Theory of the Heisenberg Superparamagnet

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The concept of uniform bulk magnetization in superparamagnetic particles is examined critically. By a straightforward idealization of the conditions met in actual superparamagnetic samples, it is shown that this concept is related to a fundamental problem of the physical statistics of magnetic first-order phase transitions. Thus, the fact that the concept is applicable to experimental data on superparamagnets has far-reaching consequences with respect to the nature of the magnetic transition at zero field.

1. INTRODUCTION

To describe superparamagnetic behavior, it is a reasonable approximation to neglect magnetic anisotropy and magnetostatic interactions. If this is done for an assembly of superparamagnetic particles at elevated temperatures there remain two causes for deviations from complete alignment of the magnetic moments parallel to the field direction: excitations of isotropic and essentially short-range exchange interactions, and excitations of Zeeman levels in the external field.

The first type of excitations is not typical for small particles only but is equally observed in bulk material where it reduces the spontaneous magnetization as the temperature rises. For the following, we call this type "exchange excitations." Excitations of the second type are typical for superparamagnetic behavior and have no corresponding effect in bulk ferromagnetism. Hence they may be called "superparamagnetic excitations."

In calculating the magnetization of a superparamagnetic assembly of particles it has been assumed quite currently that exchange excitations and superparamagnetic excitations may be treated independently in the sense of the following statements:

(1) On account of exchange interaction, for a superparamagnetic particle at a given temperature T there exists a sharply defined value of the particle magnetic moment $\mu(T)$ which is independent of magnetic field H as long as H is small compared to the exchange field. For large particles, $\mu(T)/v$ is identical to the spontaneous magnetization as measured by standard methods on a bulk sample. v is the particle volume.

(2) Since $\mu(T)$ is large on an atomic scale, the superparamagnetic excitations may be described in terms of classical Langevin statistics.

Apparently the first of these statements cannot be rigorously true in the form given above, since a superparamagnetic particle is a finite system, and hence there must be fluctuations in μ. Thus the concept has to be understood on the basis of the observation that, in general, a superparamagnetic particle contains a large number of atoms of order 10^2 to some 10^4, and, therefore, fluctuations might be expected to be relatively small. In fact, the rather intuitive view underlying the above assumption is twofold. First, the particle is thought to be large enough to show the "internal" behavior of a bulk isotropic ferromagnet. In particular, a spontaneous magnetization is assumed to exist and to be equal to the thermodynamic equilibrium spontaneous magnetization of the bulk. Second, this magnetization is assumed to be uniform throughout the particle volume, even so in a small external field which allows for superparamagnetic excitations out of the field direction of the particle magnetization as a whole, and also in zero external field.

It is the purpose of this investigation to find out what this concept would mean in terms of the Heisenberg model. On account of its isotropy and the neglect of magnetostatic interactions this model permits a straightforward idealization of a large particle by going to the limit of infinite particle size. When formulated in this manner the theoretical problem of the "large superparamagnetic particle" turns out to coincide with a well-known, yet unsolved, problem of statistical physics which may be stated in several ways. For example, one way to put the question is to ask whether on the phase transition line ($T<T_c$, $H=0$)[1] of an isotropic ferromagnet the root of the squared magnetic moment of the crystal is an extensive quantity in the thermodynamic limit $N\rightarrow\infty$, the volume density of which equals the $H\rightarrow 0^+$ limit of the thermodynamic magnetization. On account of the present efforts in the theoretical study of phase transitions, it seems of some special interest to establish and discuss the relationship between a theoretical problem typical in this field and a simple interpretation scheme which is often successfully employed in the special empirical field of superparamagnetism, even if a solution of the theoretical problem seems not in sight at present.

A careful investigation of the $H=0$ first-order phase transition for ferromagnetic spin lattices is due to Griffiths.[2] Much of the following discussion is based on his results. A modification of one of his results on the limiting behavior of probability distributions for large crystal size N is given in Sec. 4. It states that for the Heisenberg model the probability distribution of total spin absolute value cannot have a minimum of order

[1] The magnetization as a function of field is discontinuous at $H=0$ for $T<T_c$.

[2] R. B. Griffiths, Phys. Rev. **152**, 260 (1966).

e^{-N} at low total spin values for large N. The corresponding property for the probability distribution of total spin z component is trivial for the Heisenberg model but was shown by Griffiths to hold for more general cases.

Although the result for the Heisenberg model is not unexpected, the possibility of a formal proof seems of some interest, independent of the special superparamagnetic problem.

2. IDEALIZED MODEL OF SUPERPARAMAGNETISM

Since there exist excellent reviews of the field of superparamagnetism[3–5] we only present in a very cursory manner some orders of magnitude for characteristic parameters. This discussion is necessary to justify the neglect of anisotropy and magnetostatic interaction.

In order to adequately idealize the physical situation met with actual superparamagnetic samples, the observation is central that magnetostatic interaction and magnetic anisotropy might be expected to have no principal influence on magnetization on account of particle smallness.

In Table I, in terms of macroscopic quantities, characteristic energies are given related to magnetostatic interaction (column 4), crystal anisotropy (column 5), and stress anisotropy (column 6). The energies are given in units of k_BT, with k_B Boltzmann's constant and T equal to room temperature. The assumed particle sizes indicated in columns 2 and 3 are typical for experiments in the superparamagnetic range. The formulas used in the calculation of the energies are given at the top of the corresponding column and are familiar from the Stoner-Wohlfarth-Néel[6,7] theory of single-domain behavior.

TABLE I. Characteristic energies for superparamagnetic particles in units k_BT, with T equal to room temperature. [v=particle volume, N=number of atoms, I_s=saturation magnetization, K_1=first crystal anisotropy constant, λ=saturation magnetostriction coefficient, τ=stress (for τ 100 kp/mm² were adopted), A=exchange stiffness constant.]

1 Element	2 $v^{1/3}$ (Å)	3 N	4 $\pi v I_s^2$ [a]	5 $K_1 v$ [a]	6 $\frac{3}{2}\lambda\tau v$ [a]	7 $\pi^2 v^{1/3} A$ [b]
	10	85	7.5×10^{-2}	3.6×10^{-3}	1.2×10^{-3}	50
Fe	30	2300	2.0	9.7×10^{-2}	3.4×10^{-2}	150
	50	10700	9.3	0.45	0.16	250
	10	92	5.0×10^{-2}	4.5×10^{-2}	5.1×10^{-3}	50
Co[c]	30	2500	1.3	1.2	0.14	150
	50	11500	6.2	5.6	0.64	250
	10	92	6.5×10^{-3}	3.7×10^{-4}	8.7×10^{-3}	20
Ni	30	2500	0.17	1.0×10^{-2}	0.23	60
	50	11500	0.78	4.6×10^{-2}	1.1	100

[a] Numerical data taken from E. Kneller, *Ferromagnetismus* (Springer-Verlag, Berlin, 1962), Table 27.2.
[b] Data for A taken from W. Döring, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1966), Vol. 18.2, pp. 341–437, Table 3.
[c] Data for hexagonal Co. For cubic Co crystal anisotropy energies are lower by an order of magnitude roughly [C. P. Bean, J. D. Livingstone, and D. R. Rodbell, J. Phys. Radium **20**, 298 (1959)].

In column 7 a rough estimate is given of the minimum exchange energy for a state of vanishing net magnetic moment in terms of classical domain theory. $\pi^2 v^{1/3} A$ is the minimum exchange energy of a 180° Bloch wall in a cube-shaped particle.

The table clearly shows that anisotropy energies generally are of order k_BT or less and that exchange energy is by far dominant in the superparamagnetic range: The energy $I_s vH$ of interaction with the external field, too, is characteristically of order k_BT for superparamagnetic behavior. The same is true for the magnetostatic interaction energy, with some restrictions for the larger particle sizes and the elements with high saturation magnetization.

Hence for superparamagnetic particles, neither the external field nor anisotropy is responsible for homogeneity of magnetization postulated by the usual concept.[8] Instead, homogeneity over distances comparable with particle size must be enforced by the essentially short-range isotropic exchange interaction. It is characteristic for the size range of empirical superparamagnetism that the secondary magnetic energies related to the particle as a whole are of order kT or even smaller, whereas the particle is still rather large compared with the range of exchange forces usually adopted. Roughly speaking, the concept of bulk magnetization in superparamagnetic particles may be formulated as the assumption that in strictly vanishing external fields, short-range isotropic interaction enforces long-range homogeneity of magnetization, i.e., a very strong and special long-range correlation.

We emphasize that there is no possibility of testing this idea by experience with a macroscopic ferromagnetic crystal of, say, centimeter size on account of secondary effects. The reason for this is easily demonstrated from Table I by the observation that the energies in columns 4–6 are proportional to the particle volume, whereas the minimum Bloch wall energy (column 7) is proportional to the particle linear dimension. Thus, in order to rule out secondary effects in the actual measuring process of bulk spontaneous magnetization, fields have always to be incorporated which are only small compared to an effective exchange field but in any case are large enough to enforce homogeneity of magnetization over macroscopic distances. This argument remains valid even if there is no external field incorporated in the measuring process (e.g., Mössbauer techniques), since there are always fields resulting from

[3] C. P. Bean and J. D. Livingstone, J. Appl. Phys. **30**, Suppl., 120S (1959).
[4] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, pp. 271–344.
[5] E. Kneller, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1966), Vol. 18.2, pp. 438–544.
[6] E. C. Stoner and E. P. Wohlfarth, Phil. Trans. Roy. Soc. London **A240**, 599 (1948).
[7] L. Néel, Compt. Rend. **224**, 1488 (1947).
[8] Magnetostatic interaction generally favors states of inhomogeneous magnetization.

magnetostatic interaction or anisotropy which are large in the sense in question.

The concept of homogeneous bulk magnetization for a large superparamagnetic particle may be easily formulated as a well-defined mathematical problem in terms of the Heisenberg model. By doing this we arrive at a well-known hitherto unsoluble problem of statistical physics.

Let the Hamiltonian describing the magnetic properties of a superparamagnetic particle be[9]

$$\hat{H}=\hat{H}_0+\hat{H}_M \tag{1}$$

with

$$\hat{H}_0=\sum_{i\neq j} J_{ij}\hat{\mathbf{s}}_i\cdot\hat{\mathbf{s}}_j \tag{2}$$

the Heisenberg exchange interaction on some finite spin lattice and

$$\hat{H}_M=-h\sum_i \hat{s}_{iz}, \tag{3}$$

$$h=2\mu_B H \tag{4}$$

describing the interaction with the external field. μ_B is the Bohr magneton.

The spin operators $\hat{\mathbf{s}}_i$ are defined by their well-known commutation relations and their absolute value quantum number s. The spins are thought to be attached to some simple finite lattice (e.g., sc, fcc, or bcc) with all three dimensions of equal order of magnitude. In the following we think of the lattice type as specified but consider varying sizes of the crystal, characterized by the number N of lattice sites. The J_{ij} are assumed equal for equivalent pairs of lattice sites and of restricted range, i.e., J_{ij} is assumed to be zero for the distance $i\rightarrow j$ exceeding a given value. $\hat{H}$ works on the $(2s+1)^N$-dimensional space of spin states.

We should emphasize here that the really drastic simplifications introduced by choosing the model Hamiltonian are rather unimportant for this investigation which does not intend to give a good theory of superparamagnetic magnetization but to analyze the concept of bulk homogeneous magnetization in a large superparamagnetic particle introduced in Sec. 1. It is apparent from the discussion given above that, if any, the Heisenberg model should meet all the requirements for the concept to hold. Particularly the spatial degeneracy of the eigenstates guarantees a "natural" separation of the exchange and superparamagnetic excitations. Furthermore, the limit of large particle size (compared to the range of the J_{ij}) may easily be formulated in the mathematical model by going to the limit of infinite particle size in vanishing external field.

The experimental procedure to measure the bulk magnetization σ of a macroscopic crystal in finite external field is described within the model by the thermodynamic limit

$$\sigma(\beta,h)=\lim_{N\to\infty}[N^{-1}\langle\hat{S}_z\rangle_{\beta,h}{}^{(N)}]. \tag{5}$$

Here,

$$\langle\hat{O}\rangle_{\beta,h}{}^{(N)}=\mathrm{Tr}^{(N)}[\hat{O}e^{-\beta\hat{H}}]/\mathrm{Tr}^{(N)}[e^{-\beta\hat{H}}] \tag{6}$$

denotes the thermal mean value of an operator $\hat{O}$ at given temperature $\beta^{-1}=k_BT$, field h, and crystal size N. $\hat{S}_z$ is the z component of total spin:

$$\hat{\mathbf{S}}=\sum_i \hat{\mathbf{s}}_i. \tag{7}$$

The traces on the right side of (6) are taken in the system with N atoms and the limit in (5) is performed over a sequence of crystals for which all three linear dimensions uniformly tend to infinity. In the following the limit $N\rightarrow\infty$ should always be understood in this sense. This is a condition quite necessary for all results in Secs. 3 and 4 and shall not be repeated in each case. A proof that—with a restriction unimportant at this instant—the limit (5) exists is due to Griffiths.[10] The normalization in (5) is taken so as to obtain σ as the mean spin z component per lattice site.

The bulk spontaneous magnetization is

$$\sigma^*(\beta)=\lim_{h\to 0^+}\sigma(\beta,h). \tag{8}$$

The contribution of the particle of size N to the superparamagnetic magnetization is obtained in this model by

$$\mathcal{J}=2\mu_B\langle\hat{S}_z\rangle_{\beta,h}{}^{(N)}. \tag{9}$$

With the use of (1), (2), (3), and (6) we may write this as

$$\mathcal{J}=2\mu_B\beta^{-1}(\partial/\partial h)\ln\mathrm{Tr}^{(N)}[e^{-\beta\hat{H}}]. \tag{10}$$

Equation (10) may be brought to a form [Eq. (18) below] in which the effects of exchange and Zeeman excitations are separated. To do so we make use of the well-known properties which follow from the commutability of the operators $\hat{H}_0$, $\hat{\mathbf{S}}^2$, $\hat{S}_z$ and from their symmetry properties under rotations.

Let

$$|S,\alpha,M) \tag{11}$$

denote[11] a complete orthonormal set of common eigenstates of $\hat{\mathbf{S}}^2$, $\hat{S}_z$, and $\hat{H}_0$ with eigenvalues $S(S+1)$, M, and $E_0(S,\alpha)$, respectively. The quantum number α accounts for the remaining high degeneracy if S and M are fixed. The set and the α labeling may be chosen such that, apart from normalization, $|S,\alpha,M-1)$ results from $|S,\alpha,M)$ by application of the step-down operator $\hat{S}^-=\hat{S}_x-i\hat{S}_y$.

[9] Here and in the following, symbols are chosen in close analogy to Griffiths's paper (Ref. 2) in order to simplify reference.

[10] R. B. Griffiths, J. Math. Phys. 5, 1215 (1964).

[11] For convenience in notation we avoid the use of an additional label N to characterize the states (11). There is no danger of confusion since these states are used explicitly in developments only with fixed crystal size N.

The partition function in (10) may be written as

$$\mathrm{Tr}^{(N)}[e^{-\beta\hat{H}}]=\sum_{S,\alpha,M}(S,\alpha,M|e^{-\beta\hat{H}_0}|S,\alpha,M)e^{\beta hM}. \quad (12)$$

Here use was made of the commutability of $\hat{H}_0$ and $\hat{H}_M=-h\hat{S}_z$. For fixed S, α the matrix element appearing in (12)

$$G(S,\alpha,\beta)=(S,\alpha,M|e^{-\beta\hat{H}_0}|S,\alpha,M) \quad (13)$$

does not depend on M, and hence the summation over M may be performed. Introducing the "Brillouin partition function"

$$\phi(S,\beta,h)=\sum_{M=-S}^{+S}e^{\beta hM}=\frac{\sinh[\beta h\cdot(S+\frac{1}{2})]}{\sinh(\frac{1}{2}\beta h)} \quad (14)$$

familiar from the theory of ionic paramagnetism, we obtain for (12)

$$\mathrm{Tr}^{(N)}[e^{-\beta\hat{H}}]=\sum_S[\phi(S,\beta,h)\sum_\alpha G(S,\alpha,\beta)]. \quad (15)$$

Instead of the sum over α, appearing on the right of this equation, it is convenient to introduce the function

$$Q^{(N)}(S,\beta)=\frac{(2S+1)\sum_\alpha G(S,\alpha,\beta)}{\mathrm{Tr}[e^{-\beta\hat{H}_0}]}. \quad (16)$$

Thus (15) takes the form

$$\mathrm{Tr}^{(N)}(e^{-\beta\hat{H}})=\mathrm{Tr}^{(N)}(e^{-\beta\hat{H}_0})\times\sum_S Q^{(N)}(S,\beta)\cdot(2S+1)^{-1}\cdot\phi(S,\beta,h). \quad (17)$$

Combining (10), (14), and (17) we finally arrive at

$$\mathcal{G}=2\mu_B\frac{\sum_S Q^{(N)}(S,\beta)\cdot(2S+1)^{-1}\cdot\sinh[\beta h\cdot(S+\frac{1}{2})]\cdot B_\infty[\beta h\cdot(S+\frac{1}{2})]}{\sum_S Q^{(N)}(S,\beta)\cdot(2S+1)^{-1}\cdot\sinh[\beta h\cdot(S+\frac{1}{2})]}, \quad (18)$$

with

$$B_\infty[x]=\mathrm{cth}x-x^{-1}, \quad (19)$$

the classical Langevin function. In the deduction of (18), $\mathrm{tgh}(\frac{1}{2}\beta h)$ was replaced by the argument. This is legitimate for usual fields and temperatures.

The function $Q^{(N)}(S,\beta)$ introduced above has a simple meaning: It represents the probability distribution of total spin S in vanishing external field and at temperature $1/\beta$. This is most easily seen from (16) by evaluating the trace in the special system (11) and replacing the factor $2S+1$ by a summation over M. The result is

$$Q^{(N)}(S,\beta)=\frac{\sum_{\alpha,M}(S,\alpha,M|e^{-\beta H_0}|S,\alpha,M)}{\sum_{S,\alpha,M}(S,\alpha,M|e^{-\beta\hat{H}_0}|S,\alpha,M)}. \quad (20)$$

For later use we give still another representation for (20) which does not incorporate the special set of states (11). Let

$$\hat{Q}_S=\sum_{\alpha,M}|S,\alpha,M)(S,\alpha,M| \quad (21)$$

denote the projection operator onto the subspace spanned by the eigenstates of $\hat{\mathbf{S}}^2$ with fixed eigenvalue $S(S+1)$. Then we have

$$Q^{(N)}(S,\beta)=\langle\hat{Q}_S\rangle_{\beta,0}{}^{(N)} \quad (22)$$

according to (6), (20), and (21).

In (18) the superparamagnetic magnetization is represented as a weighted mean of Langevin-type contributions with different total spin S. It is just in form of the weighting factor $Q^{(N)}(S,\beta)$ that the exchange excitations enter the problem.

The concept of bulk spontaneous magnetization for large superparamagnetic particles obtains a clear-cut form in this model. It consists in assuming that the probability distribution $Q^N(S,\beta)$ of total spin in vanishing external field becomes sharply centered around the value

$$S^*=N\cdot\sigma^*(\beta) \quad (23)$$

for very large N. This condition assumed to hold and neglecting $\frac{1}{2}$, which is small compared to S^*, we immediately arrive at the usual formula for isotropic superparamagnetism, namely,

$$\mathcal{G}=2\mu_B S^* B_\infty[\beta h S^*]. \quad (24)$$

3. GRIFFITHS'S RESULT

Independently of their relation to superparamagnetism, problems closely related to those with which we are concerned have been extensively studied by Griffiths. In fact from several of his papers,[2,10,12] a rather comprehensive view may be obtained of the relation between probability distributions similar to $Q^{(N)}(S,\beta)$ for large N and the thermodynamic spontaneous magnetization defined by (8). As typical for exact results of statistical physics on problems of some complexity, the results may be represented by some inequalities. These are by far too weak to supply a solution of the physical problem, but instead serve to mediate a deeper insight into the problem. The problem of, roughly speaking, "peakedness" of $Q^{(N)}(S,\beta)$ remains unsolved. Instead, the usefulness of the method lies in the fact that it removes a tempting reasoning of some intuitive appeal which may be stated as follows: Apart from secondary effects like magnetostatic interaction it is the "nature" of the ferromagnetic state to

[12] R. B. Griffiths, J. Math. Phys. 6, 1447 (1965).

yield long range correlation of magnetization, even in exactly vanishing external field and hence there does not remain a problem.

The very outcome of Griffiths's results and their modification to be developed in Sec. 4 can be summarized into the following statement: The condition of a finite bulk spontaneous magnetization $\sigma^*(\beta)$ is by far too weak to imply the special peaked structure of the probability distribution for large N, which was discussed in the foregoing. Instead this condition turns out to be much less restrictive and to be compatible with a broad variety of possible limiting behavior of $Q^{(N)}(S,\beta)$. The very reason why there is such poor correspondence between the $h\to 0$ limit of thermodynamic magnetization, and the $N\to\infty$ limiting behavior of the probability distribution at the phase transition $h=0$ is as follows: The latter might be influenced by fluctuations of magnetization direction on a macroscopic scale which are excluded by the order of taking the limits in (5) and (8).

For a most general class of spin Hamiltonians including the Ising model and the Heisenberg model (2), Griffiths, in one of his papers,[2] supplies an extensive study of interrelations between $\sigma^*(\beta)$ defined by (8) and the probability distribution in vanishing external field of total spin z component

$$P^{(N)}(M,\beta)=\langle\hat{P}_M\rangle_{\beta,0}{}^{(N)}. \tag{25}$$

Here $\hat{P}_M$ is the projection operator onto the subspace spanned by the eigenstates of $\hat{S}_z$ with eigenvalue M. Particularly for the Heisenberg model discussed in this investigation, $\hat{P}_M$ may be written in terms of the states (11) as

$$\hat{P}_M=\sum_{S,\alpha}|S,\alpha,M)(S,\alpha,M|. \tag{26}$$

On account of spatial degeneracy, $P^{(N)}(M,\beta)$ is certainly not centered around $N\sigma^*$ for this model. Instead, it may easily be shown to be monotonically decreasing with increasing $|M|$ and hence is of little interest. However, Griffiths's technics may be extended to obtain the same results on $Q^{(N)}(S,\beta)$ in the special case of the Heisenberg model, which, for the more general Hamiltonian, where derived by him on $P^{(N)}(M,\beta)$, namely,[2] the following:

(1) The probability at fixed $\Delta>0$ for M to exceed $N(\sigma^*+\Delta)$, with σ^* given by (8), vanishes exponentially with size N of the system; i.e., Δ being given there exists a $\delta>0$ depending on Δ and independent of N such that

$$\sum_{M>N(\sigma^*+\Delta)}P^{(N)}(M,\beta)<e^{-\delta N} \tag{27}$$

holds for sufficiently large N. Define the relative z component of total spin

$$m=M/N, \tag{28}$$

and consider $P^{(N)}(M,\beta)$ as a function of m. Whereas from (27) for $m>\sigma^*(\beta)$ the limiting probability distribution for $N\to\infty$ is known to exist and to be identically zero, not even the existence of a limiting distribution is guaranteed for $m<\sigma^*(\beta)$. Instead only the limiting behavior is known of the function[13]

$$a^{(N)}(m,\beta)=-\beta^{-1}N^{-1}\ln P^{(N)}(Nm,\beta), \tag{29}$$

closely related to $P^{(N)}(M,\beta)$. In fact for finite N we obtain

$$P^{(N)}(M,\beta)=\exp[-\beta N\cdot a^{(N)}(M/N,\beta)], \tag{30}$$

and, thus, $a^{(N)}(m,\beta)$, in a most direct manner, determines $P^{(N)}(M,\beta)$. The function $a^{(N)}(m,\beta)$ is defined by (29) only for $2Ns+1$ discrete values of m, with s the atomic spin as defined in Sec. 2. If the definition is extended to all real values of m between $-Ns$ and $+Ns$ by linear interpolation, the following statements are true[2]:

(2) The limiting function

$$a(m,\beta)=\lim_{N\to\infty}a^{(N)}(m,\beta) \tag{31}$$

exists and is convex downward. Furthermore, $a(m,\beta)$ equals a constant within the interval $-\sigma^*(\beta)<m<\sigma^*(\beta)$ and exceeds this constant everywhere outside the interval. Finally, $a(m,\beta)$ is bounded and hence is continuous in the interior of the interval $-s<m<s$.

Hence, $a(m,\beta)$ gives full information on $\sigma^*(\beta)$, which is determined by the extent of the "flat bottom" of $a(m,\beta)$.[2] Moreover, as Griffiths has shown, $a(m,\beta)$ is a thermodynamic free energy which determines the magnetization at finite fields h too, in complete equivalence with (5).

It can be shown that statements (1) and (2) remain true if everywhere $P^{(N)}(M,\beta)$ is replaced by $Q^{(N)}(S,\beta)$. Since statement (1) is a consequence of statement (2) it is sufficient to reformulate the latter. It is possible to prove the following properties of $Q^{(N)}(S,\beta)$:

With $A^{(N)}(\sigma,\beta)$ defined by

$$A^{(N)}(\sigma,\beta)=-N^{-1}\beta^{-1}\ln Q^{(N)}(N\sigma,\beta), \tag{32}$$

this definition being extended to all real σ by linear interpolation, the limiting function

$$A(\sigma,\beta)=\lim_{N\to\infty}A^{(N)}(\sigma,\beta) \tag{33}$$

exists. Moreover,

$$A(\sigma,\beta)=a(\sigma,\beta) \tag{34}$$

is true. The proof is given in Sec. 4. We conclude this section with a discussion of the poor consequences on $Q^{(N)}(S,\beta)$ which result from the flat bottom property of $A(\sigma,\beta)$.

From the inversion of Eq. (32)

$$Q^{(N)}(N\sigma,\beta)=\exp[-\beta N\cdot A^{(N)}(\sigma,\beta)] \tag{35}$$

[13] Definition (29) differs from Griffiths's by an additive function $f^{(N)}(\beta)$ independent of m and defined by (47) below. Since $\lim f^{(N)}(\beta)$ is known to exist (Ref. 10), there are no difficulties in taking the limit (31). Particularly the validity of statement (2) below remains unaffected.

it is obvious that the assumption of a finite thermodynamic spontaneous magnetization $\sigma^*(\beta)$ by no means implies that $Q^{(N)}(N\sigma,\beta)$ for large N tends to a function with a sharp peak at $\sigma=\sigma^*(\beta)$ and vanishing at smaller values of σ. This would mean that $A^{(N)}(\sigma,\beta)$ for large N should obtain a relative and absolute minimum near $\sigma=\sigma^*(\beta)$, i.e., a very special structure of the function $A^{(N)}(\sigma,\beta)$. The only implication, however, on $A^{(N)}(\sigma,\beta)$ and hence $Q^{(N)}(S,\beta)$, which can be taken from (8), is the fact that for $\sigma<\sigma^*(\beta)$ each structure in $A^{(N)}(\sigma,\beta)$ must vanish in the limit. Vice versa any sequence of functions $A^{(N)}(\sigma,\beta)$ tending to a constant for $\sigma<\sigma^*$ implies (8) regardless of the structure of $A^{(N)}(\sigma,\beta)$ for finite N.

The corresponding discussion, with $Q^{(N)}(S,\beta)$ replaced by $P^{(N)}(M,\beta)$, has been given by Griffiths.[2] Perhaps the most instructive illustration of possible behavior of $A^{(N)}(\sigma,\beta)$ for finite N is supplied by Fig. 1 closely resembling a figure in Griffiths's paper.

Three possible structures of $A^{(N)}(\sigma,\beta)$ for large N are indicated. The three curves I, II, and III correspond to probability distributions $Q^{(N)}(S,\beta)$ with peaks at $S=N\sigma^*$, $S=0$, and both $S=N\sigma^*$ and $S=0$, respectively. In any case the structure in $A^{(N)}(\sigma,\beta)$ must vanish in the limit. If, however, this vanishing is weaker than N^{-1}, say of order $N^{-1/2}$, $Q^{(N)}(S,\beta)$ remains sharply peaked on account of the factor N in the exponential in (35). For case III assume that in the limiting sequence the difference between the amplitudes of the two relative minima vanishes to lower order than N^{-1}. Then essentially only one peak in $Q^{(N)}(S,\beta)$ remains for large N. As a further possibility assume that all structure in $A^{(N)}(S/N,\beta)$ with $N\to\infty$ vanishes faster than N^{-1} in a finite interval around the minimum. Then for large N the probability $Q^{(N)}(S,\beta)$ should become essentially constant within this interval. Of course, there exists a variety of other possibilities for $A^{(N)}(\sigma,\beta)$ to tend to a constant in the limit including more pathological ones which, in contrast to those discussed above, do not lead to a well-defined limiting behavior of $Q^{(N)}(S,\beta)$.

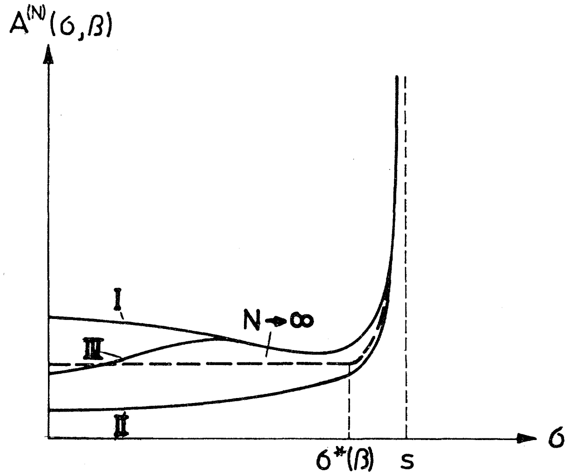

FIG. 1. Three possible types of the finite particle free energy as a function of total spin.

4. EXTENSION OF GRIFFITHS'S RESULT TO $A(\sigma,\beta)$

The proof that $A(\sigma,\beta)$ defined by the limit (33) exists and equals $a(\sigma,\beta)$ conveniently is split into two steps. First, $A(\sigma,\beta)$ may be shown to exist, to be convex downward, and to obtain its minimum[14] for $\sigma=0$. From this it is not difficult to prove the identity with $a(\sigma,\beta)$. The first property implies that $A(\sigma,\beta)$ as a function of σ is monotonic nondecreasing. In particular $A(\sigma,\beta)$ cannot exceed $A(\sigma^*,\beta)$ for $\sigma<\sigma^*$. This property is nontrivial in contrast with the corresponding property for $a(\sigma,\beta)$, which simply follows from spatial degeneracy. However, this property for $a(\sigma,\beta)$ is easily seen to have a deeper foundation by observing that Griffiths's deduction is valid for more general Hamiltonians including the Ising model. The central point entering Griffiths's deduction is the observation that it is always possible to reduce the total spin z component by introducing a border between two halves of the crystal which is characterized by an energy of order $N^{2/3}$ only and hence is not felt in the thermodynamic limit (31) defining the bulk free energy. Thus a corresponding result might be expected for $A(\sigma,\beta)$ in the Heisenberg model.

The proof may be given directly following Griffiths's scheme[15] and thus we can be brief referring to his paper for all steps except those differing. The modifications are nontrivial at one special point subsequent to Eq. (39) below.

In accord with Griffiths we introduce a border dividing the crystal of size N into two parts (1) and (2) containing N_1 and N_2 atoms, respectively, with $N_1+N_2=N$. Next the exchange Hamiltonian (2) for the whole crystal is split into

$$\hat{H}_0=\hat{H}_0^{(1)}+\hat{H}_0^{(2)}+\hat{H}', \tag{36}$$

with $\hat{H}_0^{(1)}$, $\hat{H}_0^{(2)}$, and $\hat{H}'$ those parts of $\hat{H}_0$ which contain spins of subsystem (1) only, subsystem (2) only, and of both subsystems, respectively. The inequality

$$\mathrm{Tr}^{(N)}[\hat{Q}_S e^{-\beta\hat{H}_0}]\geq e^{-\beta|\hat{H}'|}\,\mathrm{Tr}^{(N)}\{\hat{Q}_S e^{-\beta[\hat{H}_0^{(1)}+\hat{H}_0^{(2)}]}\} \tag{37}$$

may be shown to hold with arguments exactly resembling those used by Griffiths in establishing the corresponding relation with $\hat{Q}_S$ replaced by $\hat{P}_M$.[15] Here $|\hat{H}'|$ is the largest of the absolute values of the eigenvalues of $\hat{H}'$. For (37) to hold it is essential that $\hat{\mathbf{S}}^2$ commutes with each of the operators $\hat{H}_0^{(1)}$ and $\hat{H}_0^{(2)}$ and hence with $\hat{H}'=\hat{H}_0-\hat{H}_0^{(1)}-\hat{H}_0^{(2)}$. This, however,

[14] For $a(\sigma,\beta)$ the latter property is a consequence of convexity and symmetry in σ. $A(\sigma,\beta)$, however, is only defined for nonnegative σ.

[15] Reference 2, Appendix A.

is true since each component of $\hat{\mathbf{S}}$ commutes with each of the Hamiltonians. For example,

$$[\hat{S}_z,\hat{H}_0^{(1)}]=[\hat{S}_z^{(1)}+\hat{S}_z^{(2)},\hat{H}_0^{(1)}]=0 \qquad (38)$$

holds, with $\hat{S}_z^{(i)}$ the z component of the total spin operator $\hat{\mathbf{S}}^{(i)}$ of subsystem (i). Equation (38) may easily be deduced from the atomic spin commutation relations, which particularly imply:

$$\begin{aligned}[\hat{s}_{iz},\hat{\mathbf{s}}_j]&=0\,, \quad \text{for} \quad i\neq j\\ [\hat{s}_{iz}+\hat{s}_{jz},\hat{\mathbf{s}}_i\hat{\mathbf{s}}_j]&=0\,.\end{aligned} \qquad (39)$$

In what follows, Griffiths essentially makes use of the fact that a common eigenstate of $\hat{S}_z^{(1)}$ and $\hat{S}_z^{(2)}$, with eigenvalues M_1 and M_2, is an eigenstate of $\hat{S}_z$ with eigenvalue M_1+M_2. Apparently this is not generally true for the eigenstates of $[\hat{\mathbf{S}}^{(1)}]^2$, $[\hat{\mathbf{S}}^{(2)}]^2$, and $\hat{\mathbf{S}}^2$.

Hence the following developments leading to (47) below differ in both cases. Let

$$|S_1,\alpha_1,M_1;S_2,\alpha_2,M_2) \qquad (40)$$

denote a complete orthonormal set of common eigenstates of $[\hat{\mathbf{S}}^{(1)}]^2$, $\hat{S}_z^{(1)}$, $\hat{H}_0^{(1)}$, $[\hat{\mathbf{S}}^{(2)}]^2$, $\hat{S}_z^{(2)}$ and $\hat{H}_0^{(2)}$, defined completely analogous to (11). The corresponding eigenvalues of $\hat{H}_0^{(i)}$ may be $E_0^{(i)}(S_i,\alpha_i)$. Further, let $\Omega(S_1,\alpha_1,S_2,\alpha_2)$ be the $(2S_1+1)(2S_2+1)$-dimensional subspace spanned by the functions in (40) with fixed S_1, α_1, S_2, α_2, and varying M_1, M_2.

As is known from standard applications of group theory on atomic moments leading to the "vector model,"[16] a new basis can be chosen in $\Omega(S_1,\alpha_1,S_2,\alpha_2)$ which consists of functions

$$|S_1,\alpha_1;S_2,\alpha_2;S,M\} \qquad (41)$$

diagonalizing $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ with eigenvalues $S(S+1)$ and M. The total spin quantum numbers S range from $|S_1-S_2|$ to S_1+S_2.

Evaluating the trace appearing on the right side of (37) in the system (41), we obtain a sum of non-negative contributions. Retaining only those with a fixed pair S_1, S_2, and with $M=S$, we obtain the inequality

$$\mathrm{Tr}^{(N)}\{\hat{Q}_S e^{-\beta[\hat{H}_0^{(1)}+\hat{H}_0^{(2)}]}\}\geqslant\Delta(S,S_1,S_2)\times\sum_{\alpha_1,\alpha_2}\exp\{-\beta[E_0^{(1)}(S_1,\alpha_1)+E_0^{(2)}(S_2,\alpha_2)]\}\,, \qquad (42)$$

with Δ given by

$$\begin{aligned}\Delta(S,S_1,S_2)&=1 \quad \text{for} \quad S_1+S_2\geqslant S\geqslant|S_1-S_2|\\ &=0 \quad \text{otherwise}.\end{aligned} \qquad (43)$$

The two sums over α_i appearing on the right side of (42) equal

$$(2S_i+1)^{-1}\,\mathrm{Tr}^{(N_i)}[\hat{Q}_{S_i}e^{-\hat{H}_0^{(i)}}]\,, \quad i=1,\,2 \qquad (44)$$

with the trace now extended over the space of states of subsystem (i) only, and $\hat{Q}_{S_i}$ defined as the projection operator onto states with fixed total spin of the subsystem. Define the function

$$\tilde{A}^{(N)}(\sigma,\beta)=-N^{-1}\beta^{-1}\ln\mathrm{Tr}^{(N)}[\hat{Q}_{N\sigma}e^{-\beta\hat{H}_0}] \quad (45)$$

which, on account of (32), (22), and (6), is related to $A^{(N)}(\sigma,\beta)$ by

$$\tilde{A}^{(N)}(\sigma,\beta)=A^{(N)}(\sigma,\beta)-f^{(N)}(\beta)\,, \qquad (46)$$

$$f^{(N)}(\beta)=N^{-1}\beta^{-1}\ln\mathrm{Tr}[e^{-\beta\hat{H}_0}]\,. \qquad (47)$$

Now substitute (44) on the right side of (42), combine (37) and (42), and take the logarithm on both sides of the resulting inequality. The result of these manipulations may be expressed in terms of the function $\tilde{A}$ and is

$$\begin{aligned}\tilde{A}^{(N)}(N^{-1}|S_1\pm S_2|,\beta)\leqslant N^{-1}|\hat{H}'|&+N^{-1}N_1\tilde{A}^{(N_1)}(N_1^{-1}S_1,\beta)\\ &+N^{-1}N_2\tilde{A}^{(N_2)}(N_2^{-1}S_2,\beta)\\ &+N^{-1}\beta^{-1}\ln[(2S_1+1)(2S_2+1)]\end{aligned} \quad (48\pm)$$

for the cases $S=S_1+S_2$ and $S=|S_1-S_2|$.

Here the upper sign corresponds to the former, the lower sign to the latter case, and only these two special cases are needed in the following. In deducing (48±) use was made of (43), also.

Apart from the last summand on the right side, (48+) is the exact equivalent of the "basic inequality" obtained by Griffiths.[15] In what follows this last summand is unimportant since it vanishes with increasing N even stronger than $N^{-1}|\hat{H}'|$. The proceeding of the proof is completely analogous to that given in Ref. 15 and thus need not be given here. In particular the generalization of (48+) to the case of more than two subsystems is possible since the vector model works for this case as well. The proof proceeds by performing the limit $(N,N_1,N_2)\to\infty$ by a suitable sequence of crystals. The essential point is that $|\hat{H}'|$ is bounded by $C\cdot N^{2/3}$, with a constant C depending on the J_{ij} in (2) and on the special sequence chosen in taking the limit, but independent of N. Hence $N^{-1}|\hat{H}'|$ in (48+) varies like $N^{-1/3}$ and the unimportance of the last term, varying like $N^{-1}\ln N$, becomes evident. Observe that taking the limit $(N,N_1,N_2)\to\infty$ in (48+) would imply the convexity of $\tilde{A}(\sigma,\beta)$ immediately, if the limits were known to exist. For the mathematical details of the formal proof, including the proof of existence, we again refer to Refs. 15 and 12. The result is that the limiting function

$$\tilde{A}(\sigma,\beta)=\lim_{N\to\infty}\tilde{A}^{(N)}(\sigma,\beta) \qquad (49)$$

exists, is convex downward, and is independent of the special sequence of crystals chosen in taking the limit.

Moreover $\tilde{A}(\sigma,\beta)$ takes its minimum at $\sigma=0$. To prove this property assume in (48−) that N is even and $N_1=N_2=\frac{1}{2}N$. Then (48−) takes the form

$$\tilde{A}^{(N)}(0,\beta)\leqslant\tilde{A}^{(N/2)}(\sigma,\beta)+N^{-1}|\hat{H}'|+2N^{-1}\beta^{-1}\ln[N\cdot2\sigma+1]\,. \quad (50)$$

[16] For example, E. P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), Chap. 18.

From this by going to the limit of infinite particle size through a sequence of crystals with even N we obtain the desired result.

The limit $N\rightarrow\infty$ for $f^{(N)}(\beta)$ appearing in (46) and (47) exists, as was stated before.[13] Hence $A^{(N)}(\sigma,\beta)$ also tends to a limiting function $A(\sigma,\beta)$, which has the same two properties which were stated for $\tilde{A}(\sigma,\beta)$ above.

To prove that $A(\sigma,\beta)$ equals $a(\sigma,\beta)$ we make use of the fact that

$$P^{(N)}(N\sigma,\beta)-P^{(N)}(N[\sigma+\mu],\beta)=\sum_{S=N\sigma}^{N(\sigma+\mu)-1}(2S+1)^{-1}\cdot Q^{(N)}(S,\beta)\quad(51)$$

holds. Here $N\sigma$ and $N\mu$ are assumed positive and integer. Equation (51) is a direct consequence of spatial degeneracy. Another consequence is

$$(2S+1)^{-1}Q^{(N)}(S,\beta)\leqslant P^{(N)}(N\sigma,\beta),\quad\text{for}\quad S\geqslant N\sigma.\quad(52)$$

We combine (51) and (52) to obtain

$$\begin{aligned}P^{(N)}(N\sigma,\beta)\cdot\{1-P^{(N)}(N[\sigma+\mu],\beta)/P^{(N)}(N\sigma,\beta)\}&\leqslant N\mu\cdot\max_{N\sigma\leqslant S<N(\sigma+\mu)}\{Q^{(N)}(S,\beta)\}\\&\leqslant N\mu(2N+1)\cdot P^{(N)}(N\sigma,\beta).\end{aligned}\quad(53)$$

Here the maximum Q has to be taken from the S interval indicated.

Taking the logarithm and dividing by $-\beta N$ yields

$$\begin{aligned}&a^{(N)}(\sigma,\beta)-N^{-1}\beta^{-1}\\&\quad\times\ln\{1-\exp[-\beta N(a^{(N)}(\sigma+\mu,\beta)-a^{(N)}(\sigma,\beta))]\}\\&\geqslant\min_{N\sigma\leqslant S<N(\sigma+\mu)}[A^{(N)}(S/N,\beta)]-N^{-1}\beta^{-1}\ln[N\mu]\\&\geqslant a^{(N)}(\sigma,\beta)-N^{-1}\beta^{-1}\ln[N\mu(2N+1)].\end{aligned}\quad(54)$$

In the following the cases $\sigma\geqslant\sigma^*(\beta)$ and $\sigma<\sigma^*(\beta)$ are treated separately. First assume $\sigma>\sigma^*(\beta)$.

In this case $a(\sigma,\beta)$ is a monotonically increasing function of σ. This follows directly from the properties of the function a given in Sec. 3. Moreover $A(\sigma,\beta)$ is monotonically nondecreasing in any case. This follows from the fact, that $A(\sigma,\beta)$ is convex downward and assumes its minimum for $\sigma=0$. With the use of these properties we obtain from (54) by going to the limit $N\rightarrow\infty$:

$$a(\sigma,\beta)\geq A(\sigma,\beta)\geq a(\sigma,\beta).\quad(55)$$

Thus (34) is true for $\sigma>\sigma^*(\beta)$.

On account of the continuity of $a(\sigma,\beta)$ and $A(\sigma,\beta)$, which follows from convexity and boundedness,[10] (34) is valid for $\sigma=\sigma^*(\beta)$ as well.

For $\sigma<\sigma^*(\beta)$ of the two inequalities in (55) only the right one can be obtained from (54). Taking account of the flat bottom property of $a(\sigma,\beta)$ below $\sigma^*(\beta)$ we may replace $a(\sigma,\beta)$ by $a(\sigma^*,\beta)=A(\sigma^*,\beta)$ in this inequality. Thus we obtain

$$A(\sigma,\beta)\geq A(\sigma^*,\beta).\quad(56)$$

But since $A(\sigma,\beta)$ is monotonically nondecreasing, only

$$A(\sigma,\beta)=A(\sigma^*,\beta)=a(\sigma^*,\beta)=a(\sigma,\beta)\quad(57)$$

is possible for $\sigma<\sigma^*$. This completes the proof.

5. EMPIRICAL RESULT

As was stated in Sec. 3 and illustrated by the discussion of Fig. 1 the knowledge to be deduced from a finite spontaneous magnetization on the probability distribution $Q^{(N)}(S,\beta)$ is rather poor, even in the simplified model. We should emphasize that even this knowledge, summarized into the flat bottom property for $A(\sigma,\beta)$ is developed from the assumption of a nonvanishing spontaneous magnetization $\sigma^*(\beta)$ and not from a knowledge of this property, which has never been proved for the Heisenberg model. Moreover there is no chance to obtain a meaningful result from existing approximate theories on, say, quantities like $Q^{(N)}(0,\beta)/Q^{(N)}(S^*,\beta)$ for large N.

This is most obvious, and has been extensively discussed,[2] for the molecular field theory which is known to yield a hump in the thermodynamic free energy $A(\sigma,\beta)$ at $\sigma=0$, in complete disagreement with the exact result. It is a natural consequence of this situation of the theory to look for an empirical solution.

As was stated in Sec. 2 the experimental field of superparamagnetism may serve as a tool to obtain results on the probability distribution $Q^{(N)}$, and hence finite crystal free energy[17] $A^{(N)}(\sigma,\beta)$ at least for particles of size N ranging up to some 10^4. We should emphasize that this is a type of experimental information which is completely inaccessible by numerical calculations on the model, the relevant matrices of Hamiltonian and spin operators in the mathematical model being of order $(2s+1)^N$ by $(2s+1)^N$.

The experimental results are rather distinct and greatly support the existence of a finite particle free energy of type I illustrated in Fig. 1. On account of the importance for the fundamental statistical problem we briefly present some of the known experimental results. We mainly restrict the discussion to the three ferromagnetic transition elements and even doing so, do not intend completeness but refer to the exhaustive reviews existing in this field.[3–5]

There is experimental evidence for the probability distribution being centered at total spin values closely resembling the bulk spontaneous magnetization for small cobalt precipitates in copper[18,19] with particle

[17] Of course, for finite particle size the free energies $a^{(N)}(m,\beta)$ and $A^{(N)}(\sigma,\beta)$ differ. There is, however, no danger of confusion since we shall be concerned with $A^{(N)}$ only in the following.

[18] J. J. Becker, J. Metals, Trans. Am. Inst. Mining Met. Eng. **209**, 59 (1957).

[19] A. Knappwost, A. Illenberger, and L. N. Nunez, Z. Physik. Chem. **23**, 145 (1960).

sizes ranging from 10 to 30 Å, for small cobalt particles in mercury,[20] for nickel particles deposited onto silica gel catalysts,[21,22] ranging in size from 30 to 85 Å, for very small nickel clusters in Ni-Cu alloys,[23] and for iron precipitates in β-brass roughly 20 Å in diam.[24]

In all these cases the superparamagnetic "superposition principle"[5,21] holds well, indicating that the particle moment is practically unique in all states which make an appreciable contribution to the distribution. In terms of the symbols introduced in Sec. 2 the superposition principle states that the reduced plot of the experimentally accessible quantities $\mathcal{J}/\sigma^*(\beta)$ versus $\beta h\sigma^*(\beta)$ yields a unique curve for different temperatures β^{-1}. This behavior is an immediate consequence of Eqs. (23) and (24) which hold for a narrow probability distribution centered at $N\sigma^*(\beta)$.

There are a few comments necessary on the above statements. First, in most of the cases above experiments were restricted to room temperature and lower temperatures. Exceptions are those referenced under Refs. 19, 21, and 22. For nickel, results are given at temperatures up to the Curie temperature. If interpreted in terms of a spontaneous magnetization, these results[21,22] show a somewhat stronger drop of $\sigma^*(\beta)$ with temperature as compared to the bulk spontaneous magnetization. The deviations, however, are small and of order of magnitude proposed by approximate theories on account of particle smallness. A special spin-wave theoretical account for the author's results on Ni particles[22] has been given by Abbel.[25] There is no indication of a more fundamental effect related to a probability distribution deviating appreciably from the type usually assumed.

A second observation is rather essential, which strongly confirms the relatively unimportant role of anisotropy effects stated in Sec. 2: The superposition of experimental data in the reduced plot in most cases works well not only in a restricted low-field region, but over the whole range of fields. The linear portion of the magnetization curve in low fields is independent of anisotropy for general theoretical reasons.[26] However, the superposition principle should not hold over the whole field range if anisotropy were essential. This experimental finding rules out the possibility of large anisotropy as a source of long range homogeneity of magnetization. Hence, the special peaked probability distribution of total spin must be caused by exchange energy. This result from experiment is rather essential since the estimates of characteristic anisotropy energies reported in Sec. 2 are based on bulk magnetic properties and hence are not necessarily relevant for small particles too. Particularly there might be spin pinning at the particle surface. Apparently such effects are small.

A few exceptions from the rule of negligible anisotropy are typical for low temperatures[22,27] and can be accounted for by anisotropies of reasonable order of magnitude. In each of these cases anisotropy causes lower values of magnetization in the reduced plot, as compared to the superimposing magnetization curves at higher temperatures. In these cases a satisfying explanation is given in terms of a modified description of the superparamagnetic excitations, the exchange excitations and the shape of $Q^{(N)}(S,\beta)$ as a function of S remaining unaffected.

Superparamagnetic investigations have not been restricted to the pure elements. There are results on ferromagnetic alloys and compounds well fitting the general scheme of a practically unique magnetic moment for all states appreciably excited. We again refer to recent reviews of the whole field for detailed references.[4,5]

Finally, we should make mention of a few results, which at first sight are in striking disagreement with the general findings dealt with so far. These are results on Ni_3Mn,[28] on Fe-Ni-Cu alloys,[29–32] and on small iron particles in mercury.[20,33,34] For the Fe-Ni-Cu alloys the striking first results[29] have found a convincing interpretation in terms of chemical inhomogeneity of the particle-matrix boundary.[30–32] In Ni_3Mn similar metallurigical effects might be expected. Moreover, exchange interaction in this system seems far from simple[35,36] and leads to a complicated dependence of magnetic properties on precipitation conditions. Thus the concept of bulk Ni_3Mn properties for small precipitates seems oversimplified and deviations from the superposition principle are of no great significance.

The puzzling behavior of superparamagnetic iron amalgams has been discussed at length in several papers including the author's.[37–39] We do not intend to repeat this discussion but state the most recent results by Thomas[38] and Brown[39]: Magnetostatic interaction between clustered particles cannot be excluded as a

[20] E. Vogt, W. Henning, and A. Hahn, Berichte der Arbeitsgemeinschraft Ferromagnetismus 1958, 44, Riederer Stuttgart, 1959 (unpublished).
[21] C. R. Abeledo and P. W. Selwood, J. Appl. Phys. **32**, 229 (1961).
[22] A. Hahn, Ann. Physik (Leipzig) **11**, 277 (1963).
[23] H. C. van Elst, B. Lubach, and G. J. van den Berg, Physica **28**, 1297 (1962).
[24] A. E. Berkowitz and P. J. Flanders, Acta Met. **8**, 823 (1960).
[25] R. Abbel, Z. Angew. Phys. **20**, 212 (1966).
[26] A. Hahn, Z. Angew. Phys. **13**, 165 (1961).
[27] Reference 3, Fig. 10.
[28] E. Kneller, Z. Physik **152**, 574 (1958).
[29] E. Kneller, in Proceedings of the International Conference on Magnetism, Nottingham, 1964, London, 1965, p. 174 (unpublished).
[30] E. Kneller and M. Wolff, J. Appl. Phys. **37**, 1350 (1966).
[31] E. Kneller, M. Wolff, and E. Egger, J. Appl. Phys. **37**, 1838 (1966).
[32] E. Kneller and G. Trippel, J. Appl. Phys. **38**, 993 (1967).
[33] F. E. Luborsky and P. E. Lawrence, J. Appl. Phys. **32**, Suppl., 231S (1961).
[34] K. Reuter, Physik Kondensierten Materie **3**, 150 (1964).
[35] J. S. Kouvel, J. Phys. Chem. Solids **21**, 57 (1961).
[36] J. S. Kouvel, J. Appl. Phys. Suppl. **31**, 142S (1960).
[37] A. Hahn, Physik Kondensierten Materie **4**, 20, 25 (1965).
[38] H. Thomas, Z. Angew. Phys. **21**, 13 (1966).
[39] W. F. Brown, J. Appl. Phys. **38**, 1017 (1967).

source of the strong deviations from superparamagnetic superposition in this system. We feel that the complete lack of experimental information on the microscopic structure of superparamagnetic iron amalgams prevents unequivocal conclusions to be drawn from the magnetic behavior. On the other hand the results on iron precipitates in β-brass quoted above[24] clearly indicate, that iron is not an exception from the general behavior of superparamagnetic magnetization.

The general conclusion thus to be drawn from experimental results in the superparamagnetic size range is as follows:

For ferromagnetic particles containing some hundred to some 10 000 spins the finite particle free energy as a function of total spin moment S essentially has the shape indicated by curve I of Fig. 1 and characterized by a minimum near total spin values corresponding to bulk spontaneous magnetization. If a second minimum should happen to exist at lower S values this must be flatter than the former. These are rather distinct results from experiment on a problem fundamentally related to the thermodynamic nature of the ferromagnetic phase.

6. SUMMARY

The concept of uniform bulk magnetization in the finite superparamagnetic particles was reexamined. Arguments are given warranting the neglect of secondary energies on account of their smallness. When adequately idealized in terms of statistical thermodynamics, superparamagnetic magnetization and bulk spontaneous magnetization turn out to be related to substantially different quantities: the zero-field probability distribution of particle magnetic moment and the width of the thermodynamic free energy flat bottom, respectively. The difference in these quantities is independent of the effects of particle smallness on the parameters of approximate theories, say on molecular field coefficient or, in noninteracting spin-wave theory, on the spin-wave energy spectrum. It is, instead, related to a fundamental problem encountered in the theory of the magnetic first-order phase transition.

The weak implications of the free-energy characteristics on the finite-particle probability distribution of superparamagnetic moment are treated in close analogy to a discussion given by Griffiths for a related problem. An extension to the superparamagnetic case of Griffiths's calculations was found feasible. As a result, a variety of types of superparamagnetic behavior would be consistent with a given bulk spontaneous magnetization. At present, it seems not possible to decide between these possibilities mathematically.

From experiment, however, there is strong evidence that the probability distribution actually realized differs markedly from zero only within a narrow interval around a value of the moment corresponding to the homogeneous bulk spontaneous magnetization. In fact, this is the view usually adopted intuitively. The above consequences of the experimental evidence with respect to the statistical properties of a spin lattice with a short-range isotropic interaction seem to have been overlooked until now. Thus, measurements on superparamagnets appear to be a tool to obtain in this field positive results which are theoretically inaccessible.

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