On the kinetics of magnetization of suspensions of ferromagnetic particles

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According to the nature of the field and the temperature dependences of the magnetization, dilute suspensions of identical particles should be regarded as paramagnetics. Relaxation of magnetization to the equilibrium value defined by the Langevin formula is ensured by Brownian rotational motion of the particles and their spontaneous remagnetization (Néel supermagnetism). When the particle volume exceeds a certain critical value, the Brownian motion becomes the major factor. In this case a macroscopic equation of motion of the suspension magnetic moment can be derived from the Fokker–Planck equation. The former equation contains two relaxation times, one for the longitudinal and the other for the transverse magnetization components. The relaxation times are proportional to the liquid viscosity and are decreasing functions of the Langevin argument.

A suspension of very fine ($\lesssim 100$ Å) particles of a ferromagnetic material is similar in its static magnetic properties to a paramagnetic gas. In it, the role of the elementary carriers of magnetism is played by particles suspended in a liquid. For the sizes mentioned, each of them is in a uniformly magnetized single-domain state[1]. Far from the Curie temperature, the magnetic moment of an individual particle is practically independent of the temperature and equal to $\mu = M_S V$, where M_S is the saturation magnetization of the ferromagnetic material and V is the volume of the particle. Orientation of the magnetic moments in the direction of the applied field is impeded by heat motion. Allowance for both factors, just as in Langevin's classical theory of paramagnetism, leads to the formula for the magnetization of the suspension

$$M_0 = cM_s L(\mu H / kT), \quad L(\xi) = \operatorname{cth}\xi - \xi^{-1}. \tag{1}$$

The volume concentration of the solid phase, $c = nV$, is assumed to be so small that the dipole interaction between the particles can be neglected. Because of the large values of μ (10^4 to 10^5 Bohr magnetons), saturation can be observed experimentally[2] at room temperature in even very moderate fields ($\sim 10^3$ Oe).

Much more interesting are the kinetic properties of magnetic suspensions. The establishment of the equilibrium magnetization (1) is accompanied by a number of relaxational processes, of which some occur in the solid phase (that is, inside the particles themselves) and others are due to rotation of the particles in the viscous liquid. A qualitative analysis of these processes (section 1) enables us, in particular, to introduce a critical volume V_* for the superparamagnetic state[1] of colloidal particles of a ferro- or ferrimagnetic material.

To find the distribution function of the magnetic moments of particles with $V > V_*$, for which a determining role is played by Brownian rotational diffusion, in section 2 the Fokker-Planck equation is used. The characteristic values of this equation determine the spectrum of relaxation times of the distribution function W; that is, they describe the rate of approach of W(t) to the equilibrium (canonical) distribution W_0. We have calculated the dependence of the lowest (most important) levels of the spectrum of characteristic values on the Langevin argument $\xi = \mu H/kT$.

In section 3, we derive from the Fokker-Planck equation the macroscopic equation of motion of the magnetic moment of the suspension. The method used here is a modification of the well-known thermodynamic method of Leontovich[3] (the effective-field method). The equation obtained for the magnetization agrees in form with the phenomenological equation of one of the authors[4] but differs in the dependence of the relaxation time on ξ.

Comparison of the results of sections 2 and 3 shows that the relaxation times of the magnetization actually coincide with the longest relaxation times of the distribution function.

1. RANGE OF THE CHARACTERISTIC TIMES

In an external field H, the energy of a uniaxial, uniformly magnetized particle is[1]

$$U = -\mu \mathbf{e}\mathbf{H} - KV(\mathbf{en})^2, \tag{2}$$

where $K > 0$ is the effective anisotropy constant, n is the unit vector along the axis of easiest magnetization, and $\mathbf{e} = \mu/\mu$.

In equilibrium, the magnetic moment of the particle is parallel to the effective field intensity

$$\mathbf{H}_{\text{eff}} = -\mu^{-1}\partial U / \partial \mathbf{e} = \mathbf{H} + 2KM_s^{-1}(\mathbf{en})\mathbf{n}. \tag{3}$$

The precession of the vector μ, which occurs for any deviation of it from the equilibrium orientation, is described by the Landau-Lifshitz[5] equation

$$\dot{\mu} = \gamma[\mu \mathbf{H}_{\text{eff}}] - (\tau_0 \mu H_{\text{eff}})^{-1}[\mu[\mu \mathbf{H}_{\text{eff}}]]. \tag{4}^*$$

In the absence of a radiofrequency field, the Larmor precession is extinguished after a time $\tau_0 = (\alpha\gamma H_{\text{eff}})^{-1}$, with $\alpha < 0.1$. Hereafter we shall take as an estimate $\alpha = 10^{-2}$, in agreement with experimental data on ferromagnetic resonance in a colloidal suspension of nickel[6]. The effective field (3) is composed of the external field H and the anisotropy field $H_A = 2K/M_S$. For $H \ll H_A$, the relaxation time is

$$\tau_0 = M_s / 2\alpha\gamma K. \tag{5}$$

A second characteristic time, which together with τ_0 determines the rate of "solid-state" relaxation processes, is due to thermal fluctuations of the direction of the magnetic moment μ. This relaxation mechanism, first pointed out by Néel[7], is peculiar to subdomain particles: even in the absence of an external field, there is possible a reorientation of the vector μ between dif-

ferent directions of easiest magnetization, by surmounting of an energy barrier KV. The Néel fluctuation process is characterized by a remagnetization time τ_N, for which Brown[8] obtained the asymptotic formula

$$\tau_N = \tau_0 \sigma^{-1/2} e^{\sigma}, \quad \sigma = KV/kT, \tag{6}$$

correct when $\sigma \gtrsim 2$, with τ_0 from (5).

If the external conditions change over a characteristic time t', then for $t' > \tau_N$ a system of subdomain particles, embedded in a solid nonmagnetic matrix, displays paramagnetic properties—superparamagnetism[1]. This shows up in a characteristic (Langevin) dependence of the magnetization on the field and the temperature.

In suspensions of single-domain particles, the equilibrium orientation of the magnetic moments in an external field can be attained also by rotation of the particles themselves with respect to the liquid. This relaxation mechanism is described by the Brownian rotational-diffusion time

$$\tau_B = 3\eta V/kT, \tag{7}$$

where η is the dynamic viscosity of the liquid.

Thus, the dynamics of the magnetization of a suspension is linked with two fluctuation mechanisms. These mechanisms are physically different: the Néel mechanism is determined by the properties of a dispersed ferromagnetic material, the Brownian by the viscosity of the liquid. At the same time, there is a definite similarity between them: the Néel process can be considered[7] as a rotational diffusion of the magnetic moment with respect to the body of the particle, that is as a certain analog of the Brownian rotation of the particles in the liquid. Consequently, the mean square of the angular displacement of the vector μ after time t must be equal in order of magnitude to

$$\langle (\delta\theta)^2 \rangle = 2t(\tau_B^{-1} + \tau_N^{-1}). \tag{8}$$

Thus the more important mechanism is the one that is described by the shorter rotational-diffusion time.

According to (5)—(7), the equality $\tau_N = \tau_B$ holds when

$$\sigma^{-1/2} e^{\sigma} = 6\alpha\gamma\eta M_S^{-1}. \tag{9}$$

The value σ_* that is the solution of equation (9) determines a critical volume $V_* = \sigma_* kT/K$ for the superparamagnetic state of a particle. On setting $\eta = 10^{-2}$, $M_S = 1500$, $\gamma = 2 \cdot 10^7$, and $\alpha = 10^{-2}$ in (9), we find $\sigma_* \approx 4$. For the critical radius of particles of iron ($K = 4.8 \cdot 10^5$) and of hexagonal cobalt ($K = 4.5 \cdot 10^6$), at room temperature, we get 40 and 20 Å respectively. Particles with $V < V_*$ ($\tau_N < \tau_B$) are superparamagnetic. In a suspension of ferromagnetic particles, $V > V_*$ ($\tau_N > \tau_B$), and consequently the establishment of the equilibrium orientation of the magnetic moments, as is seen from (8), is guaranteed essentially by rotation of the particles; that is, the relaxation time of the magnetization of such a suspension is of the order of τ_B. For $\sigma \geq 10$, the condition

$$\tau_0 \ll \tau_B \ll \tau_N. \tag{10}$$

is satisfied. In this case, the internal state of each solid particle, during the process of magnetization of the suspension, can be considered an equilibrium state (after time τ_B the precession of the magnetic moment has become extinguished, whereas the Néel fluctuation mechanism is "frozen").

On taking into account the parallelism of the vectors μ and H_{eff}, we find from (3)

$$\mu[\mathbf{eH}] = -2KV(\mathbf{en})[\mathbf{en}]. \tag{11}$$

The right side of (11) can be written $-[\mathbf{n}, \partial U/\partial \mathbf{n}]$; that is, it is equal to the torque acting on the particle in the magnetic field. Thus the equation of rotational motion of the particle has the form

$$I\dot{\omega} + \zeta\omega = \mu[\mathbf{eH}], \tag{12}$$

where I and ω are the moment of inertia and the angular velocity; $\zeta\omega$ is the frictional torque (for a spherical particle, $\zeta = 6\eta V$). The ratio I/ζ determines the viscous time

$$\tau_s = I/\zeta = \rho_s R^2/15\eta \tag{13}$$

(ρ_S is the density and R the radius of the particle). For $R \leq 10^{-6}$ and $\eta \approx 10^{-2}$ we get $\tau_S \lesssim 10^{-10}$ sec. The smallness of τ_S permits us to neglect the inertial term in equation (12) in comparison with the viscous.

We shall hereafter suppose that, in addition to (10), the inequality $H \ll H_A$ is satisfied; that is,

$$\xi \ll \sigma, \quad \sigma \geq 10. \tag{14}$$

Then, as is seen from (3), the vector $\mu = \mu\mathbf{e}$ will be directed along the axis of easiest magnetization; consequently, in the kinematic relation

$$\dot{\mathbf{n}} = [\omega\mathbf{n}] \tag{15}$$

n may be replaced by e—the condition (14) enables us to treat each particle as a rigid magnetic dipole. Then on eliminating ω from (12) and (15), we get the equation

$$\dot{\mathbf{e}} = -(\mu/6\eta V)[\mathbf{e}[\mathbf{eH}]]. \tag{16}$$

2. RELAXATION OF THE DISTRIBUTION FUNCTION

The distribution function of particles suspended in a liquid, with respect to the orientations of their magnetic moments, is subject to the Fokker-Planck equation. On allowing for the rotational diffusion of the vector e and for its regular change (16) under the influence of the field, we get

$$\partial W/\partial t = -(2\tau_B)^{-1} \operatorname{div}[\mathbf{e}[\mathbf{e}(\nabla - \xi)]]W. \tag{17}$$

The differential operators here contain only the angular variables; in spherical coordinates, with the polar axis along ξ, equation (17) takes the standard form[3]

$$2\tau_B \sin\vartheta \frac{\partial W}{\partial t} = \frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial W}{\partial\vartheta} + \xi\sin\vartheta W\right)\right] + \frac{1}{\sin\vartheta}\frac{\partial^2 W}{\partial\varphi^2}. \tag{18}$$

The normalized stationary solution of equation (17) is

$$W_0 = \frac{\xi}{4\pi \operatorname{sh}\xi} e^{(\xi\mathbf{e})}, \quad (\xi\mathbf{e}) = \xi x, \quad x \equiv \cos\vartheta. \tag{19}$$

During the process of approach of the system to the equilibrium state (for example, after sudden switching on of the field), the distribution function can be represented in the form

$$W = W_0 + \sum_{l=1}^{\infty}\sum_{m=-l}^{l} A_{lm} f_{lm}(x) \exp\{\xi x - im\varphi - \lambda_{lm} t/2\tau_B\}. \tag{20}$$

The coefficients A_{lm} are determined by the initial conditions—the orientational configuration of the system of dipoles at the instant t = 0.

On substituting (20) in (18), we get the equation

$$(1-x^2)f_{lm}'' + [\xi(1-x^2) - 2x]f_{lm}' + \left(\lambda_{lm} - \frac{m^2}{1-x^2}\right)f_{lm} = 0, \tag{21}$$

whose characteristic values $\lambda_{lm}(\xi)$ determine the spectrum of relaxation times $\tau_{lm} = 2\tau_B\lambda_{lm}^{-1}$ of the distribution function. All that is required of the characteristic functions $f_{lm}(x)$ is finiteness in the interval $-1 \le x \le +1$.

In the absence of an external field ($\xi = 0$), equation (21) is satisfied by the associated Legendre polynomials,

$$f_{lm}(x) = \left\{\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right\}^{1/2} P_l^m(x), \quad \lambda_{lm}(0) = l(l+1).$$

The magnetic field partially removes the degeneracy with respect to m: each $(2l+1)$-fold degenerate level splits into $l+1$ levels, differing in their values of $|m|$. In the case of a weak field ($\xi < 1$), perturbation theory can be used. In the second order, we find

$$\lambda_{lm}(\xi) = l(l+1) + \frac{1}{2(2l+1)}\left\{\frac{l(l+2)[(l+1)^2-m^2]}{(l+1)(2l+3)} - \frac{(l^2-1)(l^2-m^2)}{(2l-1)l}\right\}\xi^2. \tag{22}$$

We are basically interested in the smallest characteristic numbers (the largest τ_{lm}), since, except in the earliest stages of the relaxation process, it is they that determine the rate of approach of the system to equilibrium. For the longest relaxation times we get from (22)

$$\tau_{1,0} = (1 - {}^1/_{10}\xi^2)\tau_B, \quad \tau_{1,\pm1} = (1 - {}^3/_{40}\xi^2)\tau_B. \tag{23}$$

The calculation of the characteristic values of equation (21) for $\xi \ge 1$ was done by Galerkin's method. The function f_{lm} with fixed m was approximated by a linear combination of the first twenty polynomials $P_l^m(x)$, differing with respect to the lower index. The characteristic determinant has tridiagonal form; diagonalization at each step with respect to the parameter ξ was accomplished with an electronic computer. In the $\lambda_{lm}(\xi)$ spectrum obtained, there are no intersections, so that relazation times $\tau_{1,0}$ and $\tau_{1,\pm1}$ appear fundamental over the whole interval investigated, $0 < \xi < 15$. Their dependence on ξ is shown in the figure.

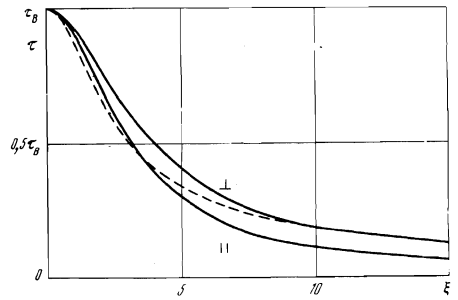
3. MACROSCOPIC EQUATION OF MOTION. RELAXATION OF THE MAGNETIZATION

Equations for the macroscopic characteristics of a magnetic suspension can be obtained by averaging of the corresponding quasimicroscopic quantities with a distribution function satisfying equation (17). For example, for the magnetization of the suspension, $n\mu\langle e\rangle$, we get from (17)

$$2\tau_B\frac{\partial}{\partial t}\langle e\rangle = -2\langle e\rangle + \xi - \langle e(e\xi)\rangle. \tag{24}$$

Equation (24) for the first moment of the distribution function contains the second moment, the equation for the second contains the third, and so on; that is, one gets, as usual, an infinite system of coupled equations. Closure can be accomplished in the effective-field approximation. In accordance with the idea of Leontovich's method[3], we shall suppose that at each instant the distribution function W(t) coincides in form with the equilibrium function W_0, but with replacement in (19) of the actual field by a certain effective field ξ_e. On performing the averaging in (24) with the distribution function introduced in this form, we get the equation for the effective field

$$2\tau_B\frac{\partial}{\partial t}\left\{L(\xi_e)\frac{\xi_e}{\xi_e}\right\} = -2\xi_e^{-1}L(\xi_e)(\xi_e - \xi) - \xi_e^{-3}\{3L(\xi_e) - \xi_e\}[\xi_e[\xi\xi_e]]. \tag{25}$$



Dependence of relaxation times on dimensionless field ξ. Solid lines: $\tau_{1,0}(\parallel)$ and $\tau_{1,\pm1}(\perp)$, calculated by Galerkin's method. These curves are approximated by the functions $\tau_\parallel$ and $\tau_\perp$ of (28) with accuracy 15% ($\parallel$) and 7% ($\perp$). Dotted lines: $\tau_\perp$ from (30).

The solution $\xi_e(\xi, t)$ of equation (25) determines the magnetization of the suspension

$$\mathbf{M} = n\mu L(\xi_e)\xi_e/\xi_e.$$

We shall consider the case of slight nonequilibrium, when the effective field is close to the actual field,

$$\xi_e = \xi + \nu, \quad \nu \ll \xi.$$

For the nonequilibrium part of the magnetization,

$$\mathbf{m} = \mathbf{M} - \mathbf{M}_0 = n\mu\{L(\xi_e)\xi_e/\xi_e - L(\xi)\xi/\xi\}$$

we get in the linear approximation with respect to ν

$$\mathbf{m} = n\mu L(\xi)\{(d\ln L(\xi)/d\ln\xi)\xi^{-3}(\xi\nu)\xi + \xi^{-1}\nu\}. \tag{26}$$

Then on carrying out the linearization of equation (25) and, in it, expressing ν in terms of m by means of (26), we get the equation of motion of the magnetization:

$$\dot{\mathbf{m}} = -\mathbf{H}(\mathbf{mH})/\tau_\parallel H^2 - [\mathbf{H}[\mathbf{mH}]]/\tau_\perp H^2, \tag{27}$$

which describes a relaxation of the components of m parallel and perpendicular to the external field with time constants

$$\tau_\parallel = \frac{d\ln L(\xi)}{d\ln\xi}\tau_B, \quad \tau_\perp = \frac{2L(\xi)}{\xi - L(\xi)}. \tag{28}$$

These formulas reduce for $\xi \ll 1$ to

$$\tau_\parallel = (1 - {}^2/_{15}\xi^2)\tau_B, \quad \tau_\perp = (1 - {}^1/_{10}\xi^2)\tau_B$$

(compare with (23)), whereas the asymptotic form for $\xi \gg 1$ gives

$$\tau_\parallel = \tau_B/\xi, \quad \tau_\perp = 2\tau_B/\xi.$$

The macroscopic relaxation times (28) are close to the quasimicroscopic $\tau_{1,m}$. For all values of ξ, the equalities

$$\tau_\parallel = \tau_{1,0}, \quad \tau_\perp = \tau_{1,\pm1}. \tag{29}$$

are satisfied with accuracy no worse than 15%.

The results obtained are easily generalized to a suspension of nonspherical particles. For example, let each particle be an ellipsoid of revolution with volume $V = {}^4/_3\pi ab^2$ and with magnetic moment directed along the nondegenerate semiaxis a of the ellipsoid. In this case all the changes in the formulas given reduce to a simple renormalization of the rotational diffusion coefficient: τ_B must be divided by a certain function $\Phi(\epsilon)$, where $\epsilon \equiv b/a$. We shall not give here the unwieldy expressions that define $\Phi(\epsilon)$ separately for oblate ($\epsilon > 1$) and prolate ($\epsilon < 1$) ellipsoids; these formulas can be found, for example, in[9]. We point out only that the value $\Phi(1) = 1$ is a maximum; that is, $\Phi(\epsilon) < 1$ for $\epsilon \ne 1$. Consequently, nonsphericity of the particles

should manifest itself in an increase of the relaxation times of the magnetization.

In closing, we mention that equation (27) can be derived also by a phenomenological method[4]. In the paper[4], a linear law was assumed for the relaxation of the vector magnetization, with time constant τ_B. An additional (Landau-Lifshitz type) relaxation term appeared as a result of allowing for the rotational degrees of freedom of the particles (the same considerations were used as in the derivation of equation (16)). In brief, $\tau_\parallel$ remained equal to the "priming" constant τ_B, whereas $\tau_\perp$ turned out to depend on the field:

$$\tau_\parallel = \tau_B, \quad \tau_\perp = 2\tau_B / [2 + \xi L(\xi)]. \tag{30}$$

Equation (27), with the relaxation times (30), was applied in[4] for calculation of the rotational viscosity $\Delta\eta$ of the suspension. This is independent of $\tau_\parallel$ and is expressed in terms of $\tau_\perp$ by the formula $\Delta\eta = \frac{1}{4}M_0 H\tau_\perp$. The $\tau_\perp$ obtained with the phenomenological derivation from (30) gives values close to the $\tau_\perp$ from (28) (see Figure). This evidently also explains the good agreement of theory[4] with experiment[10] in the dependence of the viscosity of magnetic suspensions on the field.

*$[\mu \mathbf{H}_{\text{eff}}] \equiv \mu \times \mathbf{H}_{\text{eff}}$.

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