Birefringence in a ferromagnetic liquid

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We investigate the birefringence produced when a suspension of single-domain magnetite particles is magnetized. The dependence of the difference between the refractive indices of the ordinary and extraordinary rays on the intensity of the applied field and on the temperature is obtained in experiment. The results of measurements in an alternating field are used to estimate the time of the Brownian rotational diffusion of the particles. A single-particle-model of a magnetic suspension is used for a theoretical analysis of the results.

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Colloidal suspensions of ferro- and ferrimagnets have recently come into use and designated ferroliquids.[1,2] A ferromagnetic liquid is a suspension of single-domain microcrystal (linear dimension $\sim 10^{-6}$ cm) of a magnet in a nonpolar liquid matrix (water, kerosene, toluene, etc.), stabilized by addition of a surface-active medium. The stabilizer molecules are adsorbed by the magnetic particles and produce around them strong protective sheaths, thereby ensuring a high anticoagulation stability of the colloid.

A ferroliquid polarized by an external magnetic field **H** becomes optically uniaxial. The resultant magnetooptical effects—dichroism, birefringence, anisotropy of light scattering, etc. —are quite appreciable[3–5] thereby uncovering a possibility of their practical utilization. The present paper is devoted to a study of birefringence under the influence of a constant and alternating magnetic field (the Cotton-Mouton effect) in a suspension of the iron ferrite Fe_3O_4(magnetite).

1. EXPERIMENTAL PROCEDURE

Owing to the birefringence, a linearly polarized light beam passing in a normal direction through a plane-parallel layer of magnetized suspension (the magnetization **M** lies in the plane of the layer) becomes elliptically polarized. The degree of ellipticity is determined by the difference between the refractive indices $n_\perp$ and $n_\parallel$ of the ordinary and extraordinary rays—light components with electric vectors **D** oriented perpendicular and parallel to the optical axis, the direction of which coincides with **M**. The phase difference between the components

$$\vartheta = 2\pi (l/\lambda)(n_\parallel - n_\perp), \tag{1}$$

where l/λ is the ratio of the layer thickness to the wavelength of the light, is a measurable quantity.

A block diagram of the setup for the observation of birefringence and for the measurement of the phase difference between the ordinary and extraordinary rays is shown in Fig. 1. The optical system consisted of a light source 1, light filters 2, a polarizer 3, a cell with the investigated liquid 4, and analyzer 5, a focusing system 6, and a photomultiplier 7. The light source was an incandescent lamp fed with stabilized direct current. Monochromatization was with KS 10 and ZhZS 18 filters ($\lambda = 600$ nm, $\Delta\lambda = 32$ nm). The investigated liquid was a colloidal suspension of magnetite in kerosene, prepared by the procedure of[6] and stabilized with oleic acid. The volume concentration of the solid phase was 0.02%. A cell of thickness $l = 10$ mm, filled with liquid, was placed in a thermostat between the poles of the electromagnet 8. The windings of the electromagnet were fed from a stabilized dc source 9. The signal of the FÉU-79 photomultiplier was registered with a model UI-7 electrometric amplifier 11. To study the phase relations between the external magnetic field and the light flux the electromagnet was connected to an alternating-voltage source 10 (GZ-33 generator), and signals proportional respectively to the field between the electromagnet poles and the light intensity past the analyzer were fed to a double-beam oscilloscope 12 (S1-18).

If the polarizing filters are crossed, then the intensity of the light passing through the analyzer is equal to

$$I = I_0 \sin^2 2\beta \sin^2(\vartheta/2),$$

where I_0 is the intensity of the incident light and β is the angle between the direction of the polarization of the incident beam and the magnetization vector **M**. At $\beta = 45°$, for small ϑ, we can use the approximate formula

$$I = I_0 (\vartheta/2)^2, \tag{2}$$

and whereas the error does not exceed 2% up to a phase difference 30°.

2. EXPERIMENTAL RESULTS

At a fixed temperature $T_0 = 297$ K we measured the intensity $I(H)$ of the light flux as a function of the intensity

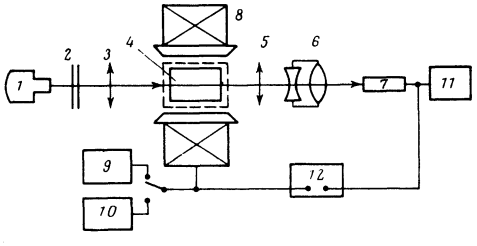

FIG. 1. Experimental setup for the study of birefringence in a magnetic suspension.

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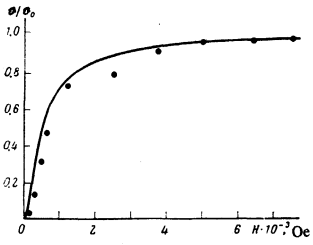

FIG. 2. Dependence of the phase difference between the ordinary and extraordinary rays on the intensity of the constant external field, $T = 297$ K. Points—experiment, curve—calculation by formula (10).

H of the constant external field. The corresponding values of $\vartheta(H)$ were calculated by formula (2). The experimental points in Fig. 2 are plotted in coordinates ϑ/ϑ_0, where ϑ_0 is the phase difference in the maximum field $H_0 = 7540$ Oe of the electromagnet. The region where the effect is saturated is quite clearly pronounced.

To assess the influence of the dichroism of the suspension of the measurement results, a special series of experiments was performed with the analyzer removed from the installations. It turned out that the magnetite ferroliquid has a weak negative dichroism. Compared with the isotropic case ($H = 0$), the intensity of a plane-parallel beam increases in a field of 400 Oe by 2% if the vector **D** of the light wave is parallel to the external field H, and decreases by 6% when $\mathbf{D} \perp \mathbf{H}$. Inasmuch as in experiments on birefringence the plane of the polarization of the beam was oriented at an angle 45° to the field direction, the dichroism effects cancelled each other in part, so that the combined change they produced in the intensity of the light flux leads to not more than a 5–7% error in the measurements.

The purpose of the temperature experiments was to establish the $\vartheta(T)$ dependence at a given external-field intensity. It turned out that in the entire investigated region 500 Oe $< H <$ 7500 Oe variation of the applied field had little effect on the results of the measurements. The character of the temperature dependence of ϑ is illustrated in Fig. 3, which shows the experimental values of $\vartheta(T)/\vartheta(T_0)$ at $H = 1000$ Oe.

Experiments on birefringence in an alternating field have made it possible to determine the relaxation properties of the effect. Figure 4 shows a photograph of the screen of a double-beam oscilloscope, with the aid of which the phase-frequency measurements were made. The phase shift between the applied field (lower trace) and the intensity of the light flux past the analyzer (upper trace) is distinctly displayed. The frequency dependence of the phase delay δ of the birefringence is shown in Fig. 5.

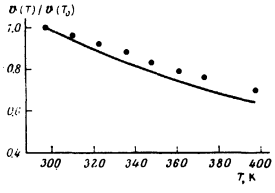

FIG. 3. Temperature dependence of the phase difference between the ordinary and extraordinary rays; $H = 1000$ Oe. Points—experiment curve—calculation by formula (10).

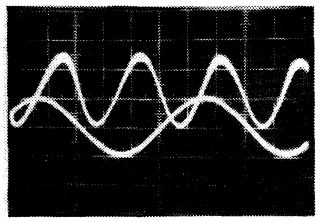

FIG. 4. Oscillogram of oscillations of external field (lower trace) and of the photomultiplier current (upper trace) in a phase-frequency experiment; sweep rate 0.5 msec/cm of screen, $\omega = 2 \times 10^3$ rad^{-1}.

3. THEORETICAL INTERPRETATION OF THE RESULTS

We start from the assumption that a ferromagnetic suspension, like a liquid crystal, becomes birefringent as a result of the nonsphericity of the particles oriented by the external field.[1)] According to electron-microscope observation data,[5,7,8] the nonsphericity of the magnetic grains of the ferroliquid is not large, but quite sufficient to cause the effects described above.

The magnetic anisotropy of the colloidal particles is due to two causes: the natural crystallograph anisotropy and the shape anisotropy. For magnetite suspensions, the second factor is the decisive one. The natural crystallographic anisotropy of Fe_3O_4 is quite small (energy density $|K| \approx 1.1 \times 10^5$ erg/cm^3 [9]), and therefore even a weak shape anisotropy

$$\Delta N > |K|/4\pi M_s^2 \approx 4 \cdot 10^{-2} \qquad (3)$$

(ΔN is the difference between the demagnetizing factors along the long and short axes, $M_s = 480$ G is the saturation magnetization of the magnetite) produces an internal field capable of exerting a decisive influence on the orientation of the magnetic moment μ of the particle. When the inequality (3) is satisfied, the vector μ is in fact parallel to the long axis of the particle. We shall describe the orientation of this axis with the aid of a unit vector **n**, whose statistical mean value $\langle \mathbf{n} \rangle$ is in this case the analog of the director of a liquid crystal. The external field H, by orienting the magnetic moments of the particles, orders by the same token the directions of their long axes, and it is this which leads in final analysis to the onset of optical anisotropy of the ferroliquid.

The macroscopic tensor of the dielectric constant of the suspension can be represented in the form

$$\varepsilon_{ik} = \varepsilon_0 [\delta_{ik} + \alpha\varphi S_{ik}], \quad S_{ik} \equiv \frac{3}{2}\left(\langle n_i n_k \rangle - \frac{1}{3}\delta_{ik} \right). \qquad (4)$$

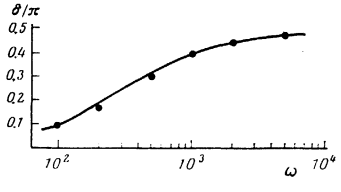

FIG. 5. Frequency dependence of the phase delay of the light flux. Points—experiment, curve—calculation by formula (15) with $\tau = 4 \times 10^{-3}$ sec.

Here ε_0 is the dielectric constant at $\mathbf{H}=0$, α is a coefficient proportional to the average nonsphericity of the particles and depends also on the ratio of the electric-polarization properties of the liquid matrix and the ferromagnetic material, and φ is the volume concentration of the solid phase. The anisotropy of the medium, just as in the case of liquid crystals, is described by the macroscopic orientation tensor S_{ik}. The correction $\varepsilon_{ik}-\varepsilon_0\delta_{ik}$ arising in the presence of an external field is small because φ is small—in the experiments discussed here $\varphi=2\times10^{-4}$.

In the optical frequency region, the magnetic permeability of the suspension should be set equal to unity[10]; we then obtain readily for the difference between the refractive indices of the ordinary and extraordinary rays, in the approximation linear in φ,

$$n_{\parallel}-n_{\perp}=\tfrac{1}{2}\alpha\varphi n_0 S_{zz} \tag{5}$$

(the z axis is parallel to $\mathbf{M}$, n_0 is the refractive index at $\mathbf{H}=0$). For the phase shift ϑ we obtain from (1) and (5)

$$\vartheta=\pi(l/\lambda)\alpha\varphi n_0 S_{zz}. \tag{6}$$

Neglecting the interparticle interaction, we calculate the orientation tensor S_{ik}. The magnetic energy of a particle with volume V_m is equal to

$$U=-\mu H\mathbf{eh}-KV_m(\mathbf{en})^2. \tag{7}$$

Here $\mathbf{e}=\boldsymbol{\mu}/\mu$, $\mathbf{h}\equiv\mathbf{H}/H$; $K>0$ is the effective uniaxial magnetic anisotropy constant and is determined, by definition, by the nonsphericity of the particle.

To calculate the macroscopic characteristics of the system in a constant external field it suffices to know the equilibrium function $W_0\sim e^{-U/kT}$ of the orientational distribution of the vectors $\mathbf{e}$ and $\mathbf{n}$:

$$W_0\sim\exp[\xi\mathbf{eh}+\sigma(\mathbf{en})^2], \tag{8}$$

where $\xi\equiv\mu H/kT$ and $\sigma\equiv KV_m/kT$. In view of the small nonsphericity of the particles, σ is likewise small, so that we can linearize (8) with respect to this parameter. For the normalized distribution function we obtain

$$W_0=(\xi/16\pi^2\operatorname{sh}\xi)\exp[\xi\mathbf{eh}]\{1+[\sigma(\mathbf{en})^2-1/3]\}. \tag{9}$$

With the aid of (7) and (9) we get

$$\vartheta=(\pi l/\lambda)\alpha\varphi n_0\int(n_z^2-1/3)W_0\,d^2\mathbf{e}\,d^2\mathbf{n}=C\sigma[1-3L(\xi)/\xi], \tag{10}$$

where $C\equiv 2\pi l\alpha n_0/15\lambda$ and $L(\xi)=\coth\xi-\xi^{-1}$ is the Langevin function. The asymptotic expressions corresponding to (10) are of the form

$$\vartheta=C\sigma\begin{cases}\xi^2/15 & (\xi\ll1)\\ 1-3/\xi & (\xi\gg1).\end{cases} \tag{11}$$

The obtained function $\vartheta(\xi)$ allows us to describe the results of the static measurements (see **Figs. 2 and 3**). From a comparison of the experimental plot of $\vartheta/\vartheta_0=f(1/H)$ in the region of strong fields ($\xi\gg1$) with the formula obtained from (11)

$$\frac{\partial}{\partial(1/\xi)}\frac{\vartheta}{\vartheta_0}=-3\left(1+\frac{3}{\xi_0}\right)$$

($\xi_0\equiv\mu H_0/kT_0$, $H_0=7540$ Oe, $T_0=297$ K—see Sec. 2) we determine the characteristic parameter of the suspension $\mu/kT\approx8.4\cdot10^{-3}$ Oe^{-1} and the corresponding magnetic[2)] volume of the particle $V_m=\mu/M_s\approx7.5\times10^{-19}$ cm^3. For the indicated value of μ/kT, the ϑ/ϑ_0 dependence calculated from formula (10) is plotted in Fig. 2. It is also easy to compare formula (10) with the temperature-measurement data. The curve (Fig. 3) plotted on the basis of (10) agrees qualitatively with the experimental results.

The alternating external field causes a reorientation of the magnetic moments of the ferroliquid particles. If the field frequency ω is low in comparison with the frequency ω_0 of the natural ferromagnetic resonance

$$\omega\ll\omega_0=2\gamma K/M_s,$$

then the rotation of the vector $\boldsymbol{\mu}$ is due only to the Brownian rotational diffusion of the particle in the liquid matrix. This relaxation process is characterized by a time $\tau=AV\eta/kT$, where η is the dynamic viscosity of the liquid and A is a coefficient equal to three for spherical particles and close to this value in the case of small nonsphericity. It is important to note that the formula for τ contains not the volume V_n of the "bare" solid particles (see footnote 2), but the total volume V of the colloidal particle (the solid plus the stabilizer sheath); as a rule,[7,11] $V\gg V_n$.

Since the amplitude of the alternating field is usually small in dynamic experiments ($\xi>\sigma$), we can neglect at low frequencies ($\omega\ll\omega_0$) the fact that the magnetic moment is not parallel to the anisotropy axis of the particle, and put $e=n$ (model of rigid dipoles[2]). The equation of motion of the orientational distribution function of rigid dipoles, derived in[12] is of the form

$$2\tau\dot{W}=i\hat{\mathbf{L}}(i\hat{\mathbf{L}}-\xi[\mathbf{e}\times\mathbf{h}])W, \tag{12}$$

where

$$\hat{\mathbf{L}}\equiv-i\left[\mathbf{e}\times\frac{\partial}{\partial\mathbf{e}}\right]$$

is the operator of infinitesimally small rotation.

From (12) we easily obtain a system of equations for the first two moments of the function W:

$$\tau\frac{d}{dt}\langle e_i\rangle=-\langle e_i\rangle+\frac{1}{2}\xi_i-\frac{1}{2}\xi_k\langle e_ie_k\rangle,$$
$$\tau\frac{d}{dt}\langle e_ie_k\rangle=\delta_{ik}-3\langle e_ie_k\rangle+\frac{1}{2}\xi_i\langle e_k\rangle+\frac{1}{2}\xi_k\langle e_i\rangle-\xi_i\langle e_ie_ke_i\rangle. \tag{13}$$

The external field has no dc component, so that at equilibrium ($\dot{W}=0$) the solution of Eq. (12) is isotropic: $W_0=\text{const}$. If the condition $\xi<1$ is satisfied, the alternating field can be regarded as a perturbation, and to make the system (13) closed we can use the following

approximate form of the distribution function:

$$W=W_0[1+a_ie_i+b_{ik}(e_ie_k-\delta_{ik}/3)]. \quad (14)$$

The coefficients a_i and b_{ik} which are to be determined do not depend on **e** and are of the order of ξ and ξ^2. Substitution of the harmonic relation $\xi=(0, 0, \xi\sin\omega t)$ in (13) leads after the use of (14) to a system of linear equations for a_i and b_{ik}. Solution of this equation makes it possible to determine the components of the tensor $\langle e_ie_k\rangle$. Calculation of ϑ (we recall that $\langle e_ie_k\rangle=\langle n_in_k\rangle$ in the rigid-dipole model) shows that the phase oscillates like $\sin^2(\omega t-\delta)$. The complete dispersion formula for ϑ has not been written out here, being too unwieldy. The expression for the phase shift δ between the absolute value of the external-field intensity and the intensity of the light passing through the ferroliquid layer (see Fig. 4) is

$$\operatorname{tg}\delta=\frac{4\omega\tau}{5}\left[1+\frac{1}{8(3+2\omega^2\tau^2)}\right]. \quad (15)$$

From a comparison of this formula with the results of the phase-frequency measurements we determined the Brownian time of rotational diffusion of the particles, $\tau\approx 4\times10^{-3}$ sec. A plot of (15) at the indicated value of τ is shown in Fig. 5.

From the obtained value of τ we can estimate the total volume of the particle, $V=\tau kT/3\eta\approx 5.3\cdot10^{-15}$ cm^3. If we take into account the presence of the nonmagnetic surface layer, the ratio of the volumes of the "dressed" and "bare" particle is $V/V_n\approx 4.6\cdot10^3$, thus indicating that the protective sheath is quite thick. We note for comparison that an investigation[11] of colloidal suspensions of iron in toluene with aluminum naphthenate as the stabilizer yielded a close result, $V/V_n\approx 2.9\times10^3$.

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[1)]We are thus considering a single-particle model: account is taken of the interaction of the magnetic moment of the particle with the internal and external fields, as well as the rotational Brownian motion. It is permissible in the case of dilute suspensions of minute particles ($\lesssim 10^{-6}$ cm), when the interparticle interaction is negligible.

[2)]According to the data of[7,8] the chemical reaction between the Fe_3O_4 and the oleic acid produces a nonmagnetic layer of iron oleate on the surface of the suspension particles. The layer thickness is of the order of the lattice constant $a=8.4$ Å of the crystalline magnetite, so that the volume V_n of the solid particle is always 2—3 times larger than the volume V_m of its ferrimagnetism-preserving core.

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