# **Thermal Fluctuations of Fine Ferromagnetic Particles**

WILLIAM FULLER BROWN, JR., FELLOW, IEEE

Abstract-Fine ferromagnetic particles jump spontaneously from one locally stable state to another; they surmount intervening energy barriers with the aid of thermal agitation. A theory of this phenomenon has as its primary goal the calculation of time constants. The elements of such a theory are presented. The emphasis is on calculations that require only elementary methods and on results that are simple enough to be easily applicable. The reader is assumed to be acquainted with the basic properties of ferromagnetic materials but not necessarily with Brownian-motion theory, on which the present theory is based.

#### I. INTRODUCTION

HEN WE MAKE a tape recording and then put the tape on the shelf, we expect to be able later to take it off the shelf, play it back, and hear what we recorded; in other words, we expect it to stay in the same magnetic state. We can, of course, put it into a new magnetic state by subjecting it to an erasure procedure or to a new recording procedure. But we should be surprised if, overnight, it jumped spontaneously from being a recording of Beethoven to being a recording of Brahms. Similarly, we can, by appropriate procedures, magnetize a "permanent" magnet in either polarity or demagnetize it, but we do not expect it to jump spontaneously from one polarity to another or to a state of zero magnetic moment.

In principle, however, any apparently stable magnetic state of a tape or magnet is only one of many local minima of the free energy; thermal agitation can cause spontaneous jumps from one such state to another. The apparent stability is due to the fact that our tape or magnet cannot get from one state to another without passing over an energy barrier that is very large in comparison with the thermal energy kT (k = Boltzmann's constant, T = absolute temperature); the probability per unit time of a jump over such a barrier is so small that the mean time we should have to wait for it far exceeds our own mean lifetime. But what is involved here is the total free energy of the system that undergoes a change during the hypothetical transition, and this energy decreases as the volume of the system decreases. For fine ferromagnetic particles at not too low temperatures, the barrier height becomes comparable with kT, and spontaneous jumps from one state to another become important [1], [2].

In the opposite limiting case, in which the barrier height is very small in comparison with kT, a ferromagnetic particle behaves like a paramagnetic atom. For a sample consisting of such particles, if interaction between the particles is negligible, the magnetization as a function of the applied field, under normal measurement conditions, exhibits no hysteresis and is determined by a Langevin function. This phenomenon is called "superparamagnetism" [3].

Under intermediate conditions, when the barrier height is neither very large nor very small in comparison with kT, the specimen neither remains in a single state for a long time nor attains statistical-mechanical equilibrium in a short time; after a change of field, it undergoes a change of magnetization that is not completed "instantly" (on the time scale of the observations) but requires some time for its completion. In a small alternating field, the resulting small change of magnetization lags behind the field. Such phenomena are described, rather loosely, by such terms as "magnetic aftereffect" and "magnetic viscosity." Their analysis requires more than a mere comparison of the sizes of an energy barrier and of kT. What is needed is a theory that covers the whole range of phenomena from quasistatic behavior to superparamagnetic. Such a theory is needed also for complete understanding of these two extremes, for each is relative to the time scale of the measurements: what appears to be an instantaneous response in measurements that take a second may show magnetic aftereffect on a nanosecond scale. The theory must therefore be a dy namic theory, describing not only states of statisticalmechanical equilibrium but also the transition to a new state after a change of the external parameters (e.g., the applied field), and even the response to constantly changing parameters.

Such a theory exists, and the purpose of the present paper is to describe it. The description is intended for readers who would like to get a general understanding of the main features and results of the theory, and who are not necessarily already acquainted either with it or with the Brownian motion theory of which it is an extension. The paper is tutorial rather than exhaustive; the reader interested in more details may consult the references. The bibliography, in turn, is introductory rather than comprehensive; the references chosen (all of which are in English) will merely guide the reader to sources of additional information about necessary physical and mathematical background or about further aspects of the theory. The emphasis is on calculations that require only elementary methods and on results that are simple enough to be easily applicable. The paper contains no new results but does present some simpler and more direct derivations of old ones, and some quantitative criteria for their applicability. Experimental results are not discussed; those will be found in appropriate references.

As is well known, a sufficiently fine, internally homogeneous ferromagnetic particle lacks the domain structure that complicates the magnetic behavior of ordinary magnetic specimens; it has a uniform vector magnetization M whose magnitude  $M_s$ , the "spontaneous magnetization," is determined by the material and the temperature, but whose direction is determined by

Manuscript received April 2, 1979; revised May 15, 1979.

The author is with the Department of Electrical Engineering, University of Minnesota, Minneapolis, MN 55455.

crystalline anisotropy, internal magnetostatic fields ("shape anisotropy"), and the field H that acts on the particle [4]. The field H may include, besides the directly controlled or "applied" field, the fields of other particles; such "magnetic interactions" between the particles greatly complicate the behavior. It will be supposed hereafter than we are dealing with particles small enough so that each is uniformly magnetized ("single-domain" particles), and far enough apart so that the magnetic interactions are negligible and H is simply the applied field (assumed to be uniform over the volume of a particle). We can then restrict ourselves to study of a single particle. For a sample consisting of many identical particles, in a uniform applied field H, the average over the particles of any component of M, say  $M_z$ , may be equated to the statistical-mechanical "ensemble" average for a single particle.

### **II. ENERGY AND FREE ENERGY**

In atomic and molecular theory, including statistical mechanics, the energy E of a system is a microscopic concept, described formally by the Hamiltonian function or by its equivalent in Lagrangian variables. A physical system in thermodynamic equilibrium at temperature T is described by a Gibbs canonical ensemble of identical systems [5], [6]. The energy E varies from one member of the ensemble to another; so does the magnetic moment  $\mu$ . The thermodynamic quantities U, the "internal energy," and m, the observable magnetic moment, are the ensemble averages,  $\langle \cdots \rangle$ , of E and  $\mu$ , respectively:  $U = \langle E \rangle$ ,  $m = \langle \mu \rangle$ . The averages are computed with the weights (per state)  $e^{-E/kT}$ ; that is, the ensemble average of any quantity u is

$$\langle u \rangle = \left( \sum_{st} u e^{-E/kT} \right) / \left( \sum_{st} e^{-E/kT} \right)$$
(1)

where the sum is over all possible states of the system.

If, as is usually the case, the convenient independent thermal variable is the temperature T rather than the entropy S, a more convenient thermodynamic potential than U is the "free energy" F = U - TS. The statistical-mechanical formula for F is

$$F = -kT \ln Z \tag{2}$$

or

$$Z = e^{-F/kT} \tag{3}$$

where Z is the "partition function"

$$Z = \sum_{st} e^{-E/kT} \tag{4}$$

In general, Z and therefore F are functions of T and of certain controllable parameters, such as the volume of a fluid or the magnetic field applied to a magnetic particle. The entropy is given by  $S = -\partial F/\partial T$ ; by use of this formula, of (2) and (4), and of the relation U = F + TS, one easily derives a formula for U and recognizes it as equivalent to the formula  $U = \langle E \rangle$ .

In one-dimensional Brownian motion, the system (a solid particle in a viscous fluid) is not in equilibrium; but if we choose as our microscopic variables, instead of the coordinates of the individual atoms or molecules of the particle and of the fluid, the coordinate x of the center of mass of the particle

and a suitable set of other coordinates  $\xi_i$ , then it may be legitimate to treat the subsystem described by the  $\xi_i$  as a system in internal thermodynamic equilibrium at each given value of x; for this subsystem, x is a parameter, as was the volume or field in the previous paragraph. The subsystem formula analogous to (3) is

$$Z_1(x) = e^{-F_1(x)/kT}$$
(5)

where  $Z_1$  is obtained by summation over the  $\xi_i$  states only, at specified x, and where  $F_1(x)$  is the subsystem free energy at the specified x. If now the whole system is in thermodynamic equilibrium, its free energy F can be found by substituting in (2) the value

$$Z = \sum_{x} Z_{1}(x) = \sum_{x} e^{-F_{1}(x)/kT}$$
(6)

This is equivalent to (4) but differs from it in that 1) we have to sum not over states of the whole system but only over states of the coordinate x; and 2) instead of a microscopic energy E, we must use the subsystem free energy  $F_1(x)$ .

If, however, we wish to study the behavior when only the  $\xi$  subsystem is in equilibrium, whereas x is not, we can treat the system as a thermodynamic system described by an independent variable x and a free energy  $F_1(x)$ . This procedure would be exact if  $F_1(x)$  were evaluated by carrying out the summations in  $Z_1(x)$ . Actually, it has to be approximated by use of symmetry arguments, truncation of infinite series, etc., and is therefore not exact; yet it may be quite adequate.

For the magnetic particle, x is replaced by two variables (e.g., angles  $\theta$  and  $\phi$ ) that describe the orientation of the magnetic moment. The subsystem free energy corresponding to  $F_1$  is the free energy  $F(\theta, \phi)$  of the particle expressed as a function of the orientation angles; its form is derived by symmetry arguments, truncation of series, etc.; it contains temperature-dependent quantities such as the anisotropy constant and  $M_s$ . When there is equilibrium with respect to the orientation angles as well as with respect to the internal variables  $\xi$ , the mean values of observable quantities, such as a component  $M_z$  of the magnetic moment, may be found by averaging over orientational states with weighting factor  $e^{-F(\theta, \phi)/kT}$ .

This analysis is based, essentially, on the assumption that the time required for attainment of internal equilibrium at given  $(\theta, \phi)$  is very short in comparison with the time for attainment of the equilibrium values of  $\theta$  and  $\phi$ .

# **III. THE DISCRETE-ORIENTATION MODEL**

When the energy barriers are large in comparison with kT, but not so large as to preclude changes of orientation altogether, we may suppose that the magnetization is always along one of the directions  $(\theta_i, \phi_i)$  of easy magnetization, but that in orientation *i* there is a probability  $v_{ij}$  per unit time of a jump to orientation *j*. The  $v_{ij}$  depend on the anisotropy constant, the field, and the temperature. For a large number *n* of identical, noninteracting particles at the same *T* and *H*, the number  $n_i$  of particles in orientation *i* then changes with time in accordance with the equation (the dot denotes time differentiation)

$$\dot{u}_{i} = \sum_{i \neq i} (\nu_{ji} n_{j} - \nu_{ij} n_{i}).$$
(7)

ł

If there are k directions of easy magnetization, there are k equations (7):  $i = 1, 2, \dots, k$ . Summation over i gives  $\sum_i \dot{n_i} = 0$ ; thus the total number n of particles remains at its initial value, and only this initial value needs to be imposed if all k equations are used. Alternatively, we may impose the condition  $\sum_i n_i = n$  at all times and drop one of the equations (7).

Some properties of the  $v_{ij}$  can be deduced by study of specific cases.

# A. Two Orientations

This is the case of a uniaxial crystal of the easy-axis type, or of a prolate spheroid, with the applied field along the axis of symmetry. Let 1 refer to the positive orientation and 2 to the negative. Then (7) reduces to

$$\dot{n}_1 = -\dot{n}_2 = \nu_{21}n_2 - \nu_{12}n_1. \tag{8}$$

On setting  $n_2 = n - n_1$  and solving the resulting differential equation, we find that  $n_1$ , and hence  $n_2$  and the relative magnetization  $M/M_s = n_1 - n_2$ , approach their final values (when  $v_{12}$  and  $v_{21}$  are constant) according to a factor  $e^{-(v_{12} + v_{21})t}$ , i.e., with time constant  $1/(v_{12} + v_{21})$ .

By analogy with various chemical processes [7], it is usual to suppose that [8]

$$v_{ij} = v_{ij}^{0} e^{-v(V_m - V_i)/kT}$$
(9)

(i = 1, j = 2 or i = 2, j = 1), where  $V_i$  is the free-energy density in orientation i and where  $V_m$  is the free-energy density at the top of the barrier between orientations i and j; v is the particle volume. The factors  $v_{ii}^0$ , if they vary with temperature, are assumed to do so slowly in comparison with the exponential variation of the other factor; often the  $v_{ii}^0$  are taken to be constant. This approximation is adequate for many purposes. For example, one application of the theory is to "magnetic granulometry": the determination of the size distribution in a powder of ferromagnetic particles by measurement of the remanence as a function of temperature [9]. Formula (9), with the appropriate numerical values (regardless of the precise form of  $v_{ii}^0$ , shows that when v/T changes by a factor of less than 3 in a certain critical part of its range, the time constant changes from  $10^{-1}$  s to  $10^{+9}$  s. Thus to a good approximation, there is a critical volume  $v_c$  such that particles with  $v < v_c$  are superparamagnetic and exhibit no hysteresis, whereas particles with  $v > v_c$  have hysteresis loops. By varying T and hence  $v_c$ and measuring the remanence, one can find the number of particles with  $v < v_c$  as a function of  $v_c$ .

In thermodynamic equilibrium,  $\dot{n}_1 = \dot{n}_2 = 0$ , and hence  $n_1/n_2 = v_{21}/v_{12}$ . One might suppose that under these conditions  $n_1$  and  $n_2$  are proportional to the Boltzmann factors  $e^{-vV_1/kT}$  and  $e^{-vV_2/kT}$ ; this would give  $v_{21}/\dot{v}_{12} = e^{-v(V_1 - V_2)/kT}$ . This relation is compatible with (9) only if  $v_{12}^0 = v_{21}^0$ . As we shall see, the  $n_i$  are not exactly proportional to the factors  $e^{-vV_i/kT}$ ; the reason is that the particles are not actually all in orientations *i* and *j* but have statistical distributions about these orientations.

In the simplest uniaxial case, the anisotropy energy density is  $K_1 \sin^2 \theta$  ( $K_1 > 0$ ), where  $\theta$  is the angle between M and the positive z axis; with a field H along the z axis, the total free energy density is [10]

$$V(\theta) = K_1 \sin^2 \theta - HM_s \cos \theta.$$
(10)

If  $|H| < 2K_1/M_s \equiv H_c$ ,  $V(\theta)$  has minima at  $\theta = 0$  and  $\pi$  and a maximum at  $\theta = \cos^{-1}(-H/H_c) \equiv \theta_m$ ; the corresponding values of V are easily found.

## B. More than Two Orientations

1) General Relations: In thermodynamic equilibrium, the  $n_i$  satisfy (7) with the left members equal to zero. The sum of the right members is zero; that is, any one of the k equations can be derived from the other k - 1, so that the determinant vanishes and the equations are compatible. Any k - 1 of them determine the ratios  $n_2:n_1, n_3:n_1$ , etc.; specification of the total number n of particles then determines the  $n_i$  themselves.

The cases of greatest interest are those of a cubic crystal, for which the anisotropy energy (truncated after its leading term) is

$$V(\alpha_1, \alpha_2, \alpha_3) = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2).$$
(11)

Here  $(\alpha_1, \alpha_2, \alpha_3)$  are the direction cosines of the magnetization with respect to the cubic axes. When  $K_1 > 0$ , V has minima at the six orientations of the type [100] (i.e.,  $\alpha_1 = 1, \alpha_2 = \alpha_3 = 0$ , M along a cube edge of the lattice); it has maxima at the eight orientations of the type [111] (M along a body diagonal) and saddle points at the twelve orientations of the type [110] (M along a face diagonal). When  $K_1 < 0$ , the minima and maxima are interchanged. The values of V for directions [100], [110], and [111] are 0,  $\frac{1}{4}K_1$ , and  $\frac{1}{3}K_1$ , respectively.

2) Cubic Crystal, Positive Anisotropy: We suppose that H = 0; then all the minima are equivalent. For  $K_1 > 0$ , let  $n_1, n_2, n_3$  be the numbers of particles with M along the positive cubic axes x, y, z, respectively, and  $n_{\bar{1}}$ , etc., the numbers along the opposite directions. To get from orientation 1 to orientation 2, a particle must surmount a single energy barrier, whose lowest point is the saddle point at orientation [110]; to get from orientation 1 to orientation  $\bar{1}$ , it must surmount two successive barriers. If the barriers are high, it is unlikely to do this in a single event; between the two surmountings, it may be considered to belong to the intermediate orientation 2, 3,  $\bar{2}$ , or  $\bar{3}$ . We may therefore set  $v_{i\bar{i}} = v_{\bar{i}\bar{i}} = 0$  (i = 1, 2, 3) and set the other  $v_{i\bar{i}}$  equal to a single value v. Equations (7) then become

$$\dot{n}_1 = \nu (n_2 + n_3 + n_{\overline{2}} + n_{\overline{3}} - 4n_1)$$
  
$$\dot{n}_{\overline{1}} = \nu (n_{\overline{2}} + n_{\overline{3}} + n_2 + n_3 - 4n_{\overline{1}})$$
(12)

and four other equations obtained from these by cyclic permutation.

$$x_{i} = n_{i} + n_{\bar{i}} \qquad y_{i} = n_{i} - n_{\bar{i}}.$$
(13)

Then, by addition and subtraction of (12), we obtain

Let

$$\dot{x}_1 = 2\nu(x_2 + x_3 - 2x_1)$$
  
$$\dot{y}_1 = -4\nu y_1$$
(14)

and four other equations obtained by cyclic permutation. The three y equations separate from the three x equations and from each other. By symmetry, the equilibrium values (which are attained at time  $t = \infty$ ) are  $n_1 = n_2 = \cdots = \frac{1}{6}$ , hence  $x_i = \frac{1}{3}$  and  $y_i = 0$ . The solutions of the y equations, for initial values  $y_{i0}$ , are

$$y_i = y_{i0} e^{-4\nu t}$$
 (15)

hence each component of the magnetization,  $M_i = M_s y_i/n$ , decays with time constant  $(4\nu)^{-1}$ .

To solve the x equations, note that  $x_1 + x_2 + x_3 = n$ , so that  $x_2 + x_3$  in the first (14) may be replaced by  $n - x_1$ , and so on. Solution of the resulting equations gives

$$x_i = \frac{1}{3}n + (x_{i0} - \frac{1}{3}n) e^{-6\nu t}.$$
 (16)

Thus the deviations of the  $x_i$  from their equilibrium values  $\frac{1}{3}n$  decay with time constant  $(6\nu)^{-1}$ ; and the behavior of the  $n_i$  themselves is governed by two time constants,  $(4\nu)^{-1}$  and  $(6\nu)^{-1}$ .

As in the case of two orientations, we may surmise that  $\nu$  is given by a formula of the form (9), with  $V_i = 0$  and  $V_m = \frac{1}{4}K_1$ ; that is,

$$v = v^0 e^{-(1/4)vK_1/kT}.$$
(17)

Here  $\nu^0$  is presumably a function of  $K_1$  and perhaps explicitly of T, but its variation with T is small in comparison with the exponential variation of the other factor.

3) Cubic Crystal, Negative Anisotropy: We again suppose that H = 0. For  $K_1 < 0$ , the eight directions of easy magnetization may be represented by the eight corners of a cube, and the intervening barriers by the six cube edges; at this point, the reader is urged to draw his own diagram. Let  $n_1$  be the number of particles with magnetization orientation [111]; let  $n_2$ ,  $n_3$ , and  $n_4$  by the numbers with magnetization along [111], [111], and [111], respectively, the three directions of easy magnetization closest to [111]; and let  $n_{\overline{i}}$  be the number in the orientation opposite to orientation *i*. We again suppose that only one barrier at a time can be surmounted; then for transitions from orientation 1, for example, we have  $v_{12} =$  $v_{13} = v_{14} = v$ ,  $v_{1\overline{1}} = v_{1\overline{2}} = v_{1\overline{3}} = v_{1\overline{4}} = 0$ . On writing (7) and on adding and subtracting the equations for  $\dot{n}_i$  and for  $\dot{n}_{\overline{i}}$ , we get the following equations for  $x_i = n_i + n_{\overline{i}}$  and  $y_i = n_i - n_{\overline{i}}$ :

$$\dot{x}_1 = \nu(x_2 + x_3 + x_4 - 3x_1) \tag{18}$$

and three equations obtained from this by cyclic permutation;

$$\dot{y}_{1} = \nu(-3y_{1} + y_{2} + y_{3} + y_{4}),$$
  

$$\dot{y}_{2} = \nu(y_{1} - 3y_{2} - y_{3} - y_{4}),$$
  

$$\dot{y}_{3} = \nu(y_{1} - y_{2} - 3y_{3} - y_{4}),$$
  

$$\dot{y}_{4} = \nu(y_{1} - y_{2} - y_{3} - 3y_{4}).$$
(19)

In (18), we may set  $x_2 + x_3 + x_4 = n - x_1$ ; we thus find that the  $x_i$  approach their equilibrium value  $\frac{1}{4}n$  with time constant  $(4\nu)^{-1}$ . The x component of magnetization is proportional to  $y_1 + y_2 + y_3 - y_4$ ; from (19) we find that the time rate of change of this quantity is  $-2\nu$  times the quantity itself; thus  $M_x$  (or  $M_y$  or  $M_z$ ) decays with time constant  $(2\nu)^{-1}$ . There is still a third time constant, as can be found by assuming  $y_i = B_i e^{-r\nu t}$  in (19); the compatibility condition can be reduced to  $(r-2)^3 (r-6) = 0$ , so that the third time constant is  $(6\nu)^{-1}$ . The distribution that decays with this time constant is one with  $y_1: y_2: y_3: y_4 = -1:1:1:1$ , as can be verified by assuming  $y_i = B_i e^{-6\nu t}$  in (19) and solving for the ratios of the  $B_i$ .

Equation (9) in this case becomes, since  $V_1 = -\frac{1}{3}|K_1|$  and  $V_m = -\frac{1}{4}|K_1|$ ,

$$v = v^0 e^{-(1/12)v |K_1|/kT}.$$
(20)

## C. Shortcomings of the Model

The discrete-orientation model is adequate when the energy barriers are large in comparison with kT, provided suitable values of the  $v_{ij}^0$  in (9) can be found. For such purposes as magnetic granulometry, any  $v_{ij}^0$  of the right order of magnitude will do; one can begin by setting  $v_{ij}^0$  equal to some parameter of the system with dimensions (time)<sup>-1</sup>, for example, the frequency of gyromagnetic precession about the minimum. Then empirical adjustments of the value can be made if they prove necessary.

For a precise analysis of transient effects, we need a better theory: one that will not only evaluate the  $v_{ij}^0$ , but give us a criterion for applicability of the discrete-orientation model, and provide alternate formulas when that model is not applicable. For the discrete-orientation theory not only fails when kT becomes comparable with the barrier height, but gives us no way of knowing how small a ratio of these two quantities is tolerable within the framework of the theory.

## **IV. BASIC EQUATIONS**

# A. The Equation of Motion (Without Fluctuations)

When thermal fluctuations are negligible, the rotation of the vector magnetization M of a single-domain particle, under the influence of a (perhaps time-dependent) "effective field"  $\mathcal{H}$ , can be described by either of two phenomenological equations: the Landau-Lifshitz and the Gilbert [11] (the relations between the two are discussed in Appendix I). We shall use the Landau-Lifshitz equation,

$$M = \gamma'_0 M \times \mathcal{H} - (\lambda/M_s^2) M \times (M \times \mathcal{H}).$$
(21)

The "gyromagnetic" parameter  $\gamma'_0$  and the "damping parameter  $\lambda$  are constants for a given material at a given temperature. The "effective field" H includes the applied field  $H_0$ , the demagnetizing field due to the particle's own magnetization, and the effect of crystalline anisotropy. If V(M) is the free energy per unit volume expressed as a function of M, then

$$\mathcal{H} = -\partial V / \partial M. \tag{22}$$

Here  $\partial/\partial M$  is an abbreviation for  $i\partial/\partial M_x + j\partial/\partial M_y + k\partial/\partial M_z$ . Because  $|M| = \text{const} = M_s$ , V is indeterminate by an arbitrary function of  $M^2$  and H by an arbitrary vector along M, which contributes nothing to  $M \times H$ . We shall use, instead of M, the unit vector along it,  $r^0 = M/M_s$ , whose Cartesian components are the direction cosines  $\alpha_i$  of M. Then  $\partial/\partial M$  may be replaced by  $M_s^{-1}\partial/\partial r^0 = M_s^{-1}\nabla$ . Here the symbol  $\nabla$  has its usual meaning in  $(r, \theta, \phi)$  space but will act only at points of the unit sphere, |r| = 1, and only on functions of the angular spherical coordinates  $(\theta, \phi)$  or of equivalent generalized coordinates; in effect it is a two-dimensional gradient operator on the surface of the unit sphere. Equation (21) now becomes

$$\dot{r}^{0} = -ar^{0} \times \nabla V + br^{0} \times (r^{0} \times \nabla V)$$
<sup>(23)</sup>

where the new gyromagnetic constant a and damping constant b are given by

$$a = \gamma_0' / M_s \qquad b = \lambda / M_s^2 \,. \tag{24}$$

Hereafter, the parameters a and b will be used instead of the parameters  $\gamma_0'$  and  $\lambda$ .<sup>1</sup>

# B. The Langevin Equation

In Brownian-motion theory, the equation of one-dimensional motion of a Brownian particle in a viscous liquid,  $m\ddot{x} = -\eta \dot{x}$ , where *m* is the particle mass and  $\eta$  a friction constant, is modified to take account of thermal agitation by adding to the viscous force  $-\eta \dot{x}$  a random term f(t) whose time and ensemble averages are zero. The resulting equation,  $m\ddot{x} = -\eta \dot{x} + f(t)$ , is called the Langevin equation [13]-[15].

The analogous procedure in our problem is to add to the effective field  $\mathcal{H} = -\partial V/\partial M$  a random term h(t), or to  $-\nabla V$  a random term  $g(t) = M_s h(t)$ , whose time and ensemble averages are zero. Then (23) becomes

$$\dot{r}^{0} = -ar^{0} \times [\nabla V - g(t)] + br^{0} \times \{r^{0} \times [\nabla V - g(t)]\}.$$
(25)

Concerning the statistical properties of g(t) we make assumptions analogous to those made in the theory of Brownian motion. If  $g(t) = ig_1(t) + jg_2(t) + kg_3(t)$ , we assume for the ensemble averages

$$\langle g_i(t) \rangle = 0, \tag{26}$$

$$\langle g_i(t) g_i(t+\tau) \rangle = \mu \delta_{ii} \delta(\tau) \tag{27}$$

where  $\mu$  is a (temperature-dependent) constant.<sup>2</sup> Equation (26) restates that the ensemble mean of g(t) is zero. Equation (27) for  $j \neq i$  states that different components of g(t) are uncorrelated; for j = i, it states that  $g_i(t)$  and  $g_i(t + \tau)$  are uncorrelated for any  $\tau$  other than 0, and that the correlation concentrated at  $\tau = 0$  is such that the random variable

$$G_{i}(\tau) = \int_{t}^{t+\tau} g_{i}(t_{1}) dt_{1}$$
(28)

<sup>1</sup>In an earlier publication [12], the following symbols were used: g' = a, h' = b.

<sup>2</sup>The  $\mu$  of [12] is the present  $\mu/M_s^2$ .

whose mean is zero, has variance  $\mu\tau$ :

$$\langle [G_i(\tau)]^2 \rangle = \left\langle \int_t^{t+\tau} dt_1 \int_t^{t+\tau} g_i(t_1) g_i(t_2) dt_2 \right\rangle$$
$$= \int_t^{t+\tau} dt_1 \int_t^{t+\tau} \langle g_i(t_1) g_i(t_2) \rangle dt_2$$
$$= \mu \int_t^{t+\tau} dt_1 \int_t^{t+\tau} \delta(t_2 - t_1) dt_2$$
$$= \mu \int_t^{t+\tau} dt_1 = \mu\tau.$$
(29)

Physically, the delta function in (27) means that the correlation time of the random field is assumed to be very short in comparison with the times over which  $\mathcal{H}$  varies and with the response time of our system, as determined by (21).<sup>3</sup> We make the further assumption that the random process  $g_i(t)$  results from the superposed effects of a large number of independent random events; then by virtue of the central limit theorem [17], the statistical distribution of the random variable  $g_i(t)$  at any time is normal (Gaussian). It follows that  $G_i(\tau)$  and any other quantities in which the  $g_i$  occur linearly also have normal distributions.

We shall call (25) the Langevin equation of our problem. When it can be linearized, direct solution of it, followed by ensemble averaging, is a practical method of solving the problem. This method will be illustrated in Section V. In most cases, however, (25) is nonlinear, and analytical solution of it is not possible. We then need a method that does not require solution of the Langevin equation.

# C. The Unit-Sphere Representation

The instantaneous orientation  $(\theta, \phi)$  of the magnetization of a particle can be represented by a point on the unit sphere, with spherical coordinates  $(1, \theta, \phi)$ . As the magnetization changes its direction, the representative point moves on the surface of the sphere.

Now consider a statistical ensemble of identical particles, and let  $W(\theta, \phi) d\Omega$  be the probability that a member of the ensemble has orientation  $(\theta, \phi)$  to within solid angle  $d\Omega$ ; the integral  $\int W d\Omega$  over the unit sphere is unity. Then W is represented by a surface density on the unit sphere. To it corresponds a current density J: since representative points are neither created nor destroyed, but can only move to new positions on the sphere, W and J satisfy the continuity equation

$$\dot{\boldsymbol{W}} = -\nabla \cdot \boldsymbol{J}. \tag{30}$$

We shall seek an expression for J based on the equation of motion (25); insertion of such an expression in (30) will give a partial differential equation to determine the distribution function W.

 $<sup>{}^{3}</sup>A$  theoretical treatment based on less restrictive assumptions has been given by Smith and de Rozario [16].

For a sample consisting of a large number n of noninteracting particles, the statistical properties of the actual collection of particles are approximately those of the statistical ensemble (population) of our theory. Then the number of particles with orientations  $(\theta, \phi)$ , to within solid angle  $d\Omega$ , is approximately  $nW(\theta, \phi) d\Omega$ . The reader may find it easier to visualize the situation by letting W be this quantity, so that  $\int W d\Omega = n$ rather than 1; he can then think of W as a density and J as a current density of representative points on the unit sphere.

# D. The Fokker-Planck Equation

Let us first suppose that the random field h(t) is absent. Then J = Wv, where v, the velocity of a representative point at the specified location  $(\theta, \phi)$ , is the value of  $\dot{r}^0$  according to (25) with g(t) = 0.

There are now two ways of taking the random field h(t) into account.

1) Intuitive Derivation: The tendency of the random thermal forces is to produce disorder: to destroy any concentration of representative points in particular regions of the unit sphere. We can describe this tendency by postulating a term in J of the form  $-k' \nabla W$ , where k' is a positive constant (at given temperature); a current of this form would rob the rich regions to feed the poor and would cease only when W became uniform. We thus get

$$\boldsymbol{J} = \boldsymbol{W}\boldsymbol{v} - \boldsymbol{k}' \boldsymbol{\nabla} \boldsymbol{W},\tag{31}$$

where v is given by (23). Insertion of (31) in (30) gives the desired partial differential equation,

$$\frac{\partial W}{\partial t} = ar^0 \cdot (\nabla V \times \nabla W) + b \nabla \cdot (W \nabla V) + k' \nabla^2 W.$$
(32)

In the first term, we have used the fact that, as is easily shown,  $\nabla \cdot (r^0 \times \nabla V) = 0$ ; in the second, that  $r^0 \times (r^0 \times \nabla V) = -\nabla V$ . Equation (32) is the "Fokker-Plank equation" of the pres-

ent problem.

The new constant k' is not independent of the previous constants. When  $\partial W/\partial t = 0$ , W must reduce to the equilibrium distribution

$$W_0 = A \ e^{-\beta V} \tag{33}$$

where

 $\beta = v/kT \tag{34}$ 

(an abbreviation we shall use frequently hereafter), and where A is a constant. Substitution of (33) in (32) shows that (32) is satisfied by  $W_0$  only if

$$k' = b/\beta. \tag{35}$$

2) Derivation from the Langevin Equation: The Fokker-Planck equation (32) can be derived directly from the Langevin equation (25); the interested reader is referred to the literature [12]-[15]. When this method is used, the last term in (32) contains the constant  $\mu$  of (27) instead of the constant k' of (31). The relation between these two constants is

$$k' = \frac{1}{2}\mu(b^2 + a^2). \tag{36}$$

nabla . (SxgradV) = gradV . (nablaxS) - S .  $(nabla \times gradV) = 0$ 

$$c_2$$
 are both positive, a saddle point if they have opposite signs;

quantities is

 $V = V_0 + \frac{1}{2} \left( c_1 \alpha_1^2 + c_2 \alpha_2^2 \right)$ 

terest to us. The Langevin equation (25), expressed to the first order of small quantities, becomes

V. CASES IN WHICH THE LANGEVIN EQUATION

IS LINEARIZABLE

There are cases in which we are interested in the behavior of

W in the vicinity of a minimum or other stationary point of

the free-energy density V. In such a case, take the z axis along

the direction of minimum (or stationary) V. Then by suitable

orientation of the x and y axes, V to the second order of small

where  $V_0$  is the value at the stationary point,  $\alpha_1$  and  $\alpha_2$  are

the direction cosines with respect to the x and y axes, and the

c are constants. The stationary point is a minimum if  $c_1$  and

the case of a maximum  $(c_1 \text{ and } c_2 \text{ both negative})$  is of no in-

A. Simplification near a Stationary Point of the Free Energy

$$\dot{\alpha}_{1} = -bc_{1}\alpha_{1} + ac_{2}\alpha_{2} + bg_{1}(t) - ag_{2}(t)$$
  
$$\dot{\alpha}_{2} = -ac_{1}\alpha_{1} - bc_{2}\alpha_{2} + ag_{1}(t) + bg_{2}(t).$$
 (38)

The Fokker-Planck equation (32) becomes

$$\partial W/\partial t = (bc_1\alpha_1 - ac_2\alpha_2) \partial W/\partial \alpha_1 + (ac_1\alpha_1 + bc_2\alpha_2) \partial W/\partial \alpha_2$$

$$+ b(c_1 + c_2)W + (b/\beta)\nabla^2 W$$
 (39)

 $(\nabla^2 = \partial^2/\partial\alpha_1^2 + \partial^2/\partial\alpha_2^2)$ ; in the last term, we have used (35). The element of solid angle is  $d\Omega = d\alpha_1 d\alpha_2/(1 - \alpha_1^2 - \alpha_2^2)^{1/2}$ ; in the linear approximation, this becomes simply  $d\alpha_1 d\alpha_2$ . The current density (31) becomes

$$J_{1} = -(c_{1}b\alpha_{1} - c_{2}a\alpha_{2})W - (b/\beta) \partial W/\partial\alpha_{1}$$
  

$$J_{2} = -(c_{1}a\alpha_{1} + c_{2}b\alpha_{2})W - (b/\beta) \partial W/\partial\alpha_{2}$$
(40)

 $J_1$  and  $J_2$  are the components along the  $\alpha_1$  and  $\alpha_2$  axes, respectively.

## B. Behavior near an Isotropic Minimum

In this case,  $c_1 = c_2 = c > 0$ .

1) Equilibrium and Quasiequilibrium: In equilibrium,

$$W = A'e^{-\beta V} \cong A' \exp \left[-\beta V_0 - \frac{1}{2}\beta c(\alpha_1^2 + \alpha_2^2)\right]$$
  
=  $A \exp \left[-\frac{1}{2}\beta c(\alpha_1^2 + \alpha_2^2)\right]$  (41)

where  $A = A'e^{-\beta V_0}$ . If  $\beta c$  is sufficiently large, this formula is valid out to values of  $\alpha_1^2 + \alpha_2^2$  at which W becomes negligible. For the unit sphere as a whole, a formula of the form (41) will be valid within a region  $\Omega_i$  about each minimum. If the equilibrium is complete, the constant A' will be the same for all minima and can be found by setting the sum of the integrals of W over the regions  $\Omega_i$  equal to unity. The contribution of parts of the unit sphere outside the regions  $\Omega_i$  may be neglected, since there W is exponentially small; for the same reason, the integration over each region  $\Omega_i$  can be extended over

(37)

the range  $-\infty < \alpha_1 < +\infty, -\infty < \alpha_2 < +\infty$  (when the element of solid angle is written  $d\alpha_1 d\alpha_2$ ).

We are interested also in the case in which relative equilibrium has been established within each region  $\Omega_i$ , but the distribution between the different regions has not yet attained equilibrium becasue of the high energy barriers between the regions. In this case we can again use formula (41), but with different values of A' for different regions. The integral of W over region  $\Omega_i$  then gives the probability that a representative point is in region  $\Omega_i$ ; or approximately, for an actual collection of identical noninteracting particles, the fractional number of particles  $n_i/n$  with orientations close to direction *i*. With the approximation already described, this gives

$$n_i/n = A \left[ \int_{-\infty}^{+\infty} \exp\left(-\frac{1}{2}\beta c\alpha^2\right) d\alpha \right]^2 = 2\pi A/\beta c.$$
 (42)

It may be legitimate to assume an equilibrium *relative* distribution at distances too far from the minimum to permit the approximation (41). This will not invalidate the calculation just made, since W at such distances is too small to introduce appreciable error in the relation (42). But at such distant points we must use the exact formula  $W = A'e^{-\beta V} = Ae^{-\beta(V-V_0)}$  instead of the approximation (41). We then get

$$W = (n_i/n) \left(\beta c/2\pi\right) e^{-\beta (V - V_0)}.$$
(43)

This relates the value of W at any point within the quasiequilibrium region about a minimum to the relative number of particles in that region.

Given such quasiequilibrium, the condition for validity of the relation (43) is that  $\exp(-\frac{1}{2}\beta c\alpha^2)$  must become negligibly small while  $\alpha^2$  is still negligibly small, so that the linear approximation is still justified. If we simultaneously require  $\exp(-\frac{1}{2}\beta c\alpha^2) \leq \epsilon_1$  and  $\alpha^2 \leq \epsilon_2$ , where  $\epsilon_1$  and  $\epsilon_2$  are specified small quantities, we must have

$$\beta c \ge (2/\epsilon_2) \ln (1/\epsilon_1). \tag{44}$$

If  $\epsilon_1 = \epsilon_2 = \epsilon$ , then for  $\epsilon = 0.1$ , 0.01, and 0.001 we get  $\beta c \ge 4.6 \times 10^1$ ,  $9.2 \times 10^2$ , and  $1.4 \times 10^4$ , respectively. Similar conditions may be derived for validity of the relations to be derived in Sections V-C, -D, and -E.

2) Solution of the Langevin Equation: In order to judge the legitimacy of our assumptions about the relative times for establishment of various degrees of equilibrium, we need an estimate of the time necessary to establish the relative equilibrium discussed in 1). For this purpose, we must solve the Langevin equation (38) or the Fokker-Planck equation (39) for the case  $c_1 = c_2 = c > 0$ .

The Langevin equation is complicated by the presence of the gyromagnetic terms  $ac\alpha_2$  in  $\dot{\alpha}_1$  and  $-ac\alpha_1$  in  $\dot{\alpha}_2$ . This complexity can be removed by using direction cosines  $\alpha'_1$ ,  $\alpha'_2$  referred to axes that rotate with angular velocity

$$\omega = -ca \tag{45}$$

and that coincide with the xy axes at time 0. The resulting equations are easily solved; and by carrying out appropriate ensemble averages, we find that if the initial values  $(\alpha_{10}, \alpha_{20})$  are the same for all members of the ensemble (as could be ac-

complished by initial application and removal of a large field),  $\alpha'_1$  and  $\alpha'_2$  have means

$$\langle \alpha_1' \rangle = \alpha_{10} e^{-cbt} \qquad \langle \alpha_2' \rangle = \alpha_{20} e^{-cbt} \tag{46}$$

and variances and covariance  $(\delta \alpha'_i \equiv \alpha'_i - \langle \alpha'_i \rangle)$ 

$$\langle \delta \alpha_1'^2 \rangle = \langle \delta \alpha_2'^2 \rangle = \sigma^2 = \sigma_0^2 \left[ 1 - e^{-2cbt} \right]$$
$$\langle \delta \alpha_1' \delta \alpha_2' \rangle = 0 \tag{47}$$

where

$$\sigma_0^2 = \mu (b^2 + a^2)/2cb = k'/cb = 1/\beta c = kT/vc.$$
(48)

Equations (46) show that in the rotating axes, the mean magnetization decays, with time constant 1/cb, toward the direction of minimum V; in fixed axes, it executes a damped precession about this direction. Equations (47) show that  $\alpha'_1$  and  $\alpha'_2$  are uncorrelated and have a common variance that is initially zero and that approaches, with time constant 1/2cb, the value  $\sigma_0^2 = 1/\beta c$ . Transformation back to fixed axes at  $t = \infty$  shows that  $\alpha_1$  and  $\alpha_2$  then are uncorrelated and have zero mean and variance  $1/\beta c$ , in accordance with the Boltzmann distribution (41).

Since the  $g_i(t)$  are normal random variables, so are the  $\alpha'_i$ ; and being uncorrelated normal random variables, they are independent.

3) Solution of the Fokker-Planck Equation: The Fokker-Planck equation (39), with  $c_1 = c_2 = c$ , contains terms in  $\alpha_1 \partial W / \partial \alpha_2$  and  $\alpha_2 \partial W / \partial \alpha_1$  that prevent solution by separation of the variables  $\alpha_1$  and  $\alpha_2$ . These terms can be removed by the same transformation that was used for the Langevin equation. The equation can then be solved by separation of variables. The mathematics from that point on is essentially the same as in Uhlenbeck and Ornstein's treatment of Brownian motion [18], [19]. For arbitrary initial conditions, one can expand W as a series of terms that decay with reciprocal time constants (m + n)bc, where m and n are nonnegative integers (the term m = n = 0 is the equilibrium solution) [18]. For the special initial conditions considered in 2) above, one can use either the series method or a more direct one [19] in which, instead of W, one uses the "characteristic function" [20] of the distribution (essentially the Fourier transform of W); the results are the same as before.

From the results of this and the preceding subsection, we may conclude that quasiequilibrium about a minimum of V is established in a time of the order of 1/cb.

# C. Behavior near an Anisotropic Minimum

When  $c_2 \neq c_1$ , the quasiequilibrium calculations of Section V-B1) require only trivial modifications. In (41),  $c(\alpha_1^2 + \alpha_2^2)$  must be replaced by  $c_1\alpha_1^2 + c_2\alpha_2^2$ ; in (42) and (43), c must be replaced by  $(c_1c_2)^{1/2}$ .

The Langevin equation can be solved by standard methods, such as the Laplace transform. The transient parts of the solution contain terms in  $e^{s_1 t}$  and  $e^{s_2 t}$ , where  $s_1$  and  $s_2$  are the roots of

$$(s+bc_1)(s+bc_2) + a^2c_1c_2 = 0.$$
<sup>(49)</sup>

The time for attainment of equilibrium may be estimated as the reciprocal of the smaller of  $-s_1$  and  $-s_2$  when they are real, and of their common real part when they are complex. This time is of the order of  $1/bc_1$  and  $1/bc_2$  when these are of the same order.

Solution of the Fokker-Planck equation is more difficult and is not necessary for our purposes.

# D. Behavior near a One-Dimensional Maximum

When the system is symmetric about an axis (as in the case of a uniaxial crystal in the form of a prolate spheroid, with the crystal and spheroid axes coincident and the field along this axis), V is a function of a single variable  $\theta$ , the angle between M and the axis of symmetry. If W is initially symmetric about this axis, it will remain so. Any energy barrier will be at some value  $\theta_m$  of  $\theta$  and will extend around a parallel of latitude on the unit sphere, a total distance  $2\pi \sin \theta_m$ . In the local axes of Section V-A, if we take  $\alpha_2$  along the direction of increasing  $\theta$ , V and W are independent of  $\alpha_1$ ; in the Fokker-Planck equation (39),  $c_1 = 0$  and  $c_2 = -c'$ , where c' > 0. Thus

$$\frac{\partial W}{\partial t} = -bc'\alpha \frac{\partial W}{\partial \alpha} - bc'W + (b/\beta) \frac{\partial^2 W}{\partial \alpha^2}.$$
 (50)

We have dropped the subscript on  $\alpha_2$ .

We are interested in the case in which the regions on opposite sides of the barrier, and not too close to it, are practically in internal equilibrium, as described in Section V-B, but are not yet in equilibrium with each other. We can describe this situation by saying that for sufficiently large  $|\alpha|$ , W is approximately equal to  $A'e^{-\beta V(\alpha)}$  for  $\alpha > 0$  and to  $B'e^{-\beta V(\alpha)}$  for  $\alpha < 0$ , with  $A' \neq B'$ . We suppose that this becomes true at small enough values of  $|\alpha|$  so that the approximation  $V = V_m + \frac{1}{2}c_2\alpha_2^2 = V_m - \frac{1}{2}c'\alpha^2$  is still valid; here  $V_m$  is the value of V at the maximum. Then the values of W at such values of  $\alpha$  are  $A \exp(\frac{1}{2}\beta c'\alpha^2)(\alpha > 0)$  and  $B \exp(\frac{1}{2}\beta c'\alpha^2)(\alpha < 0)$ , where  $A = A'e^{-\beta Vm}$  and  $B = B'e^{-\beta Vm}$ .

$$W = U \exp\left(\frac{1}{2}\beta c'\alpha^2\right)$$

(51)

then the limiting values of U are A and B. The partial differential equation satisfied by U is

$$\partial^2 U/\partial \alpha^2 + \beta c' \alpha \, \partial U/\partial \alpha = (\beta/b) \, \partial U/\partial t.$$
(52)

The time-independent solution  $(\partial U/\partial t = 0)$  is found by elementary integration and is

$$U = C_1 \phi(\alpha \beta^{1/2} c'^{1/2}) + C_2$$
 falta signo "-" en el (53)  
here exponente

where

$$\phi(x) = (2/\pi)^{1/2} \int_0^x \exp\left(\frac{1}{2}\zeta^2\right) d\zeta.$$
 (54)

For |x| >> 1,  $\phi(x) = +1$  for x > 0 and = -1 for x < 0.

On imposing the boundary conditions U = A for  $\alpha \beta^{1/2} c'^{1/2}$ large and positive, = B for  $\alpha \beta^{1/2} c'^{1/2}$  large and negative, we find a time-independent distribution that satisfies our conditions:

$$W = \exp\left(\frac{1}{2}\beta c'\alpha^{2}\right)\left[\frac{1}{2}(A+B) + \frac{1}{2}(A-B)\phi(\alpha\beta^{1/2}c'^{1/2})\right].$$
(55)

To maintain such a distribution indefinitely would require continuous destruction of representative points (or of particles) at  $\alpha = +\infty$  and creation of them at an equal rate at  $\alpha = -\infty$ , or vice versa, so as to keep the numbers there constant despite the flow across the barrier; otherwise, A and B will change with time, approaching the values that correspond to equilibrium for the whole system. We may neglect this fact if, as we are assuming, the time for attainment of equilibrium between regions is very long in comparison with the time for attainment of equilibrium within a region.

To the time-independent solution (55) may be added timedependent solutions of (52), determined by the initial conditions. These solutions decay with time constants whose reciprocals are multiples of bc'. Thus the barrier attains a steady-flow situation in a time comparable with that in which the neighborhood of a minimum attains equilibrium (since normally c' for a maximum of V and  $c_1$  and  $c_2$  for a minimum are of the same order).

The current density  $J_2$  across the barrier is, by (40),

$$J_{2} = c'b\alpha W - (b/\beta) \partial W/\partial\alpha = -\exp\left(\frac{1}{2}\beta c'\alpha^{2}\right)(b/\beta) \partial U/\partial\alpha$$
$$= -(A - B)b(c'/2\pi\beta)^{1/2}.$$
 (56)

There is also a component  $J_1 = -c' \alpha \alpha W$  along the barrier; this represents a mean gyroscopic precession about the symmetry axis. The total current  $I_2$  across the barrier is found by multiplying  $J_2$  by the barrier length  $2\pi \sin \theta_m$ . debe ser  $\alpha$ 

Let  $P_1$  and  $P_2$  be two points, in the regions a > 0 and a < 0, respectively, far enough from  $\alpha = 0$  so that the corresponding values of W have their limiting values  $W_1 = A'e^{-\beta V'_1}$  and  $W_2 = B'e^{-\beta V'_2}$ , respectively, where  $V'_1$  and  $V'_2$  are the values of V at  $P_1$  and  $P_2$ . In terms of  $W_1$  and  $W_2$ , we have  $A = A'e^{-\beta V_m} = W_1e^{-\beta(V_m - V'_1)}$  and  $B = B'e^{-\beta V_m} = W_2e^{-\beta(V_m - V'_2)}$ . Thus

$$I_{2} = -b(2\pi c'/\beta)^{1/2} \left[ W_{1} e^{-\beta (V_{m} - V_{1}')} - W_{2} e^{-\beta (V_{m} - V_{2}')} \right] \sin \theta_{m}.$$
(57)

Equation (57) relates the rate of flow of representative points across the barrier to the values of W at two points on opposite sides of the barrier, and far enough from it to be within the regions of quasiequilibrium for the corresponding minima.

#### E. Behavior near a Saddle Point

In a more general situation, flow of representative points occurs across barriers that are not of uniform height; the flow across any barrier will be concentrated near the point of least height, i.e., a saddle point of V: say a minimum with respect to  $\alpha_1$  and a maximum with respect to  $\alpha_2$ . Then in (39),  $c_1 > 0$  and  $c_2 < 0$ ; let  $c_2 = -c'_2$ , where  $c'_2 > 0$ . As in Section V-D, we suppose that away from the barrier  $W = A'e^{-\beta V}$  for  $\alpha_2 > 0$ ,  $= B'e^{-\beta V}$  for  $\alpha_2 < 0$ , and that these limiting values are realized while  $|\alpha_2|$  is still small enough to justify the linear approximation in  $\alpha_2$ . We also suppose that W decreases rapidly enough with increasing  $|\alpha_1|$  to become negligible within the range of validity of the linear approximation in  $\alpha_1$ . As before, we seek a relation between the flow  $I_2$  across the barrier and the values of W at two points on opposite sides of the barrier, and not too close to it.

Let  $W = U \exp \left[-\frac{1}{2}\beta(c_1\alpha_1^2 - c_2'\alpha_2^2)\right]$ . Then U satisfies the equation

$$(\beta/b) \,\partial U/\partial t = \nabla^2 U + \beta(-c_1 \alpha_1 + \rho c_2' \alpha_2) \,\partial U/\partial \alpha_1 + \beta(\rho c_1 \alpha_1 + c_2' \alpha_2) \,\partial U/\partial \alpha_2$$
(58)

where

$$\rho = a/b. \tag{59}$$

Equation (58) does not yield to an attempt to separate the variables  $\alpha_1$  and  $\alpha_2$  (the separation of t from them is easy enough), because of the gyromagnetic terms containing  $\rho$ . These terms cannot be removed by any orthogonal transformation (rotation of axes). They can, however, be removed by a nonorthogonal transformation to variables  $z_p = \sum_i q_{pi} \alpha_i$ , with the  $q_{pi}$  suitably chosen. The penalty is that a cross term containing  $\partial^2 U/\partial z_1 \partial z_2$  now appears; but it turns out that when  $\partial U/\partial t = 0$ , there are solutions that are functions only of  $z_1$  or only of  $z_2$ , and in such solutions the cross term drops out.

We therefore seek, directly, a solution of (58) of the form U = f(z), where

$$z = q\alpha_1 + \alpha_2 \tag{60}$$

with q to be determined. (For q = 0, z will reduce to  $\alpha_2$ ). On substituting U = f(z) in (58), we get a result that reduces to an ordinary differential equation in z only if a certain linear combination of  $\alpha_1$  and  $\alpha_2$  is identically equal, except for a multiplicative constant L, to the linear combination z. On imposing this condition, we get two equations that can be solved for L and q. On substituting these values in the differential equation and integrating it, we get

$$U = C_1 \int_0^{q\alpha_1 + \alpha_2} \exp\left(-\frac{1}{2}\beta c''\xi^2\right) d\xi + C_2$$
(61)

where

$$q = (2\rho c'_2)^{-1} \left\{ -(c_1 + c'_2) + \left[ (c_1 + c'_2)^2 + 4\rho^2 c_1 c'_2 \right]^{1/2} \right\}$$
(62)

and

$$c'' = \rho c_1 c_2' / q (c_1 + c_2'). \tag{63}$$

This is the solution that approaches finite values as  $|\alpha_2|$  increases. There is another solution, corresponding to a minus sign before the radical in (62), which becomes infinite as  $|\alpha_2| \rightarrow \infty$ ; it corresponds to the other  $z_p$  and is not useful here.

 $C_1$  and  $C_2$  are now determined by the conditions at large positive and negative  $|\alpha_2|\beta^{1/2}c_2^{\prime 1/2}$ . The evaluation of  $J_2$  by (40) and of  $I_2 = \int_{-\infty}^{+\infty} J_2 d\alpha_1$  is straightforward; in the integral for  $I_2$ , the term in  $J_2$  that contains U can be transformed, by integration by parts, to one that contains  $\partial U/\partial \alpha_1$ , so that the integral over  $\xi$  disappears. We get, instead of (57) of the onedimensional case,

$$I_{2} = -G(b/\beta)(c_{2}'/c_{1})^{1/2} \left[W_{1}e^{-\beta(V_{s}-V_{1}')} - W_{2}e^{-\beta(V_{s}-V_{2}')}\right]$$
(64)

where  $V_s$  is the value of V at the saddle point, and where

$$G = 1 + \rho q = (2c'_2)^{-1} \{ (c'_2 - c_1) + [(c_1 + c'_2)^2 + 4\rho^2 c_1 c'_2]^{1/2} \}.$$
(65)

For given b, the value of  $\rho$  affects  $I_2$ , and hence the rate of approach to an equilibrium distribution of representative points between the two minima, only through the factor G. This factor reduces to unity when  $\rho = 0$  (i.e.,  $a = 0, b \neq 0$ : damping but no gyromagnetic torque in the Landau-Lifshitz equation of motion (23)).

Although (57) and (64) have much in common, the temperature dependence (recall that  $\beta = v/kT$ ) of the pre-exponential factors is quite different in the two cases.

Time-dependent solutions of (58) can be expected to decay with time constants of the order of 1/bc'.

## VI. THE UNIAXIAL CASE

# A. The Fokker-Planck Equation

We turn now to consideration of the Fokker-Planck equation (32) in situations in which the corresponding Langevin equation (25) cannot be linearized. Though the Fokker-Planck equation itself is linear in either case, it is much more complicated in the latter case than in the former.

In this part we shall consider the special case in which V is a function of  $\theta$  only, independent of  $\phi$ . Then if W is initially independent of  $\phi$ , it will by symmetry remain so. In this case, (32) reduces to

$$\frac{\partial W}{\partial t} = \frac{b}{\beta \sin \theta} \frac{\partial}{\partial \theta} \left\{ \sin \theta \left[ \beta \frac{dV}{d\theta} W + \frac{\partial W}{\partial \theta} \right] \right\}.$$
 (66)

The gyromagnetic terms (those containing a) have disappeared. The only effect of the gyromagnetic term in the equation of motion is that the current density J of representative points has a  $\phi$  component; that is, there is a mean precession of the magnetization about the symmetry axis. This part of J is divergenceless and does not affect the evolution of W.

If we set  $W = Ue^{-\beta V}$  and change to  $x = \cos \theta$  as independent variable, we can put (66) into the form

$$\frac{\beta}{b}\frac{\partial U}{\partial t} = (1 - x^2)\frac{\partial^2 U}{\partial x^2} - \left[2x + \beta(1 - x^2)\frac{dV}{dx}\right]\frac{\partial U}{\partial x}.$$
 (67)

The boundary conditions are: finiteness of U at  $x = \pm 1$ .

The time-independent solution  $(\partial U/\partial t = 0)$  can be found by direct integration. The general solution in this case is

$$U = C_1 + C_2 \int_0^x (1 - \xi^2)^{-1} e^{+\beta V(\xi)} d\xi.$$
 (68)

For finiteness at  $x = \pm 1$ ,  $C_2 = 0$ ; then  $W = C_1 e^{-\beta V}$ , the expected equilibrium solution.

Time-dependent solutions are of the form

$$U = X(x) e^{-pt} \tag{69}$$

where X(x) satisfies the ordinary differential equation

$$\frac{d^2 X}{dx^2} - \left[\frac{2x}{1-x^2} + \beta \frac{dV}{dx}\right] \frac{dX}{dx} + \frac{\lambda}{1-x^2} X = 0,$$
 (70)

with  $\lambda = p/b$ . (Note the new use of the symbol  $\lambda$ ; the Landau-Lifshitz  $\lambda$  has been absorbed into the constant b.) If the eigenvalues  $\lambda_n$  of the parameter  $\lambda$  can be found, the characteristic reciprocal time constants  $p_n$  will be given by

$$p_n = \lambda_n b/\beta = \lambda_n bkT/v. \tag{71}$$

The case of greatest interest is that of a particle with uniaxial crystalline anisotropy and with a field H applied along its axis: from (10),

$$V = K_1(1 - x^2) - HM_s x (K_1 > 0).$$
(72)

When H = 0, (70) for this case reduces to

$$\frac{d^2 X}{dx^2} - \left[\frac{2x}{1-x^2} - 2\beta K_1 x\right] \frac{dX}{dx} + \frac{\lambda}{1-x^2} X = 0.$$
(73)

Equation (73) has two regular singularities, at x = +1 and at x = -1, and an irregular singularity at  $x = \infty$  [21]. These properties take it outside the classes of second-order differential equations that are easily solved: Fuchsian, especially hypergeometric (these have only regular singularities), and confluent hypergeometric (these have an irregular singularity at  $\infty$  and only one regular finite singularity) [21]. If one seeks a series solution,  $X = \sum_n a_n x^{\rho+n}$ , one obtains a recurrence relation that contains three successive *a*'s rather than two, so that no simple explicit formula for the coefficients can be obtained. If one performs an integral transformation (e.g., a Fourier transformation), one obtains for the transformed variable a differential equation that is as complicated as the original equation. Therefore, one must resort to approximate or numerical methods.

# B. Limiting Cases

1) Low Energy Barrier (High Temperature),  $\beta |V| \ll 1$ : In the limit  $\beta \to 0$ , (70) becomes Legendre's equation, with eigenvalues  $\lambda_n = n(n+1)$   $(n=0, 1, \cdots)$ ; the eigenvalue 0 corresponds to the equilibrium solution, which is simply W = const. The other eigenvalues determine reciprocal time constants  $p_n$  that are integral multiples of  $b/\beta$ .

For  $\beta |V|$  nonzero but small, perturbation theory can be used, and  $\lambda_n$  can be expressed as the first few terms of a series in a small parameter, e.g.,  $\beta K_1$  for (73) [12], [22].

2) High Energy Barrier (Low Temperature),  $\beta |V| \gg 1$  the Kramers Method: For this case, we can use the ideas presented in Sections V-B and -D: that the time to attain relative equilibrium in the region about a minimum of V is very short in comparison with the time to attain equilibrium between different minima.

For simplicity, we consider the case of two minima,  $V_1$  and  $V_2$ , at  $\theta = 0$  and  $\pi(x = +1 \text{ and } -1)$ , respectively, separated by a maximum  $V_m$  at  $\theta = \theta_m$ . Near the minimum at  $\theta = 0$ 

$$V \simeq V_1 + \frac{1}{2}c^{(1)}\theta^2 \tag{74}$$

where  $c^{(1)} = (d^2 V/d\theta^2)_{\theta=0}$ . With the z axis along the direction  $\theta = 0, \alpha_1^2 + \alpha_2^2 = \sin^2 \theta \cong \theta^2$ , so that

$$V \cong V_1 + \frac{1}{2}c^{(1)}(\alpha_1^2 + \alpha_2^2)$$

and in (43),  $c_1 = c_2 = c^{(1)}$ ; thus the value of W at a point  $P_1$  close to the barrier, but still within the region of quasiequi-

librium about  $\theta = 0$ , is

$$W_1 = (n_1/n) \left(\beta/2\pi\right) c^{(1)} e^{-\beta \left(V_1' - V_1\right)}$$
(75)

where  $V'_1$  is the value of V at  $P_1$ . For the minimum about  $\theta = \pi$ , a similar equation holds. Now by (57), the current of representative points across the barrier from 2 to 1 is  $(\alpha \cong \theta_m - \theta)$ 

$$I_{21} = -b (2\pi c'/\beta)^{1/2} \cdot [W_1 e^{-\beta (V_m - V_1')} - W_2 e^{-\beta (V_m - V_2')}] \sin \theta_m.$$
(76)

On inserting (75) and its  $P_2$  counterpart in (76), we get

$$nI_{21} = b(\beta c'/2\pi)^{1/2} \cdot [n_2 c^{(2)} e^{-\beta (V_m - V_2)} - n_1 c^{(1)} e^{-\beta (V_m - V_1)}] \sin \theta_m.$$
(77)

For an ensemble of identical noninteracting particles,  $nI_{21} = \dot{n}_1 = -\dot{n}_2$  in the discrete-orientation model; therefore, the coefficients of  $n_1$  and of  $n_2$  in (77) must be equal to  $-\nu_{12}$  and  $\nu_{21}$ , respectively, in (8). Thus we get (i = 1, j = 2 or i = 2, j = 1)

$$v_{ij} = v_{ij}^0 e^{-\beta (V_m - V_i)}$$
(78)

where

$$v_{ii}^0 = b(\beta c'/2\pi)^{1/2} c^{(1)} \sin \theta_m.$$
<sup>(79)</sup>

Equation (78) is equivalent to (9), but we now have an explicit formula for  $v_{ij}^0$ . It does indeed depend on *T*, both directly through the factor  $\beta^{1/2} (\propto T^{-1/2})$  and indirectly, through the temperature dependence of  $c', c^{(i)}$ , and b.

Having found  $\nu_{12}$  and  $\nu_{21}$ , we can find the time constant  $\tau = 1/(\nu_{12} + \nu_{21})$  (see Section III-A). This method of evaluating  $\tau$  is an adaptation to the present case of a method developed by Kramers for handling the escape of Brownian particles over potential barriers [23].

3) High-Energy Barrier, Asymptotic Expansion: For the particular case of (73), a correction to the Kramers formula has been obtained in the form of an asymptotic series [24]. In this case  $V_m - V_i = K_1$ ,  $c^{(i)} = c' = 2K_1$ ,  $\theta_m = \pi/2$ , and  $v_{12}^0 = v_{21}^0 = 2b\beta^{1/2}\pi^{-1/2}K_1^{3/2}$ ; hence the reciprocal time constant  $p_0 = v_{12} + v_{21}$  according to (78) and (79) is  $4b\beta^{1/2}\pi^{-1/2}K_1^{3/2} \cdot e^{-\beta K_1}$ , and the corresponding eigenvalue of  $\lambda$  in (73) is

$$\lambda_0 = \beta p_0 / b = (2\kappa^3 / \pi)^{1/2} e^{-(1/2)\kappa}, \tag{80}$$

where

$$\kappa = 2\beta K_1 = 2K_1 v/kT. \tag{81}$$

The asymptotic series for  $\lambda$  is

$$\lambda^{-1} = \lambda_0^{-1} (1 + 2/\kappa + 7/\kappa^2 + 36/\kappa^3 + 249/\kappa^4 + \cdots).$$
 (82)

The error may be expected to be comparable with the first omitted term; therefore this formula can give very accurate values of  $\lambda$  when  $\kappa$  is large.

According to (82), the fractional error by use of the leading term only (Kramers approximation) is of the order of  $2/\kappa = 2/2\beta K_1 = 2/\beta c^{(i)}$ ; if this is to be a negligibly small quantity  $\epsilon$ ,  $\beta c^{(i)}$  should be no smaller than  $2/\epsilon$ . This is con-

sistent with the estimate  $(2/\epsilon) \ln (1/\epsilon)$  obtained in Section V-B1). Equation (82) omits an exponentially small correction that will be significant when  $\kappa$  is only moderately large.

### C. Intermediate Energy Barrier: Numerical Solution

When  $\beta |V| \sim 1$ , we must resort to numerical methods. These have been applied to the case when V is given by (72), both for H = 0 [22] and for  $H \neq 0$  [25]. One can express U either as a series of Legendre polynomials or as an ordinary power series. The three-term recurrence formula is quite amenable to a purely numerical method; one procedure for handling such problems, when the object is to find the smallest eigenvalue of a parameter, has been described by Jeffreys and Jeffreys [26].

The difficulty with the numerical method is that as  $\kappa$  becomes larger and larger, one needs more and more terms of the series (which for numerical calculations must always be truncated after a finite number of terms); and because of cancellation of terms, one needs more and more figures in the calculation (try calculating  $e^{-30}$  directly by the series formula!). Thus with a given number of figures and a given amount of available computer time, there is a limit to how large a  $\kappa$  is manageable.

Before this point is reached, however, the asymptotic formula (82) can take over. Thus in the case of the free-energy formula (72) with H=0, the leading time constant is now known accurately over the whole  $\kappa$  range. Extension of the same methods to the case  $H \neq 0$  or to a more complicated uniaxial-anisotropy formula presents, in principle, no difficulty.

## VII. MORE COMPLICATED CASES

In the general case  $V = V(\theta, \phi)$ , the Fokker-Planck equation (32) becomes

$$\frac{\partial W}{\partial t} = \frac{a}{\sin \theta} \left( \frac{\partial V}{\partial \theta} \frac{\partial W}{\partial \phi} - \frac{\partial V}{\partial \phi} \frac{\partial W}{\partial \theta} \right) + b \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial V}{\partial \theta} \cdot W \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left( \frac{\partial V}{\partial \phi} \cdot W \right) \right] + \frac{b}{\beta} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial W}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2 W}{\partial \phi^2} \right) \right].$$
(83)

The assumption  $W = F(\theta, \phi) e^{-pt}$  reduces (83) to a partial differential equation for  $F(\theta, \phi)$ , containing a parameter  $\lambda = \beta p/b$  whose eigenvalues (determined by the condition of finiteness over the unit sphere) are to be found. The eigenvalue  $\lambda = 0$  corresponds to the equilibrium solution  $F = Ae^{-\beta V}$ . For  $\lambda \neq 0$ , even with the simplest forms of  $V(\theta, \phi)$  that are of interest, the variables  $\theta$  and  $\phi$  do not separate: assumption of a series  $\sum_m [f_m(\theta) \cos m\phi + g_m(\theta) \sin m\phi]$  leads to coupled differential equations for the functions  $f_m$  and  $g_m$ , and assumption of a series  $\sum_{mn} (A_{mn} \cos m\phi + B_{mn} \sin m\phi) P_n^m$  (cos  $\theta$ ) leads to an infinite set of simultaneous equations for the coefficients  $A_{mn}$  and  $B_{mn}$ . Approximate and numerical methods are again necessary.

# A. Limiting Cases

1) Low Energy Barriers (High Temperature): For  $\beta = 0$ , the differential equation for  $F(\theta, \phi)$  reduces to the differential

equation of the spherical harmonics; thus the eigenvalues of  $\lambda$  for  $\beta = 0$  are again n(n + 1), and for small  $\beta$  one can use perturbation theory.

2) High Energy Barriers (Low Temperature): In this case, we can use the same method as for the uniaxial case, except that the flow of representative points from one minimum of V to another is now concentrated near saddle points, and instead of (57) we must use (64). The result is that the  $v_{ij}$  of (7) are given by

$$\nu_{ij} = G(b/2\pi) (c_2'/c_1)^{1/2} (c_1^{(i)} c_2^{(i)})^{1/2} e^{-\beta (V_S - V_i)}.$$
(84)

Here  $V_i$  and  $V_S$  are, respectively, the values of V at the minimum i and at the saddle point between i and j;  $c_1^{(i)}$  and  $c_2^{(i)}$  are the constants in the expansion of V about i,  $V = V_i + \frac{1}{2}(c_1^{(i)}\alpha_1^2 + c_2^{(i)}\alpha_2^2) + \cdots; c_1$  and  $c_2'$  are the coefficients in the expansion about the saddle point,  $V = V_S + \frac{1}{2}(c_1\alpha_1^2 - c_2'\alpha_2) + \cdots$  (of course,  $\alpha_1$  and  $\alpha_2$  have different meanings in the two expansions); and G is given by (65). Equation (84) applies to two minima separated by a single barrier; as in Section III-B2) and 3), we set  $v_{ij} = 0$  for two minima separated by two or more barriers.

For a cubic crystal with  $K_1 > 0$ , in zero field (Section III-B2), we find  $V_i = 0$ ,  $V_S = \frac{1}{4}K_1$ ,  $c_1^{(i)} = c_2^{(i)} = 2K_1$ ,  $c_1 = K_1$ ,  $c_2' = 2K_1$ , and hence in (12)

$$\nu = G \cdot 2^{1/2} \pi^{-1} b K_1 e^{-(1/4)\beta K_1}, \quad (K_1 > 0)$$
(85)

where

$$G = \frac{1}{4} + \frac{1}{4} (9 + 8\rho^2)^{1/2}.$$
(86)

For a cubic crystal with  $K_1 < 0$ , in zero field (Section III-B3), we find  $V_i = -\frac{1}{3} |K_1|$ ,  $V_S = -\frac{1}{4} |K_1|$ ,  $c_1^{(i)} = c_2^{(i)} = (4/3) |K_1|$ ,  $c_1 = 2 |K_1|$ ,  $c_2' = |K_1|$ , and hence in (18) and (19)

$$\nu = G \cdot 2^{1/2} (3\pi)^{-1} b |K_1| e^{-(1/12)\beta |K_1|}, \quad (K_1 < 0)$$
 (87)

where

$$G = -\frac{1}{2} + \frac{1}{2} \left(9 + 8\rho^2\right)^{1/2}.$$
(88)

Recall that the reciprocal time constants of the discrete-orientation model are  $4\nu$  and  $6\nu$  for  $K_1 > 0$  and are  $2\nu$ ,  $4\nu$ , and  $6\nu$ for  $K_1 < 0$ ; the mean magnetization decays with reciprocal time constant  $4\nu$  for  $K_1 > 0$  and  $2\nu$  for  $K_1 < 0$ .

The cubic cases have been worked out directly by Eisenstein and Aharoni [27] and by Smith and de Rozario [16]. The results of Eisenstein and Aharoni are equivalent to (85)-(88) only when  $\rho = 0$ , so that G = 1. The discrepancy when  $\rho \neq 0$ can be attributed to their assumption that W near the saddle point is even in  $\alpha_1$ ; (61) shows that this is true only when  $\rho = 0$ , so that q = 0. The results of Smith and de Rozario are equivalent to (85)-(88).<sup>4</sup>

We can now derive a criterion for applicability of the highbarrier formula (84). The reciprocal time constant for estab-

<sup>&</sup>lt;sup>4</sup>Note that the  $\nu$  of (85) and (87) is differently defined from the  $\nu$  of Eisenstein and Aharoni [27], which differs from it by a factor 4 when  $K_1 > 0$  and by a factor 3 when  $K_1 < 0$ . Eisenstein and Aharoni [27, p. 1283] correctly interpreted the discrepancy between their formulas and those of Smith and de Rozario [16]. The printed version of the article by Smith and de Rozario [16] corrects errors present in the preprint. The symbol q in their (81) is evidently a misprint for 9.

lishment of equilibrium between minima is of the order of  $v_{ij}$ ; for establishment of relative equilibrium (quasiequilibrium) about a minimum, of the order of  $bc_1^{(i)}$  or  $bc_2^{(i)}$ . The ratio of the former to the latter, if  $c'_2 \sim c_1$ , is of the order of  $e^{-\beta(V_S - V_i)}$ , which is less than 0.001 if  $\beta(V_S - V_i)$  is larger than 6.91. The assumptions made about these time constants will then be justified. The conditions assumed in Section V-B-E, e.g., that exp  $(-\frac{1}{2}\beta c'\alpha_2^2)$  becomes small while  $\alpha_2^2$  is still small, are more stringent (in the cubic case, both  $\beta c'$  and  $\beta(V_S - V_i)$  are of the order of  $\beta|K_1|$ ).

# B. Cubic Crystals: Numerical Solution

Eisenstein and Aharoni [27] have evaluated the longest time constants by numerical methods for cubic crystals with positive and with negative  $K_1$ . There is still a range of  $\beta | K_1 |$  in which numerical calculation was not feasible and in which the oneterm asymptotic approximation (84) is not yet reliable. The derivation of an asymptotic series analogous to (82) presents difficulties not present in the uniaxial case.

## C. Other Methods

Instead of dealing directly with the probability density W, one may consider its moments  $m_{lmn} = \int W \alpha_1^l \alpha_2^m \alpha_3^n d\Omega$ ; for example, in the uniaxial case,  $m_n = 2\pi \int_0^{\pi} W \cos^n \theta \sin \theta \, d\theta =$  $2\pi \int_{-1}^{+1} Wx^n dx$  (n = 1, 2, ...). The first-order moments (e.g., l = m = 0, n = 1) are proportional to the components of the magnetic moment and are therefore of direct interest. An expression for  $dm_{lmn}/dt$  can be obtained by multiplying the Fokker-Planck equation by  $\alpha_1^l \alpha_2^m \alpha_3^n d\Omega$  and integrating; if V is a polynomial in the direction cosines  $\alpha_i$ , the right member can be transformed, by partial integration, to an expression involving only the moments. But the expression for  $dm_{lmn}/dt$ involves moments of higher order, and so one gets an infinite system of coupled differential equations. As in many such problems in statistical physics, one can "close" the system by introducing an approximate expression for the moments of some definite order in terms of moments of lower order, and thus get an approximate solution of the problem. This method has been applied to several problems, including ones that relate to a mechanism of magnetization relaxation not considered here, and possibly important when the magnetic particles are suspended in a liquid: Brownian rotation of the particle itself (rather than of the magnetic moment with respect to the particle) [28]-[31].

#### VIII. CONCLUSION

The basic theory described in Section IV appears to be adequate; the difficulties in applying it are chiefly mathematical ones, resulting from the complexity of the Fokker-Planck partial differential equation (32).

Solutions for small energy barriers pose no serious difficulty but have so far not proved of much interest experimentally. Large energy barriers can be treated fairly satisfactorily by the Kramers method; essentially this consists of solving, in each of several regions on the unit sphere, an approximate Fokker-Planck equation based on a linearized form of the Langevin equation valid in that region, and then joining these solutions together. In principle this is a straightforward procedure, and in the uniaxial case the result is well established; but in the cubic case the discrepancies noted in Section VII-A1), demonstrate that some algebraic cleaning up is still necessary. Once the Kramers calculation has been carried out and the  $v_{ij}$  have been found, their relation to the time constants of the discrete-orientation model (Section III-B2) and 3)) is a matter on which there is no disagreement [16], [27].

The Kramers formula is the leading term in an asymptotic series; evaluation of additional terms would insure accuracy at values of  $\beta |V| = |V| v/kT$  that need not be quite so large, and would provide means of estimating the error. This has been achieved in the simplest uniaxial case but presents, in the cubic case, difficulties not yet overcome.

For intermediate energy barriers, numerical calculations, or approximate methods, such as the moment method with truncation of the infinite chain of equations, are necessary. The numerical calculations can be carried out successfully provided  $\beta |V|$  is not too large; they become impractical at a value at which the Kramers approximation is still inaccurate. The gap is filled by the complete asymptotic expansion, which in the cubic case is still to be derived.

Thus the simplest uniaxial case may be considered completely solved; more complicated uniaxial cases can in principle be solved equally completely by the same techniques; the cubic cases are still subject to some incompleteness and uncertainty; and more complicated cases, such as a cubic crystal in an applied field, remain to be investigated.

#### APPENDIX I

# THE GILBERT AND LANDAU-LIFSHITZ EQUATIONS

The Gilbert equation is

$$\dot{M} = \gamma_0 M \times (\mathcal{H} - \eta \dot{M}) \tag{A1}$$

where  $\gamma_0$  is a "gyromagnetic" and  $\eta$  a "damping" parameter. Equation (A1) can be put into the form (21) by the following steps. Operation with  $M \cdot \text{gives } M \cdot \dot{M} = 0$  (or  $d(M^2)/dt = 0$ ; thus the differential equation guarantees constancy of the magnitude of M). Operation with  $M \times$ , use of  $M \cdot \dot{M} = 0$ , and substitution of the result in the last term of (A1) give an equation that can be solved for  $\dot{M}$ . The result is (21) with

$$\gamma_0' = \gamma_0 / (1 + \gamma_0^2 \eta^2 M_s^2), \ \lambda = \gamma_0^2 \eta M_s^2 / (1 + \gamma_0^2 \eta^2 M_s^2).$$
(A2)

The inverse relations are

$$\gamma_0 = \gamma'_0 + \lambda^2 / \gamma'_0 M_s^2$$
  $\eta = \lambda / [(\gamma'_0 M_s)^2 + \lambda^2].$  (A3)

To any specified real value of  $\gamma_0$  and real positive value of  $\eta$  correspond a real value of  $\gamma'_0$  and real positive value of  $\lambda$ , and vice versa; but if the "gyromagnetic" parameter of one equation is held constant while the "damping" parameter is varied, the "gyromagnetic" parameter of the other equation will not remain constant. If  $\eta = 0$ ,  $\lambda = 0$ , and vice versa; in this limiting case of no damping,  $\gamma'_0 = \gamma_0$ , both equations reduce to  $\overline{M} = \gamma_0 M \times \mathcal{H}$ , and the common value of  $\gamma_0$  and  $\gamma'_0$  is presumably at least approximately equal to the gyromagnetic ratio for an electron spin. The same mechanisms that cause damping produce a deviation of the "gyromagnetic" parameter from this value in at least one of the equations, and quite possibly in both.

The Gilbert equation has the theoretical advantage that it can be derived from a classical Lagrangian function and Rayleigh dissipation function. But if we were to start with it in the present problem, the first step would be to transform it to the Landau-Lifshitz form. Consequently, our final formulas are simpler when expressed in terms of the Landau-Lifshitz parameters than of the Gilbert. Equivalent formulas in terms of the Gilbert parameters can be found by the substitutions (A2).

#### REFERENCES

- [1] I. S. Jacobs and C. P. Bean, "Fine particles, thin films and exchange anisotropy," in Magnetism, vol. III, G. T. Rado and H. Suhl, Eds. New York: Academic, 1963, pp. 271-350.
- [2] E. P. Wohlfarth, "Permanent magnet materials," in Magnetism, vol. III, G. T. Rado and H. Suhl, Eds. New York: Academic, 1963, pp. 351-393.
- [3] C. P. Bean and J. D. Livingston, "Superparamagnetism," J. Appl. Phys., vol. 30, Supplement, pp. 120S-129S, Apr. 1959.
- [4] A. H. Morrish, The Physical Principles of Magnetism. New York: Wiley, 1965, pp. 340-360.
- [5] E. A. Guggenheim, "Thermodynamics, classical and statistical," in *Encyclopedia of Physics*, vol. III/2, S. Flügge, Ed. Berlin: Springer-Verlag, 1959, pp. 1-118. See especially pp. 47-59.
- [6] E. W. Montroll, "Principles of statistical mechanics and kinetic theory of gases," in *Handbook of Physics*, 2d ed., E. U. Condon and H. Odishaw, Eds. New York: McGraw-Hill, 1967, pp. 5-13-5-33. See especially sect. 8, pp. 5-21-5-33.
- [7] S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes. New York: McGraw-Hill, 1941.
- [8] L. Néel, "Theoretical remarks on ferromagnetism at low temperatures," in Progress in Low Temperature Physics, vol. 1, C. J. Gorter, Ed. Amsterdam: North-Holland, 1955, pp. 336-343.
- [9] L. Weil, "Experimental research on ferromagnetism at very low temperatures," in Progress in Low Temperature Physics, vol. 1, C. J. Gorter, Ed. Amsterdam: North-Holland, 1955, pp. 347-350.
- [10] Ref. [4], p. 350.
- [11] Ref. [4], pp. 543 and 549.
- [12] W. F. Brown, Jr., "Thermal fluctuations of a single-domain
- particle," Phys. Rev., vol. 130, pp. 1677-1686, June 1963. S. Chandresekhar, "Stochastic problems in physics and astron-omy," Rev. Mod. Phys., vol. 15, pp. 1-89, Jan. 1943. See es-[13] pecially pp. 20-44.

- [14] M. C. Wang and G. E. Uhlenbeck, "On the theory of the Brownian motion II," Rev. Mod. Phys., vol. 17, pp. 323-342, Apr.-July 1945. See especially pp. 331-332.
- [15] Selected Papers on Noise and Stochastic Processes, N. Wax, Ed. New York: Dover, 1954. Contains reprints of Refs. [13], [14], and [18].
- [16] D. A. Smith and F. A. de Rozario, "A classical theory of superparamagnetic relaxation," J. Magnetism and Magnetic Materials, vol. 3, pp. 219-233, Sept./Oct. 1976.
- [17] H. Cramér, Mathematical Methods of Statistics. Princeton, NJ: Princeton Univ. Press, 1946, pp. 213-218.
- [18] G. E. Uhlenbeck and L. S. Ornstein, "On the theory of the Brownian motion," Phys. Rev., vol. 36, pp. 823-841, Sept. 1, 1930.
- [19] Ref. [14], pp. 341-342.
- [20] Ref. [17], pp. 100-102.
- [21] E. D. Rainville, Intermediate Differential Equations, 2d ed. New York: Chelsea, 1972, pp. 63-67 and ch. 6-11.
- A. Aharoni, "Thermal agitation of single domain particles," Phys. [22] Rev. B, vol. 135, pp. 447-449, July 1964.
- [23] Ref. [13], pp. 63-68.
- [24] W. F. Brown, Jr., "Time constants of superparamagnetic particles," Physica, vols. 86-88 B, pp. 1423-1424, 1977 (Proc. International Conference on Magnetism, ICM '76).
- [25] A. Anaroni, "Effect of a magnetic field on the superparamagnetic relaxation time, Phys. Rev., vol. 17, pp. 793-796, Jan. 1969.
- [26] H. Jeffreys and B. S. Jeffreys, Methods of Mathematical Physics, 3d ed. Cambridge and London, England: Cambridge Univ. Press, 1956, pp. 485-487 (pp. 455-456 in 1st ed., 1946; pp. 485-487 in 2d ed., 1950).
- [27] I. Eisenstein and A. Aharoni, "Asymptotic superparamagnetic time constants for cubic anisotropy. I. Positive anisotropy. II. Negative anisotropy constant," Phys. Rev. B, vol. 16, pp. 1278-1284 and 1285-1290, Aug. 1977.
- [28] V. A. Ignatchenko and R. S. Gekht, "Dynamic hysteresis of a superparamagnet," Sov. Phys. JETP, vol. 40, pp. 750-754, Oct. 1974.
- [29] Yu. L. Raikher and M. I. Shliomis, "Theory of dispersion of the magnetic susceptibility of fine ferromagnetic particles," Sov. Phys. JETP, vol. 40, pp. 526-532, Sept. 1974.
- [30] M. I. Shliomis, "Magnetic Fluids," Sov. Phys. Usp., vol. 17, pp. 153-169, Sept.-Oct. 1974.
- M. A. Martsenyuk, Yu. L. Raikher, and M. I. Shliomis, "Kinetics [31] of magnetization of suspensions of ferromagnetic particles," Sov. Phys. JETP, vol. 38, pp. 413-416, Feb. 1974.