. **12**, 391 (1963). However, since the connection between probability and the theorem on convexity of $a(m)$ can easily lead to confusion if misunderstood (see references in the article by Hill), a brief discussion here may not be out of place.

[18] M. E. Baur and L. H. Nosanow, J. Chem. Phys. **37**, 153 (1962).

[18a] *Note added in proof.* N. D. Mermin and H. Wagner, Phys. Rev. Letters (to be published) have recently shown that one- and two-dimensional Heisenberg ferromagnets cannot exhibit a spontaneous magnetization in the sense of definition A above.

[19] C. N. Yang, Phys. Rev. **85**, 808 (1952).

[20] S. Katsura, Progr. Theoret. Phys. (Kyoto) **11**, 476 (1954).

[21] R. Peierls, Proc. Cambridge Phil. Soc. **32**, 477 (1936).

[22] R. B. Griffiths, Phys. Rev. **136**, A437 (1964).

[23] R. L. Dobrushin, Teoriya Veroyatnostei i ee Primeneniya **10**, 209 (1965). The argument has recently been extended to the case of interactions involving other than nearest neighbors by J. Ginibre, A. Grossman, and D. Ruelle, Commun. Math. Phys. (to be published).

tonian $\mathcal{H}_0$ commutes with all three components of the total angular momentum:

$$\mathbf{S}=\sum_i \mathbf{S}_i.$$

Consequently for each state E and z component of magnetization M there is a set of states degenerate in energy with z components of magnetization $M-1$, $M-2$, $\cdots$ $1-M$, $-M$. And thus $p_M(0)$ as defined in (10) is monotone decreasing in $|M|$. In particular, it is impossible for $p_{Nm}(0)$ to have two peaks. Perhaps of more interest in this case is the probability distribution for the total-angular-momentum quantum number S_T. One might suppose that the appearance of spontaneous magnetization would correspond for large N to a sharp peak in the probability around some value of $S_T/N=m_s$. In this case one would expect $p_{Nm}(0)$ to be essentially constant for $-m_s<m<m_s$, and close to zero outside this region. Only further investigation can confirm or rule out this possibility.

VI. CONCLUSION

We hope the above discussion has served to indicate some of the ambiguities and problems which beset the discussion of spontaneous magnetization in idealized magnetic systems. Since these systems provide some of the simplest examples of phase transitions, it seems safe to assume that analogous problems exist in discussing liquid-vapor transitions, order-disorder phenomena, and the like.

Even the few relationships among different definitions obtained above depend in a critical way upon the fact that $\mathfrak{M}$ and $\mathcal{H}_0$ commute. Cases where this does not occur—e.g., the spontaneous sublattice magnetizations in ordinary antiferromagnets—present nontrivial problems which we believe are worthy of further research.

ACKNOWLEDGMENTS

A preliminary version of this paper was prepared while the author was a National Science Foundation Postdoctoral Fellow at the University of California, San Diego. Financial support of the Foundation and the hospitality of the Physics Department are both gratefully acknowledged.

APPENDIX A: EXISTENCE AND PROPERTIES OF THE FREE ENERGY $a(m)$

We assume that $\mathfrak{M}$ and $\mathcal{H}_0$ commute; in this case the free energy

$$a_N(N^{-1}M)=-\beta^{-1}N^{-1}\ln\mathrm{Tr}[P_M e^{-\beta\mathcal{H}_0}] \qquad \text{(A1)}$$

is the lattice equivalent of the Helmholtz free energy for a gas as calculated in the canonical ensemble. Since the analogous problem for a continuum gas has been discussed in detail[24] and the mathematical techniques are similar, our comments will be brief. For simplicity, we set $g\mu$ equal to 1.

The definition (A1) may be extended to all values of m in the closed interval $[-S, S]$ by linear interpolation between the discrete values for which Nm is an eigenvalue of $\mathfrak{M}$. As the eigenvalues of $\mathcal{H}_0$ lie in some interval of the form[6] $[-CN, CN]$ and the trace (A1) contains at least 1 and at most $(2S+1)^N$ nonzero terms, we have the bounds

$$-C-\beta^{-1}\ln(2S+1)\leq a_N(m)\leq C. \qquad \text{(A2)}$$

We suppose that our system of N atoms is composed of two subsystems 1 and 2 (e.g., two halves of a cube) containing K and L atoms, respectively, with $K+L=N$. The Hamiltonian $\mathcal{H}_0^{(1)}$ contains all terms in $\mathcal{H}_0$ involving only atoms in system 1 and $\mathcal{H}_0^{(2)}$ is similarly defined for system 2. Thus

$$\mathcal{H}_0=\mathcal{H}_0^{(1)}+\mathcal{H}_0^{(2)}+\mathcal{H}', \qquad \text{(A3)}$$

where $\mathcal{H}'$ includes all terms in $\mathcal{H}_0$ which simultaneously involve at least one atom in each subsystem, that is, $\mathcal{H}'$ constitutes a "surface energy." Further, if $\mathfrak{M}_1$ and $\mathfrak{M}_2$ are total magnetization operators for the subsystems, we shall assume that each operator commutes[25] with both $\mathcal{H}_0^{(1)}$ and $\mathcal{H}_0^{(2)}$. Therefore $\mathfrak{M}=\mathfrak{M}_1+\mathfrak{M}_2$, since it commutes with $\mathcal{H}_0$, also commutes with $\mathcal{H}'$ as well as $\mathcal{H}_0^{(1)}$ and $\mathcal{H}_0^{(2)}$. Consequently, in evaluating the trace (A1) we may substitute (A3) and regard the matrices $\mathcal{H}_0^{(j)}$ and $\mathcal{H}'$ as restricted to the subspace of eigenvectors of $\mathfrak{M}$ with eigenvalue M; that is, all other elements of these matrices may be set equal to zero without altering (A1). One may then show by the techniques of Ref. 4 that

$$\mathrm{Tr}[P_M e^{-\beta\mathcal{H}_0}]=\tau\,\mathrm{Tr}[P_M \exp-\beta(\mathcal{H}_0^{(1)}+\mathcal{H}_0^{(2)})], \qquad \text{(A4)}$$

where

$$|\ln\tau|\leq\beta|\mathcal{H}'| \qquad \text{(A5)}$$

and $|\mathcal{H}'|$, the matrix norm used in Appendix B, denotes the largest of the absolute values of the eigenvalues of $\mathcal{H}'$. We remark that (A4) with the bound (A5) depends in an essential way on the fact that $\mathfrak{M}$ commutes with $\mathcal{H}_1$ and the $\mathcal{H}_0^{(j)}$.

Let $P_M^{(1)}[P_M^{(2)}]$ be defined for the subsystem 1[2] in analogy with P_M. The relation

$$P_M=\sum_R P_R^{(1)}P_{M-R}^{(2)} \qquad \text{(A6)}$$

permits us to express the right side of (A4) as a sum of positive terms

$$\tau\sum_R \mathrm{Tr}_1[P_R^{(1)}\exp(-\beta\mathcal{H}_0^{(1)})] \times\mathrm{Tr}_2[P_R^{(2)}\exp(-\beta\mathcal{H}_0^{(2)})], \qquad \text{(A7)}$$

where $\mathrm{Tr}_1[\mathrm{Tr}_2]$ denotes the trace over all states of system 1 [2].

[24] D. Ruelle, Helv. Phys. Acta **36**, 183 (1963); **36**, 789 (1963); M. E. Fisher, Arch. Ratl. Mech. Anal. **17**, 377 (1964).

[25] $\mathfrak{M}_1$ commutes with $\mathcal{H}_0^{(2)}$ and $\mathfrak{M}_2$ with $\mathcal{H}_0^{(1)}$ because they operate within different subsystems.

Define $a_K(m)$ and $a_L(m)$ for subsystems 1 and 2, respectively, in analogy with (A1). Combining (A1), (A4), (A5), and (A7) we obtain the basic inequality

$$a_N(KN^{-1}m_1+LN^{-1}m_2)\leq KN^{-1}a_K(m_1)+LN^{-1}a_L(m_2)+N^{-1}|\mathcal{H}'|. \quad \text{(A8)}$$

The derivation of (A8) has been carried out only for appropriate discrete values of m_1 and m_2. Its extension to all values in $[-S, S]$ with the a's defined by linear interpolation [see paragraph following (A1)] is immediate, as is its generalization to the case of more than two subsystems.

The remainder of the proof is carried out in close analogy with arguments given elsewhere,[6] so we omit details. For a given m, one considers a sequence of cubes $k=2, 3, \cdots$ containing $N_k=2^{3k}$ atoms and shows that

$$a_{2^{3k}}(m)+d_k \quad \text{(A9)}$$

is monotonically decreasing in k, where d_k is a suitable sequence of numbers going to zero as $k\to\infty$. As the $a_N(m)$ are bounded from below by (A2), the sequence possesses a limit $a(m)$ as k becomes infinite. One can then show that the same limit is obtained for other simple sequences of finite systems (e.g., rectangular parallelepipeds with all three edges going to infinity).

The limiting free energy $a(m)$ is convex downwards, bounded by (A2), and therefore continuous[26] in the *interior* of the interval $[-S, S]$. The presence or absence of jump discontinuities at the end points [i.e., one may have $a(S)>\lim(m\to S)a(m)$] is a delicate manner we shall not discuss here.[27] The functions $a_N(m)$ are not, in general, convex in m. For fixed m they are, on the other hand, monotone decreasing and convex upwards in T, and this property is "automatically" inherited by the limiting function $a(m)$.

The equivalence of $f(H)$ and $a(m)$ for the thermodynamic description of the system may be shown as follows. Using the definitions (4) and (A1), we have

$$e^{-\beta N f_N(H)}=\sum_M e^{\beta HM}\exp[-\beta N a_N(N^{-1}M)]. \quad \text{(A10)}$$

The sum contains $2NS+1$ non-negative terms. It must be greater than the maximum term and less than $2NS+1$ times the maximum term. Thus we may write

$$f_N(H)\leq \tilde{f}_N(H)\leq f_N(H)+(\beta N)^{-1}\ln(2NS+1), \quad \text{(A11)}$$

where

$$\tilde{f}_N(H)=\min_m[a_N(m)-mH] \quad \text{(A12)}$$

is the Legendre transform[28] of the function $a_N{}^c(m)$, the "convex-cover" of $a_N(m)$; that is, it is convex downwards and, for every m, greater than or equal to any convex-downwards function everywhere smaller than $a_N(m)$.

The sequence $a_N{}^c(m)$ converges to the same limit as the $a_N(m)$. For the special sequence (A9) this follows from the fact that $a(m)$ is a convex-downwards function less than $a_{2^{3k}}(m)+d_k$, and thus less than $a_{2^{3k}}{}^c(m)+d_k$, for every k. Convergence of the former sequence thus implies convergence of the latter. Extension of this result to other than the standard sequence is not difficult.

Now (A11) shows that $\tilde{f}_N(H)$ converges to the same limit as $f_N(H)$, namely $f(H)$. But as $\tilde{f}_N$ and $a_N{}^c$ are convex functions related by a Legendre transformation; the same is true of the limits $f(H)$ and $a(m)$.[28]

APPENDIX B: PROOF THAT $m_N(H)$ IS ANALYTIC FOR A FINITE SYSTEM

For a system of N spins, $\mathcal{H}_0$ and $\mathfrak{M}$ are bounded Hermitian matrices in a $d=(2S+1)^N$-dimensional space. We shall show that

$$Z_N(H)=\mathrm{Tr}[e^{-\beta(\mathcal{H}_0-H\mathfrak{M})}] \quad \text{(B1)}$$

is an entire function of H. For the case where $\mathcal{H}_0$ and $\mathfrak{M}$ commute this follows immediately from the fact that Z is a finite polynomial[3] in $e^{-g\mu\beta H/2}$. When $\mathcal{H}_0$ and $\mathfrak{M}$ do not commute, the exponential can be expanded in an infinite series of terms, each a product of H to some power multiplied by factors of β, $\mathcal{H}_0$, and $\mathfrak{M}$. The series formed by taking the trace of each term it absolutely convergent, and may therefore be rearranged as a convergent series in powers of H. To prove absolute convergence we introduce a matrix norm[29] with the properties

$$\begin{aligned}|\mathfrak{A}+\mathfrak{B}|&\leq|\mathfrak{A}|+|\mathfrak{B}|,\\ |\mathfrak{A}\mathfrak{B}|&\leq|\mathfrak{A}||\mathfrak{B}|,\\ |b\mathfrak{A}|&=|b||\mathfrak{A}|,\\ |\mathrm{Tr}[\mathfrak{A}]|&\leq d|\mathfrak{A}|,\end{aligned} \quad \text{(B2)}$$

where $\mathfrak{A}$ and $\mathfrak{B}$ are matrices and b a number. The series for $Z_N(H)$ is then bounded by

$$d\exp\{\beta|\mathcal{H}_0|+\beta|H||\mathfrak{M}|\}. \quad \text{(B3)}$$

Finally we note that for H real, $Z_N(H)$ is the trace of a positive matrix and cannot vanish. Thus $f_N(H)$ is an analytic function for real H and so is its derivative $m_N(H)$.

[26] Reference 15, p. 91.

[27] The continuity of the ground-state energy at the end points for a particular case of the Hamiltonian (2) with spin $\frac{1}{2}$ has been proved by C. N. Yang and C. P. Yang, Phys. Rev. **147**, 303 (1966).

[28] Reference 6, Appendix C.

[29] P. R. Halmos, *Finite-Dimensional Vector Spaces* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958), pp. 176 ff.