Thermal Fluctuations of a Single-Domain Particle

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A sufficiently fine ferromagnetic particle has a uniform vector magnetization whose magnitude is essentially constant, but whose direction fluctuates because of thermal agitation. The fluctuations are important in superparamagnetism and in magnetic aftereffect. The problem is approached here by methods familiar in the theory of stochastic processes. The "Langevin equation" of the problem is assumed to be Gilbert's equation of motion augmented by a "random-field" term. Consideration of a statistical ensemble of such particles leads to a "Fokker-Planck" partial differential equation, which describes the evolution of the probability density of orientations. The random-field concept, though convenient, can be avoided by use of the fluctuation-dissipation theorem. The Fokker-Planck equation, in general, is complicated by the presence of gyroscopic terms. These drop out in the case of axial symmetry: then the problem of finding nonequilibrium solutions can be restated as a minimization problem, susceptible to approximate treatments. The case of energy barriers large in comparison with kT is treated both by approximate minimization and by an adaptation of Kramers' treatment of the escape of particles over barriers. The limits of validity of the discrete-orientation approximation are discussed.

1. INTRODUCTION

A SUFFICIENTLY fine ferromagnetic particle consists of a single magnetic "domain."[1] The direction of its magnetization $\mathbf{M}$ is determined by the applied field $\mathbf{H}$ and by internal forces. Let the free energy per unit volume be $V(\theta,\phi)$, where θ and ϕ are angular coordinates that describe the orientation of $\mathbf{M}$; and let v be the volume of the particle. When the difference between the maximum and minimum values of $V(\theta,\phi)v$ is very large in comparison with the thermal energy kT, we may (for any reasonable measurement times) ignore thermal agitation and calculate the static magnetization curves by simply minimizing V (with respect to θ and ϕ) at each $\mathbf{H}$. This is the familiar Stoner-Wohlfarth[2] calculation; it leads to hysteresis, because in certain field ranges there are two or more minima, and transitions between them are neglected. When the differences in $V(\theta,\phi)v$ are very small in comparison with kT, thermal agitation causes continual changes in the orientation of the moment of an individual particle; and in an ensemble of such particles, it maintains a distribution of orientations characteristic of statistical equilibrium, so that the number of particles with orientation within solid angle $d\Omega(=\sin\theta d\theta d\phi)$ is proportional to $e^{-Vv/kT}d\Omega$. The behavior is like that of an ensemble of paramagnetic atoms; there is no hysteresis. This phenomenon is called "superparamagnetism."[3] Under intermediate conditions, changes of orientation occur, with relaxation times comparable with the time of a measurement; the result is an observable lag of magnetization changes behind field changes, a phenomenon called "magnetic after effect" or "magnetic vicosity."[4] Each of the three types of behavior—stable ferromagnetism, superparamagnetism, and lagging response—is useful for some purposes but undesirable for others, so that theoretical understanding of each is of practical importance. Furthermore, an understanding of the nonequilibrium behavior of this relatively simple system may contribute to the understanding of more complicated processes, such as thermal nucleation of domain structures.[5]

This problem can be approached through simplifications that have proved successful in the theory of the Brownian motion and other stochastic processes.[6] The most important simplification is the assumption that the random thermal forces have correlation times much shorter than the response times of the system (e.g,. of the Brownian particle). This simplification makes possible the replacement of an integral equation (the Smoluchowski or Chapman-Kolmogoroff equation) by a partial differential equation (the Fokker-Planck equation). In effect, it reduces the random forces to a "purely random" process, with a "white" spectrum. According to the quantum-mechanical Nyquist formula,[7,8] the spectrum of thermal-agitation forces may be regarded as white up to a frequency of order kT/h ($\approx 10^{13}$ sec^{-1} at room temperature); this corresponds to correlation times of order 10^{-13} sec. The response time of a single-domain particle is of the order of the reciprocal of its gyromagnetic resonance fre-

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[1] For a summary of the theory, see W. F. Brown, Jr., *Magnetostatic Principles in Ferromagnetism* (North-Holland Publishing Company, Amsterdam, 1962), Chap. 6.

[2] E. C. Stoner and E. P. Wohlfarth, Phil. Trans. Roy. Soc. (London) **A240**, 599 (1948).

[3] For a review, see C. P. Bean and J. D. Livingston, Suppl. J. Appl. Phys. **30**, 120S (1959).

[4] L. Néel, Ann. Géophys. **5**, 99 (1949).

[5] A. Aharoni, J. Appl. Phys. **33**, 1324 (1962).

[6] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943), Chap. II; M. C. Wang and G. E. Uhlenbeck, *ibid.* **17**, 323 (1945). Both these papers are reprinted in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, Inc., New York, 1954).

[7] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

[8] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, London, 1958), Chap. 12.

quency, i.e., $\approx 10^{-10}$ sec.[9] The basic assumption of the Brownian-motion treatment is, therefore, allowable.

In previous treatments of this problem,[3] it has usually been assumed that $(V_{\max}-V_{\min})v/kT$ is large enough to justify a discrete-orientation model. Thus, when $V=V(\theta)$, with minima V_1 and V_2 at $\theta=0$ and π and with a maximum V_m at $\theta_m(0<\theta_m<\pi)$, it is assumed that n_1 particles of an ensemble have $\theta=0$ (orientation 1) and n_2 have $\theta=\pi$ (orientation 2), and that a particle in orientation i $(=1$ or $2)$ has probability ν_{ij} per unit time of jumping to orientation j $(=2$ or $1)$. The approach to statistical equilibrium is then described by the equation

$$\dot{n}_1=-\dot{n}_2=n_2\nu_{21}-n_1\nu_{12}. \tag{1.1}$$

By analogy with other such problems, one writes

$$\nu_{ij}=c_{ij}e^{-(V_m-V_i)v/kT} \tag{1.2}$$

and sets c_{ij} equal to some quantity associated with the particle and having the dimensions of a frequency—for example, the natural frequency of gyromagnetic precession about orientation i. This simple model will break down eventually as v/T decreases, because the distribution will no longer be sufficiently concentrated near $\theta=0$ and π. One purpose of the present work is to find at what v/T the model becomes unreliable.

The first detailed calculation was that of Néel.[4] Some steps in Néel's derivation fall short of completeness,[10] and it provides no criterion for the validity of the discrete-orientation model.

Stacey[11] has proposed for "a domain or domain wall" a formula of the form (1.2) with $c_{ij}=(\pi^2/6\sqrt{3})(kT/h)$. He derives this formula by assuming that the random forces have an upper cutoff frequency of order kT/h (he thereby omits the zero-point energy of the equivalent oscillators), and by identifying the energy available for surmounting the barrier with an energy associated with the random field. Thus, he neglects altogether the process by which the system under study acquires the energy from the random field; that is, he assumes an instantaneous response of the moment to the field. According to the estimates presented above, it is this response time, and not the correlation time of the field, that limits the rate of fluctuation of the moment.

The theory to be presented is based on a Brownian-motion approach. It uses the discrete-orientation simplification only as an approximation valid under certain special conditions. The basic model is described in detail in Sec. 2; the corresponding Fokker-Planck equation is derived in Sec. 3. Further calculations, related to the case of axial symmetry, are presented in Sec. 4. Conclusions are drawn in Sec. 5.

[9] For example, W. F. Brown, Jr., J. P. Hanton, and A. H. Morrish [Suppl. J. Appl. Phys. **31**, 214S (1960)], Table I, find resonance frequencies of 4.45 to 5.20 kMc/sec for four γ-Fe_2O_3 powders of different axial ratios.

[10] W. F. Brown, Jr., Suppl. J. Appl. Phys. **30**, 130S (1959).

[11] F. D. Stacey, Proc. Phys. Soc. (London) **73**, 136 (1959).

2. BASIC MODEL

An individual particle has uniform vector magnetization $\mathbf{M}$, of magnitude M_s determined by the temperature T. The orientation of $\mathbf{M}$ is described by angles θ and ϕ such that $M_x=M_s\sin\theta\cos\phi$, $M_y=M_s\sin\theta\sin\phi$, $M_z=M_s\cos\theta$. A particle with orientation (θ,ϕ) will be assumed to be in internal thermodynamic equilibrium at temperature T, with Helmholtz free energy per unit volume $A(\theta,\phi,T)$ determined by crystalline anisotropy, magnetic self-energy ("shape anisotropy"), or both. The particle is not necessarily in external equilibrium with the applied field $\mathbf{H}$. The Gibbs free energy per unit volume is[12] $V(\theta,\phi,T,H)=A(\theta,\phi,T)-\mathbf{M}\cdot\mathbf{H}$, which we shall write simply $V(\theta,\phi)$; the total (Gibbs) free energy is $V(\theta,\phi)v$, where v is the particle volume.

In the absence of thermal agitation, changes of $\mathbf{M}$ are assumed to obey Gilbert's[13] equation

$$d\mathbf{M}/dt=\gamma_0\mathbf{M}\times[-\partial V/\partial\mathbf{M}-\eta d\mathbf{M}/dt], \tag{2.1}$$

where γ_0 is the ratio of magnetic moment to angular momentum, and where η is a dissipation constant; $\partial V/\partial\mathbf{M}$ means the vector whose components are $\partial V/\partial M_x$, etc. [If Eq. (2.1) is solved for $d\mathbf{M}/dt$, the result is of the same form as the Landau-Lifshitz[14] equation.] When $V=-\mathbf{M}\cdot\mathbf{H}$, $-\partial V/\partial\mathbf{M}=\mathbf{H}$; thus in general $-\partial V/\partial\mathbf{M}$ represents the conservative part, and $-\eta d\mathbf{M}/dt$ the dissipative part, of an "effective field."

A particle with instantaneous moment-orientation (θ,ϕ) can be represented by a point on the unit sphere. A statistical ensemble of such particles can be represented by a distribution of points over the unit sphere, with surface density $W(\theta,\phi,t)$; as the particles undergo changes of moment orientation, the representative points move, and there is a net surface-current density $\mathbf{J}$. The total number of points is conserved; we may normalize $\int W d\Omega$ to unity, so that W is a probability density, or to some large number, so as to avoid the mental difficulty of a fractional number of points in $d\Omega$. Because of the conservation of points, W and $\mathbf{J}$ satisfy a continuity equation

$$\partial W/\partial t=-\nabla\cdot\mathbf{J}; \tag{2.2}$$

here and hereafter, expressions containing the operator ∇ are to be expressed in spherical coordinates with the radial terms omitted. In the absence of thermal agitation, $\mathbf{J}=W\mathbf{v}$, where $\mathbf{v}$ is the velocity of a representative point at (θ,ϕ); that is, $\mathbf{v}=(d\mathbf{M}/dt)/M_s$, where $d\mathbf{M}/dt$ can be found from Eq. (2.1). Insertion of this $\mathbf{J}$ into Eq. (2.2) gives a partial differential equation for $W(\theta,\phi,t)$; it describes how W would decay toward static equilibrium under conditions of appreciable dissipation but negligible thermal agitation. We shall

[12] See reference 1, p. 96 ff.

[13] T. L. Gilbert, Phys. Rev. **100**, 1243 (1955).

[14] L. Landau and E. Lifshitz, Phys. Z. Sowjetunion **8**, 153 (1935).

see later [cf. Eq. (3.22)] that this is the limiting case $T/v \to 0$.

We now suppose that in the presence of thermal agitation, the dissipative "effective field", $-\eta d\mathbf{M}/dt$ in Eq. (2.1), describes only the statistical (ensemble) average of rapidly fluctuating random forces, and that for an individual particle this expression must be augmented by a term $\mathbf{h}(t)$ whose statistical average is zero. Thus, the "Langevin equation" [15] of our stochastic process is

$$(d\mathbf{M}/dt)=\gamma_0\mathbf{M}\times[-\partial V/\partial\mathbf{M}-\eta(d\mathbf{M}/dt)+\mathbf{h}(t)]. \quad (2.3)$$

Concerning the components $h_i(t)$ $(i=1, 2, 3)$ of the "random field" $\mathbf{h}(t)$ we make the following assumptions: that the process $\mathbf{h}(t)$ is stationary; that the joint distribution of any finite set of the quantities $h_{i'}(t')$, $h_{i''}(t'')$, $\cdots$ is normal (Gaussian), with means equal to zero; that $h_i(t)$ and $h_j(t+\tau)$ are correlated only for time intervals τ much shorter than the time required for an appreciable change of $\mathbf{M}$ according to Eq. (2.1); and that the statistical properties of $h_i(t)$ are independent of the orientation of the x, y, and z axes.

These assumptions, apart from the last, are similar to those made about random forces in Brownian motion theory.[6] The last assumption, that the statistical properties are isotropic, is made primarily to simplify the calculation; the anisotropic case will be discussed briefly at the end of Sec. 3.

By virtue of the correlation assumptions, we may simplify the process to a purely random one and write the correlation functions

$$\langle h_i(t)h_j(t+\tau)\rangle=\mu_{ij}\delta(\tau), \quad (2.4)$$

where, because of the stationarity, μ_{ij} is a constant; $\langle\ \rangle$ means "statistical average of." For isotropy of the statistical properties, $\mu_{ij}=\mu\delta_{ij}$, where μ is a single constant. Thus

$$\langle h_i(t)\rangle=0, \quad \langle h_i(t)h_j(t+\tau)\rangle=\mu\delta_{ij}\delta(\tau). \quad (2.5)$$

It follows that if

$$K_i\equiv\int_t^{t+\Delta t} h_i(t')dt', \quad (2.6)$$

then

$$\langle K_i\rangle=0, \quad \langle K_iK_j\rangle=\mu\delta_{ij}\Delta t. \quad (2.7)$$

The next step is to use the Langevin equation (2.3) and the statistical properties of $\mathbf{h}(t)$ to calculate the quantities needed in the Fokker-Planck equation. The calculation can be carried out either in angular coordinates (θ,ϕ) or in Cartesian coordinates (x,y,z) in the space of representative points, in which the unit sphere is $x^2+y^2+z^2=1$. That Cartesian coordinates can be used results from the fact that Eq. (2.3) keeps each representative point on a sphere $x^2+y^2+z^2=\text{const}$; we may, therefore, replace the surface density $W(\theta,\phi)$ by a volume density of representative points, ultimately to be of the form $\delta(r-1)W(\theta,\phi)$. The Cartesian method has the advantage of symmetry but is no less laborious; we shall therefore present only the (θ,ϕ) method.

This calculation will be carried out in Sec. 3. First, however, we digress to present a simpler, intuitive method of taking account of thermal agitation in Eq. (2.2). As has been seen, $\mathbf{J}$ in the absence of thermal agitation is equal to $W\mathbf{v}$, where $\mathbf{v}$ is $(d\mathbf{M}/dt)/M_s$ as computed from Eq. (2.1), i.e., with neglect of thermal agitation. Let us now add to this $\mathbf{J}$ a diffusion term $-k'\nabla W$; its tendency is to make the distribution more nearly uniform. Direct justification of this intuitive procedure would be difficult; but in fact it gives the same result as the Fokker-Planck method of Sec. 3, with considerably less labor.

The intuitive procedure gives for the components of J

$$\left.\begin{aligned} J_\theta&=-\left[\left(h'\frac{\partial V}{\partial\theta}-g'\frac{1}{\sin\theta}\frac{\partial V}{\partial\phi}\right)W+k'\frac{\partial W}{\partial\theta}\right],\\ J_\phi&=-\left[\left(g'\frac{\partial V}{\partial\theta}+h'\frac{1}{\sin\theta}\frac{\partial V}{\partial\phi}\right)W+k'\frac{1}{\sin\theta}\frac{\partial W}{\partial\phi}\right],\end{aligned}\right\} \quad (2.8)$$

where

$$h'=\frac{\eta}{(1/\gamma_0^2)+\eta^2M_s^2}, \quad g'=\frac{1/\gamma_0}{M_s[(1/\gamma_0^2)+\eta^2M_s^2]}; \quad (2.9)$$

substitution of (2.8) in (2.2) gives

$$\begin{aligned}\frac{\partial W}{\partial t}=&\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\left[\left(h'\frac{\partial V}{\partial\theta}-g'\frac{1}{\sin\theta}\frac{\partial V}{\partial\phi}\right)W+k'\frac{\partial W}{\partial\theta}\right]\right\}\\ &+\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\left\{\left(g'\frac{\partial V}{\partial\theta}+h'\frac{1}{\sin\theta}\frac{\partial V}{\partial\phi}\right)W\right.\\ &\left.+k'\frac{1}{\sin\theta}\frac{\partial W}{\partial\phi}\right\}. \quad (2.10)\end{aligned}$$

The Fokker-Planck method will lead directly to the partial differential equation (2.10), without introduction of the current-density components J_θ and J_ϕ.

3. THE FOKKER-PLANCK EQUATION

Let $x_1=\theta$, $x_2=\phi$; and let $P(x_1,x_2,t)dx_1dx_2$ be the probability of a value in dx_1dx_2 at time t. Then the Fokker-Planck equation is[16]

$$\frac{\partial P}{\partial t}=-\frac{\partial}{\partial x_i}(A_iP)+\frac{1}{2}\frac{\partial^2}{\partial x_i\partial x_j}(B_{ij}P). \quad (3.1)$$

Summation over repeated subscripts is understood. The quantities A_i and B_{ij} are functions of x_1 and x_2 defined

[15] S. Chandrasekhar, reference 6, Eq. (184); M. C. Wang and G. E. Uhlenbeck, reference 6, Eq. (48).

[16] S. Chandrasekhar, reference 6, p. 31 ff.; M. C. Wang and G. E. Uhlenbeck, reference 6, Eq. (39a).

by

$$A_i=\lim_{\Delta t\to 0}\frac{1}{\Delta t}\langle\Delta x_i\rangle,\quad B_{ij}=\lim_{\Delta t\to 0}\frac{1}{\Delta t}\langle\Delta x_i\Delta x_j\rangle,\qquad(3.2)$$

where Δx_i is the change in x_i in time Δt; the statistical averages $\langle\ \rangle$ are to be evaluated by use of the Langevin equation (2.3) and the statistical properties (2.5) of $\mathbf{h}(t)$.

If Eq. (2.3) is written in angular coordinates and the resulting two simultaneous equations are solved for $\dot\theta$ and $\dot\phi$, the result is

$$\begin{aligned}\dot\theta&=h'P_\theta'-g'(\sin\theta)^{-1}P_\phi',\\ \dot\phi&=g'(\sin\theta)^{-1}P_\theta'+h'(\sin\theta)^{-2}P_\phi'.\end{aligned}\qquad(3.3)$$

Here h' and g' are given by Eq. (2.9), and

$$P_\theta'=-\partial V/\partial\theta+P_\theta,\quad P_\phi'=-\partial V/\partial\phi+P_\phi,\qquad(3.4)$$

where P_θ and P_ϕ are the contributions of $\mathbf{h}(t)$ to the generalized forces (torques) corresponding to θ and ϕ:

$$\begin{aligned}P_\theta&=M_s\{h_1(t)\cos\theta\cos\phi+h_2(t)\cos\theta\sin\phi-h_3(t)\sin\theta\},\\ P_\phi&=M_s\{-h_1(t)\sin\theta\sin\phi+h_2(t)\sin\theta\cos\phi\}.\end{aligned}\qquad(3.5)$$

Equations (3.3), when expressed directly in terms of the random-field components $h_i(t)$, are of the form

$$\dot x_i=F_i(x)+G_{ik}(x)h_k(t)\quad(i=1,2,\cdots,n),\qquad(3.6)$$

where x represents the n variables $x_1, x_2, \cdots, x_n$ (here, $n=2$), and summation over m values of k (here, $m=3$) is understood. In the corresponding equations of standard Brownian-motion theory, $F_i(x)$ and $G_{ik}(x)$ are constants; the nonlinearity of the present problem complicates the calculation. To evaluate A_i and B_{ij} by Eqs. (3.2), we need Δx_i only to terms of order Δt for A_i and only to terms of order $(\Delta t)^{1/2}$ for B_{ij}. For a typical member of the ensemble, Δx_i itself is of order $(\Delta t)^{1/2}$, since $\int_t^{t+\Delta t}h_k(t')dt'$ is of this order by the second Eq. (2.7).

For simplicity of notation, shift the origins so that at the beginning of the interval Δt considered, $t=0$ and $x_i=0$. Expand $F_i(x)$ and $G_{ik}(x)$ in Taylor's series:

$$\begin{aligned}F_i(x)&=F_i+F_{i,j}x_j+\tfrac12F_{i,jl}x_jx_l+\cdots,\\ G_{ik}(x)&=G_{ik}+G_{ik,j}x_j+\tfrac12G_{ik,jl}x_jx_l+\cdots,\end{aligned}\qquad(3.7)$$

where, for example, $F_{i,j}$ means $\partial F_i/\partial x_j$ evaluated at $x_1=x_2=\cdots=0$. Then by integration of Eq. (3.6) with respect to t, we get

$$\begin{aligned}x_i(t)=F_it+F_{i,j}\int_0^t x_j(t_1)dt_1+\cdots+G_{ik}\int_0^t h_k(t_1)dt_1\\ +G_{ik,j}\int_0^t x_j(t_1)h_k(t_1)dt_1+\cdots.\end{aligned}\qquad(3.8)$$

From (2.7) it follows that the terms on the right in (3.8) are of the following orders in the small quantities x and t: t, xt, $\cdots$, $t^{1/2}$, $xt^{1/2}$, $\cdots$. We deduce that x is of order $t^{1/2}$ and that the terms are of the following orders in t: t, $t^{3/2}$, $\cdots$, $t^{1/2}$, t, $\cdots$. To the first order in t,

$$x_i(t)=F_it+G_{ik}\int_0^t h_k(t_1)dt_1+G_{ik,j}\int_0^t x_j(t_1)h_k(t_1)dt_1;\qquad(3.9)$$

and in the last integral we may express $x_j(t_1)$ to order $t^{1/2}$, namely, as $G_{jl}\int_0^{t_1}h_l(t_2)dt_2$. Thus,

$$x_i(t)=F_it+G_{ik}\int_0^t h_k(t_1)dt_1+G_{ik,j}G_{jl}\int_0^t dt_1\int_0^{t_1}h_k(t_1)h_l(t_2)dt_2.\qquad(3.10)$$

The second term is of order $t^{1/2}$, the others of order t; therefore, to the first order in t

$$x_i(t)x_j(t)=G_{ik}G_{jl}\int_0^t dt_1\int_0^t h_k(t_1)h_l(t_2)dt_2.\qquad(3.11)$$

We now take the statistical average in (3.10) and (3.11) divide by t, and let $t\to 0$. It is easily seen that the double integral in (3.10) is half that in (3.11). Thus, by use of (2.7)

$$A_i=\lim_{t\to0}\frac1t\langle x_i(t)\rangle=F_i+\tfrac12\mu G_{ik,j}G_{jk},\qquad(3.12)$$

$$B_{ij}=\lim_{t\to0}\frac1t\langle x_i(t)x_j(t)\rangle=\mu G_{ik}G_{jk}.\qquad(3.13)$$

In the original notation, at the instant t considered the variables have values x_i; the functions F_i, G_{jk}, and $G_{ik,j}=\partial G_{ik}/\partial x_j$ are evaluated at these values of the x's.

In standard Brownian-motion theory, quantities such as $\langle x_i(t)x_j(t)x_p(t)\rangle$ vanish faster than Δt, so that Eq. (3.1) contains no partial derivatives of third or higher order. This remains true here, for the only effect of the variability of F_i and G_{ik} in (3.6) is to add terms of still higher order in Δt.

In the present application

$$\begin{aligned}F_1&=-h'V_\theta+g'(\sin\theta)^{-1}V_\phi,\\ F_2&=-g'(\sin\theta)^{-1}V_\theta-h'(\sin\theta)^{-2}V_\phi,\end{aligned}\qquad(3.14)$$

where

$$V_\theta\equiv\partial V/\partial\theta,\text{ etc.};$$

and

$$\begin{aligned}M_s^{-1}G_{11}&=h'\cos\theta\cos\phi+g'\sin\phi,\\ M_s^{-1}G_{12}&=h'\cos\theta\sin\phi-g'\cos\phi,\\ M_s^{-1}G_{13}&=-h'\sin\theta,\\ M_s^{-1}G_{21}&=g'\cot\theta\cos\phi-h'\csc\theta\sin\phi,\\ M_s^{-1}G_{22}&=g'\cot\theta\sin\phi+h'\csc\theta\cos\phi,\\ M_s^{-1}G_{23}&=-g'.\end{aligned}\qquad(3.15)$$

Partial differentiation of Eqs. (3.15) with respect to θ and ϕ gives the formulas for the twelve quantities $G_{ik,j}$ ($i,j=1,2$; $k=1,2,3$). Substitution of the values of F_i, G_{jk}, and $G_{ik,j}$ in Eqs. (3.12) and (3.13) gives

$$\begin{aligned}A_1&=-h'V_\theta+g'(\sin\theta)^{-1}V_\phi+\tfrac12\mu M_s^2(h'^2+g'^2)\cot\theta,\\ A_2&=-g'(\sin\theta)^{-1}V_\theta-h'(\sin\theta)^{-2}V_\phi,\end{aligned}\qquad(3.16)$$

$$\begin{aligned}B_{11}&=\mu M_s^2(h'^2+g'^2),\\ B_{12}&=B_{21}=0,\\ B_{22}&=\mu M_s^2(h'^2+g'^2)\csc^2\theta.\end{aligned}\qquad(3.17)$$

Substitution of (3.16) and (3.17) in (3.1) gives the partial differential equation satisfied by P. By the definitions of P and W,

$$P=W\sin\theta.\qquad(3.18)$$

With some rearranging and some manipulating of derivatives, the equation satisfied by W can be reduced to the form (2.10), with

$$k'=\tfrac12\mu M_s^2(h'^2+g'^2)=\frac{\tfrac12\mu\gamma_0^2}{1+\gamma_0^2\eta^2M_s^2}.\qquad(3.19)$$

To relate the constant k' or μ to other constants, we impose the requirement that in statistical equilibrium ($\partial W/\partial t=0$), W must reduce to

$$W_0=A_0e^{-V(\theta,\phi)v/kT}\qquad(3.20)$$

in accordance with statistical mechanics. Substitution of (3.20) in (2.10) leads to an identity only if

$$k'=kTh'/v,\qquad(3.21)$$

whence

$$\mu=2kT\eta/v.\qquad(3.22)$$

Without the terms in g', the partial differential equation (2.10) would be formally the same as the

corresponding equation for an electrically permanently polarized particle or molecule (as in Debye's theory of polar molecules) with inertia neglected. In the magnetic problem ordinary inertia plays no role, but instead we have the gyroscopic terms in g'. In statistical equilibrium these terms cancel out of the partial differential equation (2.10) but not out of the current-density components (2.8); there is a steady divergenceless current density, i.e., a mean precession, even in equilibrium.

By assuming a solution of the form $T(t)F(\theta,\phi)$, we can show that the general solution of Eq. (2.10) is of the form

$$W=W_0+\sum_{n=1}^{\infty} A_n F_n(\theta,\phi)e^{-p_n t}, \tag{3.23}$$

where F_n satisfies (2.10) with $\partial/\partial t$ replaced by $-p_n$. The eigenvalues p_n and the corresponding eigenfunctions F_n are determined by the requirements of single-valuedness and of finiteness; the equilibrium term W_0 is the eigenfunction corresponding to the eigenvalue $p_0=0$. The constant A_0 in W_0 is determined by the normalization condition, the constants A_n by the initial conditions, e.g., by the prescribed values of W at $t=0$. Solution for $F_n(\theta,\phi)$ by separation of the variables θ and ϕ is in general not possible, because V in general depends on both variables and because derivatives with respect to both occur in the gyroscopic terms.

At this point two facts are helpful. First, except in the very early stages of an approach to equilibrium, the only appreciable time-dependent term in Eq. (3.23) will be the term $n=1$, corresponding to the longest finite time constant $1/p_1$. Second, the problems of greatest interest are those in which the free-energy density has axial symmetry, $V=V(\theta)$. If the initial distribution also has axial symmetry (e.g., when a uniaxial particle is subject to a change in value of an applied field always directed along the particle axis), we may assume $W=W(\theta)$. The gyroscopic terms then drop out of Eq. (2.10) (though there is still a current density J_ϕ), and the equation for F_n reduces to an ordinary differential equation. Section 4 will be devoted to this case.

First, however, we stop to consider the second Eq. (2.5) and its anisotropic generalization (2.4) from a different point of view. Choose new coordinate axes with Oz along the direction that $\mathbf{M}$ has at some instant t_0. Consider a time interval (t_1,t_2) about t_0; take t_2-t_1 short enough so that throughout it M_x and M_y (referred to the new axes) are small, but still long in comparison with the correlation times of the thermal fluctuations. Then by expressing Gilbert's equation (2.1) to the first order of small quantities and solving for $\dot{M}_x$ and $\dot{M}_y$, we find

$$\left.\begin{aligned}\dot{M}_x&=M_s^2(h'\mathcal{H}_x-g'\mathcal{H}_y),\\ \dot{M}_y&=M_s^2(g'\mathcal{H}_x+h'\mathcal{H}_y),\end{aligned}\right\} \tag{3.24}$$

where

$$\mathcal{H}_x=-\partial V/\partial M_x,\quad \mathcal{H}_y=-\partial V/\partial M_y; \tag{3.25}$$

we suppose V expressed in the form $V(M_x,M_y)$. To the linearized set of equations (3.24) we may apply the fluctuation-dissipation theorem[17] and the theory associated with it. We then regard Eqs. (3.24) as describing only the behavior of the statistical means of M_x and M_y; on these are superposed spontaneous fluctuations δM_x and δM_y, whose statistical properties (and those of their time derivatives) can be found by use of the standard formulas of the theory. From this point of view the "random-field" components h_x, h_y are formal concepts, introduced for convenience, and defined as the values of $\mathcal{H}_x$ and $\mathcal{H}_y$ necessary, according to Eqs. (3.24), to produce the fluctuations $\delta\dot{M}_x$ and $\delta\dot{M}_y$. In this way we find

$$\langle h_i(t)h_j(t+\tau)\rangle=(2kT\eta/v)\delta_{ij}\rangle(\tau) \tag{3.26}$$

for $i,j=1,2$ in the new xyz axes. The component h_3 has no effect and may be assigned at will. If we require it to have such properties that (3.26) holds also when $i=3$ or $j=3$ or both, then (3.26) becomes invariant to a rotation of the coordinate axes and, therefore, holds for $i,j=1,2,3$ in the original axes, in which $\mathbf{M}$ has an arbitrary direction. We may now remove the restriction to a short time interval, since the same result follows for any t_0.

Equation (3.26) is equivalent to the second Eq. (2.5) with μ given by Eq. (3.22). From this alternative derivation it can be seen that the anisotropic generalization would require not only replacement of (2.5) by (2.4), but also replacement of the damping term $-\eta d\mathbf{M}/dt$ in Gilbert's equation (2.1) by an anisotropic term.

Strictly, the moment of a particle undergoes thermal fluctuations of its magnitude as well as of its direction. The exchange forces keep the fluctuations of magnitude small, and in the present calculation we simply neglect them.

4. THE CASE OF AXIAL SYMMETRY

When V and W are independent of ϕ, Eqs. (2.8) and (2.10) reduce to

$$\left.\begin{aligned}J_\theta&=-[h'(\partial V/\partial\theta)W+k'\partial W/\partial\theta],\\ J_\phi&=-g'(\partial V/\partial\theta)W,\end{aligned}\right\} \tag{4.1}$$

$$\frac{\partial W}{\partial t}=\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\left[h'\frac{\partial V}{\partial\theta}W+k'\frac{\partial W}{\partial\theta}\right]\right\}; \tag{4.2}$$

Equation (3.23) reduces to

$$W=W_0+\sum_{n=1}^{\infty} A_n F_n(\theta)e^{-p_n t}, \tag{4.3}$$

with

$$W_0=A_0 e^{-V(\theta)v/kT}. \tag{4.4}$$

The only effect of the gyroscopic properties is the presence of a current component J_ϕ, which can be ignored in the calculation of W. With

$$x\equiv\cos\theta \tag{4.5}$$

as independent variable, Eq. (4.2) takes the form

$$\frac{\partial W}{\partial t}=\frac{\partial}{\partial x}\left\{[1-x^2]\left[h'\frac{\partial V}{\partial x}W+k'\frac{\partial W}{\partial x}\right]\right\}. \tag{4.6}$$

When $\partial W/\partial t=0$, the differential equation can be integrated directly; imposition of the conditions of

[17] See reference 7; H. B. Callen, M. L. Barasch, and J. L. Jackson, Phys. Rev. **88**, 1382 (1952); H. B. Callen and R. F. Greene, *ibid.* **86**, 702 (1952); R. F. Greene and H. B. Callen, *ibid.* **88**, 1387 (1952); reference 8.

finiteness at $x=\pm 1$ leads again to the equilibrium solution W_0.

The differential equation satisfied by F_n can be written

$$\frac{d}{dx}\left\{[1-x^2]e^{-\beta V}\frac{d}{dx}[e^{\beta V}F]\right\}+\lambda F=0, \tag{4.7}$$

where

$$\beta\equiv v/kT, \quad \lambda\equiv pv/kTh. \tag{4.8}$$

If

$$F=e^{-\beta V}\phi(x), \tag{4.9}$$

this becomes

$$\frac{d}{dx}\left\{(1-x^2)e^{-\beta V}\frac{d\phi}{dx}\right\}+\lambda e^{-\beta V}\phi=0. \tag{4.10}$$

The eigenvalues λ_n are determined by the requirement that ϕ must be finite at $x=\pm 1$. The lowest eigenvalue is $\lambda_0=0$; it corresponds to the equilibrium solution $\phi_0=$const. (Note that the symbol ϕ is now being used in a new sense.)

A. General Principles

Analytical solution of Eq. (4.10) is easy only when $V=$const, or for any finite $V(x)$ in the limit $\beta\rightarrow 0$, i.e., $T\rightarrow\infty$. Then

$$\lambda_n=n(n+1), \quad \phi_n=P_n(x), \tag{4.11}$$

where $P_n(x)$ is a Legendre polynomial. This solution may be used as a starting point in a perturbation calculation for small $\beta(V_{\max}-V_{\min})$.

For other conditions, a more useful starting point is the restatement of the problem as a minimization problem.[18] The nth eigenfunction ϕ_n of Eq. (4.10) minimizes the functional

$$D[\phi]\equiv\int_{-1}^{1}(1-x^2)e^{-\beta V}[\phi'(x)]^2dx \tag{4.12}$$

under the constraints of constant

$$H[\phi]\equiv\int_{-1}^{1}e^{-\beta V}[\phi(x)]^2dx \tag{4.13}$$

and of vanishing

$$H[\phi,\phi_m]\equiv\int_{-1}^{1}e^{-\beta V}\phi(x)\phi_m(x)dx \tag{4.14}$$

for $m=0, 1, 2, \cdots, n-1$; λ_n is equal to the corresponding minimized value of $D[\phi]/H[\phi]$. We are primarily interested in the value of p_1 and, therefore, [cf. the second Eq. (4.8)] of λ_1. For it, the last set of constraints reduces to the single constraint

$$\int_{-1}^{1}e^{-\beta V}\phi_1(x)dx=0, \tag{4.15}$$

since $\phi_0(x)=$const. By approximate minimization one can evaluate λ_1 approximately; and by two approximate minimizations, of which one errs (if at all) upward and the other (if at all) downward, one can set upper and lower bounds to λ_1, and thus to p_1.

When $\beta(V_{\max}-V_{\min})\gg 1$, the case usually encountered, one can use either the approximate method just described or the following physical principle: When high (as compared with kT) energy barriers separate the minima of vV, equilibrium within the distribution about a minimum will be established much faster than equilibrium between different minima. Therefore, except in the initial stages of a transient process, it is legitimate to assume that the distribution about the minimum θ_i is of the form $B_i(t)e^{-\beta V(\theta)}$; the problem then reduces to finding the variation with time of the functions $B_i(t)$, which can be related to quantities $n_i(t)$ [cf. Eq. (1.1)] that describe the relative numbers of particles with orientations near θ_i. A method of formulating and solving this problem is suggested by Kramers' treatment of the escape of particles over potential barriers.[1]

These various approximations will be discussed in the following subsections, B through D.

B. Low-Energy-Barrier Approximation

By standard perturbation theory,[20] we can derive the following series solution of Eq. (4.10) in powers of β:

$$\phi_n=u_n+\beta\sum_m{}' V_{nm}u_m/[n(n+1)-m(m+1)]+\cdots, \tag{4.16}$$

$$\lambda_n=n(n+1)+\beta V_{nn}+\beta^2\sum_m{}' V_{nm}V_{mn}/[n(n+1)-m(m+1)]+\cdots; \tag{4.17}$$

here u_n is the nth normalized eigenfunction for the unperturbed case $V=$const,

$$u_n=[(2n+1)/2]^{1/2}P_n(x), \tag{4.18}$$

and

$$V_{nm}=\int_{-1}^{1}(1-x^2)\frac{du_n}{dx}\frac{dV}{dx}u_m dx. \tag{4.19}$$

In the case of greatest interest, a particle with uniaxial anisotropy constant K in a longitudinal field H,

$$\begin{aligned}V&=-HM_s\cos\theta+K\sin^2\theta\\&=-HM_s x-Kx^2+\text{const.}\end{aligned} \tag{4.20}$$

In this case

$$V_{nm}=-HM_s a_{nm}-2Kb_{nm}, \tag{4.21}$$

[18] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 1, p. 398.

[19] H. A. Kramers, Physica 7, 284 (1940); S. Chandrasekhar, reference 6, pp. 63–70.

[20] R. Courant and D. Hilbert, reference 18, pp. 343–346. In the present case the perturbation $\beta V'(x)$ affects the term in $d\phi/dx$ rather than the term in ϕ in the differential equation, but the changes required are minor. Formulas read from books on quantum mechanics are too specialized in that they assume that the matrix (V_{nm}) is Hermitian; here it is not, for in general V_{nm} and V_{mn} are real and unequal.

where

$$\begin{aligned} a_{n(n-1)}&=n(n+1)/[(2n-1)(2n+1)]^{1/2},\\ a_{n(n+1)}&=-n(n+1)/[(2n+1)(2n+3)]^{1/2},\\ b_{nn}&=n(n+1)/\{(2n-1)(2n+3)\}, \end{aligned} \tag{4.22}$$

$$\begin{aligned} b_{n(n-2)}&=(n-1)n(n+1)/\\ &\quad\{(2n-1)[(2n-3)(2n+1)]^{1/2}\}, \end{aligned} \tag{4.23}$$

$$\begin{aligned} b_{n(n+2)}&=-n(n+1)(n+2)/\\ &\quad\{(2n+3)[(2n+1)(2n+5)]^{1/2}\}; \end{aligned}$$

the other a's and b's vanish. Thus

$$\lambda_1=2-\frac{4}{5}\beta K+\frac{96}{875}(\beta K)^2+\frac{1}{5}(\beta HM_s)^2+\cdots. \tag{4.24}$$

Unfortunately, these formulas apply to the case of least interest, the case in which βK $(=Kv/kT)$ and βHM_s $(=HM_sv/kT)$ are small.

C. High-Energy-Barrier Approximation

Formulas for the case $v(V_{\max}-V_{\min})\gg kT$ can be derived by two methods: the Kramers method and the method of approximate minimization. We consider for simplicity the case in which $V(\theta)$ has a minimum V_1 at $\theta=0$, a minimum V_2 at $\theta=\pi$, and a maximum V_m at $\theta=\theta_m$ $(0<\theta_m<\pi)$, with $\beta(V_m-V_1)\gg1$ $(i=1, 2)$.

In the *Kramers method*[19] we assume from the outset that equilibrium has been attained within the regions $0\leqslant\theta\leqslant\theta_1$ and $\theta_2\leqslant\theta\leqslant\pi$ separately $(\theta_1<\theta_m<\theta_2)$ and that all but a very small fraction of the members of the ensemble have orientations within one or the other of these regions. The choice of θ_1 and θ_2 is not critical, since most of the particles have orientations very close to 0 or π; all that is required is that $e^{-\beta V(\theta_i)}$ be very small in comparison with $e^{-\beta V_i}$ but very large in comparison with $e^{-\beta V_m}$ $(i=1, 2)$, conditions easily satisfied when $\beta(V_m-V_i)\gg1$.

In the regions $(0,\theta_1)$ and (θ_2,π) we have

$$W(\theta)=W_ie^{-\beta[V(\theta)-V_i]}, \quad (i=1,2) \tag{4.25}$$

where $W_1\equiv W(0)$ and $W_2\equiv W(\pi)$. Almost all the particles in $(0,\theta_1)$ have orientations very close to 0, and almost all in (θ_2,π) have orientations very close to π. If we normalize $\int W d\Omega$ to be the total number n of particles, then the numbers n_1 and n_2 in the two groups are

$$n_i=2\pi W_ie^{\beta V_i}I_i, \tag{4.26}$$

with

$$I_1=\int_0^{\theta_1}e^{-\beta V(\theta)}\sin\theta d\theta, \quad I_2=\int_{\theta_2}^{\pi}e^{-\beta V(\theta)}\sin\theta d\theta. \tag{4.27}$$

Because of the rapid decrease of the exponential factor with distance from the minimum of V, we may in I_1 replace $V(\theta)$ by its Taylor's series about 0, truncated at the θ^2 term (the θ term vanishes); replace $\sin\theta$ by θ; and replace the upper limit θ_1 by ∞. With these approximations and the corresponding approximations in I_2, we get

$$I_i=e^{-\beta V_i}/\beta k_i, \tag{4.28}$$

where

$$k_1\equiv V''(0), \quad k_2\equiv V''(\pi). \tag{4.29}$$

In the region (θ_1,θ_2), W is very small; but it must be sufficient to maintain a small net flow of representative points from the overpopulated toward the underpopulated minimum. We assume that this flow can be approximated sufficiently by a divergenceless current density, so that the total current $I=2\pi(\sin\theta)J_\theta$ is independent of θ. Then by the first Eq. (4.1), since $k'=h'/\beta$,

$$\frac{\partial W}{\partial\theta}+\beta\frac{\partial V}{\partial\theta}W=-\frac{\beta I}{2\pi h'\sin\theta}. \tag{4.30}$$

On multiplying by the integrating factor $e^{\beta V}$ and integrating from θ_1 to θ_2, we get

$$We^{\beta V}\Big|_{\theta_1}^{\theta_2}=-(\beta I/2\pi h')I_m, \tag{4.31}$$

where

$$I_m=\int_{\theta_1}^{\theta_2}e^{\beta V}d\theta/\sin\theta. \tag{4.32}$$

In this case we replace V by its Taylor's series about the *maximum*, truncated at the $(\theta-\theta_m)^2$ term; replace $\sin\theta$ by $\sin\theta_m$; and integrate from $-\infty$ to $+\infty$. Then

$$I_m=(2\pi/\beta k_m)^{1/2}e^{\beta V_m}/\sin\theta_m, \tag{4.33}$$

where

$$k_m\equiv-V''(\theta_m). \tag{4.34}$$

Now by Eqs. (4.25), the left member of Eq. (4.31) is $W_2e^{\beta V_2}-W_1e^{\beta V_1}$; or by Eq. (4.26), $(n_2/I_2-n_1/I_1)/2\pi$. Equation (4.31) relates this to the current, I, from the region $(0,\theta_1)$ to the region (θ_2,π). But since practically all the representative points are in these regions, $I=-\dot n_1=\dot n_2$. Equation (4.31), therefore, gives

$$\dot n_1=-\dot n_2=\frac{h'}{\beta I_m}\left(\frac{n_2}{I_2}-\frac{n_1}{I_1}\right). \tag{4.35}$$

This is of the form (1.1), with

$$\nu_{ij}=h'/\beta I_mI_i \quad (i=1,\ j=2 \text{ or } i=2,\ j=1). \tag{4.36}$$

With the approximations (4.28) and (4.33), this becomes

$$\nu_{ij}=c_{ij}e^{-\beta(V_m-V_i)}, \tag{4.37}$$

with

$$c_{ij}=h'k_i(\sin\theta_m)(\beta k_m/2\pi)^{1/2}. \tag{4.38}$$

When V is given by Eq. (4.20), with $K>0$, there are two minima whenever $|H|M_s<2K$. If, following Néel,[4] we define a critical field H_c by

$$H_cM_s\equiv2K, \tag{4.39}$$

then the condition for existence of two minima is $|H|<H_c$. The maximum is at

$$\cos\theta_m=-H/H_c\equiv-\epsilon. \tag{4.40}$$

In this case

$$V_1=-HM_s,\ V_2=+HM_s,\ V_m=\tfrac{1}{2}H_cM_s(1+\epsilon^2), \tag{4.41}$$

$$k_1=H_cM_s(1+\epsilon),\quad k_2=H_cM_s(1-\epsilon),\quad k_m=H_cM_s(1-\epsilon^2). \tag{4.42}$$

Formula (4.44) gives

$$\left.\begin{matrix}c_{12}\\ c_{21}\end{matrix}\right\}=h'\left(\frac{v}{2\pi kT}\right)^{1/2}(H_cM_s)^{3/2}(1\pm\epsilon)^2(1\mp\epsilon) \tag{4.43}$$

$$=\frac{\gamma_0^2\eta M_s}{1+(\gamma_0\eta M_s)^2}\left(\frac{vH_c^3M_s}{2\pi kT}\right)^{1/2}(1-\epsilon^2)(1\pm\epsilon). \tag{4.44}$$

Numerical calculations based on this formula were reported earlier.[10]

To attack the case $\beta(V_m-V_i)\gg1$ by the *method of approximate minimization*, we note that with θ as variable the quantity to be minimized is

$$D[\phi]\equiv\int_0^\pi e^{-\beta V}(d\phi/d\theta)^2\sin\theta d\theta \tag{4.45}$$

and that the constraints are

$$H[\phi]\equiv\int_0^\pi e^{-\beta V}\phi^2\sin\theta d\theta=\text{const}\equiv H \tag{4.46}$$

and

$$H[\phi,\phi_0]\equiv\int_0^\pi e^{-\beta V}\phi\sin\theta d\theta=0. \tag{4.47}$$

Because of the constraint (4.47), ϕ must change sign in $(0,\pi)$. Because of the exponential factor, $H[\phi]$ and $H[\phi,\phi_0]$ depend mostly on the values of ϕ near 0 and π and not on the details of the change from $\phi_1\equiv\phi(0)$ to $\phi_2\equiv\phi(\pi)$, provided it is not concentrated near these points; on the other hand $D[\phi]$ can be kept small only by concentrating the large values of $|d\phi/d\theta|$ near θ_m. We can, therefore, expect to get a good approximation, when $\beta(V_m-V_i)\gg1$, by constraining ϕ to have constant values ϕ_1 in $(0,\theta_1)$ and ϕ_2 in (θ_2,π) and minimizing $D[\phi]$ under the modified constraints $H_1[\phi]=H$ and $H_1[\phi,\phi_0]=0$, where in H_1 the integration extends from 0 to θ_1 and from θ_1 to π, with omission of the very small contribution from the interval (θ_1,θ_2). The choice of θ_1 and $\theta_2(0<\theta_1<\theta_m<\theta_2<\pi)$ is, as before, not critical.

The modified constraints are equivalent to

$$\begin{aligned}\phi_1^2I_1+\phi_2^2I_2&=H,\\ \phi_1I_1+\phi_2I_2&=0,\end{aligned} \tag{4.48}$$

where I_1 and I_2 are again defined by Eqs. (4.27). Equations (4.48) can be solved for ϕ_1 and ϕ_2 (except for an indeterminacy of sign):

$$\begin{aligned}&\phi_1=C/I_1,\quad \phi_2=-C/I_2,\\ &C^2=H/[(1/I_1)+(1/I_2)].\end{aligned} \tag{4.49}$$

We may, therefore, minimize $D[\phi]$ for specified $\phi(\theta_1)=\phi_1$ and $\phi(\theta_2)=\phi_2$. Then in (θ_1,θ_2), ϕ satisfies

$$\frac{d}{d\theta}\left(e^{-\beta V}\frac{d\phi}{d\theta}\sin\theta\right)=0. \tag{4.50}$$

Integration gives

$$d\phi/d\theta=Ae^{\beta V}/\sin\theta, \tag{4.51}$$

and further integration from θ_1 to θ_2 gives

$$AI_m=\phi_1-\phi_2, \tag{4.52}$$

where I_m is defined by Eq. (4.32); this evaluates A. To evaluate $\lambda_1=D[\phi]/H$ we now substitute (4.51) in (4.45) with limits θ_1 and θ_2, since elsewhere $d\phi/d\theta=0$; insert the value of A from (4.52); substitute the values of ϕ_1 and ϕ_2 from (4.49); and divide by H. Thus,

$$p_1=\frac{\lambda_1h'}{\beta}=\frac{h'}{\beta}\frac{1}{I_m}\left(\frac{1}{I_1}+\frac{1}{I_2}\right). \tag{4.53}$$

This method gives directly the reciprocal p_1 of the longest finite time constant. To find the same quantity by the Kramers method, we set $n_2=n-n_1$ ($n=$const) in Eq. (4.35) and transpose the n_1 term to the left; p_1 is the coefficient of n_1. It is equal to $\nu_{12}+\nu_{21}$ and is again given by Eq. (4.53). Thus, the minimization method gives the same time constant as the Kramers method. It also gives formulas for

$$W=e^{-\beta V}(A_0+A_1\phi e^{-p_1t})$$

in the various regions $(0,\theta_1)$, (θ_1,θ_2), and (θ_2,π); these may now be interpreted physically in terms of n_1 and n_2, with the same results as by the Kramers method. The minimization method has the advantage that it justifies, on the basis of a purely mathematical approximation, simplifications which have to be injected arbitrarily in the Kramers calculation; in particular, it avoids the arbitrary assumption of a divergenceless **J** in (θ_1,θ_2).

The further simplifications that follow from the approximations (4.28) and (4.33) may now be introduced as in the Kramers method. Then

$$p_1=\nu_{12}+\nu_{21}=c_{12}e^{-\beta(V_m-V_1)}+c_{21}e^{-\beta(V_m-V_2)}, \tag{4.54}$$

where c_{12} and c_{21} are given by Eq. (4.38).

In equilibrium, Eq. (1.1) with the approximations (4.37)–(4.38) gives

$$n_2/n_1=\nu_{12}/\nu_{21}=(k_1/k_2)e^{-\beta(V_2-V_1)}. \tag{4.55}$$

In general, $k_1\neq k_2$, and, therefore, $n_2/n_1\neq e^{-\beta(V_2-V_1)}=e^{-v(V_2-V_1)/kT}$. The violation of the Boltzmann distribution law is only apparent. The n_1 particles with orientations in $(0,\theta_1)$ are not equivalent to n_1 particles each of orientation $\theta=0$ and free energy V_1v; they

constitute an ensemble with partition function $Z_1=2\pi\nu I_1$ and Gibbs free energy[21] (per particle) $G_1=-kT\ln Z_1$, where $\nu d\Omega$ is the number of microstates for which the moment orientation is within solid-angle element $d\Omega$. It is this free energy G_1, not the value vV_1 characteristic of particles with θ exactly zero, that must be used in the Boltzmann factors to find n_1 and n_2 in equilibrium. With the approximation (4.28),

$$e^{-G_1/kT}=Z_1=2\pi\nu I_1=(2\pi\nu/\beta k_1)e^{-\beta V_1}; \tag{4.56}$$

a similar formula holds with subscript 2. The equilibrium n_i's are in the ratio

$$n_2/n_1=e^{-(G_2-G_1)/kT}=(k_1/k_2)e^{-\beta(V_2-V_1)}, \tag{4.57}$$

in agreement with (4.55).

One can change the power of T in the coefficient of the exponential function in ν_{ij} by including or not including a particular free-energy term, such as that just discussed, in the argument of the exponential. Such terms may be different for single-domain particles, for domain walls, and for other models of magnetization reversal. Therefore, no great significance can be attached to formulas for c_{ij} [in Eqs. (4.37)] that are derived without consideration of the specific properties of the model.

The approximate-minimization method described is easily extended to the case in which $V(\theta)$ has more than two minima separated by energy barriers large in comparison with kT. The results are the same as would be obtained by assuming that n_i particles of the ensemble have orientations near the minimum θ_i and that

$$\dot{n}_i=\sum_j{}' (n_j\nu_{ji}-n_i\nu_{ij}), \tag{4.58}$$

and evaluating the ν_{ij}'s by the Kramers method.

D. Other Approximations

The method of approximate minimization can be used to obtain approximate values of the p_i's and ϕ_i's, and in particular of p_1 and ϕ_1, when neither of the inequalities $v(V_{\max}-V_{\min})\gtrless kT$ is satisfied.

For example, assume a solution of the form $(x=\cos\theta)$

$$\phi=\Sigma_n C_n x^n, \tag{4.59}$$

where the sum may include even or odd powers or both and as many terms as one wishes. Then

$$D[\phi]=\Sigma_n\ \Sigma_m\ C_nC_m nm(q_{n+m-2}-q_{n+m}), \tag{4.60}$$

$$H[\phi]=\Sigma_n\ \Sigma_m\ C_nC_m q_{n+m}, \tag{4.61}$$

where

$$q_\nu=\int_{-1}^{1} e^{-\beta Vx}x^\nu dx. \tag{4.62}$$

The extrema of $D[\phi]/H[\phi]$ satisfy

$$\delta D[\phi]-\lambda\delta H[\phi]=0, \tag{4.63}$$

where

$$\lambda=D[\phi]/H[\phi], \tag{4.64}$$

and where the variables are the C_n's. This gives the homogeneous system of linear equations in the C_n's

$$\Sigma_m\,[nm(q_{n+m-2}-q_{n+m})-\lambda q_{n+m}]C_m=0; \tag{4.65}$$

the compatibility condition is

$$|[nm(q_{n+m-2}-q_{n+m})-\lambda q_{n+m}]|=0. \tag{4.66}$$

If the term C_0x^0 is included in (4.59), one solution will be $\lambda=0$, $C_0\neq0$, $C_n=0$ for $n\neq0$; this is the equilibrium solution of the original problem and is rigorous. Any other solution ϕ_n of (4.65) and (4.66) then automatically satisfies the orthogonality conditions $H[\phi,\phi_m]=0$ with respect to the equilibrium function $\phi_0=C_0$ and to previously obtained approximate solutions ϕ_m of the form (4.59) $(m=1, 2, \cdots, n-1)$. The desired approximate value of λ_1 for the original problem is therefore the smallest *nonvanishing* eigenvalue of (4.66). The term C_0x^0 need not be included in (4.59) if the condition $H[\phi,1]=0$ is satisfied by symmetry.

In the case of a uniaxial particle in zero field,[12] with $V=-Kx^2$,

$$q_\nu=2\int_0^1 \exp(\alpha x^2)x^\nu dx, \tag{4.67}$$

where

$$\alpha=Kv/kT; \tag{4.68}$$

q_0 can be found from tables[22,23] of $\int_0^x \exp(t^2)dt$, and recurrence formulas for the other q_ν's can be derived by integration by parts. One can then solve with successively larger numbers of terms in Eq. (4.59) until the agreement of successive values is satisfactory. The labor would be considerable.

Since this method introduces constraints in the minimizations, it gives a value of λ_1 that errs, if at all, upward; it therefore provides an upper bound for λ_1. In general, minimization of $D_1[\phi]/H_1[\phi]$ will give an upper bound to λ_1 if $D_1[\phi]\geqslant D[\phi]$ and $H_1[\phi]\leqslant H[\phi]$ for every ϕ and if the minimization is performed either rigorously or under constraints; it will give a lower bound if $D_1[\phi]\leqslant D[\phi]$ and $H_1[\phi]\geqslant H[\phi]$ and if the minimization is performed rigorously. It is difficult to obtain useful lower bounds because of the last condition.[24]

In the case $V=-Kx^2$, a lower bound can be found by replacing the factor $e^{-\beta V}=\exp(vKx^2/kT)=\exp(\alpha x^2)$ by 1 in $D[\phi]$ and by e^α in $H[\phi]$. The eigenvalues of λ in the resulting minimization problem are then $\epsilon^{-\alpha}$ times the eigenvalues of λ in the original problem with $V=\text{const}$; therefore $\lambda_n\geq n(n+1)e^{-\alpha}$, and in particular

$$\lambda_1\geq 2e^{-\alpha}. \tag{4.69}$$

The discrete-orientation approximation (4.54), for $V=-Kx^2$, gives

$$\lambda_1=(4/\sqrt{\pi})\alpha^{3/2}e^{-\alpha}, \tag{4.70}$$

which is compatible with (4.69) only if $\alpha\geq(\pi/4)^{1/3}=0.92$. Thus for $\alpha<0.92$, the value of λ_1 by (4.70) is certainly too small.

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[21] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), pp. 67–68. Let the system under consideration be the particle plus an ideal permanent-magnet field source, so that the energy ϵ_s in microstate s includes the energy of the microscopic moments in the field. Then $vV(\theta)$ is the free energy of a particle specified to have orientation θ, whereas G_1 is the free energy of one specified only to have an orientation in $(0,\theta_1)$. Therefore, $e^{G1/kT}=\Sigma_s e^{-\epsilon_s/kT}$ and $e^{-vV(\theta)/kT}=\Sigma_{s(\theta)}e^{-\epsilon_s/kT}$, where the first sum is over microstates compatible with an orientation in $(0,\theta_1)$ and the second over microstates compatible with the specified θ. It follows that $e^{-G1/kT}=\Sigma_k \nu_k e^{-vV(\theta k)/kT}\Delta\Omega_k$, where $\nu_k\Delta\Omega_k$ is the number of microstates with $\theta=\theta_k$ to within solid angle $\Delta\Omega_k$, and the summation is over $\Delta\Omega_k$'s for which θ is in $(0,\theta_1)$. On going over to an integral we get Eq. (4.56) if we suppose that $\nu_k=\nu$, independent of θ_k.

[22] H. G. Dawson, Proc. London Math. Soc. **29**, 519 (1898); E. Jahnke and F. Emde, *Tables of Functions* [(B. G. Teubner, Leipzig, 1933), 4th ed. (Dover Publications, Inc., New York, 1945)], p. 32.

[23] N. Arley, *On the Theory of Stochastic Processes and Their Application to the Theory of Cosmic Radiation* (John Wiley & Sons, Inc., New York, 1943), pp. 222–227.

[24] Other methods of obtaining lower bounds are discussed by S. H. Gould, *Variational Methods for Eigenvalue Problems* (University of Toronto Press, Toronto, 1957).

E. Application

For any specific form of the function $V(\theta)$ or $V(x)$ ($x=\cos\theta$), the methods described in Secs. 4B–D can be used to calculate λ_1 and hence p_1, and also ϕ_1 if it is of interest; some of these methods can be extended to λ_n and ϕ_n with $n>1$. Except in the trivial case $V=$const, it is necessary to use approximate formulas; but accurate values can be found at the cost of computational labor, and upper and lower bounds to λ_n can be established by the general methods described in Sec. 4D.

The case of greatest interest is the case $V=K\sin^2\theta - HM_s\cos\theta$, a uniaxial particle in a longitudinal field[12]; and here the most important question is to how small a value of v/T the high-energy-barrier approximation, which leads to Eqs. (4.44) and (4.54), is legitimate. A partial answer to this question in the case $H=0$, where Eq. (4.54) is equivalent to Eq. (4.70), was given in the discussion of Eq. (4.69): The formula is certainly wrong if $\alpha\equiv Kv/kT=H_cM_sv/2kT$ is less than 0.92. A more stringent criterion could be established by numerical calculations based on Eq. (4.66) in the range $\alpha\approx 1$. A less satisfactory method is to compare values of λ_1 (or p_1) based on the high-energy-barrier approximation with values based on the low-energy-barrier formula (4.24). Such a calculation, for the iron particles considered in reference 10, shows that the two formulas agree in order of magnitude at $\alpha=0.5$ ($1/p_1=2.8\times10^{-10}$ sec by the first formula, 1.4×10^{-10} sec by the second) but disagree by two orders of magnitude at $\alpha=0.05$ (3.5×10^{-9} sec vs 1.2×10^{-11} sec; the high-energy-barrier formula gives a spurious minimum of $1/p_1$ as a function of v/T at $v/T=k/H_cM_s$, when $\alpha=1/2$). For order of magnitude, therefore (and this is often all that matters), the high-energy-barrier formula seems to be useful even slightly below the point ($\alpha=0.92$) at which it becomes certainly wrong. For iron particles at room temperature,[10] this corresponds to a spherical particle of radius about 40 Å.

5. CONCLUSIONS

The Brownian-motion approach to this problem is based on legitimate simplifications, and it yields to analysis up to the point where a partial differential equation is to be solved. Beyond this point, analytical methods fail except in trivial cases. When $V=V(\theta)$, the approximate methods developed seem adequate for all cases of interest. When $V=V(\theta,\phi)$, practical techniques of solution remain to be developed. Formulation of the problem as a minimization problem seems possible only when the gyroscopic terms drop out, as they do when $V=V(\theta)$.

The analysis of the case $V=V(\theta)$ shows that the high-energy-barrier approximation is usually sufficient; this reduces the continuous distribution of orientations effectively to a discrete distribution and leads to formulas (1.1)–(1.2) and to numerical calculations of the type illustrated in reference 10. Further study of the case $V=V(\theta,\phi)$ might, therefore, aim specifically at developing a high-energy-barrier approximation for this case.

Formulas for the case $V=V(\theta,\phi)$ would have another application, quite apart from superparamagnetism and magnetic viscosity. When one attempts to calculate static magnetization curves of a single-domain crystal, one finds that the initial orientation sometimes becomes unstable while two or more other equilibrium orientations are still stable.[25] One must then determine to which of the remaining orientations an irreversible jump can occur, and with what probabilities. This problem can be studied by use of Eq. (2.10).

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[25] C. E. Johnson, Jr., and W. F. Brown, Jr., Suppl. J. Appl. Phys. **32**, 243S (1961).