Magnetic fluids

M. I. Shliomis

Polymer Physics Division, Ural Scientific Center, USSR Academy of Sciences, Perm'

Usp. Fiz. Nauk **112**, 427–458 (March 1974)

Interest in fluids with strong magnetic properties has developed in recent years in connection with technical applications. Artificially created magnetic fluids are suspensions of very fine ($\sim 10^{-6}$ cm) particles of ferromagnetic material in ordinary (as a rule nonconducting) liquids. This review briefly describes the methods of preparation and considers the stability problems of magnetic colloids. It deals principally with their physical and hydrodynamic properties. It summarizes the results of theoretical and experimental investigations of the effect of a magnetic field on the equilibrium conditions and on the character of the motion of the suspensions. A considerable part of the article is devoted to an analysis of critical phenomena—instability of the free surface of the liquid in an external field and thermoconvective instability. The mechanisms of relaxation of the magnetization of a suspension are discussed; the most important of these are rotational Brownian motion of the particles and the Néel fluctuation mechanism, which leads to the superparamagnetism of subdomain particles of a ferromagnetic material. Important differences are noted between the hydrodynamics of suspensions of superparamagnetic and of ferromagnetic particles. In the latter case it is necessary to take account of rotation of the particles themselves, which greatly complicates the picture of the interaction of hydrodynamic and magnetic phenomena. Consideration is given to various effects caused by internal rotation: anisotropy of the viscosity and of the magnetic susceptibility, entrainment of the suspension by a rotating field, and dependence of the kinetic coefficients on the field intensity.

CONTENTS

1. INTRODUCTION

With respect to its magnetic properties, any single-phase fluid is dia- or paramagnetic, so that its magnetic susceptibility is extremely small. For example, the volume susceptibility of liquid oxygen—an anomalously strong paramagnet—is only 3×10^{-4} at 90° K. The magnetic susceptibility is at least an order of magnitude smaller for concentrated solutions of paramagnetic salts and of certain free radicals. As regards ferromagnets, as far as is known they do not exist in the liquid phase, although the problem of whether they are possible in principle is at present unsolved. But a liquid medium with strong magnetic properties can be obtained by colloidal dispersion of ferromagnetic particles in an ordinary liquid. Such a two-phase system is very sensitive to a magnetic field and in many respects behaves like a uniform fluid. Existing technology today makes it possible to obtain colloids with initial susceptibility 0.05—0.10, and with saturation magnetization 30-35 G, attainable in fields of intensity 8-10 kOe.

The synthesis and the systematic study of the properties of magnetic fluids was started a few years ago by Rosensweig's research group[1-9]. The not altogether felicitous term "ferrofluid," proposed in one of the first papers[2] on the hydrodynamics of magnetic suspensions ("ferrohydrodynamics"), became established in the scientific literature. We remark at once that the ferrofluids under discussion here have little in common with the magnetic composites used for visualization of domain boundaries[10] or in magnetic clutches[11] and which came into use early in the last fifty years. In these, the suspensions used were of a ferromagnetic powder (usually carbonyl iron) in a mineral or silicone oil. The mean dimensions of the particles were 4—12 μm. The technical application of such suspensions was based on their property of congealing under the influence of a magnetic field.

Ferrofluids differ from these coarse suspensions primarily by the much smaller (by three orders!) dimensions of the suspended particles: depending on the ferromagnetic material used, their mean diameter varies from 30 to 150 Å. The smallness of the dimensions of the particles, in combination with the measures always applicable for prevention of coagulation, guarantees high stability of the magnetic colloids: they undergo practically no aging or separation, they remain liquid in a magnetic field, and after removal of the field they fully recover their characteristics.

The experimental and theoretical data so far obtained enable us to put together a more or less complete presentation of the physical properties and hydrodynamics of magnetic fluids. The only review pertaining to this subject, by Bertrand[12], is concerned basically with the preparation of ferrofluids and with the prospects for their use in technology. In the article being presented, we have attempted to fill in the gaps that exist, paying primary attention to the physical side of the subject.

2. STATIC PROPERTIES OF MAGNETIC SUSPENSIONS

(a) Colloidal systems. The very existence of a colloidal suspension assumes, obviously, that the solid particles suspended in the liquid do not settle under the influence of the force of gravity. For this purpose the velocity of Brownian (thermal) motion of the particles

must be no smaller than the settling velocity determined by Stokes's formula. Hence an upper estimate of the dimensions of a suspended particle:

$$d \leqslant \left(\frac{\eta^2 kT}{\rho_s (\Delta\rho)^2 g^2}\right)^{1/7}, \qquad (2.1)$$

where $\Delta\rho = \rho_s - \rho_f$ is the difference of densities of the solid and liquid phases. Depending on the viscosity η of the liquid, formula (2.1) gives $d_{max} \sim 10^{-3} - 10^{-4}$ cm at room temperature. In practice, in stable colloids the dimensions of the particles lie within the limits 10^{-7} to 10^{-4} cm.

In a state of thermodynamic equilibrium, the height distribution of the particles obeys the barometric law

$$n(z) \sim \exp\left[-\frac{(\Delta\rho) Vgz}{kT}\right] \qquad (2.2)$$

(V is the volume of the particles). Consequently, in order that there shall not be concentration gradients of gravitational origin, the height h of the container must be sufficiently small:

$$h < \frac{kT}{(\Delta\rho) Vg}. \qquad (2.3)$$

For $\Delta\rho = 10$ g/cm^3, T = 300°K, and d = 200 Å, we must have h < 1 cm. We remark, however, that the time t′ for establishment of the equilibrium distribution (2.2) for colloidal particles is very large, and an originally uniform system remains uniform over a long period of time t < t′. In order of magnitude, $t' = h^2/D$, where $D \sim kT/\eta d$ is the diffusion coefficient of the suspended particles. For h ~ 1 cm, d ~ 10^{-6} cm, and $\eta \sim 10^{-2}$ g/cm sec, the uniformity is preserved for several weeks.

Whereas in ordinary suspensions gradients of the particle concentration are produced by Archimedean forces alone, for magnetic suspensions, placed in a nonuniform field H, a role analogous to that of the gravitational field is played by gradients of the magnetic field. In a nonuniform field, a particle with magnetic moment m is subject to a force[13] $\mathbf{m} \cdot \nabla\mathbf{H}$. In estimating the size of this force, one must remember that for such particle dimensions (d ~ 100 Å) as are used in stable magnetic colloids, each suspended particle is an individual magnetic domain[14]. Calculation of the critical dimensions, below which a particle becomes absolutely single-domain, leads to values of d from several hundreds of angstroms (330 and 760 Å for iron and nickel respectively)[15] to several thousands of angstroms for materials with strong magnetic anisotropy (4×10^3 and 13×10^3 Å for manganese-bismuth alloy and for barium ferrite[16]). The magnetic moment of a uniformly magnetized (single-domain) particle is $m = M_S V$, where M_S is the saturation magnetization of the particle material. Thus the ratio of the magnetic force $M_S V|\nabla H|$ to the Archimedean $(\Delta\rho)Vg$ is independent of the particle dimension. For $|\nabla H| > g(\Delta\rho)/M_S$, the magnetic forces dominate over the gravitational. In this case, in formulas (2.1) and (2.3), which determine the maximum permissible linear dimensions of the particles and of the container, $\Delta\rho \cdot g$ must be replaced by $M_S|\nabla H|$.

(b) **Preparation and stability of magnetic colloids.** Colloidal ferromagnets must be stabilized to exclude possible coagulation. Stabilization is accomplished by adsorption on to the surface of the dispersed particles of ions, with formation of double ionic layers, or by means of surface-active substances (soaps, alcohols, fatty acids). The molecules of these substances form on the solid particles adsorbed lavers with definite orientations of the polar groups.[1)] This leads to the appearance of a potential barrier that prevents coagulation: in order for the particles suspended in the liquid to approach each other, work must be expended to overcome the forces of molecular bonding between the molecules of the liquid and the adsorbed layer. The width of the potential barrier in the case of fatty acids is about 20 Å.

Rosensweig, Kaiser, et al. worked with ferrofluids obtained by grinding ferrite powders (mostly magnetite) in ball mills. The grinding is continued several weeks in the presence of the carrying liquid, in which the stabilizing agent is dissolved from the very beginning. Used as a base are kerosene, water, and fluoro-organic and silicone liquids; the stabilizer is often oleic acid. In[17], the dispersion obtained after grinding was centrifuged 20 minutes in a field of 17 000 G, after which the unsettled fraction was separated. In various suspensions described in[17], the mean diameter of the magnetite particles varied from 50 to 90 Å, with particle concentration $n \sim 10^{16}$–10^{18} cm^{-3}.

Colloids of magnetite are prepared also by chemical precipitation[18] of Fe_3O_4 particles from a solution of salts of di- and trivalent iron, by acting on the solution with an excess of alkali. The precipitate obtained is washed and is then separated to a colloidal state in weak hydrochloric acid or in a solution of oleic acid in a nonpolar liquid.

Exceptionally high stability is exhibited by colloids of cobalt particles, stabilized by polymeric materials with molecular weight 10^4 and larger[19,20]. The method proposed by Thomas[19] for preparing such colloids consists in thermal decomposition of dicobalt octacarbonyl in toluene or chlorobenzene, containing in dissolved form a suitable polymer. By changing the $Co_2(CO)_8$ concentration, the temperature, and the composition of the polymer, it is possible to vary the dimensions of the particles of metallic cobalt between 20 and 300 Å; in each case, about 85% of the particles differ in their dimensions by less than a factor two from the mean value.

In[21], an electrocondensation method was used for dispersion of iron in toluene: evaporation and condensation of the metal in a high-frequency spark discharge. Aluminum naphthanate served as a stabilizer.

In a number of researches, attempts were made to produce a magnetic suspension on the basis of liquid metals. Such ferrofluids, in contrast to existing ones, would possess high electrical and thermal conductivity and a high boiling point. These qualities, in conjunction with strong magnetic properties, would guarantee them a wide application in various areas of technology, including the conversion of heat to mechanical or electrical energy[5] (a ferrohydrodynamic generator). The electrocondensation method was used to obtain particles of iron[22] and gadolinium[23] in mercury. Ferrofluids of Ni-Fe alloys on a mercury base were prepared by the method of electrolytic precipitation[24]. Also used as carrier liquids were tin, ingas (an indium-gallium-tin alloy), and bismuth alloys[25]. The basic difficulty in the way of production of an electroconductive ferrofluid is the lack of effective methods for stabilizing it.

Two mechanisms promote the coagulation of magnetic colloids: molecular attraction between the suspended particles, and the dipole-dipole interaction that is spe-

cific to magnetic particles. The latter has, for contact of the particles, the order of magnitude m^2/d^3, so that it is possible to introduce a dimensionless "coupling constant"

$$\lambda = \frac{m^2}{d^3 kT}. \qquad (2.4)$$

For single-domain particles, for which $m = M_S V$, λ is proportional to the volume of the particle. For example, for magnetite (M_S = 450 G) at room temperature ($kT = 4 \times 10^{-14}$ erg) the value $\lambda = 1$ is obtained for particles of diameter d = 90 Å. For $\lambda < 1$ the determining role is played by van der Waals forces. With increase of the particle dimensions, the contribution of the magnetic interaction to the resultant balance of interparticle forces increases.

The effect of magnetic attraction on the stability of disperse ferromagnets, stabilized by the electrostatic forces of repulsion between ions of double electric layers, was considered by Bibik and Lavrov[26] in the spirit of the Deryagin-Landau[27] theory of the stability of lyophobic sols. The interaction energy W of two spherical particles is composed of van der Waals and magnetic attractions and electrostatic repulsion. The dependence of W on the shortest distance ϵ between the sphere surfaces can have the following four basic forms (Fig. 1). Obviously, only when a curve of type 1 or 2 is realized will the ionic layers prevent conglomeration of the particles. A limit of stability must occur when the peak of the maximum of $W(\epsilon)$ is located at the level of the axis of abscissas (curve 3). The critical thickness ϵ_c decreases with increase of λ, and for $\lambda \gtrsim 10^3$ the magnetic colloid can no longer be stabilized by electrostatic forces. Its uniformity, however, is disturbed much sooner. For $\lambda \gg 1$ the magnetic attraction of the particles leads to formation of spatial structures[26]—chains, rings, clusters—because of the occurrence of a minimum of the total energy W at appreciable distances between the particles (curve 2 in Fig. 1).

Figure 2 shows electron-microphotographs of colloidal particles of cobalt[20]. Most of the particles in

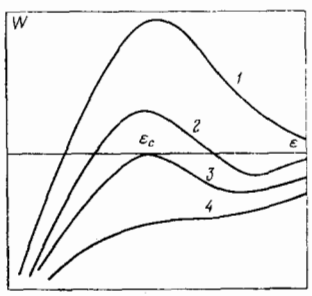

FIG. 1

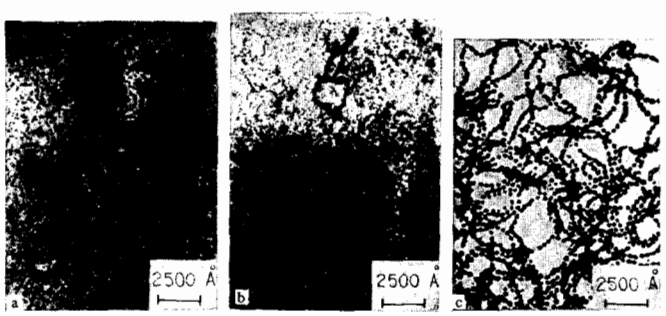

FIG. 2

Fig. 2a have dimensions less than 100 Å. Formation of chain aggregates begins (Fig. 2b) at somewhat larger mean dimensions. Finally, still coarser particles (200–400 Å) are completely joined into chains (Fig. 2c).

In those colloids in which spontaneous agglomeration of the particles does not occur, an external magnetic field may produce reversible agglomeration. This is evidenced, for example, by the effect of a field on the transparency of colloids of magnetite[28]: the transparency decreases in a magnetic field (aggregation) and is restored after removal of the field (disintegration of the aggregates). In[29], experiments were performed with dispersions of ferrite particles (~ 200 Å) in water. Electron microscopy showed that the agglomerates that originated under the influence of the field formed a regular system of lines parallel to the magnetic-intensity vector. Depending on the method of preparation of the electron-optic replica[29], the distance between neighboring chains of particles amounted to 4000 or 8000 Å.

(c) Formation of chains and clusters. Interesting results pertaining to the formation of chains of colloidal magnetic particles and to the effect of a uniform magnetic field on this process were obtained by de Gennes and Pincus[30]. They considered some of the properties of the equation of state of a "rarefied gas" of ferromagnetic particles suspended in an inert liquid. They allowed for the departure of the gas from ideality so far as this resulted from the magnetic attraction between the particles constituting the gas (electrostatic and van der Waals forces were disregarded).

The energy of interaction of two magnetic dipoles, located at a distance **r** from each other, is

$$W_{12} = r^{-3}[(\mathbf{m}_1\mathbf{m}_2) - 3(\mathbf{m}_1\mathbf{r})(\mathbf{m}_2\mathbf{r})r^{-2}].$$

In an external magnetic field strong enough to aline the particles completely,

$$\xi \gg 1, \quad \xi \gg \lambda \quad (\xi \equiv mH/kT),$$

the binary correlation function has the form

$$g(\mathbf{r}) = \begin{cases} 0 & (r < d), \\ \exp[\lambda (d/r)^3 (3\cos^2\theta - 1)] & (r > d), \end{cases} \qquad (2.5)$$

where θ is the angle between **r** and **H**. The second virial coefficient is expressed by the formula[31]

$$B = \frac{1}{2}\int [1 - g(\mathbf{r})]\, d^3\mathbf{r}. \qquad (2.6)$$

For small λ the integrand in (2.6) is nearly zero. Upon retaining the term linear in λ in the expansion of the exponential in (2.5), we find that the coefficient B depends considerably on the shape of the container in which the colloid is held. If the container is an ellipsoid of revolution with its axis of symmetry parallel to the applied field, then

$$B = \frac{1}{2}\left(N - \frac{4\pi}{3}\right)\lambda d^3 \quad (\lambda \ll 1, \xi \gg 1),$$

where N is the demagnetizing factor of the ellipsoid in the direction of its axis of symmetry ($0 < N < 4\pi$). Thus the sign of B depends on the shape of the chamber, and in the case of an oblate ellipsoid ($B > 0$) it corresponds to a repulsion between the particles.

In the limit of large λ, the most important region in (2.6) is $r \sim d$ and $\theta \approx 0$ or π. The asymptotic formula for B is

$$B_\infty = -\frac{\pi}{18}\frac{d^3}{\lambda^2}e^{2\lambda} \quad (\xi \gg \lambda \gg 1).$$

By considering pair correlations between particle positions, de Gennes and Pincus found that in strong external fields, at small concentrations of the suspended particles, ferromagnetic grains tend to form chains parallel to the field direction. The mean number of particles in a chain is

$$\nu_\infty = (1 - 2n \mid B_\infty \mid)^{-1}. \tag{2.7}$$

Formula (2.7) has meaning, obviously, so long as $2n|B_\infty| \leq 1$, i.e.,

$$\varphi \leqslant \lambda^3 e^{-2\lambda} \tag{2.8}$$

(ϕ = nV is the volume concentration of the solid phase). The condition (2.8) evidently determines the radius of convergence of an expansion in powers of the density; the inequality $n|C| < |B|$, where C is the third virial coefficient, leads to (2.8) if one takes $|C| \sim B^2$, as in simple monatomic gases. We may suppose that when the condition (2.8) is violated, not chains but clusters will form in the liquid.

At zero external field and $\lambda \gg 1$, there also exists a certain number of chains. Their mean length,

$$\nu_0 = (1 - 2n \mid B_0 \mid)^{-1} \quad (B_0 = B_\infty \lambda^{-1}) \tag{2.9}$$

is smaller than in a strong field, and they are oriented in a random manner.

(d) **Static magnetic properties.** The magnetic properties of a suspension are determined both by the state of the solid particles and by their degree of ordering. Processes occurring in the solid phase have an appreciable influence on the properties of a magnetic colloid only at temperatures close to the Curie temperature of a ferromagnet or to the Néel and compensation temperatures of a ferrimagnet. Far from the Curie temperature, each single-domain particle possesses a magnetic moment m that is practically constant in magnitude.

For $\lambda < 1$ one can neglect the spatial correlations between different particles; and if in addition $\phi \ll 1$, one can neglect also the correlation between the directions of their magnetic moments. Such a uniform and isotropic "ferromagnetic fluid" behaves with respect to an external field like a paramagnet in which the elementary carriers of the magnetism are the suspended particles. The magnetic moment of a particle exceeds the moment of an individual atom by 4 to 5 orders of magnitude, so that here the term "superparamagnetism" —introduced by Bean[32] to describe the behavior of systems of single-domain particles in a field—is entirely appropriate.

Orientation of the magnetic moments in the direction of the applied field is impeded by thermal motion. Allowance for both factors, as in Langevin's classical theory of paramagnetism, leads to the formula for the magnetization of a ferrofluid

$$M = M_0 L\left(\frac{mH}{kT}\right), \qquad M_0 = nm = \varphi M_s, \quad L(\xi) = \operatorname{cth}\xi - \xi^{-1}. \tag{2.10}$$

Because of the large magnitude of the moment m, nonlinear effects show up rather early: at room temperature, the value $\xi \approx 1$ has already been reached at fields $H \sim 10^2$ Oe. The asymptotic forms of the Langevin function are described by the initial section of the magnetization curve,

$$\xi \ll 1: \; M = \chi_0 H, \quad \chi_0 = \frac{nm^2}{3kT} = \frac{2}{\pi}\varphi\lambda, \tag{2.11}$$

and the approach to saturation,

$$\xi \gg 1: \quad M = M_0 - \frac{nkT}{H}. \tag{2.12}$$

For large volume concentrations of the ferromagnetic material ($\phi \sim 0.1$), the initial magnetic permeability may differ markedly from unity. In this case it is no longer permissible to neglect the interaction between the magnetic moments of the particles (we shall as before neglect the spatial correlation of the particles, supposing that $\lambda < 1$). Allowance for the dipole-dipole interaction can be made by a method similar to that used in the Debye-Onsager theory of polar liquids (see[33]). As a result, formula (2.11) is replaced by

$$M = \chi H, \quad \chi = \frac{\mu - 1}{4\pi}, \quad \frac{(\mu-1)(2\mu+1)}{\mu} = 4\pi\frac{nm^2}{kT}.$$

The superparamagnetism of magnetic colloids was first observed by Elmore[34]. His experiments laid the basis for magnetic granulometry[35]—a method of determining the dimensions of fine particles of a ferromagnetic material by magnetic measurements. The method is based on a comparison of an experimental magnetization curve with the Langevin curve: by appropriate choice of the "scale factor" m in the argument of the Langevin function, coincidence of the two curves can be achieved. Since the magnetic moment of a single-domain particle is $(\pi/6)M_S d^3$, the "right choice" of m at the same time determines also the mean diameter of the particles. More accurately, two mean diameters can be determined: one, d_0, from the data in weak fields; the other d_∞, in strong. It is always true that $d_0 > d_\infty$, since in weak fields the chief contribution to the magnetization is made by the coarse particles, which are easily oriented by a magnetic field, whereas the approach to saturation is determined by the fine particles, orientation of which requires large fields.

Figure 3a shows an experimental magnetization curve[36] of a colloidal dispersion of magnetite in kerosene, with a slight addition of oleic acid as a stabilizer. The measurements were made at temperature 290°K. Figure 3b shows the experimental values of the magnetization as a function of H^{-1}. The latter dependence, as is seen from the graph, is linear in strong fields, in complete agreement with (2.12). By use of formulas (2.11)–(2.12) and of data taken from the graphs of Fig. 3.

$$M_0 = 33.8 \text{ G}, \quad \chi_0 \equiv \left(\frac{\partial M}{\partial H}\right)_{H=0} = 8\cdot 10^{-2},$$
$$nkT \equiv \left(H^2 \frac{\partial M}{\partial H}\right)_{H\to\infty} = \operatorname{tg}\alpha = 2.1\cdot 10^4 \text{ erg/cm}^3,$$

we find: $d_0 = 100$ Å, $d_\infty = 65$ Å.

In the ferrofluid discussed above, the volume concentration of the solid phase, calculated from the density of the colloid, was $\varphi_\rho = 0.12$. At the same time, the volume concentration determined from the magnetization ($\varphi = M_0/M_S$) is only 0.075. One reason capable of

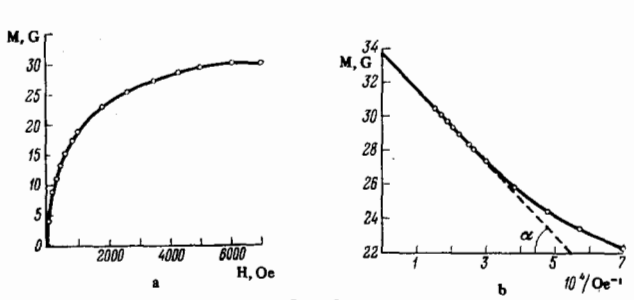

FIG. 3

producing such a discrepancy ($\varphi/\varphi_\rho = 0.62$) might be a dependence of the saturation magnetization of the solid phase on the degree of its dispersion. But experiments of various authors, discussed in[37], have detected no decrease of the spontaneous magnetization of subdomain particles (diameter down to 20 Å) in comparison with the magnetization of bulk material. The most plausible explanation of the difference between φ and φ_ρ is contained in the paper of Kaiser and Miskolczy[17]: the molecules of oleic acid adsorbed on the surface of the particles can, by entering into a reaction with the Fe_3O_4, form iron oleate, which possesses no magnetic properties. For this reason the "magnetic diameter" of each particle decreases by the amount 2ϵ, where ϵ is the thickness of the nonmagnetic spherical layer.

A better agreement is observed[17,36] between the experimental magnetization curves and theoretical curves calculated with the formula

$$M = M_s\left(\varphi_\rho \Big/ \sum_i n_i d_i^3\right) \sum_i n_i (d_i - 2\varepsilon)^3 L\left[\frac{M_s H}{kT}\frac{\pi}{6}(d_i - 2\varepsilon)^3\right],$$

if one takes $\epsilon = 8.3$ Å (this is the lattice constant of the cubic structure of magnetite). The distribution of particle dimensions was determined in the cited papers by means of an electron microscope.

As was stated above, strong dipole interaction between magnetic grains ($\lambda \gg 1$) produces condensation of the gas of particles, with formation of linear chains or clusters. The initial magnetic susceptibility of the suspension is given in this case by the formula

$$\chi = \frac{nm^2}{3kT}\frac{1}{1 - 2n|B_0|(1 - 4\lambda^{-1})} \qquad (2.13)$$

with B_0 from (2.9). The square of the angle between the magnetic moments of neighboring grains in the chain is in order of magnitude equal to λ^{-1}. Therefore for $\nu_0 < \lambda$ each chain resembles a short rod with magnetic moment $m\nu_0$, directed along the axis of the rod. In the case under consideration ($\lambda \gg 1$, $\nu_0 < \lambda$) one can neglect the term $4\lambda^{-1}$ in (2.13); this formula then takes the form

$$\chi = \frac{nm^2}{3kT}\nu_0.$$

For $\nu_0 > \lambda$, the chains are strongly curved. For very large ν_0 ($2n|B_0| \to 1$), we get from (2.13)

$$\chi = \frac{nm^2}{3kT}\frac{\lambda}{4}.$$

With increase of the intensity of the external field, the chains straighten, and their mean length increases (compare (2.7) and (2.9). For $\xi \gg \lambda$ all the chains are oriented along the field[30]

3. RANGE OF CHARACTERISTIC TIMES

(a) **Mechanisms of relaxation of the magnetization.** So far, in discussing the superparamagnetism of suspensions, we have considered only their magnetostatic properties—the magnetization obeys Langevin's law—and have ignored the kinetics of the magnetization process.

What are the characteristic times that determine the behavior of an individual ferromagnetic particle in a magnetic field? In order to respond to this question, we shall consider the simplest model, a suspension of spherical single-domain particles of a uniaxial magnetic crystal, supposing that the first anisotropy constant $K > 0$. Let the unit vector **n** be directed along the axis of easiest magnetization of one of the particles. In an external field H the energy of the particle is given by the formula[14]

$$U = U_0 - mH\cos\vartheta - KV\cos^2(\psi - \vartheta) \qquad (3.1)$$

(the angles are defined by Fig. 4). If the particle is deprived of the freedom to rotate (for example, by freezing the suspension), then the angle ψ, depending on the direction of H, can take an arbitrary value; but the angle θ, which determines the direction of the effective field H_{eff}, is found from the equation $\partial U/\partial\vartheta = 0$, that is

$$mH\sin\vartheta = KV\sin 2(\psi - \vartheta). \qquad (3.2)$$

In equilibrium, m and H_{eff} are parallel. Every departure of the magnetic moment of the particle from the equilibrium orientation is accompanied by a precession of the vector m about the direction of H_{eff} with the Larmor frequency $\omega_0 = \gamma H_{eff}$. In the absence of a radio-frequency field, the extinction time of the precession is[38]

$$\tau_0 = (\alpha\gamma H_{eff})^{-1}, \qquad (3.3)$$

where α is a dimensionless attenuation parameter, by use of which the Landau-Lifshitz[39] equation can be written in the form

$$\dot{\mathbf{M}} = -\gamma[\mathbf{M}\times\mathbf{H}_{eff}] - \alpha\frac{\gamma}{M}[\mathbf{M}\times[\mathbf{M}\times\mathbf{H}_{eff}]]. \qquad (3.4)$$

In the review of Skrotskiĭ and Kurbatov[38] it was mentioned that in the majority of experiments on ferromagnetic resonance the relation $\alpha < 0.1$ is satisfied. Anderson and Donovan[40] observed natural (that is, in the absence of an external biasing field) ferromagnetic resonance in a colloidal suspension of nickel in diethylphthalate. The value of α, determined from the width of the resonance absorption line, is according to the data[40] about 10^{-2}. We shall hereafter adopt this value of α for estimates.

The effective field H_{eff} is composed of the external field H and the anisotropy field $H_a = 2K/M_S$. For $H \ll H_a$, formula (3.3) takes the form

$$\tau_0 = \frac{M_s}{2\alpha\gamma K}. \qquad (3.5)$$

A second characteristic time, which along with τ_0 determines the rate of occurrence of relaxation processes within the particle itself, is connected with thermal fluctuations of the directions of the magnetic moment m. This relaxation mechanism, first pointed out by Néel[41], is specific to subdomain particles: even in the absence of an external field, reversal of their magnetization is possible by surmounting of the energy barrier KV between different directions of easy magnetization. The probability of a transition from the state with m = mn to the state with m = −mn is proportional to exp(−KV/kT); that is, it depends strongly on the dimensions of the particle. For the relaxation time τ_N

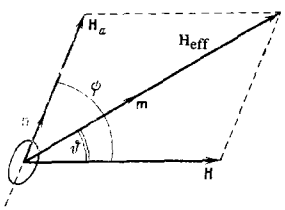

FIG. 4

characterizing the Néel process, Brown[42] obtained the asymptotic formula

$$\tau_N = \tau_0 \sigma^{-1/2} e^{\sigma} \quad \left(\sigma \equiv \frac{KV}{kT}\right), \tag{3.6}$$

valid for $\sigma \geq 2$, with τ_0 from (3.5). If the duration t′ of the magnetization measurement process satisfies the condition $t' > \tau_N$, then each particle behaves superparamagnetically, and this is manifested in a characteristic (Langevin) dependence of the magnetization of the system of particles on field and temperature[32]. In the comprehensive review of Bean and Livingston[37], a detailed discussion is presented on the superparamagnetism of systems of subdomain particles embedded in a solid nonmagnetic matrix: fine precipitations of iron in brass and of cobalt in copper, and iron and cobalt amalgams (the latter at temperatures below the melting point of mercury).

In a suspension of single-domain particles, the equilibrium orientation of the magnetic moments in an applied field can be attained also by rotation of the particles themselves with respect to the liquid matrix. This mechanism of relaxation of the magnetization is characterized by the Brownian rotational-diffusion time[33]

$$\tau_B = \frac{3V\eta}{kT}. \tag{3.7}$$

Thus the dynamics of magnetization of a suspension is related to two fluctuation mechanisms. They are physically different: one (the Néel) is determined by the properties of the ferromagnet, the other (the Brownian) by the viscosity of the liquid. At the same time, there is a definite similarity between the two mechanisms: the Néel process may be regarded[41] 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. Hence it is clear that the mean square of the angular displacement of the vector m over a time t must be (in order of magnitude)

$$\langle(\delta\theta)^2\rangle = 2t\,(\tau_B^{-} + \tau_N^{-}),$$

and that consequently the more important relaxation mechanism is the one that is characterized by the shorter rotational-diffusion time. According to (3.5)–(3.7), equality of the characteristic times, $\tau_N = \tau_B$, occurs when

$$\sigma^{-3/2} e^{\sigma} = 6\alpha\gamma\eta M_s^{-1}. \tag{3.8}$$

This equation, solved for σ, determines the critical dimension for a superparamagnetic (in the Néel-Bean sense) state of a particle suspended in a liquid with viscosity η. On setting $\eta = 10^{-2}$, $M_S = 1500$, $\gamma = 1.7 \times 10^7$, and $\alpha = 10^{-2}$ in (3.8), we find $\sigma_* \approx 4$. For the critical diameter d_* of particles of iron ($K = 4.8 \times 10^5$) and of hexagonal cobalt ($K = 4.5 \times 10^6$) we get 85 and 40 Å, respectively, at $kT = 4 \times 10^{-14}$. In suspensions of particles with $d > d_*$ (and consequently $\tau_N > \tau_B$), establishment of the equilibrium orientation of the magnetic moments is guaranteed basically by the Brownian motion of the particles; that is, the relaxation time τ of the magnetization is in order of magnitude equal to[2)] τ_B. We note that in case the condition

$$\tau_0 \ll \tau_B \ll \tau_N \tag{3.9}$$

is satisfied, then in the process of relaxation of the magnetization of a suspension the internal state of each solid particle may be considered an equilibrium state: during the time τ_B the precession of the magnetic moment has time to become extinguished, whereas the Néel fluctuation mechanism is "frozen." The condition (3.9) is well satisfied when $\sigma \geq 2\sigma_*$.

In the case $\sigma < \sigma_*$, the chief relaxation mechanism is the Néel, so that $\tau \sim \tau_N$. Finally, in a strong magnetic field, when $H \gg H_a$ (that is, $\xi \gg \sigma$), τ is smallest and is equal to $\tau_0 = (\alpha\gamma H)^{-1}$.

(b) **Rotational motion of the particles and relaxation of the anisotropy.** On a particle in a magnetic field there acts a torque $\partial U/\partial\psi$, where U is the expression given above for the energy, and a frictional torque[43] $-6V\eta\dot{\psi}$. The resulting equation of motion[44]

$$I_0\ddot{\psi} + 6V\eta\dot{\psi} + KV \sin 2(\psi - \vartheta) = 0 \tag{3.10}$$

(I_0 is the moment of inertia of the spherical particle) must be supplemented by the relation between the angles ψ and θ. For the latter one can use (3.2) if one neglects motion of the particle caused by the precession of the vector magnetic moment. Such neglect is justified by the fact that the period of the Larmor precession is always several orders of magnitude smaller than the characteristic turning time τ_t of the particle.

For a similar reason, it is possible in the equation of motion to neglect the inertial term in comparison with the viscous, if $\tau_t \gg \tau_S = I_0/6\eta V$. In order of magnitude, the "viscous time" $\tau_S \sim 10^{-11}$ sec at $d \sim 100$ Å and $\eta \sim 10^{-2}$ g/cm sec. The remaining terms of Eq. (3.10) describe a relaxation process, as a result of which the axis of easiest magnetization of the particle sets itself parallel to the direction of the applied field. In the limiting cases of strong or weak external fields (in comparison with the anisotropy field $H_a = 2K/M_S$), we have from (3.10) and (3.2)

$$6V\eta\dot{\psi} = \begin{cases} -KV \sin 2\psi & (H \gg H_a), \\ -mH \sin\psi & (H \ll H_a). \end{cases}$$

Hence we find the characteristic turning time of the particle

$$\tau_t = \begin{cases} 6\eta/M_s H_a = 3\eta/K & (H \gg H_a), \\ 6\eta/M_s H & (H \ll H_a). \end{cases} \tag{3.11}$$

It is now easy to demonstrate the correctness of the assumptions adopted above, $\omega_0\tau_t \gg 1$ and $\tau_t \gg \tau_S$: we have

$$\omega_0\tau_t = \frac{6\eta\gamma}{M_s} \geqslant 10^3 \text{ and } \tau_t/\tau_s \geqslant \frac{180\eta^2}{K\rho_s d^2} \geqslant 10^3$$

for $M_S \sim 10^3$ G and $K \sim 10^6$ erg/cm³.

Thus the magnetic field as an orienting factor plays a double role. First, it produces magnetization of the suspension by orienting the magnetic moments of the particles. Second, by lining up the axes of easiest magnetization the magnetic field causes anisotropy of the mechanical properties of the ferrofluid. We shall explain the last statement. In hydrodynamic motion of a medium with velocity v, each element of the fluid rotates with local angular velocity $\Omega = (\text{curl } v)/2$. In the absence of a field, particles suspended in the liquid also rotate with the same angular velocity. A magnetic field hampers the motion of the particles in those parts of the liquid where the vectors H and Ω are not parallel. This braking effect, caused by the magnetic torques, leads to anisotropy of the viscosity tensor (see Sec. 5(c)). There is here an analogy with a plasma, in which the magnetic field (because of cyclotron rotation of the charged particles) hampers the processes of transfer in a trans-

verse direction, whereas along the field the particles move freely.

But in order that the mechanical anisotropy induced by the magnetic field may manifest itself, it is necessary that its relaxation time τ_t be less than the rotational diffusion time τ_B of the particles (the latter plays the same role here as does the free-path time of the particles of a plasma). The condition $\tau_t \ll \tau_B$ with the aid of (3.7) and (3.11) reduces to the form $\sigma \gg 1$ (when $\xi \gg \sigma$) or $\xi \gg 1$ (when $\xi \ll \sigma$). Thus only when

$$\sigma \gg 1 \tag{3.12}$$

can the anisotropy of the ferrofluid be appreciable. On the other hand, if the condition

$$\sigma \ll 1, \tag{3.13}$$

the inverse of the preceding, is satisfied, then a suspension of spherical magnetic particles is isotropic in arbitrary external fields. In this case $\tau_t \gg \tau_B$, and because of rapid chaotic (Brownian) rotational fluctuations of the particles no preferred orientation of their easy axes succeeds in establishing itself. One can say that in a time τ_B the particle "forgets" its orderly rotation, caused by the magnetic torque.

The next chapter treats the hydrodynamics of an isotropic ($\sigma \ll 1$) ferrofluid.

4. QUASISTATIONARY FERROHYDRODYNAMICS

(a) Equations of motion of a ferrofluid. In the motion of a magnetic suspension in a nonuniform field, there acts on each particle a force[13]

$$\mathbf{f} = (\mathbf{m}\nabla)\,\mathbf{H}. \tag{4.1}$$

This force and the Stokes drag coefficient determine the regular component of the Brownian velocity of the particle with respect to the liquid,

$$\mathbf{u} = \frac{M_s d^2}{18\eta} L(\xi)\,\nabla H. \tag{4.2}$$

The velocity u is insignificantly small—it does not exceed 10^{-5} cm/sec for $d \sim 10^{-6}$ cm and $|\nabla H| \sim 10^3$ Oe/cm. By neglecting the relative (translational) motion of the gas of particles and of the liquid, one can construct a single-fluid hydrodynamics of a magnetic suspension.

The state of motion of a nonconducting ferrofluid changes under the influence of a volume magnetic force

$$\mathbf{F} = (\mathbf{M}\nabla)\,\mathbf{H}, \tag{4.3}$$

which is most simply obtained from (4.1) by summing over all the particles contained in unit volume; in the last expression, $\mathbf{M} = \sum_{i=1}^{n} \mathbf{m}_i$ is the magnetization of the suspension, and H is the magnetic field averaged over a volume large in comparison with n^{-1}. The relation between M and H is determined by the equation for dM/dt, which describes the dynamics of the magnetization, and Maxwell's equations

$$\operatorname{div}(\mathbf{H} + 4\pi\mathbf{M}) = 0, \quad \operatorname{rot}\mathbf{H} = 0. \tag{4.4}$$

By use of (4.4), F can be expressed in the form

$$F_i = \frac{\partial t_{ik}}{\partial x_k}, \quad t_{ik} = \frac{1}{4\pi}\left(H_i B_k - \frac{1}{2} H^2 \delta_{ik}\right). \tag{4.5}$$

Besides the force (4.1), a particle in a magnetic field is subject to a torque, which however may be neglected if the inequality (3.13) is satisfied. The condition $\sigma \ll 1$ means that the dimensions of the particles lie in the range of thorough-going superparamagnetism[32]; that is, there is no connection between the orientation of a particle and the direction of its magnetic moment. The relaxation of the magnetization of the suspension to the equilibrium value

$$\mathbf{M} = \varphi M_s L(\xi)\frac{\mathbf{H}}{H} \tag{4.6}$$

is determined in this case by the "solid body" time τ_0, which is incommensurably small in comparison with any hydrodynamic times. Equation (4.6) can be violated only in an alternating magnetic field whose frequency is close to the Larmor frequency.

The last formula and the condition (4.4) for absence of currents enable us to write

$$\mathbf{F} = (\mathbf{M}\nabla)\,\mathbf{H} = M\nabla H, \tag{4.7}$$

so that the hydrodynamic equations for an incompressible ferrofluid will be[1]

$$\rho\left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\nabla)\,\mathbf{v}\right] = -\nabla p + \eta\Delta\mathbf{v} + M\nabla H, \qquad \operatorname{div}\mathbf{v} = 0. \tag{4.8}$$

To these equations must still be added the equation of heat transfer[43]

$$\rho T\left(\frac{\partial s}{\partial t} + \mathbf{v}\nabla s\right) = \kappa\nabla^2 T + \frac{\eta}{2}\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right)^2, \tag{4.9}$$

where s is the mass density of entropy and κ is the coefficient of heat conductivity.

Equations (4.4), (4.6), (4.8), and (4.9) constitute the complete system of equations of Rosensweig-Neuringer ferrohydrodynamics[1]. It is natural to call this hydrodynamics, which uses the equation of "magnetic state" (4.6) instead of the equation of motion of M, quasistationary. The assumptions made in the theory[1] about the instantaneous relaxation of the magnetization and the absence of anisotropy are satisfied, as has been shown, when $\sigma \ll 1$.

(b) Isothermal equilibria and flows. In the absence of outside sources of heat, the flow of a suspension in a nonuniform magnetic field may be considered isothermal, if we disregard internal sources, weak as a rule, due to viscous dissipation of energy and to the magnetocaloric effect[14]—the cooling of a magnet on withdrawal from a field. For T = const it follows from (4.6) and (4.7) that

$$\mathbf{F} = nkTL(\xi)\nabla\xi = nkT\nabla\ln\frac{\operatorname{sh}\xi}{\xi}, \tag{4.10}$$

thereafter, the equation of motion (4.8) takes the standard form of the Navier-Stokes equation, in which the role of the pressure is played by the quantity

$$p_{\text{eff}} = p - nkT\ln(\xi^{-1}\operatorname{sh}\xi). \tag{4.11}$$

The derivability of the magnetic force (4.10) from a potential points to the importance of Bernoulli's theorem for vortex-free motion of a ferrofluid[1]. For stationary flow in the field of gravity we have

$$p + \rho g z + \frac{\rho v^2}{2} - nkT\ln\frac{\operatorname{sh}\xi}{\xi} = \text{const}. \tag{4.12}$$

This formula is very useful for qualitative investigation of the distributions of velocity and pressure in a nonuniform magnetic field. For v = 0 ("ferrohydrostatics"),

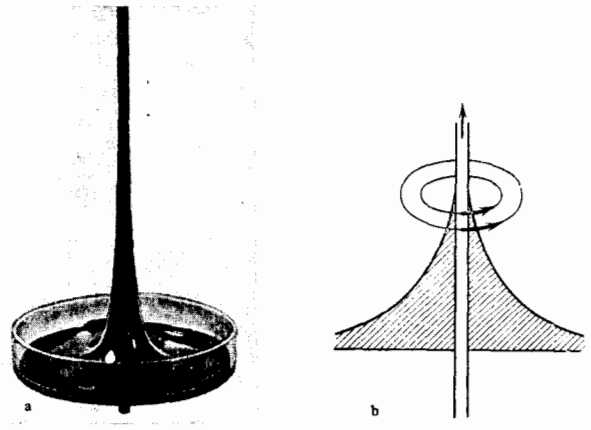

FIG. 5

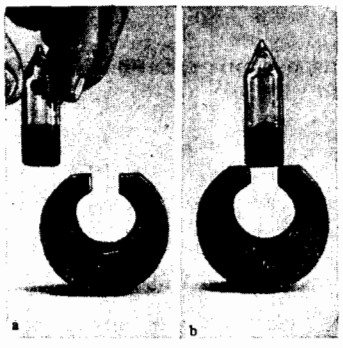

FIG. 6

Eq. (4.12) predicts an increase of pressure in those parts of the liquid where the field is stronger. This effect is demonstrated by Figs. 5(a) and 6, from an article of Rosensweig[8]. Figure 5(a) shows the free surface of a ferrofluid in the magnetic field of a straight current. The latter flows along a metal rod that pierces the dish containing the liquid (see the diagram in Fig. 5(b)).

In a nonuniform field, a nonmagnetic body immersed in a magnetic fluid experiences an additional Archimedean force, along the direction of diminution of the field intensity. Unit volume of the test body is acted upon by a force $\mathbf{F}_b = -\mathbf{F}$. In the case $\xi \ll 1$, formula (4.10) simplifies, and we then have

$$\mathbf{F}_b = -\frac{\chi}{2}\nabla H^2, \quad \chi = \frac{nm^2}{3kT}.$$

Thus a nonmagnetic body in a ferrofluid behaves like a diamagnet with volume susceptibility $\chi_b = -\chi$ and can be kept in equilibrium by static magnetic fields (magnetic suspension). Figure 6 shows an ampoule containing ferrofluid, into which has been placed a nonmagnetic (nylon) ball. The density of the ball is larger than the density of the liquid, and therefore in Fig. 6(a) it is not visible. In a nonuniform magnetic field (Fig. 6(b)) the pressure in the lower part of the ampoule is increased because of the magnetic pressure, and the ball has floated to the surface.

We consider as a further example a free horizontal jet (p, z = const) that traverses a region in which a magnetic field has been produced. According to Eq. (4.12) the velocity of the liquid should increase on entry into the field and decrease on exit from it. With change of the velocity, there will obviously be also a change of the cross-sectional area of the jet. This fact can be used[1,9] for introduction of signals into a hydraulic control system by means of a magnetic field.

A nonuniform field can itself become a reason for motion of the liquid, if the magnetic pressure is not equilibrated by the hydrostatic (see (4.11)). In calculating the gradient of the magnetic pressure one must use Maxwell's equations (4.4), which together with (4.6) impose limits on the possible geometry of the field. We shall show, for example, the possible arrangement of a plane Poiseuille flow caused by magnetic forces[45].

Let a layer of ferrofluid be bounded by immovable solid surfaces $z = \pm h$. Equation (4.12) is satisfied by a field with components

$$H_x = Gz, \quad H_y = 0, \quad H_z = H_0 + Gx. \tag{4.13}$$

One-dimensional stationary flow with velocity $v = v_x(z)$ in the section $-l < x < l$ is realized if the gradient of the intensity is small in the sense $Gl \ll H_0$. In the approximation linear in Gl/H_0, Eq. (4.4.1) is satisfied identically, and from the equation of motion (4.8) we find

$$v = \frac{GM(\xi_0)}{2\eta}(h^2 - z^2), \quad \xi_0 = \frac{mH_0}{kT}. \tag{4.14}$$

On comparing this with ordinary Poiseuille flow, we conclude that the role of the drop in pressure δp is here played by the quantity $M\delta H$. We shall make an estimate of the effect. In a strong field H_0 (i.e. for $\xi_0 \gg 1$) we may put $M = 30-40$ G; then for $\delta H = 3 \times 10^3$ Oe we get an effective $\delta p \approx 0.1$ atm.

It is interesting to compare the mean flow velocity of (4.14), $\bar{v} = (3\eta)^{-1}GMh^2$, with the velocity (4.2) of motion of the particles with respect to the liquid matrix, $u = (18\eta\varphi)^{-1}GMd^2$. The condition $u \ll \bar{v}$ that permits neglect of the relative motion of the particles and the liquid reduces to the inequality

$$\varphi \gg \left(\frac{d}{h}\right)^2, \tag{4.15}$$

satisfaction of which is already guaranteed at insignificant concentrations of the dispersed ferromagnetic material: for particle diameter $d \sim 10^{-6}$ cm and layer thickness $h \sim 0.1$ cm, it is sufficient to have $\varphi \gg 10^{-10}$, which corresponds to $n \gg 10^8$ cm^{-3}.

(c) Stability of the surface in a uniform field. Capillary gravitational waves. The equilibrium surface of a ferrofluid forms under the influence of three kinds of force: gravity, surface tension, and magnetic forces. In the case in which the uniform magnetic field is vertical, it can be shown that there is a critical value H_* of the intensity, above which a plane shape of the surface of separation of the magnetic and nonmagnetic media is unstable with respect to small perturbations. The equilibrium contour for $H > H_*$ is stationary waves.

Instability of the boundary between a ferrofluid and the atmosphere was first observed by Cowley and Rosensweig[3]. They also calculated the critical magnetization

$$M_*^2 = \frac{\sqrt{\rho g \alpha}}{2\pi}\left(1 + \frac{1}{\sqrt{\mu\hat{\mu}}}\right), \quad \mu \equiv \frac{B_*}{H_*}, \quad \hat{\mu} \equiv \left(\frac{\partial B}{\partial H}\right)_{H_*} \tag{4.16}$$

(α is the coefficient of surface tension). Quantities relating to the atmosphere will be denoted below by the index e. In (4.16) we have set $\mu_e = 1$, $\rho_e = 0$. We shall estimate the value of M_*. For a ferrofluid with a kerosene base[3] we may take $\rho \approx 1$ g/cm^3, $\alpha = 28$ dyn/cm. The critical magnetization depends only slightly on the

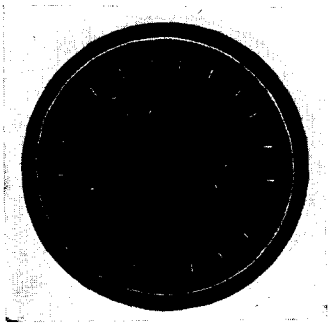

FIG. 7

value of $(\mu\hat{\mu})$: a change of $(\mu\hat{\mu})$ over the range $(1, \infty)$ does not take M_* outside the interval 5–7 G. Such values of M can be attained in the linear part of the magnetization curve (see Fig. 3(a)), so that in the neighborhood of H_* it is permissible to consider that $\mu = \hat{\mu} = \text{const}$ with respect to H.

When there is a linear relation between M and H, it is convenient to go over from the critical magnetization (4.16) to the critical intensity:

$$(H_*^e)^2 = (\mu H_*)^2 = 8\pi \frac{\mu(\mu+1)}{(\mu-1)^2} \sqrt{\rho g \alpha}. \qquad (4.17)$$

This same formula (with replacement of H by E and of μ by ϵ) determines the onset of instability of the free surface of a liquid dielectric in a constant vertical electric field[46]. If the liquid is a conductor, then in (4.17), after the indicated substitution, it is necessary to go to the limit $\epsilon \to \infty$: the electric field does not penetrate into the conducting medium. The stability condition obtained in this case, $E_e^2 < 8\pi\sqrt{\rho g \alpha}$, was first found by Frenkel[47] and was corroborated by experiments[46,48].

Figure 7, taken from[3], shows a photograph of the free surface of a ferrofluid in a uniform field $H = 1.03\ H_*$, produced by a Helmholtz coil. In the picture are visible, in the top plane, waves (peaks) that form a regular hexagonal lattice. This picture and the very nature of the phenomenon under consideration remind us of Benard's convective cells, which occur in a horizontal layer of a liquid at supercritical temperature gradients.

One can offer the following qualitative explanation[49] of the condition for appearance of ripples on the surface of a liquid. Suppose that in a uniform vertical field there has arisen a wave-shaped warping (perturbation) of the surface of the ferrofluid. The field intensity near the bulges of the perturbations is increased (the lines of force of the magnetic field are concentrated), but in the hollows it is decreased in comparison with the equilibrium value. Therefore the perturbation of the magnetic force is directed upward at the bulges but downward in the hollows; that is, it has a tendency to amplify the perturbation of the surface. On the other hand, the surface-tension and Archimedean forces are directed opposite to the displacement of the parts of the surface from the equilibrium position; that is, they impede the displacement. As long as the warping of the surface is small, all the forces produced by it—magnetic, surface-tension, and Archimedean—are proportional to the value of the displacement. It is important that the coefficients of proportionality between the last two forces and the displacement—the elastic coefficients—depend only on the properties of the liquid. But the "elastic" coefficient in the perturbation of the magnetic force is not

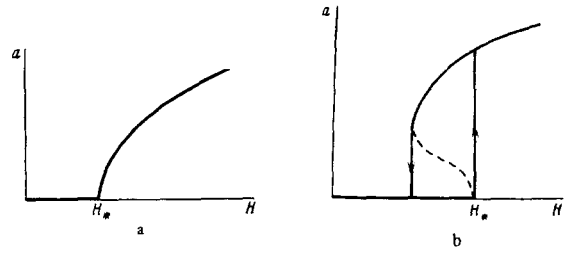

FIG. 8

determined solely by the properties of the liquid (its magnetic permeability) but is also proportional to the square of the intensity of the applied field. Therefore at sufficiently large intensities, the destabilizing magnetic force exceeds the sum of the other two forces, and the displacement of the surface will increase; that is, instability sets in.

A theoretical investigation of the nature of the transition from a plane to a wavy surface was undertaken by Zaĭtsev and Shliomis[50]. The value $H = H_*$ is a point of bifurcation, above which, in principle, two types of wave excitation are possible—soft and hard. Belonging to one or the other type is determined by the dependence of the amplitude a of the warping of the surface on the supercriticality parameter $H - H_*$: in the soft regime, a vanishes along with this difference (Fig. 8(a)); in the hard, the amplitude remains finite at $H = H_*$. In the latter case hysteretic effects can be observed (see Fig. 8(b)).

The equilibrium contour of the liquid-air separation surface is determined by the condition for balance of the forces acting on the surface[13]:

$$(p - p_c) n_i = (t_{ik} - t_{ik}^e) n_k + \alpha (r_1^{-1} + r_2^{-1}) n_i; \qquad (4.18)$$

here t_{ik} is the Maxwell tensor (4.5), and n is the outward normal vector to the surface of the ferrofluid. For two-dimensional perturbations[50] $z = \zeta(x)$ of an initially plane surface $z = 0$, there remains in the last term of (4.18), which determines the capillary pressure, a single radius of curvature $r = -(1 + \zeta'^2)^{3/2}/\zeta''$.

Equation (4.18) for the tangential components is satisfied identically by virtue of the boundary conditions

$$\mu H_n = H_n^e, \quad H_\tau = H_\tau^e \qquad (4.19)$$

on the surface $z = \zeta$. By using these conditions and taking account of the absence of volume forces (equilibrium),

$$\operatorname{grad}\left(p + \rho g z - \frac{\mu-1}{8\pi} H^2\right) = 0,$$

we can write the normal component of (4.18) in the form

$$\rho g \zeta - \frac{\alpha \zeta''}{(1+\zeta'^2)^{3/2}} = \frac{\mu-1}{8\pi} H^2 + \frac{(\mu-1)^2}{8\pi} H_n^2 + \text{const}. \qquad (4.20)$$

The field intensity H is composed of a uniform part $H_0 = (0, 0, H_0)$ and the perturbation $h = -\nabla\varphi(x, z)$ due to the warping of the surface. The potentials φ and φ_e satisfy Laplace's equation. For H_0 close to H_*, a solution of the system (4.19)–(4.20) was constructed[50] from a power series in the amplitude (the quasilinear method):

$$\begin{aligned}
\zeta(x) &= a\cos kx + a^2\beta\cos 2kx + \ldots,\\
\varphi(x, z) &= aAe^{kz}\cos kx + a^2Be^{2kz}\cos 2kx + \ldots,\\
\varphi_e(x, z) &= aA_e e^{-kz}\cos kx + a^3B_e e^{-2kz}\cos 2kx + \ldots,\\
H_0 &= H_* + a^2H^{(2)} + \ldots, \quad k = k_* + a^2k^{(2)} + \ldots
\end{aligned}$$

In the linear approximation, the critical field (4.17) and the wave number $k_* = \sqrt{\rho g/\alpha}$ of the critical pertur-

bation are determined. In the third approximation $H^{(2)}$ is calculated; this enables us to find the amplitude of the wave:

$$ak_* = \sqrt{F(\mu)\frac{H_0 - H_*}{H_*}}, \quad F(\mu) = \frac{32(\mu+1)^2}{42\mu - 11(\mu^2+1)}. \qquad (4.21)$$

The function $F(\mu)$ changes sign at $\mu = \mu_* \approx 3.54$; that is, the nature of the instability depends on the magnetic permeability of the liquid. If $\mu < \mu_*$, then $F > 0$, and the instability is soft: near H_* the height of the waves is proportional to $\sqrt{H_0 - H_*}$ (Landau's law). If $\mu > \mu_*$, there follows from (4.21) the possibility of a wavy contour in the subcritical range of fields—a situation characteristic of hard instability.

Gaĭlitis[51] considered perturbations of hexagonal structure,

$$\zeta(x, y) = a\left[\cos kx + \cos\frac{k}{2}(x + y\sqrt{3}) + \cos\frac{k}{2}(x - y\sqrt{3})\right] + O(a^2),$$

which corresponds to the experimentally observed picture (Fig. 7). The results of the first approximation agree with[50], since the linear problem is degenerate and its solution for $H_0 = H_*$ is an arbitrary superposition of plane waves of the same length. But already in the second approximation the degeneracy is removed, and instead of (4.21) one gets

$$ak_* = \frac{8(\mu+1)}{3(\mu-1)}\frac{H_* - H_0}{H_*}. \qquad (4.22)$$

This result, in the opinion of Gaĭlitis, indicates the hard character of the instability; the failure of this to show up in the experiment[3] can be explained by the small value of the threshold jump.

Mention was made above of the equilibrium shape of the surface and, in this connection, of static (frozen) waves. Propagation of plane waves

$$\zeta \sim \exp[i(\omega t - k_x x - k_y y)]$$

of small amplitude on the surface of a magnetic fluid was observed by Zelazo and Melcher[52]. In a uniform field, normal to the unperturbed surface ($H = H_z$), the relation between ω and k is determined by the equation

$$\omega^2 = gk + \frac{\alpha}{\rho}k^3 - \frac{k^2H^2}{4\pi\rho}\frac{\mu(\mu-1)^2}{(\mu+1)^2} \quad (k^2 = k_x^2 + k_y^2).$$

Hence it is evident that with increase of the field intensity, the phase velocity of the waves slows down, and at $H = H_*$ there occurs the static instability ($\omega = 0$), considered above, of the plane surface with respect to waves with $k = k_*$.

In a tangential field $H = H_x$, the dispersion relation has the form

$$\omega^2 = gk + \frac{\alpha}{\rho}k^3 + \frac{k_x^2H^2}{4\pi\rho}\frac{(\mu-1)^2}{\mu+1}.$$

In this case, waves propagated along the field ($k_y = 0$, $k_x = k$) have the largest velocity. We note that a tangential field has no destabilizing effect on the stability of the surface.

(d) **Thermoconvective instability.** In a nonuniform field, mechanical equilibrium of a nonuniformly heated magnetic fluid is in general impossible. At the basis of the mechanism of thermomagnetic convection[53] lies the temperature dependence of the magnetization: under otherwise equal conditions, the colder elements of the fluid are more strongly magnetized, and therefore they are also subject to a larger force in the direction of $\nabla(H^2)$. The gradients of the magnetic intensity here play the same role as does the gravitational field in the mechanism of ordinary thermogravitational convection, based on the thermal expansion of the fluid.

The equilibrium equation

$$\nabla p = M\nabla H + \rho\mathbf{g} \qquad (4.23)$$

requires that the magnetic force and the force of gravity shall be equilibrated at each point by the pressure gradient. On applying the operation curl to equation (4.23), we obtain a necessary condition for equilibrium[1,45,58],

$$\left[\nabla T, \left(\frac{\partial M}{\partial T}\nabla H + \frac{\partial \rho}{\partial T}\mathbf{g}\right)\right] = 0,$$

from which it is evident that equilibrium is possible if T = const or if the gradients of the temperature and of the field are vertical. In the latter case, however, there arises the question of the stability of the possible equilibrium.

One must begin the investigation of convective stability with a transformation of the general heat-transfer equation (4.9). We choose p, T, and H as independent thermodynamic coordinates, so that, for example,

$$\nabla s = \left(\frac{\partial s}{\partial T}\right)_{p,H}\nabla T + \left(\frac{\partial s}{\partial p}\right)_{T,H}\nabla p + \left(\frac{\partial s}{\partial H}\right)_{p,T}\nabla H. \qquad (4.24)$$

By using the equilibrium equation (4.23) and the thermodynamic identity

$$d\Phi = -s\,dT + \frac{1}{\rho}dp + \frac{M}{\rho}dH$$

(Φ is the thermodynamic potential per unit mass), we get from (4.24)

$$\rho\nabla s = \frac{\rho c}{T}\nabla T + \left(\frac{\partial \rho}{\partial T}\right)_{p,H}\mathbf{g} + \left(\frac{\partial M}{\partial T}\right)_{p,H}\nabla H,$$

where $c \equiv c_{p,H} = T(\partial s/\partial T)_{p,H}$ is the specific heat at constant field and pressure. The derivative $\partial s/\partial t$ is transformed analogously; then the equation of heat conduction in a time-invariant magnetic field takes the form

$$\rho c\left(\frac{\partial T}{\partial t} + v\nabla T\right) + vT\left[\left(\frac{\partial \rho}{\partial T}\right)_p\mathbf{g} + \left(\frac{\partial M}{\partial T}\right)_H\nabla H\right] = \kappa\nabla^2 T + \frac{\eta}{2}\left(\frac{\partial v_l}{\partial x_k} + \frac{\partial v_k}{\partial x_l}\right)^2. \qquad (4.25)$$

The terms in square brackets describe an adiabatic change of temperature due to (1) compressibility[43] and (2) the magnetocaloric effect[14]:

$$\delta T_1 = \frac{T}{\rho c}\left(\frac{\partial \rho}{\partial T}\right)_p g\delta z, \quad \delta T_2 = -\frac{T}{\rho c}\left(\frac{\partial M}{\partial T}\right)_H \delta H.$$

Mechanical equilibrium of the fluid in a field H(z) at temperature T(z) will be stable if arbitrary small perturbations of a standing mode, characterized by velocity v, temperature θ, and pressure q, decay with time. Linearized with respect to these quantities, the equations of motion (4.8) (to the right side of the first of these, ρg must be added) and the equation of heat conduction (4.25) have the form

$$\begin{aligned} \rho\dot{\mathbf{v}} &= \eta\nabla^2\mathbf{v} + (\beta\rho g + \gamma MG)\,\theta\mathbf{k} - \nabla q, \quad \operatorname{div}\mathbf{v} = 0, \\ \rho c\dot{\theta} &= \kappa\Delta\theta + [\rho cA - T_0(\beta\rho g + \gamma MG)](\mathbf{vk}), \end{aligned} \qquad (4.26)$$

where k is a unit vector directed upward, along the z axis, and

$$A = -\frac{dT}{dz}, \quad G = -\frac{dH}{dz}, \quad \beta = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p, \quad \gamma = -\frac{1}{M}\left(\frac{\partial M}{\partial T}\right)_H.$$

The density, the magnetization, and their temperature coefficients β and γ are taken for some constant average values of the temperature, $T_0 = \langle T(z)\rangle$, and the field, $H_0 = \langle H(z)\rangle$.

At the limit of stability, when equilibrium is replaced by stationary convective motion, the excitations neither decay nor build up; that is, they are entirely independent of time. With appropriate choice of units[54], the dimensionless equations of neutral perturbations obtained from (4.26) remain the same as in the problems of ordinary convection[55]:

$$\nabla^2\mathbf{v} + R\theta\mathbf{k} = \nabla q,\ \Delta^2\theta + (\mathbf{kv}) = 0,\quad \operatorname{div}\mathbf{v} = 0,$$

but with another dimensionless combination of parameters in the role of Rayleigh's number[54]:

$$R = (\varkappa\eta)^{-1}l^4(\beta\rho g + \gamma MG)\,|\rho cA - T_0(\beta\rho g + \gamma MG)| \qquad (4.27)$$

(l is a characteristic dimension of the container).

Convection occurs for values of R larger than a certain critical value R_0. The latter depends only on the geometry of the chamber and the boundary conditions at its surface; for example, for a plane layer of liquid, on whose boundaries $v = \theta = 0$, the number R_0 is 1708 for a horizontal position of the layer and 1558 for a vertical.

Mechanical equilibrium of an isothermal (A = 0) liquid is always stable: to it corresponds a negative "Rayleigh number"

$$R = -(\beta\rho g + \gamma MG)^2 T_0 l^4 (\varkappa\eta)^{-1},$$

so that the inequality $R < R_0$ is known to be satisfied.[3)] The crisis of equilibrium sets in when

$$A = \frac{1}{\rho c}\left[\frac{\varkappa\eta R_0}{l^4(\beta\rho g + \gamma MG)} + T_0(\beta\rho g + \gamma MG)\right]. \qquad (4.28)$$

In a chamber of small size, the chief factors in stability are the viscosity and the heat conductivity: for

$$l^4 \ll \frac{R_0\varkappa\eta}{T_0(\beta\rho g + \gamma MG)^2} \qquad (4.29)$$

the second (adiabatic) term in (4.28) can be omitted. In this case the effective Rayleigh number (4.27) takes the simpler form[59]

$$R = \frac{\rho c}{\varkappa\eta} A l^4(\beta\rho g + \gamma MG).$$

In another limiting case, when it is possible to neglect the stabilizing effect of dissipation, the threshold value of the temperature gradient is determined by the "generalized Schwarzschild criterion"

$$A = \frac{T_0}{\rho c}(\beta\rho g + \gamma MG).$$

We shall compare the effectiveness of the gravitational and magnetic mechanisms of convection. For a suspension with kerosene base, $\beta\rho \approx 5\times10^{-4}$ g/cm^{3}deg. In the room-temperature range, we may set $\gamma \gtrsim 10^{-3}$ (that is, no smaller than in solid ferromagnets) and $M \approx 30$ G. With such parameters of the medium and with $G \gtrsim 100$ Oe/cm, the magnetic mechanism is the main one[60]; that is, $\gamma MG \gg \beta\rho g$. The inequality (4.29) reduces in this case to $l^4 \ll 10^7 G^{-2}$ (we have taken for the estimate $R_0 \sim 10^3$, $\varkappa \sim 10^4$ erg/cm sec deg, $\eta \sim 10^{-2}$ g/cm sec).

In the preceding analysis, the field gradient G was considered a given quantity. This approach is justified if $G \gg G_i$, where G_i is the gradient of the magnetic intensity induced by the temperature gradient A. We shall estimate the value of G_i. Let the ferrofluid be in a uniform field $H = (0, 0, H_e)$ at temperature T(z). The dependence of M on T leads to the result that the field inside the fluid is nonuniform: from equation (4.4.1) follows

$$G_i = -\frac{dH_i}{dz} = 4\pi\left(\frac{\partial M}{\partial T}\right)_H \frac{dT}{dz} = 4\pi\gamma MA. \qquad (4.30)$$

The magnetic forces due to G_i have a marked influence on the beginning of convection only in very thin layers[61], in which the critical temperature gradient is large. The condition $\gamma MG_i \ll \beta\rho g$, which permits neglect of the magnetic forces due to G_i, reduces with the aid of (4.28) and (4.30) to

$$l^4 \gg 4\pi R_0\left(\frac{\gamma M}{\beta\rho g}\right)^2 \frac{\varkappa\eta}{\rho c}.$$

For the values of the parameters quoted above, this inequality holds true down to $l = 1$ mm.

Specific problems of nonisothermal ferrohydrodynamics that have been treated are the conditions for occurrence of convection in a cylindrical layer of liquid heated from inside, in the field of a straight wire[45]; the effect of a uniform vertical field on the Rayleigh instability of a horizontal layer[61]; and also some problems of convective heat exchange in a boundary layer about a cold rod in a nonuniform magnetic field[62].

5. A MAGNETIC SUSPENSION AS A FIELD WITH INTERNAL ROTATION

(a) Stress tensor and equation for the magnetization. Quasistationary ferrohydrodynamics considers the particles of a suspension as points, for which the concept of intrinsic (axial) rotation does not exist. The applicability of such a model to real suspensions is limited by the condition (3.13): the volume of an individual particle must be small in the sense that $V \ll kT/K$. Allowance for the rotational degrees of freedom of the particles, which is necessary when the contrary inequality is satisfied, requires a very radical modification of the equations of ferrohydrodynamics.

The internal angular momentum of the suspension[63] can serve as a macroscopic characteristic of the intrinsic rotation of the particles. Its volume density S, in the case of small concentrations of identical spherical particles, can be written as $S = I\omega_S$, where $I = nI_0$ is the sum of the moments of inertia of the spheres in unit volume, and ω_S is their mean ordered angular velocity.[4)] In a hydrodynamic description of the suspension as a homogeneous continuous medium, the internal moment S must be treated as an independent function along with the velocity of the medium, the density, and the pressure.

A characteristic of a fluid with internal rotation is asymmetry of the stress tensor[64-66]: the laws of conservation of momentum and of angular momentum are expressed by the equations

$$\rho\frac{dv_i}{dt} = \frac{\partial\sigma_{ik}}{\partial x_k},\quad \frac{dS_{ik}}{dt} = \sigma_{ki} - \sigma_{ik},$$
$$\left(\frac{d}{dt} = \frac{\partial}{\partial t} + v_k\frac{\partial}{\partial x_k},\quad S_{ik} = e_{ikl}S_l\right). \qquad (5.1)$$

On including in the stress tensor σ_{ik}, calculated in[66], the Maxwell tensor t_{ik} from (4.5), we get for a magnetic suspension

$$\sigma_{ik} = -\left[p + \frac{S}{I}(S - I\Omega)\right]\delta_{ik} + \eta\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right) + \frac{1}{2\tau_s}(S_{ik} - I\Omega_{ik}) + \frac{1}{4\pi}\left(H_iB_k - \frac{1}{2}H^2\delta_{ik}\right), \qquad (5.2)$$
$$\Omega_{ik} = \frac{1}{2}\left(\frac{\partial v_k}{\partial x_i} - \frac{\partial v_i}{\partial x_k}\right) = e_{ikl}\Omega_l.$$

From (5.1) and (5.2), by use of Maxwell's equations

(4.4) and the condition of incompressibility of the medium div v = 0, we find

$$\rho\frac{d\mathbf{v}}{dt}=-\nabla\left[p+\frac{S}{I}(S-I\Omega)\right]+\eta\nabla^2\mathbf{v}+(M\nabla)H+\frac{1}{2\tau_s}\operatorname{rot}(S-I\Omega), \quad (5.3)$$

$$\frac{dS}{dt}=[M\times H]-\frac{1}{\tau_s}(S-I\Omega). \quad (5.4)$$

The system obtained must be supplemented by yet another equation, relating **M** and **S**. In magnetic suspensions there is between these quantities no direct relation like, for example, that exists in liquids with gyromagnetic properties[67,68], where **M** = γ**S**. The magnetization of a system of "classical" particles in principle is independent of their state of rotation, so that the analogy that suggests itself, between the internal angular momentum of a suspension and spin, is by no means complete.

The missing equations can be obtained by the following simple considerations[69]. For a fixed element of volume of the suspension, we introduce a local frame of reference Σ′ in which the mean angular velocity of the particles is zero. We suppose further that in the system Σ′ the magnetization is described by a linear relaxation equation

$$\frac{d'M}{dt}=-\frac{1}{\tau}(M-M_0)$$

with M_0 determined by formula (4.6). The frame of reference Σ′ is rotating with respect to a fixed system Σ with angular velocity $\omega_S = S/I$. By use of the well-known kinematic relation between the rates of change of a vector in the systems Σ and Σ′, we get the equation for the magnetization in the fixed frame of reference,

$$\frac{dM}{dt}=\frac{1}{I}[S\times M]-\frac{1}{\tau}(M-M_0). \quad (5.5)$$

When $\sigma \gg 1$, the only condition under which it is necessary to take account of the intrinsic rotation of the particles, the inequality (3.9) is satisfied—the magnetic moment is "frozen" into the body of the particle, i.e., the relaxation time τ of the magnetization is determined by the Brownian time τ_B. The latter has order of magnitude 10^{-6} sec at room temperature and for d ~ 100 Å. As for the "viscous" time τ_S, which characterizes the rate of relaxation of the angular momentum **S**, it is (under the same conditions) five orders smaller than τ_B:

$$\frac{\tau_s}{\tau_B}=\frac{\rho_s kT}{30\pi\eta^2 d}\sim 10^{-5}.$$

The smallness of τ_S permits us to neglect in (5.4) the derivative dS/dt, which could become comparable with S/τ_S only at those frequencies of alternation ω of the field ($\omega \sim \tau_S^{-1} \sim 10^{11}$ sec^{-1}) at which the rigid-dipole model itself becomes inappropriate[5)] because of Larmor precession of the magnetic moments of the particles[71].

On neglecting the inertial term in (5.4), we find from this equation

$$S = I\Omega + \tau_s[M\times H]. \quad (5.6)$$

Now the internal angular momentum is eliminated from the remaining equations of the system. The stress tensor (5.2) becomes symmetric:

$$\sigma_{ik}=(\ldots)\delta_{ik}+\eta\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}\right)+\frac{1}{2}(M_iH_k-M_kH_i)+\frac{1}{4\pi}H_iB_k$$
$$=(\ldots)\delta_{ik}+\eta\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}\right)+\frac{1}{2}(M_iH_k+M_kH_i), \quad (5.7)$$

as must be true also when dS/dt = 0 (see (5.1)), and the equation of motion of the magnetic moment (5.5) takes the form

$$\frac{dM}{dt}=[\Omega,\ M]-\frac{1}{\tau_B}\left(M-M_0\frac{H}{H}\right)-\frac{\tau_s}{I}[M\times[M\times H]]. \quad (5.8)$$

The last (relaxational) term in this equation appeared as a result of allowance for the rotational degrees of freedom of the particles. Like the analogous term in the Landau-Lifshitz equation (3.4), it describes a process of approach of the vector **M** to its equilibrium orientation, which proceeds without change of the length of this vector. To sum up, the relaxation times of the longitudinal and transverse components of the magnetization are different. On substituting in (5.8)

$$M=\frac{M_0}{H}H+\mu \quad (5.9)$$

and supposing that the liquid is immovable (**v** = **Ω** = 0), we get in the approximation linear in μ the equation

$$\frac{\partial\mu}{\partial t}=-\frac{H(\mu H)}{\tau_\parallel H^2}-\frac{[H\times[\mu\times H]]}{\tau_\perp H^2} \quad (5.10)$$

with the relaxation times

$$\tau_\parallel=\tau_B,\ \tau_\perp=\tau_B\left(1+\frac{\tau_s\tau_B}{I}M_0H\right)^{-1}=\frac{2\tau_B}{2+\xi L(\xi)}. \quad (5.11)$$

Thus with phenomenological allowance for the internal rotation, there develops a dependence of $\tau_\perp$ on the field intensity, whereas $\tau_\parallel$ remains unchanged and equal to the "priming" constant τ_B.

(b) Dependence of relaxation times on field intensity. In order to make more precise the dependence of the relaxation times of the magnetization of a suspension on the field intensity, we shall give here, following[72], a derivation of the macroscopic equation (5.10) from the kinetic equation, which is the Fokker-Planck equation for Brownian particles.

In an external field **H** = (kT/m) ξ the distribution function w of particles suspended in a liquid with respect to orientations of their dipole moments obeys the equation[73]

$$2\tau_B\sin\vartheta\frac{\partial w}{\partial t}=\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial w}{\partial\vartheta}+\xi w\sin\vartheta\right)\right]+\frac{1}{\sin\vartheta}\frac{\partial^2 w}{\partial\varphi^2}. \quad (5.12)$$

For what follows, it is convenient to rewrite (5.12) in vector form, introducing the unit vector **e** = m/m in the direction of the magnetic moment of the particle and the "angular momentum" operator $\hat{\mathbf{I}} = -i\mathbf{e}\times\nabla$. With this notation, Eq. (5.12) takes the form

$$2\tau_B\dot{w}=i\hat{\mathbf{I}}(i\hat{\mathbf{I}}-[\mathbf{e}\times\xi])\,w. \quad (5.13)$$

The stationary normalized solution of equation (5.13) is the Gibbs distribution

$$w_0=\frac{\xi}{4\pi\operatorname{sh}\xi}e^{\xi\mathbf{e}}, \quad (5.14)$$

and averaging of the "microscopic" vector **e** with the function w_0 gives for the equilibrium magnetization of the suspension the well-known result

$$M_0=nm\langle\mathbf{e}\rangle_0=nmL(\xi)\frac{\xi}{\xi}. \quad (5.15)$$

The equation of motion of **M** must be obtained by averaging **e** with the nonstationary distribution function satisfying the complete equation (5.13). By taking account of the anti-Hermitian character of the operator $i\hat{\mathbf{I}} = \mathbf{e}\times\nabla$, it is easy to obtain from (5.13) an equation for an arbitrary moment of the distribution function. It turns out that the equation for the first moment,

$$2\tau_B\frac{\partial}{\partial t}\langle\mathbf{e}\rangle=-2\langle\mathbf{e}\rangle-\langle[\mathbf{e}\times[\mathbf{e}\times\xi]]\rangle \quad (5.16)$$

contains the second moment $\xi_k\langle e_i e_k\rangle$, the equation for the second moment contains the third, etc.; that is, one obtains, as usual, an infinite system of coupled equations. Closure can be effected in the effective-field approximation, by use of an idea of the well-known thermodynamic method of Leontovich[74].

We shall suppose that at each instant the distribution function w(t) coincides in form with the stationary solution w_0 of the Fokker-Planck equation, but with replacement in (5.14) of the actual field ξ by some effective field $\xi_*(t)$. Then any instantaneous value of the magnetization

$$\mathbf{M} = nmL(\xi_*)\frac{\boldsymbol{\xi}_*}{\xi_*} \tag{5.17}$$

can be regarded[74] as an equilibrium value (compare (5.15)) in the presence of an additional field $\nu = \xi_* - \xi$. On carrying out the averaging in (5.16) with a distribution function introduced in the indicated manner, we obtain the equation for the effective field

$$2\tau_B \frac{\partial}{\partial t}\left[L(\xi_*)\frac{\boldsymbol{\xi}_*}{\xi_*}\right] = -2\xi_*^{-1}L(\xi_*)(\boldsymbol{\xi}_* - \boldsymbol{\xi}) - \xi_*^{-2}[3L(\xi_*) - \xi_*][\boldsymbol{\xi}_* \times [\boldsymbol{\xi} \times \boldsymbol{\xi}_*]]. \tag{5.18}$$

We shall consider the case of slight nonequilibrium, when the effective field is close to the actual ($\nu \ll \xi$). For the nonequilibrium part of the magnetization, $\mu = \mathbf{M} - \mathbf{M}_0$, we find from (5.15) and (5.17) in the approximation linear in ν

$$\boldsymbol{\mu} = nmL(\xi)\left[\left(\frac{d\ln L(\xi)}{d\ln \xi} - 1\right)\xi^{-3}\boldsymbol{\xi}(\boldsymbol{\xi}\boldsymbol{\nu}) + \xi^{-1}\boldsymbol{\nu}\right]. \tag{5.19}$$

Now by linearizing equation (5.18) and in it expressing ν in terms of μ by means of (5.19), we obtain the equation of motion of the magnetization in the form (5.10), with the relaxation times

$$\tau'_{\parallel} = \frac{d\ln L(\xi)}{d\ln \xi}\tau_B, \qquad \tau'_{\perp} = \frac{2L(\xi)}{\xi - L(\xi)}\tau_B. \tag{5.20}$$

Graphs of these functions are shown in Fig. 9. There also, dotted, is shown $\tau_\perp$, found earlier, (5.11). We note that for the relaxation time of the magnetization components perpendicular to the field, formulas (5.11) and (5.20) give close values at any ξ: in a strong magnetic field, $\tau_\perp$ and $\tau'_\perp$ approach the common asymptote $2\tau_B/\xi = 6\eta/M_S H$ (compare (3.11)), while for $\xi \ll 1$ we have

$$\tau_\perp = \left(1 - \frac{1}{6}\xi^2\right)\tau_B, \quad \tau'_\perp = \left(1 - \frac{1}{10}\xi^2\right)\tau_B.$$

The field dependence of $\tau'_\parallel$ is similar:

$$\tau'_\parallel = \tau_B \times \begin{cases} \left(1 - \frac{2}{15}\xi^2\right) & (\xi \ll 1), \\ \xi^{-1} & (\xi \gg 1). \end{cases}$$

(c) **Rotational viscosity.** In the derivation of Einstein's formula[75] for the viscosity of a suspension of spherical particles,

$$\eta = \eta_0\left(1 + \frac{5}{2}\varphi\right) \tag{5.21}$$

no allowance is made for the possibility of an ordered rotation of the spheres with respect to the liquid. The additional internal friction that arises when there is noncoincidence of the angular velocity $\boldsymbol{\omega}_S$ of the particles with the local angular velocity $\boldsymbol{\Omega} = (\text{curl } \mathbf{v})/2$ of the liquid must manifest itself in an increase of the effective viscosity of the suspension. We note at once that this additional "rotational" viscosity can be observed only in cases in which the difference $\boldsymbol{\Omega} - \boldsymbol{\omega}_S$ is maintained by the moments of some external forces, acting directly on the particles of the suspension. In the contrary case,

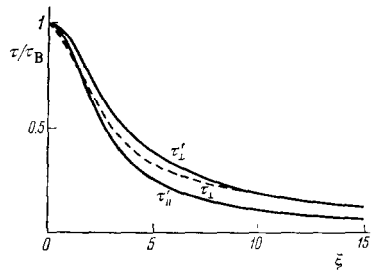

FIG. 9

equalization of the angular velocities $\boldsymbol{\omega}_S$ and $\boldsymbol{\Omega}$ occurs in a very short time $\tau_S \sim 10^{-9}$–10^{-11} sec (for spheres of diameter 10^{-5}–10^{-6} cm).

The concept of rotational viscosity enables us to explain the experimentally observed[7,76,77] increase of the viscosity of magnetic suspensions under the influence of a magnetic field. We shall first give a qualitative explanation of this effect.

We consider the motion of an individual spherical particle in a uniform shear flow ($\boldsymbol{\Omega}$ = const, plane Couette flow). In the absence of a field, the particle "rolls" freely along the appropriate shear plane, with angular velocity $\boldsymbol{\omega}_S$ equal to $\boldsymbol{\Omega}$. In a magnetic field, there acts on the particle a torque $\mathbf{m} \times \mathbf{H}$ that changes its state of rotation. As a consequence of this, there arises a frictional torque $6\eta V(\boldsymbol{\Omega} - \boldsymbol{\omega}_S)$; that is, the magnetic field "turns on" a mechanism of rotational viscosity.[6)] The latter attains its limiting value (saturation) when "rolling" of the particle is replaced by "slipping": a field of sufficiently large intensity guarantees constancy of the particle's orientation, not allowing it to twist with the liquid.

The orienting influence of the field (mH) is opposed by the hydrodynamic forces ($6\eta V\Omega$) and the Brownian motion (kT). The quantities indicated in parentheses, of the dimensions of torque, characterize the effectiveness of the factors enumerated above. In the absence of rotational diffusion, complete orientation of the magnetic moments would be attained for $mH \gg 6\eta V\Omega$; that is, for single-domain particles, in fields $H \gg 6\eta\Omega/M_S$. The value $H \sim 1$ Oe satisfies the last inequality for any reasonable values of Ω. Hence it is clear why a theory of rotational viscosity that does not allow for thermal motion[79,80] predicts saturation of the viscosity at weak fields.

For colloidal suspensions, the condition

$$\frac{3\eta V\Omega}{kT} = 2\Omega\tau_B \ll 1,$$

is always satisfied, so that the chief disorienting influence on the magnetic moments of the particles is rotational Brownian motion. Saturation of the viscosity as a function of the field must consequently set in at $mH \gg kT$; that is, at $\xi \gg 1$.

A quantitative theory of rotational viscosity (with allowance for Brownian motion) is given in[69].

We shall consider stationary flow of a suspension in a uniform magnetic field. In a quiescent liquid, the stationary solution of equation (5.8) is $\mathbf{M} = \mathbf{M}_0$. The magnetization of a moving suspension differs, of course, from $\mathbf{M}_0$, but the difference $\mathbf{M} - \mathbf{M}_0 \equiv \mu$ is small in proportion to the smallness of $\Omega\tau_B$. Treating μ and $\Omega\tau_B$ as quantities of the first order, we find from (5.8) in the linear approximation

$$\mu = \tau_\perp \frac{M_0}{H}[\Omega \times H]. \qquad (5.22)$$

By use of the last formula, the magnetization of the suspension can be described in the form $M_i = \chi_{ik}H_k$, where

$$\chi_{ik} = \frac{M_0}{H}(\delta_{ik} - \tau_\perp \Omega_{ik}).$$

As is evident, the antisymmetric part of the magnetic susceptibility tensor is determined by the vorticity of the flow.

On eliminating **M** from the expression (5.7) for the stress tensor, we get

$$\sigma_{ik} = (\ldots)\delta_{ik} + \eta_{iklm}\frac{\partial v_l}{\partial x_m} + \frac{1}{4\pi}H_iB_k \qquad (5.23)$$

with a viscosity tensor consisting of an isotropic (ordinary) part, with coefficient η, and an anisotropic part

$$\eta^a_{iklm} = \frac{1}{4}\tau_\perp M_0 H^{-1}[\delta_{il}H_kH_m - \delta_{lm}H_kH_l - \delta_{kl}H_iH_m + \delta_{km}H_iH_l]. \qquad (5.24)$$

The tensor $\eta^a_{ikl\mathrm{m}}$ is antisymmetric with respect to the indices i, k and l, m and symmetric with respect to interchange of pairs of these indices.

We shall calculate the frictional force acting on a solid surface past which the liquid is flowing. We choose a local system of coordinates with the x axis along the velocity of flow and the z axis along the normal to the surface. The force acting on unit area is $f_x = \sigma_{xz} - \sigma'_{xz}$, where σ'_{ik} is the Maxwell stress tensor in the solid body. By using the boundary conditions of continuity of H_x and B_z, we get from (5.23)–(5.24)

$$f_x = \left[\eta + \frac{1}{4}\tau_\perp \frac{M_0}{H}(H_x^2 + H_z^2)\right]\frac{\partial v_x}{\partial z}.$$

The quantity added to the ordinary viscosity in this expression must be regarded as rotational viscosity

$$\eta_r = \frac{1}{4}\tau_\perp M_0 H \sin^2\alpha, \qquad (5.25)$$

where α is the angle between the vectors **H** and Ω. The vanishing of η_r for $\mathbf{H} \| \Omega$ is simply explained: orientation of the magnetic moment of the particle along **H** does not impede its rotation with angular velocity Ω about the same direction.

In weak fields, $\tau_\perp \approx \tau_B$ and the expansion of η_r in powers of ξ begins with terms of the second order:

$$\eta_r = \frac{1}{4}\eta\varphi\xi^2\sin^2\alpha \quad (\xi \ll 1). \qquad (5.26)$$

In a strong field, when $\tau_\perp \approx 2\tau_B/\xi$, the rotational viscosity reaches the limiting value[7)]

$$\eta_r = \frac{3}{2}\eta\varphi\sin^2\alpha \quad (\xi \gg 1). \qquad (5.27)$$

In general, the formula

$$\eta_r(\xi) = \frac{3}{2}\eta\varphi F(\xi)\sin^2\alpha \qquad \left(F(\xi) = \frac{\xi - \mathrm{th}\,\xi}{\xi + \mathrm{th}\,\xi}\right), \qquad (5.28)$$

obtained from (5.25) after substitution of $\tau_\perp$ from (5.11), applies for arbitrary ξ. The dependence on the field, approximately that of $F(\xi)$, remains such if $\tau_\perp$ is replaced by $\tau'_\perp$ from (5.20).

On including η_r in the Einstein formula (5.21), we have to the first order in the concentration

$$\eta(\xi) = \eta_0\left[1 + \frac{\varphi}{2}\left(5 + 3\,\frac{\xi - \mathrm{th}\,\xi}{\xi + \mathrm{th}\,\xi}\sin^2\alpha\right)\right]. \qquad (5.29)$$

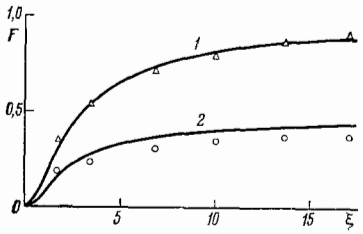

FIG. 10

In the experiments of McTague[76] the viscosity of a magnetic colloid (particles of cobalt in toluene) was messured on the basis of the time of flow through a round capillary (Poiseuille's method) placed in a uniform magnetic field. The experimental points shown in Fig. 10 were obtained with two different orientations of the field with respect to the velocity of flow: curve 1 corresponds to $\mathbf{H} \| \mathbf{v}$, curve 2 to $\mathbf{H} \perp \mathbf{v}$. In Poiseuille flow the isolines of vorticity (Ω = const) are concentric circles in a cross-sectional surface of the capillary. Therefore in case 1 the angle $\alpha = \pi/2$ at each point of the flow, while in case 2 it takes all values from 0 to 2π, so that $\sin^2\alpha = 1/2$.

According to (5.28) we should consequently have

$$\eta_r^{(1)} = \frac{3}{2}\eta\varphi F(\xi), \quad \eta_r^{(2)} = \frac{1}{2}\eta_r^{(1)}. \qquad (5.30)$$

The curves in Fig. 10 calculated from these formulas are in agreement with experiment.

We note that in case 2, when the local viscosity depends on α, the flow loses its axial symmetry[82]. But the intensity of the "secondary" flows caused by the field is very small: in order to calculate corrections to the velocity of the basic motion, it is necessary in the expansion of μ in powers of $\Omega\tau_B$ to keep higher-order terms that were neglected in (5.22). It is interesting that when these terms are taken into account, the stress tensor becomes a nonlinear function of the velocity gradients; that is, in a magnetic field the suspension acquires non-Newtonian properties[69,80,83,84]. One must remember, however, that there exists also another, far more serious reason for the non-Newtonian character of magnetic suspensions. This is the dipole interaction of the particles, which is capable, as was mentioned above, of leading even to the formation of chain aggregates. Against the background of this latter effect, non-Newtonian behavior due to finiteness of the value of $\Omega\tau_B$ can scarcely be noticed.

(d) **Entrainment of a suspension by a rotating field.** Entrainment of a nonconducting fluid by a rotating magnetic field was first observed by Zwetkoff[85] in experiments with n-azoxyanisole. The molecules of this liquid crystal possess a diamagnetic anisotropy and tend to arrange themselves in the field in such a way that the longest dimension of the molecule is parallel to the field intensity.

In ferromagnetic suspensions the rotational effect is of course much more pronounced.[4] The magnetic moments of the particles "follow" after the direction of the field, so that rotation of the field causes rotation of the particles. Because of the friction experienced in such a rotation by each particle, the liquid does not remain in the quiescent state but gradually begins to rotate. Thus there occurs a transformation of part of the internal angular momentum of the suspension into a

visible (hydrodynamic) motion of it. The mechanism of this transformation is very curious.

Each particle, by entraining the adjacent layer of viscous liquid, becomes a center of microscopic vorticity, whose dimensions do not exceed the mean distance between particles. From the point of view of the mechanics of a continuous medium, such a motion of the suspension is no longer hydrodynamic. Averaging of the microvortices over physically small elements of volume also does not lead to a resultang hydrodynamic motion in the simple case in which the particles are uniformly distributed in the liquid and rotate with the same angular velocity ω_S. "Macroscopic" vorticity Ω = (curl v)/2 is possible only with nonuniform spatial distribution of the internal angular momentum $\mathbf{S} = I\boldsymbol{\omega}_S$. This is easily seen from the equation of motion (5.3) of the liquid, where the term containing curl **S** is the volume force density. There is here an analogy with the Amperian model, which explains the magnetic moment of magnets by means of molecular currents (see, for example, the book by Tamm[86]). The density of molecular currents is proportional to curl M. If M = const, then the elementary currents of neighboring "molecules" compensate each other. The same thing occurs with microvortices when **S** = const.

The distribution of internal angular momentum in an arbitrary bounded volume is already nonuniform because of the fact that near the fixed solid boundaries of the chamber the rotation of the particles is impeded. In order to satisfy the boundary conditions for **S**,[8] it is necessary to include in (5.4) a term $D_S\nabla^2\mathbf{S}$, where D_S is the coefficient of diffusion of the internal moment.

In reference[88] the complete system of equations of the theory is solved for the case in which the suspension fills a long cylinder of radius R, placed in a uniform rotating field perpendicular to the axis of the cylinder. We shall not present the results of the calculation here, since in some details they disagree with the experimental results of Moskowitz and Rosensweig[4] and especially of Bibik et al.[89] We shall merely indicate the character of the distribution of velocity and of internal moment over the cross section of the cylinder. The nonvanishing components of these vectors (v_φ and S_z in coordinates r, φ, z) are expressed in terms of Bessel functions of imaginary argument $I_n(r/\delta)$, where $\delta = \sqrt{D_S\tau_S}$. Comparison of calculated and experimental data gives for the diffusion length δ a value of order 10^{-4} cm, so that the condition $R/\delta \gg 1$ is satisfied. In this case, as is evident from the asymptotic form of the Bessel functions

$$\frac{I_n(r/\delta)}{I_n(R/\delta)} \approx e^{-(R-r)/\delta},$$

the gradients of velocity and of moment are concentrated in a narrow boundary layer of thickness δ. In all the remaining volume of the cylinder (the core), the liquid rotates like a solid body, and the internal angular momentum is constant.

[1)]For example, in aqueous colloid the polar COOH groups of the fatty acids are oriented into the water. For colloidal systems in an organic medium, stabilization is accomplished when the hydrocarbon chains of the surface-active molecules are rotated into the medium.

[2)]We disregard for the present the dependence of τ on H, which is important in strong fields (on this topic see Sec. 5 (b)).

[3)]An erroneous conclusion about convective instability and "thermoconvective explosion" of an isothermal ferrofluid [56-58] was based on incorrect neglect of the compressibility in the heat-conduction equation: in the cited papers, the term containing ∇p in (4.24) was not taken into account; see in this connection [90] and the note added in proof in [54].

[4)]It is implied, of course, that the averaging is over elements of volume that are large in comparison with n^{-1} but small in comparison with hydrodynamic dimensions.

[5)]Despite an opinion that is encountered [70], a phenomenological description of magnetic suspensions cannot be given in general form for arbitrary external influences, properties, and degree of dispersion of the ferromagnetic material.

[6)]If the particle is not spherical, then the field prevents it from still flowing in symmetric (vortex-free) flow. In this case there appear additional coefficients of viscosity, dependent on the form of the particles and on the field intensity. For a suspension of ellipsoids of revolution, magnetized along an axis of symmetry, the viscosity tensor was calculated in [78].

[7)]We recall that this result ($\eta_r^{max}/\eta \sim \phi$) refers to suspensions of ferromagnetic particles ($\sigma \gg 1$) with "frozen in" magnetic moments ($\sigma \gg \xi$). For suspensions of superparamagnetic particles ($\sigma \ll 1$) one gets [81] instead of (5.27) $\eta_r^{max}/\eta \sim \sigma^2\phi$. The smallness of this quantity justifies the application to such suspensions of the Rosensweig-Neuringer [1] isotropic model (with a single viscosity coefficient).

[8)]Different variants of the boundary conditions are discussed in [87].

[1] J. L. Neuringer and R. E. Rosensweig, Phys. Fluids 7, 1927 (1964).
[2] R. E. Rosensweig, J. W. Nestor, and R. S. Timmins, A. I. Ch. E.-I. Chem. E. Symp. Series, No. 5, 104 (1965).
[3] M. D. Cowley and R. E. Rosensweig, J. Fluid Mech. 30, 671 (1967).
[4] R. Moskowitz and R. E. Rosensweig, Appl. Phys. Lett. 11, 301 (1967).
[5] E. L. Resler and R. E. Rosensweig, AIAA J. (Am. Inst. Aeronaut. Astronaut.) 2, 1418 (1964); J. Eng. for Power (Trans. Am. Soc. Mech. Eng., Ser. A) 89, 399 (1967).
[6] R. E. Rosensweig, AIAA J. (Am. Inst. Aeronaut. Astronaut.) 4, 1751 (1966); Nature (Lond.) 210, 613 (1966).
[7] R. E. Rosensweig, R. Kaiser, and G. Miskolczy, J. Colloid Interface Sci. 29, 680 (1969).
[8] R. E. Rosensweig, Intern. Sci. Tech., No. 55, 48 (July 1966).
[9] R. E. Rosensweig, New Scientist 29, 146 (1966) (Russ. transl.: Usp. Fiz. Nauk 92, 339 (1967)); Indust. Res. 12, 36 (1970).
[10] N. S. Akulov, Ferromagnetizm (Ferromagnetism), M.-L., ONTI, 1940.
[11] V. G. Mogilevskiĭ, Élektromagnitnye poroshkovye mufty i tormoza (Electromagnetic Powder Clutches and Brakes), M.-L., "Energiya," 1964.
[12] A. R. V. Bertrand, Rev. Inst. Franç. Bétrole 25, 16 (1970).
[13] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), M., Fizmatgiz, 1957 (Translation: Pergamon Press (Addison-Wesley), 1960).
[14] S. V. Vonsovskiĭ, Magnetizm (Magnetism), M., "Nauka," 1971.
[15] W. F. Brown, Jr., Ann. N. Y. Acad. Sci. 147, 463 (1969).
[16] E. P. Wohlfarth, Adv. Phys. 8, 87 (1959) (Russ. transl.: É. Vol'fart, Magnitno-tverdye materialy, M.-L. Gosénergoizdat, 1963).
[17] R. Kaiser and G. Miskolczy, J. Appl. Phys. 41, 1064 (1970).
[18] W. C. Elmore, Phys. Rev. 54, 309 (1938).
[19] J. R. Thomas, J. Appl. Phys. 37, 2914 (1966).
[20] P. H. Hess and P. H. Parker, J. Appl. Polym. Sci. 10, 1915 (1966).

[21]E. N. Mozgovoĭ and É. Ya. Blum, Magnit. gidrodin., No. 4, 18 (1971) [Magnetohydrodynamics (1971)].
[22]F. E. Luborsky and J. D. Opie, J. Appl. Phys. 34, 1317 (1963).
[23]P. G. Shepherd, J. Popplewell, and S. W. Charles, J. Phys. D3, 1985 (1970).
[24]P. G. Shepherd and J. Popplewell, Phil. Mag. 23, 239 (1971).
[25]I. Ya. Kagan, V. G. Rykov, and E. I. Yantovskiĭ, Magnit. gidrodin. 6, No. 2, 155 (1970) [Magnetohydrodynamics 6, 441 (1970)].
[26]E. E. Bibik and I. S. Lavrov, Kolloid. zh. 27, 652 (1965).
[27]B. V. Deryagin and L. D. Landau, Zh. Eksp. Teor. Fiz. 11, 802 (1941); 15, 663 (1945).
[28]E. E. Bibik, I. S. Lavrov, and O. M. Merkushev, Kolloid. zh. 28, 631 (1966).
[29]P. Goldberg, J. Hansford, and P. J. van Heerden, J. Appl. Phys. 42, 3874 (1971).
[30]P. G. de Gennes and P. A. Pincus, Phys. Kondens. Mater. 11, 189 (1970).
[31]L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), M., "Nauka," 1964 (translation: Pergamon Press (Addison-Wesley), 1969).
[32]C. P. Bean, J. Appl. Phys. 26, 1381 (1955); I. S. Jacobs and C. P. Bean, in Magnetism (G. T. Rado and H. Suhl, editors), vol. 3 (Academic Press, 1963), p. 271.
[33]Ya. I. Frenkel', Kineticheskaya teoriya zhidkosteĭ (Kinetic Theory of Liquids), Collection of Selected Works, vol. 3, M.-L., izd. AN SSSR, 1952 (translation: Oxford Univ. Press, 1946; Dover, 1955).
[34]W. C. Elmore, Phys. Rev. 54, 1092 (1938).
[35]C. P. Bean and I. S. Jacobs, J. Appl. Phys. 27, 1448 (1956).
[36]E. E. Bibik, B. Ya. Matygullin, Yu. L. Raĭkher, and M. I. Shliomis, Magnit. gidrodin., No. 1, 68 (1973) [Magnetohydrodynamics (1973)].
[37]C. P. Bean and J. D. Livingston, J. Appl. Phys. 30, 120S (1959).
[38]G. V. Skrotskiĭ and L. V. Kurbatov, in Ferromagnitnyĭ rezonans (Ferromagnetic Resonance) S. V. Vonsovskiĭ, ed.), M., Fizmatgiz, 1961.
[39]L. D. Landau and E. M. Lifshitz, Phys. Z. Sowjetunion 8, 153 (1935) (Russian translation: L. D. Landau, Collected Works, vol. 1, M., "Nauka," 1969, p. 128). (Reprinted in Collected Papers of L. D. Landau (D. ter Haar, ed.), Pergamon Press, 1965, p. 101).
[40]J. C. Anderson and B. Donovan, Proc. Phys. Soc. Lond. 73, 593 (1959).
[41]L. Néel, C. R. Acad. Sci. (Paris) 228, 664 (1949); Ann. Geophys. 5, 99 (1949).
[42]W. F. Brown, Jr., Phys. Rev. 130, 1677 (1963); J. Appl. Phys. 34, 1319 (1963).
[43]L. D. Landau and E. M. Lifshitz, Mekhanika sploshnyx sred (Mechanics of Continuous Media), M., Gostekhizdat, 1953 (translation: Fluid Mechanics, Pergamon Press (Addison-Wesley), 1959).
[44]J. J. Newman and R. B. Yarbrough, J. Appl. Phys. 39, 5566 (1968); IEEE Trans. Magn. Mag-5, 320 (1969).
[45]V. M. Zaĭtsev and M. I. Shliomis, Zh. Prikl. Melch. i Tekhn. Fiz. 9, No. 1, 41 (1968) [J. Appl. Mechs. and Techn. Phys. 9, 24 (1968)].
[46]J. R. Melcher, Field-Coupled Surface Waves, M. I. T. Press, Cambridge, Mass., 1963.
[47]Ya. I. Frenkel', Zh. Eksp. Teor. Fiz. 6, 347 (1936).
[48]G. I. Taylor and A. D. McEwan, J. Fluid Mech. 22, 1 (1965).
[49]V. A. Briskman and G. F. Shaĭdurov, Uch. zap. Permskogo un-ta (Scientific Notes of Perm University), No. 216 (Gidrodinamika (Hydrodynamics), issue 2), 229 (1970).
[50]V. M. Zaĭtsev and M. I. Shliomis, Dokl. Akad. Nauk SSSR 188, 1261 (1969) [Sov. Phys.-Doklady 14, 1001 (1970)].
[51]A. Gaĭlitis, Magnit. gidrodin. 5, No. 1, 68 (1969).
[52]R. E. Zelazo and J. R. Melcher, J. Fluid Mech. 39, 1 (1969) [Magnetohydrodynamics 5, No. 1, 44 (1969)].
[53]D. I. Ageĭkin, Dokl. Akad. Nauk SSSR 74, 229 (1950).
[54]M. I. Shliomis, Izv. Akad. Nauk SSSR Mekh. Zhidk. i Gaza, No. 6, 130 (1973).
[55]G. Z. Gershuni and E. M. Zhukhovitskiĭ, Konvektivnaya ustoĭchivnost' neszhimaemoĭ zhidkosti (Convective Stability of Incompressible Liquids), M., "Nauka," 1972.
[56]B. M. Berkovskiĭ and V. G. Bashtovoĭ, Magnit. gidrodin., No. 2, 24 (1971) [Magnetohydrodynamics (1971)].
[57]V. G. Bashtovoĭ, B. M. Berkovskiĭ, and A. K. Sinitsyn, Magnit. gidrodin., No. 1, 12 (1972) [Magnetohydrodynamics (1972)].
[58]B. M. Berkovskiĭ and V. G. Bashtovoĭ, Proc. 4th All-Union Conf. on Heat and Mass Exchange, vol. 1, Part 2, Minsk, ITMO Akad. Nauk BSSR, 1972, p. 385; B. M. Berkovskiĭ, Author's abstract of doctoral dissertation (Minsk, 1971).
[59]D. P. Lalas and S. Carmi, Phys. Fluids 14, 436 (1971).
[60]R. A. Curtis, Phys. Fluids 14, 2096 (1971).
[61]B. A. Finlayson, J. Fluid Mech. 40, 753 (1970).
[62]J. L. Neuringer, Int. J. Non-linear Mech. 1, 123 (1966).
[63]V. S. Sorokin, Zh. Eksp. Teor. Fiz. 13, 306 (1943).
[64]S. R. de Groot and P. Mazur, Non-Equilibrium Thermodynamics, North-Holland, 1962 (Russ. transl., M., "Mir," 1964).
[65]É. L. Aéro, A. N. Bulygin, and E. V. Kuvshinskiĭ, Prikl. Mat. i Mekh. 29, 297 (1965) [J. Appl. Math and Mechs. 29, 333 (1965)].
[66]M. I. Shliomis, Zh. Eksp. Teor. Fiz. 51, 258 (1966) [Sov. Phys.-JETP 24, 173 (1967)].
[67]M. I. Shliomis, Zh. Eksp. Teor. Fiz. 53, 1125 (1967) [Sov. Phys.-JETP 26, 665 (1968)].
[68]Yu. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. 59, 2059 (1970) [Sov. Phys.-JETP 32, 1116 (1971)].
[69]M. I. Shliomis, Zh. Eksp. Teor. Fiz. 61, 2411 (1971) [Sov. Phys.-JETP 34, 1291 (1972)].
[70]V. M. Suyazov, Prikl. Mekh. i Tekhn. Fiz. 11, No. 2, 12 (1970); No. 4, 40 (1970) [J. Appl. Mechs. and Techn. Phys. 11, 209 and 557 (1970); Magnit, gidrodin., No. 2, 3 (1971) [Magnetohydrodynamics (1971)].
[71]C. Caroli and P. Pincus, Phys. Kondens. Mater. 9, 311 (1969).
[72]M. A. Martsenyuk, Yu. L. Raĭkher, and M. I. Shliomis, Zh. Eksp. Teor. Fiz. 65, 834 (1973) [Sov. Phys.-JETP 38, 413 (1974)].
[73]M. A. Leontovich, Statisticheskaya fizika (Statistical Physics), M., Gostekhizdat, 1944.
[74]M. A. Leontovich, Vvedenie v termodinamiky (Introduction to Thermodynamics), M., Gostekhizdat, 1956.
[75]A. Einstein, Ann. Phys. (Leipz.) 19, 289 (1906); 34, 591 (1911) (Russ. transl.: Collected Scientific Works, vol. 3, M., "Nauka," 1966, p. 75). (English translation in A. Einstein, Investigations on the Theory of the Brownian Movement, Methuen, 1926; Dover, 1956).
[76]J. P. McTague, J. Chem. Phys. 51, 133 (1969).
[77]E. N. Mozgovoĭ, É. Ya. Blum, and A. O. Tsebers, Magnit. gidrodin., No. 1, 61 (1973) [Magnetohydrodynamics (1973)].

[78]M. A. Martsenyuk, Zh. Prikl. Melch. i Tekhn. Fiz. No. 5, 75 (1973) [Appl. Mechs. and Techn. Phys. (1973)].
[79]W. F. Hall and S. N. Busenberg, J. Chem. Phys. 51, 137 (1969).
[80]H. Brenner, J. Colloid Interface Sci. 32, 141 (1970).
[81]A. O. Tsebers, Magnit. gidrodin., No. 3, 33 (1973) [Magnetohydrodynamics (1973)].
[82]L. G. Leal, J. Fluid Mech. 46, 395 (1971).
[83]H. Brenner and M. H. Weissman, J. Colloid Interface Sci. 41, 499 (1972).
[84]A. C. Levi, R. F. Hobson, and F. R. McCourt, Can. J. Phys. 51, 180 (1973).
[85]V. Zwetkoff, Acta Physicochimica URSS 10, 555 (1939) (in German).
[86]I. E. Tamm, Osnovy teorii élektrichestva (Foundations of the Theory of Electricity), M., Gostekhizdat, 1957.
[87]D. W. Condiff and J. S. Dahler, Phys. Fluids 7, 842 (1964).
[88]V. M. Zaĭtsev and M. I. Shliomis, Zh. Prikl. Mekh. i Tekhn. Fiz. 10, No. 5, 11 (1969) [J. Appl. Mechs. and Techn. Phys. 10, 696 (1969)].
[89]E. E. Bibik and A. A. Simonov, IFZh 22, 343 (1972); E. E. Bibik and V. E. Skobochkin, ibid. 22, 687 (1972).
[90]V. G. Bashtovoĭ and B. M. Berkovskiĭ, Magnit. gidrodin., No. 3, 3 (1973) [Magnetohydrodynamics (1973)].

Translated by W. F. Brown, Jr.