Theory of physical properties of magnetic liquids with chain aggregates

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The effect of chain-shaped aggregates on the equilibrium and kinetic properties of magnetic liquids is analyzed under the assumption that the chains can be modeled as straight and rigid. The magnetization, relaxation time, and rheological properties of magnetic liquids with such chain-shaped formations are calculated. © *1995 American Institute of Physics.*

1. INTRODUCTION

Magnetic liquids (or ferrocolloids) are suspensions of small single-domain particles, whose sizes are generally on the order of hundreds of angstroms, in a liquid carrier medium. These systems have attracted research interest because of a combination of factors: they have good fluidity, they respond actively to an external magnetic field, and one can control their physical properties by means of external fields. Early work on magnetic liquids is reviewed in Refs. 1 and 2.

Many of the phenomena which occur in magnetic liquids result from a competition between the Brownian motion of the particles and their magnetic-dipole interaction, which is effectively manifested as an interparticle attraction. Foremost among these phenomena are a "gas-liquid" condensation phase separation in unbounded volumes[3–6] and the formation of domain structures in thin layers of magnetic liquids.[7,8]

Some statistical-thermodynamic models of undiluted magnetic liquids incorporating a dipole–dipole interparticle interaction were proposed in Refs. 3–6. Magnetic liquids were treated there as homogeneous phases; the formation of any heterogeneous structures in them was ignored. On the other hand, numerical simulations and actual experiments show that such structures form extremely frequently in dispersions of dipole particles. It appears that the heterogeneous structures which arise in polar dispersions (this category includes, in addition to magnetic liquids, suspensions of paramagnetic and multidomain particles, electrorheological suspensions, etc.) arise most frequently in the form of linear chain-shaped aggregates.[9–12]

A first attempt to theoretically describe magnetic liquids with chain structures was undertaken in Ref. 13, but the entities considered there were not chains in the usual sense of the word but anisotropic homophase condensations of particles. The distributions of chains with respect to the number of particles in them were calculated by chemical-kinetics methods in Refs. 14 and 15, but the effect of the chains on macroscopic properties of magnetic liquids was not analyzed there.

An analysis of chain aggregates and their effect on macroscopic properties of magnetic liquids with the help of general considerations of the Frenkel theory of heterofluctuations was carried out in Ref. 16. The goals of that paper were to develop and refine the results of Ref. 16. It is not possible to carry out a rigorous theoretical analysis of the structure of undiluted magnetic liquids, especially if they contain different types of heterogeneous aggregates. In order to focus our attention specifically on the chains, we adopt the following assumptions.

1. We treat the small magnetic particles as identical balls of radius a in which magnetic moments are frozen. The magnitude of these moments, m, is given and constant.

2. We ignore the existence of heterophase structures other than linear-chain aggregates. Actually, there may be conglomerates of ferromagnetic particles (e.g., rings[17] or droplets[18]) along with chains, but we cannot deal with all types of heterostructures in one study, and it is reasonable to take them up individually.

3. We ignore fluctuations in the shape of the chains. We assume them to be straight, rod-shaped aggregates consisting of particles which are in contact (or nearly in contact) and which are bound exclusively by magnetic-dipole forces. We assume that the magnetic moments of the particles are directed along the line passing through their centers. This assumption must be justified for dilute magnetic liquids in which the small particles have large magnetic moments. The validity of this assumption will be established below.

4. We assume that the ferrocolloid is so sparse that we can ignore any interaction between particles in different chains. We ignore interactions of single particles with chains or with each other.

5. We restrict the analysis to systems for which the energy of the magnetic-dipole interaction of neighboring particles in a chain is much larger than that of the interaction of the particle with the magnetic field. If this condition does not hold, or if the opposite condition holds, then each small particle interacts individually with the magnetic field, and the effect of the chains on the magnetic properties of the magnetic liquid is very slight (although the presence of the chains may have substantial effects on optical, rheological, and other physical properties of magnetic liquids).

2. FREE ENERGY OF A COLLOID

We treat the chains as heterophase fluctuations. Using Frenkel's theory[19] along with the assumptions just listed, we write the free energy per unit volume of the ferrocolloid as follows:

$$F=T\sum_{i=1}^{\infty}\left(g_n \ln\frac{g_n v}{e}+g_n f_n\right), \quad v=\frac{4\pi a^3}{3}. \tag{1}$$

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Here T is the absolute temperature in energy units, n is the number of particles in a chain, g_n is the number of such chains per unit volume, and f_n is a dimensionless "internal" free energy of a chain of n particles. The first term in square brackets in (1) is the entropy of a gas of n-particle chains due to their translational motion.

To calculate f_n we use the nearest-neighbor method, which incorporates only the magnetic-dipole interaction between directly adjacent particles in the chain. Straightforward estimates show that for straight chains this approximation leads to a relative error of less than 20% in the limit $n\to\infty$. For short chains the error is even smaller.

The dimensionless internal free energy of an n-particle chain is

$$f_n=-\ln(Z_n), \tag{2}$$

$$Z_n=\int_{|\mathbf{r}_{i,i+1}|\geq 2a}\exp\left(\boldsymbol{\alpha}\sum_{i=1}^{n}\boldsymbol{\nu}_i\right)\times\exp\left(-\sum_{i=1}^{n-1}U(\boldsymbol{\nu}_i,\boldsymbol{\nu}_{i+1},\mathbf{r}_{i,i+1})2(T)^{-1}\right)\times\prod_{i=1}^{n}\frac{d\boldsymbol{\nu}_i}{(2\pi)^2}\prod_{i=1}^{n-1}\frac{d\mathbf{r}_{i,i+1}}{v^{n-1}},\quad \boldsymbol{\alpha}=\frac{m\mathbf{H}}{T}.$$

Here $\mathbf{H}$ is the magnetic field, $\boldsymbol{\nu}_i$ is a unit vector specifying the orientation of the moment of the ith particle, and U is the potential of the dipole–dipole interaction between two ferromagnetic particles.

To calculate f_n we need to adopt a convention about the word "chain." First, it is clear that if the magnetic particles and the stabilizing layers around them are essentially incompressible, then the probability for the formation of an aggregate of particles in physical contact with each other is zero, since any fluctuation will destroy the point contact between the particles. At a formal level, this means that if we require $|\mathbf{r}_{i,i+1}|=2a$ in (2) then we obtain $Z_n=0$ and $f_n=\infty$ as a result of the integration. Below we take the word "chain" to mean a linear sequence of particles in which neighboring particles are so close to each other that the energy of their magnetic interaction is larger than the thermal energy of the system. This definition ensures a strong correlation between the positions and orientations of the particles.

By virtue of our definition of a chain, the integration over $\mathbf{r}_{ij}$ in (2) must be carried out over the entire volume v_0, which is equal to half the volume within which the energy of the magnetic-dipole interaction between the ith particle and the $(i+1)$st particle exceeds T in order of magnitude. The integration must be carried out over specifically half this volume, since for a fixed position of the ith particle, the $(i+1)$st particle must not enter the region belonging to the $(i-1)$st.

To pursue this discussion, we introduce a dimensionless parameter of the interparticle interaction: $\gamma=m^2/8a^3T$. It is easy to see that $\varepsilon=2\gamma$ is the dimensionless energy of two particles which are in contact and which have parallel magnetic moments, directed along the line connecting the centers of the particles. Clearly, chains can arise only if ε is significantly larger than one, and we will take this point into account below.

The most favorable arrangement of particles—that which minimizes the net potential energy of their interaction in the linear chain—is that of direct head-to-tail contact and the formation of a straight, rod-shaped aggregate. Noting that we have $\varepsilon\gg 1$ and $\varepsilon\gg\alpha$ by virtue of the limitation adopted above, using the known approximation of the leading term, and noting that the available volume for a particle belonging to a chain is v_0, we find the following result, working by a procedure analogous to that used in the van der Waals theory (Ref. 20, for example):

$$Z_n\approx\frac{\exp[\varepsilon(n-1)]}{4\pi}\left(\frac{v_0(n-1)}{v}\right)^{(n-1)/2}\int\exp(\boldsymbol{\alpha}n\boldsymbol{\nu}_1)d\boldsymbol{\nu}_1. \tag{3}$$

Since we have $\varepsilon n\gg 1$, we find, to logarithmic accuracy

$$Z_n\approx\frac{\exp[\varepsilon(n-1)]}{4\pi}\int\exp(\boldsymbol{\alpha}n\boldsymbol{\nu}_1)d\boldsymbol{\nu}_1=\exp[\varepsilon(n-1)]\,\frac{\sinh(\alpha n)}{\alpha n}. \tag{4}$$

This approximation will be used below.

Substituting (4) into (2), and then substituting the result into (1), we find

$$F=T\sum g_n\left(\ln\frac{g_n}{e}-\left[\varepsilon(n-1)-\ln\frac{\sinh(\alpha n)}{\alpha n}\right]\right). \tag{5}$$

3. SIZE DISTRIBUTION OF THE CHAINS

Let us calculate the distribution of chains with respect to the number of particles in them, g_n. At equilibrium this distribution function should minimize F under the normalization condition

$$\sum_{n=1}^{\infty}ng_n=\frac{\rho}{v}, \tag{6}$$

where ρ is the volume fraction of the disperse phase. The ratio ρ/v is then the number of particles per unit volume.

Minimizing (5) under (6), and carrying out some standard manipulations, we find

$$g_n=\frac{x^n}{v}\,\frac{\sinh(\alpha n)}{\alpha n}\exp(-\varepsilon),\quad x=\exp(\varepsilon+\lambda), \tag{7}$$

where λ is an undetermined Lagrange multiplier. To find this multiplier, we need to substitute (7) into (6). As a result we find an equation for x:

$$\sum_n x^n\sinh(\alpha n)=y;\quad y=\alpha\rho\exp\varepsilon. \tag{8}$$

It is convenient to transform the left side of (8):

$$\sum_n x^n \sinh(\alpha n)=\frac{1}{2}\left(\sum_n (x\exp\alpha)^n-\sum_n [x\exp(-\alpha)]^n\right)$$

$$=\frac{x\sinh\alpha}{1-2x\cosh\alpha+x^2}. \tag{9}$$

Substituting (9) into (8), we find the equation

$$x^2-x\left(2\cosh\alpha+\frac{\sinh\alpha}{y}\right)+1=0.$$

A solution of this equation which satisfies the condition $x<1$ ensures the convergence of the left side of (8):

$$x=\frac{2y\cosh\alpha+\sinh\alpha-\sqrt{(2y\cosh\alpha+\sinh\alpha)^2-4y^2}}{2y}. \tag{10}$$

In the absence of an external magnetic field ($\alpha\to 0$), we find, by combining (7) and (10),

$$g_n(\alpha=0)=g_{n0}=\frac{1}{v}x_0^n\exp(-\varepsilon),$$

$$x_0=\frac{1+2\rho\exp\varepsilon-\sqrt{1+4\rho\exp\varepsilon}}{2\rho\exp\varepsilon}. \tag{11}$$

In a very strong field, $\alpha\gg 1$, we have

$$g_n(\alpha=\infty)=g_{n\infty}=\frac{\exp(-\varepsilon)}{2v}\frac{1}{\alpha n(1+1/2y)^n}. \tag{12}$$

The mean number of particles in a chain in an arbitrary magnetic field is

$$\langle n\rangle=\frac{\Sigma_n n g_n}{\Sigma_n g_n}=\frac{\alpha\rho\exp\varepsilon}{\Sigma_n x^n\sinh(\alpha n)n^{-1}}. \tag{13}$$

We transform the denominator in (13):

$$\sum_n x^n\frac{\sinh(\alpha n)}{n}$$

$$=\frac{1}{2}\left\{\sum_n\frac{(x\exp\alpha)^n}{n}-\sum_n\frac{[x\exp(-\alpha)]^n}{n}\right\}$$

$$=\frac{1}{2}\left[\int_0^{x\exp\alpha}\sum_n s^{n-1}ds-\int_0^{x\exp(-\alpha)}\sum_n s^{n-1}ds\right]$$

$$=\frac{1}{2}\ln\frac{1-x\exp(-\alpha)}{1-x\exp\alpha}. \tag{14}$$

Substituting (14) into (13), we find our final expression for $\langle n\rangle$. For the case $\alpha=0$ (no field), we have

$$\langle n\rangle=\frac{\rho\exp\varepsilon(1-x_0)}{x_0}. \tag{15}$$

Under the conditions $\varepsilon\gg\alpha\rho\gg 1$ we find

$$\langle n\rangle\approx 2\rho\exp\varepsilon\frac{\alpha}{\ln(2\alpha\rho)+\varepsilon}. \tag{16}$$

Let us now find the condition for the applicability of the model of straight, rod-shaped aggregates. We denote by θ_{ij} the angle between the magnetic moment of the ith particle in the chain and the radius vector connecting the center of this particle to the center of the jth particle. It is easy to see that in the absence of a magnetic field the mean value is, in order of magnitude, $\langle\theta_{i,i+1}^2\rangle\sim\varepsilon^{-1}$ ($\varepsilon\gg 1$). Using known results from the theory of ideal polymer chains, we can estimate the persistence length l of a chain of magnetic particles not in a field:

$$l\sim\frac{d}{|\ln\langle\cos\theta_{i,i+1}\rangle|}\sim\frac{d}{\langle\theta_{i,i+1}^2\rangle}\sim d\varepsilon,$$

where $d\sim 2a$ is the diameter of a particle. The model adopted here is valid under the condition $l>d\langle n\rangle$, i.e., $\langle n\rangle<\varepsilon$.

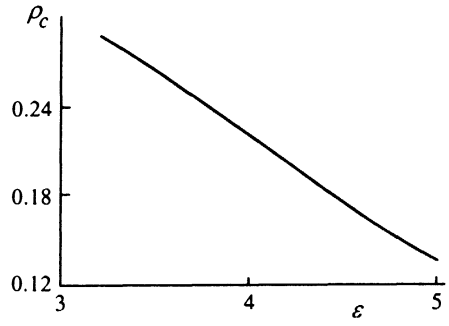

FIG. 1. Upper limit on the volume fraction of particles for validity of the model of straight aggregates, ρ_c, as a function of the interparticle interaction parameter ε.

Figure 1 shows values of ρ_c for which we have $\langle n\rangle=\varepsilon$ according to calculations from Eq. (15). These values are the upper limits on ρ for the applicability of our model of straight, rod-shaped aggregates in the case $\alpha=0$. Since a magnetic field stretches a chain out along field lines, this model is clearly applicable in a nonvanishing field at $\rho>\rho_c$.

Figures 2 and 3 show $\langle n\rangle$ versus the dimensionless magnetic field α and the total volume fraction of the particles, ρ. These curves agree qualitatively with the experimental results of Ref. 11. It is a very complicated matter to make a quantitative comparison, since we do not find in Ref. 11 the information which we would need to determine the radius or magnetic moment of the small particles.

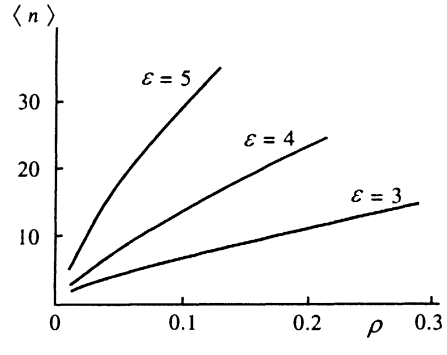

FIG. 2. Mean number of particles in a chain, $\langle n\rangle$, versus the volume fraction of particles, ρ, for $\alpha=5$ and various values of ε (the curve labels). The curves are cut off at $\rho=\rho_c(\varepsilon)$ (Fig. 1).

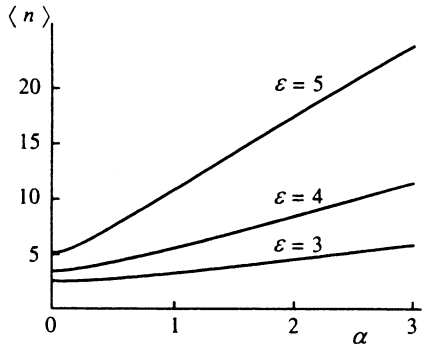

FIG. 3. Mean number of particles in a chain, $\langle n \rangle$, versus the dimensionless magnetic field α for $\rho=\rho_c(\varepsilon=5)=0.135$ and various values of ε (the curve labels).

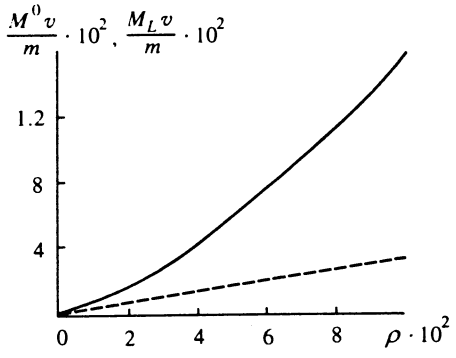

FIG. 4. Magnetization of the colloid, M^0, versus the volume fraction of particles, ρ, as calculated from Eq. (17) (solid curve; $\varepsilon=4$) and from the Langevin magnetization M_L (dashed curve). The dimensionless field is $\alpha=0.1$.

In very strong fields, in which the condition $\alpha>\varepsilon$ definitely holds, the plot[11] of $\langle n \rangle$ versus α approaches a horizontal asymptote. This situation, however, lies outside the framework of the approximations adopted here.

4. EQUILIBRIUM MAGNETIZATION

The equilibrium magnetization $\mathbf{M}^0$ of a magnetic liquid, as the mean magnetic moment per unit volume, can now be correctly defined by

$$\mathbf{M}^0=-\left.\frac{\partial F}{\partial \mathbf{H}}\right|_{g_n}=-\frac{m}{T}\left.\frac{\partial F}{\partial \boldsymbol{\alpha}}\right|_{g_n}=m\sum_n nL_1(\alpha n)g_n\frac{\mathbf{H}}{H}, \quad (17)$$

where

$$L_1(x)=\coth x-1/x \quad (18)$$

is the Langevin function.

In a very weak field ($\alpha\to 0$) we would have

$$M^0\approx\frac{\alpha}{3}m\sum_n n^2 g_{n0}=\frac{x_0 m\alpha}{3v}\exp(-\varepsilon)\frac{1+x_0}{(1-x_0)^3}. \quad (19)$$

If the parameter ε, of the magnetic–dipole interaction of the particles, is large, we have

$$x_0\approx 1-(\rho\exp\varepsilon)^{-1/2}, \quad \rho\exp(\varepsilon)\gg 1,$$

and expression (19) becomes

$$M^0=\frac{m\alpha}{3v}\exp\left(\frac{\varepsilon}{2}\right)\rho^{3/2}. \quad (20)$$

If we assume at the outset that there are no chains ($g_n=\delta_{1n}\rho/v$, where δ_{ij} is the Kronecker delta), then we find from (17) the ordinary Langevin formula for the magnetization of an ideal superparamagnetic gas, M_L:

$$M_L=\frac{m\rho}{v}L_1(\alpha). \quad (21)$$

In the limit $\alpha\to 0$ we find

$$M_L=\frac{m\alpha}{3v}\rho.$$

Comparing (20) with the latter relation, we see that the formation of chains in which the magnetic moments of the individual ferromagnetic particles are strongly correlated with each other leads to a substantial increase in the magnetization of the colloid. This conclusion is illustrated by Fig. 4, which compares calculations of the magnetization from Eqs. (17) and (21).

We note that the functional dependence of M on ρ, the volume fraction of the particles, is not analytic. Similar nonanalytic functions describing the behavior of physical properties as a function of the concentration of particles in systems with a large correlation radius are well known. They are encountered in the Debye–Hückel theory of electrolytes, in polymer theory,[21] in the theory of critical phenomena, and elsewhere. In our own case, the correlation radius is on the order of the average length of a chain, which may be considerably greater than the size of an individual particle, as can be seen from (14)–(16).

5. MAGNETIZATION RELAXATION IN ROTATING FIELDS

A key problem in the physics of magnetic liquids is to calculate their behavior under nonequilibrium conditions. Macroscopic equations for the flow of dilute ferrocolloids and for the relaxation of their magnetization in varying external fields were apparently derived most correctly in Ref. 22. Numerical simulations[23] have demonstrated that this approach is highly accurate.

There have been a fairly large number of studies (e.g., Refs. 10, 24, and 25) aimed at determining how interparticle interactions influence the kinetics of the magnetization reversal of magnetic liquids in which the particle concentration is not small. It was concluded in Ref. 26 from an analysis of many experiments that the magnetic–dipole interaction of the particles has essentially no effect on the magnetization relaxation times. A similar result was derived theoretically in Ref. 27. However, the topic discussed in Ref. 27 was a homogeneous magnetic liquid of moderate concentration, without any heterophase aggregates. The magnetic liquids studied in Ref. 26 apparently also had a homogeneous structure. On the other hand, it seems obvious that heteroaggregates which stem from the magnetic-dipole interaction of particles

TABLE I. Parameters of the equations of motion of solid prolate ellipsoids.

n	λ_n	δ_n	ρ_n	α_n	β_n	ζ_n	χ_n
1	0.0000	1.00	0.00	2.50	0.00	0.00	0.00
2	0.6000	1.50	1.06	2.17	2.71	0.660	2.83
3	0.8000	2.34	2.46	2.09	5.62	0.573	7.61
4	0.8824	3.40	4.13	2.05	8.99	0.455	13.1
5	0.9231	4.64	6.04	2.04	12.9	0.365	19.2
7	0.9600	7.65	10.5	2.02	22.0	0.247	33.0
10	0.9802	13.4	18.7	2.01	39.3	0.156	58.0
15	0.9912	25.9	36.1	2.00	76.9	0.088	110
20	0.9950	41.9	57.6	2.00	125	0.058	175
30	0.9978	83.7	113	2.00	250	0.031	341
40	0.9988	138	183	2.00	414	0.019	551
50	0.9992	205	268	2.00	614	0.014	807
70	0.9996	374	482	2.00	1123	0.008	1450
100	0.9998	721	916	2.00	2162	0.004	2752

are capable of significantly influencing not only the equilibrium but also the nonequilibrium characteristics of magnetic liquids.[10,12]

Below we analyze the relaxation of the magnetization of a ferrocolloid toward an external magnetic field which is changing in direction but not strength; we take account of the existence of straight chain aggregates. A straightforward analysis shows that the nature of the relaxation processes should depend strongly on the relation between the dimensionless magnetic field α and the parameter ε, of the interparticle interaction. Specifically, if $\alpha \gg \varepsilon$, then each particle of a chain in a rotating field should rotate in a process which is independent of the other particles. In this case, only the hydrodynamic interaction of particles will affect the kinetics of the reorientation of the particles (as in the cases discussed in Refs. 26 and 27). If the condition $\alpha \ll \varepsilon$ holds, in contrast, the chains rotate as a whole in a field. This is the case which we will look at.

In order to derive some understandable results and to develop a method of study, we restrict the analysis to the slightly nonequilibrium situation, and we ignore hydrodynamic forces which would break up the chain as it undergoes reorientation. It is a straightforward matter to derive a condition under which this approximation can be realized. We denote by ω the field rotation frequency. In the zero-delay approximation, which is essentially always valid for magnetic liquids, the angular rotation velocity of a chain which does not become deformed and which does not rupture is also equal to ω. In order of magnitude, the hydrodynamic force which displaces neighboring particles with respect to each other is given by $F_h \sim \eta_0 \omega d^2$, where η_0 is the viscosity of the carrier medium, and d is again the diameter of the particle. When the displacements of two neighboring particles make small angles θ with the chain axis, the force of their magnetic interaction is $F_m \sim \varepsilon T \theta / d$. If the chain does not rupture, we have $F_m = F_h$ and thus $\theta \sim \eta_0 d^3 \omega / (\varepsilon T)$. A chain can be assumed to be a straight, rod-shaped aggregate if $\theta \langle n \rangle \ll 1$. We then estimate an upper bound on ω:

$$\omega \ll \frac{T\varepsilon}{\eta_0 d^3 \langle n \rangle}.$$

For aqueous colloids with particles on the order of 100 Å in radius, at room temperature, this inequality holds if $\omega \ll 10^6 \varepsilon / \langle n \rangle$ s^{-1}. In experiments of which we are aware, the field rotation frequency was very often far below 10^6 Hz.

We thus again assume that the chains are straight, rod-shape aggregates, with the distribution with respect to the number of particles given in (7), (10).

In a description of the hydrodynamic interaction of a rod-shaped chain with the surrounding medium, we model the chain as an ellipsoid of revolution whose semimajor axis is equal to na (where n is again the number of particles in the chain), and whose semiminor axis is a. A point of fundamental importance is that the volume of this ellipsoid is equal to the total volume of the particles making up the chain. The volume fraction of these ellipsoids is therefore equal to the volume fraction of disperse particles in the colloid.

We introduce $\varphi_n(\mathbf{e})$, which is a normalized distribution function of the unit vector $\mathbf{e}$, which is itself directed along the magnetic moment of the particles in a rigid chain of n particles. The Fokker–Planck equation for $\varphi_n(\mathbf{e})$ takes the following form in the approximation of the chain as an ellipsoid of revolution:[28]

$$\frac{\partial \varphi_n}{\partial t} + D_n \alpha n \left[(e_j e_m h_m - h_j) \frac{\partial \varphi_n}{\partial e_j} + 2 e_j h_j \varphi_n \right] + \lambda_n (e_s \gamma_{sl} - e_m e_s e_l \gamma_{ms}) \frac{\partial \varphi_n}{\partial e_l} + \omega_{ls} e_s \frac{\partial \varphi_n}{\partial e_l} - 3 \lambda_n e_l e_s \gamma_{ls} \varphi_n = D_n \left[\frac{\partial^2 \varphi_n}{\partial e_j^2} - 2 e_s \frac{\partial \varphi_n}{\partial e_s} - e_j e_s \frac{\partial^2 \varphi_n}{\partial e_s \partial e_j} (1 - \delta_{sj}) \right],$$

$$\lambda_n = \frac{n-1}{n+1}, \quad j, m, s = x, y, z, \quad D_n = \frac{T}{6 \eta_0 v n^2 \delta_n},$$

$$h_j = \frac{H_j}{H},$$

$$\gamma_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right); \quad \omega_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right). \tag{22}$$

Here D_n is the coefficient of rotational diffusion of the ellipsoid modeling the chain, $\mathbf{u}$ is the average macroscopic flow velocity of the suspension, and δ_n is a coefficient, whose value is given in Ref. 28 and also in Table I of the presentpaper. A repeated index in (22) and below means a summation.

We now consider a system which is macroscopically at rest ($u\equiv 0$). Multiplying both sides of (22) by the components of the vector $\mathbf{e}$, and taking an average over all possible orientations of this vector, we find (cf. Ref. 28)

$$\frac{\partial\langle e_k\rangle_n}{\partial t}=-2D_n\langle e_k\rangle_n+D_n a n(h_k-\langle e_k e_j\rangle h_j),$$
$$\langle\ldots\rangle=\int\ldots\varphi_n(\mathbf{e})d\mathbf{e}. \tag{23}$$

The components of the macroscopic magnetization vector $\mathbf{M}$ are given by

$$M_k=m\sum_n ng_n\langle e_k\rangle_n. \tag{24}$$

As mentioned above, g_n can now be chosen in the same form (7), (10) as for a magnetic liquid at equilibrium. The problem is thus to calculate $\langle e_k\rangle$ under nonequilibrium conditions.

It is not possible to solve Eq. (22) analytically for arbitrary α (some asymptotic solutions are given in Ref. 28). At this point we adopt the effective field approximation, as developed in Ref. 22 in an analysis of relaxation phenomena in dilute ferrocolloids.

We seek a solution of (22) as a function corresponding to the equilibrium distribution of orientations of the chain, but in some effective field $\mathbf{H}_{en}$ rather than in the actual field $\mathbf{H}$:

$$\varphi_n=\frac{\alpha_{en}n}{4\pi\sinh(\alpha_{en}n)}\exp(\boldsymbol{\alpha}_{en}n\mathbf{e}),\quad \boldsymbol{\alpha}_{en}=\frac{m\mathbf{H}_{en}}{T}. \tag{25}$$

There is nothing new in the form of (25) itself: we have simply replaced the unknown φ_n by the new unknown $\mathbf{H}_{en}$. We can take a fundamental step forward by assuming (as Ref. 22) that $\mathbf{H}_{en}$ is a constant, independent of $\mathbf{e}$. Also using our approximation that deviation from equilibrium is only slight, we assume that the strong inequality $\delta H_n\ll H$ holds, where $\delta\mathbf{H}_n=\mathbf{H}_{en}-\mathbf{H}$. Using (25), we find, in the linear approximation in $\delta\alpha n/\alpha$,

$$\langle e_k\rangle_n=\langle e_k\rangle_n^0+\delta\langle e_k\rangle_n,$$
$$\delta\langle e_k\rangle_n=\frac{L_1(\alpha n)}{\alpha}\delta\alpha_k+\left(\frac{\partial L_1(\alpha n)}{\partial\alpha}-\frac{L(\alpha n)}{\alpha}\right)h_k h_j\delta\alpha_{jn},$$
$$\alpha n(h_k-\langle e_k e_j\rangle_n h_j)=2\langle e_k\rangle_n+\langle e_k e_j\rangle_n^0 n\delta\alpha_{jn}-n\delta\alpha_{kn}, \tag{26}$$
$$\delta\boldsymbol{\alpha}_n=\boldsymbol{\alpha}_{en}-\boldsymbol{\alpha},\quad h_j=H_i/H,\quad i,\ j,\ k=x,\ y,\ z.$$

Here and below, a superscript zero denotes the equilibrium value of a moment calculated with the help of function (25), with the effective field $\mathbf{H}_{en}$ replaced by the actual field $\mathbf{H}$.

Substituting (26) into (25), we find

$$\frac{d\langle e_k\rangle_n}{dt}=D_n[\langle e_k e_j\rangle_n^0 n\delta\alpha_{jn}-n\delta\alpha_{kn}]. \tag{27}$$

After calculating the equilibrium moment $\langle e_k e_j\rangle^0$ (detailed formulas for equilibrium moments of this type are written out in the Appendix), we find

$$\frac{d\langle e\rangle_{\|n}}{dt}=-2D_n\frac{L_1(\alpha n)}{\alpha}\delta\alpha_{\|n},$$
$$\frac{d\langle e\rangle_{\perp n}}{dt}=-D_n\frac{\alpha n-L_1(\alpha n)}{\alpha}\delta\alpha_{\perp n}. \tag{28}$$

Here the $\|$ and $\perp$ denote the components of the vectors which are respectively parallel and perpendicular to the external field $\mathbf{H}$.

We can determine the parameters $\delta\alpha_{\|n}$ and $\delta\alpha_{\perp n}$ by using the second equation in (28). As a result we find

$$\langle e\rangle_{\|n}-\langle e\rangle_n^0=\frac{\partial L_1(\alpha n)}{\partial\alpha}\delta\alpha_{\|n},\quad \langle e\rangle_{\perp n}=\frac{L_1(\alpha n)}{\alpha}\delta\alpha_{\perp n}. \tag{29}$$

Using (29) to eliminate the components of $\delta\alpha$ from (28), we find relaxation equations for the components $\langle\mathbf{e}\rangle_n$:

$$\frac{d\langle e\rangle_{\|n}}{dt}=-\frac{\langle e\rangle_{\|n}-\langle e\rangle_n^0}{\tau_{\|n}},\quad \frac{d\langle e\rangle_{\perp n}}{dt}=-\frac{\langle e\rangle_{\perp n}}{\tau_{\perp n}}, \tag{30}$$
$$\tau_{\|n}=\frac{1}{2D_n}\frac{\alpha}{L_1(\alpha n)}\frac{\partial L_1(\alpha n)}{\partial\alpha},\quad \tau_{\perp n}=\frac{1}{D_n}\frac{L_1(\alpha n)}{\alpha n-L_1(\alpha n)}.$$

With $n\equiv 1$, Eqs. (30) become the results of Ref. 22.

When multiplied by mn, Eqs. (30) describe the relaxation of the magnetic moment of an n-particle chain in a rotating magnetic field. Our problem now is to go over from the characteristics of individual chains to the characteristics of the suspension as a whole. Since it is difficult to find a compact solution of this problem for the general case, we will discuss one special (but typical) case. We assume that the magnetic field is rotating at a constant frequency ω in the x, y plane [i.e., $h_x=\cos\omega t$, $h_y=\sin\omega t$]. Using the known solution for the motion of the magnetization of a magnetic liquid in rotating fields (see, for example, Refs. 1, 2, and 28), and also using (30), we find

$$\langle e_x\rangle_n=\frac{\langle e_x\rangle_n^0-\langle e_y\rangle_n^0\omega\tau_{\perp n}}{1+\tau_{\perp n}\tau_{\|n}\omega^2},$$
$$\langle e_y\rangle_n=\frac{\langle e_x\rangle_n^0\omega\tau_{\perp n}+\langle e_y\rangle_n^0}{1+\tau_{\perp n}\tau_{\|n}\omega^2}, \tag{31}$$
$$\langle e_x\rangle_n^0=L_1(\alpha n)\cos\omega t,\quad \langle e_y\rangle_n^0=L_1(\alpha n)\sin\omega t.$$

Multiplying both sides of (31) by mng_n, summing over n, and using (24), we find

$$M_x=\sum_n\frac{\mu_{nx}^0 g_n}{1+\tau_{\perp n}\tau_{\|n}\omega^2}-\sum_n\frac{\mu_{ny}^0 g_n\omega\tau_{\perp n}}{1+\tau_{\perp n}\tau_{\|n}\omega^2},$$
$$M_y=\sum_n\frac{\mu_{nx}^0 g_n\omega\tau_{\perp n}}{1+\tau_{\perp n}\tau_{\|n}\omega^2}+\frac{\mu_{ny}^0 g_n}{1+\tau_{\perp n}\tau_{\|n}\omega^2}, \tag{32}$$

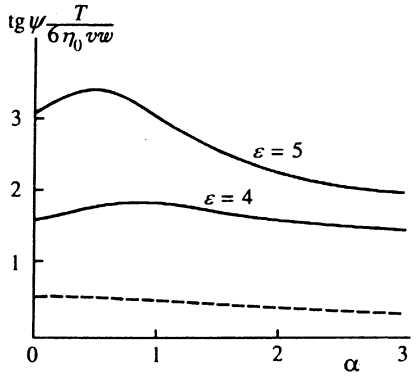

FIG. 5. Plot of tan ψ vs the dimensionless magnetic field α according to calculations from (34) for ε=4,5 (solid curves) and with Eq. (35) (broken curve); ρ=0.13.

$$\mu_{ni}^0 = mn\langle e_i\rangle^0.$$

From Eqs. (32) we can determine the angle ψ between the magnetization **M** and the rotating field. For this purpose we rewrite (32) as follows:

$$M_x = A\cos(\omega t-\psi);\quad M_y = A\sin(\omega t-\psi),$$

$$A\cos\psi = \sum_n \frac{L_1 g_n}{1+\omega^2\tau_{\perp n}\tau_{\parallel n}},$$

$$A\sin\psi = \sum_n \frac{L_1 g_n \omega\tau_{\perp n}}{1+\omega^2\tau_{\perp n}\tau_{\parallel n}}.$$

We thus find

$$\tan\psi = \frac{\Sigma_n n L_1 g_n \omega\tau_{\perp n}(1+\omega^2\tau_{\perp n}\tau_{\parallel n})^{-1}}{\Sigma_n n L_1 g_n (1+\omega^2\tau_{\perp n}\tau_{\parallel n})^{-1}}. \tag{33}$$

At low rotation frequencies, expression (33) simplifies, becoming

$$\tan\psi = \omega\frac{\Sigma_n n\tau_{\perp n} L_1(\alpha n) g_n}{\Sigma_n n L_1(\alpha n) g_n}. \tag{34}$$

In the absence of chains ($g_n = c\delta_{n1}$) we find a known result:

$$\tan\psi = \omega\tau_{\perp 1}. \tag{35}$$

Figure 5 shows results calculated for tan ψ from Eqs. (34) and (35). It can be seen from these curves that tan ψ increases with ε, the parameter of the magnetic-dipole interaction. This increase can be explained on the basis of an increase in the relative number of longer chains, for which the magnetization-reversal time scales τ_n increase with increasing n. The nonmonotonic behavior of tan ψ as a function of the dimensionless field α is explained on the basis of a competition between two mechanisms. On the one hand, an increase in α is accompanied by an increase in the average length of the chains. This increase leads to a decrease in the rotational mobility of the chains and thus an increase in tan ψ. On the other hand, each chain is oriented to a greater extent by the field along the field, and this effect reduces tan ψ.

Using (35), we can determine the transverse relaxation time $\tau_\perp = \omega^{-1}\tan\psi$ of a magnetic liquid with chain aggregates, by analogy with the relaxation time of a ferrocolloid with particles which are not in aggregates. It is easy to show that $\tau_\perp$ increases with increasing ε. This conclusion contradicts the results of Ref. 10, where it was assumed that all the chains have an identical, fixed length. The latter assumption is a very crude one, and it may even lead to qualitative errors.

6. RHEOLOGICAL PROPERTIES OF A MAGNETIC LIQUID

The effect of chain structures on the rheological properties of polar dispersions—magnetic liquids, magnetorheological and electrorheological suspensions, etc.—has been studied by many investigators.[9,12,29,30] Detailed numerical calculations of the viscosity of magnetic liquids whose particles were collected in identical chains, with a length assumed known, were carried out in Ref. 12.

Our purpose in this section of the paper is to analytically calculate rheological characteristics of magnetic liquids with chain aggregates which contain random numbers of particles, in a steady-state external magnetic field. We assume that the flow of the system is in a steady state, is laminar, and is so slow that we can ignore the effect of the deviation from equilibrium on the dimensions and shape of the chains. A condition for the validity of this approximation can easily be established by comparing the hydrodynamic force F_h, which tends to decouple two particles, with the magnetic-adhesion force of the particles, F_m. In order of magnitude we have $F_h \approx \eta_0 d^2 E$ and $F_m \approx \theta T\varepsilon/d$, where E is the gradient of the flow velocity. The condition under which a chain cannot be broken up is

$$F_m = F_h,$$

and the condition under which it cannot be deformed is

$$\theta\langle n\rangle \ll 1.$$

The condition we are seeking is thus

$$E \ll \frac{T\varepsilon}{\eta_0 d^3\langle n\rangle}.$$

It can be concluded from the estimates derived above in the analysis of the magnetization relaxation in rotating fields that this strong inequality often holds in real situations.

Again, we treat the chain as a sequence of particles in contact with each other. To incorporate the hydrodynamic interaction of the chain with the surrounding medium we model the chain as a prolate spheroid with semiminor axis a and semimajor axis na. Using known results from the statistical hydromechanics of dilute suspensions of spheroidal particles,[28] we write an expression for the components of the average viscous stress tensor σ in the linear approximation in the components of the tensor gradient of the average flow velocity **u**:

$$\sigma_{ik} = \sigma_{ik}^s + \sigma_{ik}^a,$$

$$\sigma_{ik}^s = -\eta_0\langle\langle\rho_n\langle e_j e_s\rangle_n^0\rangle\rangle\gamma_{js}\delta_{ik} + 2\eta_0\gamma_{ik}$$

$$+\eta_0\{\langle\langle(2\alpha_n)\rangle\rangle\gamma_{ik}+\langle\langle(\zeta_n+\beta_n\lambda_n)\langle e_ie_j\rangle_n^0\rangle\rangle\gamma_{ij}$$
$$+\langle\langle(\zeta_n+\beta_n\lambda_n)\langle e_ie_j\rangle_n^0\rangle\rangle\gamma_{ji}+\langle\langle\beta_n\langle e_je_k\rangle_n^0\rangle\rangle\omega_{ij}$$
$$+\langle\langle\beta_n\langle e_je_i\rangle_n^0\rangle\rangle\omega_{kj}+(\chi_n-2\beta_n\lambda_n)$$
$$\times\langle e_ie_je_ke_s\rangle_n^0\rangle\rangle\gamma_{js}\},$$

$$\sigma_{ik}^a=\frac{\alpha T}{2v}\langle\langle\langle e_i\rangle_n h_k-\langle e_k\rangle_n h_i\rangle\rangle. \tag{36}$$

Here again,

$$\gamma_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right),\quad \omega_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}-\frac{\partial u_j}{\partial x_i}\right),$$

$$\langle\langle\cdots\rangle\rangle=\sum_n\cdots vng_n,$$

$$h_i=\frac{H_i}{H},\quad i,\ j,\ k,\ s,\ x_i,\ x_j=x,\ y,\ z,\quad \lambda_n=\frac{n-1}{n+1}.$$

The tensors $\boldsymbol{\sigma}^s$ and $\boldsymbol{\sigma}^a$ are the symmetric and antisymmetric parts of $\boldsymbol{\sigma}$; the superscript zero again means the equilibrium moments of the unit vector $\mathbf{e}$, and δ_{ij} is the Kronecker delta. The parameters ρ_n, α_n, β_n, ζ_n, and χ_n were calculated in Ref. 28 (where, however, the subscripts n were not written on these parameters; otherwise they are denoted here as in Ref. 28). For reference, we show in Table I the values of these parameters taken from Ref. 28.

Since we are assuming that the chains do not rupture and are not deformed, we can calculate the distribution function g_n, used in (28) in the determination of the mean values $\langle\langle\cdots\rangle\rangle$, in the same way as for the equilibrium situation, in a first approximation [see Eqs. (7), (8)]. Accordingly, expressions (32) and the data in Table I make it possible to calculate all the quantities which appear in the definition of $\boldsymbol{\sigma}^s$. To calculate the components of the antisymmetric tensor $\boldsymbol{\sigma}^a$, on the other hand, we need to find the components of the nonequilibrium vector moment $\langle\mathbf{e}\rangle_n$, as can be seen from (36).

To determine $\langle\mathbf{e}\rangle_n$ exactly, we need to solve Eq. (22) for the orientation distribution function $\varphi_n(\mathbf{e})$ of an ellipsoidal magnetic particle in an steady-state external field and in a medium in shear motion. Exact analytic solutions of the equation can be derived only in the limits of very strong and very weak fields (the mathematical problems which arise are discussed in detail in Ref. 28).

At this point we make use of some ideas from the effective-field method. Remaining in the linear approximation in γ_{ij} and ω_{ij}, we write the nonequilibrium distribution function $\varphi_n(\mathbf{e})$ in the form

$$\varphi_n=\frac{\alpha n}{4\pi\sinh(\alpha n)}\exp(\alpha\mathbf{e})\left[1+\frac{\lambda_n}{2D_n}(e_ie_j-\langle e_ie_j\rangle^0)\gamma_{ij}\right.$$
$$\left.+\frac{1}{D_n}b_ne_i\omega_{ij}h_j\right];\quad b_n=\text{const}. \tag{37}$$

The function φ_n is normalized (to one); furthermore, for irrotational flows ($\omega_{ij}=0$) this function is an exact solution of steady-state equation (22). We find the quantity b_n from the equation for the first moment of the function φ_n, which is, in the steady-state case,

$$-2D_n\langle e_k\rangle_n+\lambda_n(\langle e_j\rangle_n^0\gamma_{jk}+\langle e_ke_je_s\rangle_n^0\gamma_{js})+\omega_{kj}\langle e_j\rangle_n^0$$
$$+D_n\alpha n(h_k-\langle e_ke_j\rangle_n h_j)=0. \tag{38}$$

Substituting (37) into (38), and carrying out some simple calculations, we find b_n and $\langle e_{xy}\rangle_n$:

$$b_n=\frac{\langle e_z\rangle_n^0}{2\langle e_x^2\rangle_n^0+\alpha n\langle e_x^2e_z\rangle_n^0},$$

$$\langle e_l\rangle_n=\frac{1}{D_n}b_n\langle e_l^2\rangle_n^0+\frac{\lambda_n}{D_n}\langle e_l^2e_z\rangle_n^0\gamma_{lz},\quad l=x,\ y. \tag{39}$$

Here and below, the z axis is directed along the external magnetic field $\mathbf{H}$.

Using (39) in (36), we find the components of the antisymmetric stress tensor:

$$\sigma_{lz}^a=-\sigma_{zl}^a=\frac{\alpha T}{2v}\langle\langle\langle e_l\rangle_n\rangle\rangle$$
$$=\frac{\alpha T}{2v}\left(\left\langle\left\langle\frac{b_n}{D_n}\langle e_l^2\rangle_n^0\right\rangle\right\rangle\omega_{lz}\right.$$
$$\left.+\left\langle\left\langle\frac{\lambda_n}{D_n}\langle e_l^2e_z\rangle_n^0\right\rangle\right\rangle\gamma_{lz}\right). \tag{40}$$

Substituting (40) into (36), we find our final expressions for the tensor $\boldsymbol{\sigma}$ in the linear approximation in γ_{ij} and ω_{ij}. It is not difficult to see that this representation can be written in the form of a Leslie-Eriksen tensor, and Parodi's relation holds.

To illustrate the results we consider two examples of simple shear flow.

1. The flow velocity $\mathbf{u}$ is perpendicular to the field $\mathbf{H}$, and the gradient of this velocity is directed along $\mathbf{H}$:

$$u_x=Ez,\quad u_y=u_z=0,\quad E=\text{const}.$$

In this case we have $\gamma_{xz}=\gamma_{zx}=\omega_{xz}=-\omega_{zx}=E/2$, and the other components γ_{ij} and ω_{ij} are zero.

Using these relations in (39), (40), and noting that we have $h_z=1$ and $h_x=h_y=0$ by virtue of our choice of coordinate system, we find, after some straightforward manipulations,

$$\sigma_{xz}=\eta_1E,\quad \eta_1=\eta_1^s+\eta_1^a,$$
$$\eta_1^s=\eta_0\left(1+\left\langle\left\langle\alpha_n+\frac{\zeta_n+\beta_n\lambda_n}{2}(\langle e_x^2\rangle_n^0+\langle e_z^2\rangle_n^0)\right.\right.\right.$$
$$\left.\left.\left.+\frac{\beta_n}{2}(\langle e_z^2\rangle_n^0-\langle e_x^2\rangle_n^0)+(\chi_n-2\lambda_n\beta_n)\langle e_x^2e_z^2\rangle_n^0\right\rangle\right\rangle\right),$$
$$\eta_1^a=\frac{\alpha T}{4}\left\langle\left\langle\frac{b_n}{D_n}\langle e_l^2\rangle_n^0\right\rangle\right\rangle+\left\langle\left\langle\frac{\lambda_n}{D_n}\langle e_l^2e_z\rangle_n^2\right\rangle\right\rangle. \tag{41}$$

Here η_1 is an effective viscosity of the colloid for the type of flow specified above, and η_1^s and η_1^a are components of η_1 corresponding to symmetric and antisymmetric stresses. The

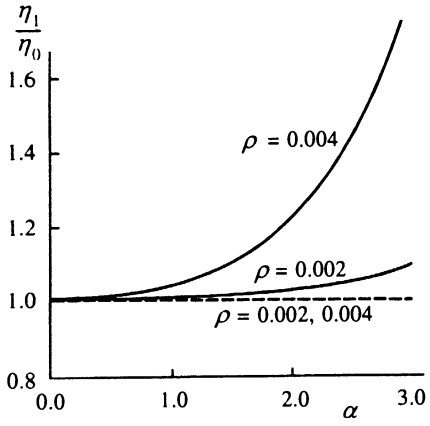

FIG. 6. Values of the effective viscosity η_1 calculated from Eq. (41) (solid curves) and calculated under the assumption of isolated particles (dashed curve). The curve labels are the values of ρ; $\varepsilon=4$.

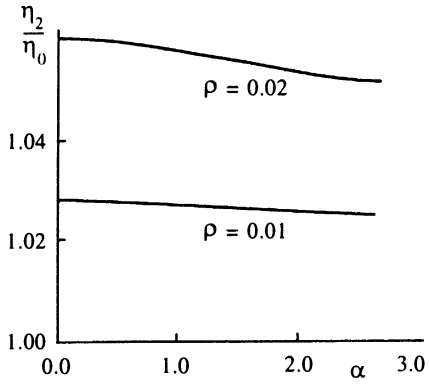

FIG. 8. Effective viscosity η_2^s calculated from Eq. (41) for $\varepsilon=4$ and various values of ρ (the curve labels).

equilibrium moments in (41) can easily be calculated with the help of the relations given in the Appendix.

Figures 6 and 7 show results calculated for η_1, in comparison with corresponding quantities found in Ref. 22 for an extremely dilute colloid with isolated, noninteracting particles (the results of Ref. 22 can be found from (41) by assuming $g_n=\rho\delta_{1n}/v$ in the calculation of the mean values $\langle\langle\cdots\rangle\rangle$. We see that the presence of the chains causes a significant increase in η_1, even for small values of ρ. This may be the reason why the results found in several experiments on the rheology of dilute magnetic liquids have not agreed with the Einstein formula, even in the absence of a field.

With $\rho\geqslant 0.01$, Eqs. (41) show that, even at $\alpha\sim 2$–3, the effective viscosity η_1^a is higher than the viscosity of the carrier liquid, η_0, by several orders of magnitude, while we have $\eta_1^s\sim\eta_0$. In this situation, however, the model of chains which are not interacting hydrodynamically is not valid. On the other hand, such a rapid increase in η_1^a with increasing α supports the assertion that the extremely pronounced increase in the viscosity of magnetic liquids and magnetorheological suspensions in an external field which has been observed in many experiments may be a consequence of not only the formation of an infinite cluster of particles but also the formation of finite chains.

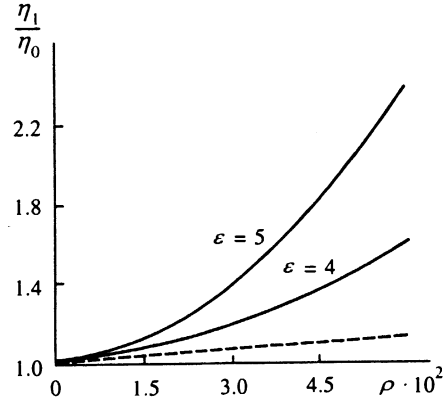

FIG. 7. Effective viscosity of the magnetic liquid vs the volume fraction of particles, ρ, in the absence of a field ($\alpha=0$). Solid curves—calculated from Eq. (41), $\varepsilon=4,5$; dashed curve—calculated from the Einstein formula.

2. We now assume that both the velocity **u** and its gradient are perpendicular to the field:

$$u_x=Ey, \quad u_y=u_z=0, \quad E=\text{const}.$$

In this case we have $\gamma_{xy}=\gamma_{yx}=\omega_{xy}=-\omega_{yx}=(1/2)E$, and the other components of the tensors γ and ω are zero. The nonvanishing components of the stress tensor are

$$\sigma_{xy}=\sigma_{xy}^s=\eta_2^s E, \quad \sigma_{ij}^a=0, \tag{42}$$

$$\eta_2^s=\eta_0\left[1+\left\langle\left\langle \alpha_n+\frac{\zeta_n+\beta_n\lambda_n}{2}\left(\langle e_x^2\rangle_n^0+\langle e_y^2\rangle_n^0\right)\right.\right.\right.$$

$$\left.\left.\left.+(\chi_n-2\lambda_n\beta_n)\langle e_x^2 e_y^2\rangle_n^0\right\rangle\right\rangle\right].$$

The role of the effective viscosity is now played by only its symmetric component η_2^s. Figure 8 shows results calculated for it. It is slightly surprising to see the decrease in η_2^s with increasing magnetic field, despite the increase in the number of particles in the chains. This result is explained by noting that the field is now orienting the chains is such a way that perturbations caused by the chains in the flow of the carrier liquid decrease.

Accordingly, chain aggregates should arise at sufficiently large values of ε, even in very dilute magnetic liquids, and these aggregates should substantially alter macroscopic properties of these systems. Since the average length of the chains increases with increasing ε, the magnetization relaxation time and the effective viscosity increase, rather than decreasing or remaining essentially constant, as was asserted in Refs. 10–12.

In conclusion we should point out that the model of rigid straight rods, combined with the neglect of correlations between particles in different chains, constitutes a very strong approximation, so the use of our results in cases with $\varepsilon\gg 1$ may be only a more or less fortuitous extrapolation. We should warn against attempts to directly generalize the re-

sults derived here to grossly nonequilibrium processes, whose analysis would require consideration of the change in the distribution g_n and also the deformation of the chain aggregates. The effects caused by long-range correlations, by the connection of particles to chains from the side, and by deformations of chains deserve separate study.

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APPENDIX

Straightforward calculations lead to the following values of the equilibrium moments $\langle ... \rangle_n^0$ (cf. Ref. 28):

$$\langle e_i \rangle_n^0 = h_i L_{1n},$$

$$\langle e_i e_k \rangle_n^0 = \tfrac{1}{2}(1 - L_{2n})\delta_{ik} + \tfrac{1}{2}(3L_{2n} - 1)h_i h_k,$$

$$\langle e_i e_k e_j \rangle_n^0 = \tfrac{1}{2}(L_{1n} - L_{3n})(\delta_{ik}h_i + \delta_{ij}h_k + \delta_{kj}h_j) + \tfrac{1}{2}(5L_{3n} - 3L_{1n})h_i h_j h_k,$$

$$\begin{aligned}\langle e_i e_k e_l e_m \rangle_n^0 = {} & \tfrac{1}{8}(1 - 2L_{2n} + L_{4n})(\delta_{ik}\delta_{lm} + \delta_{im}\delta_{kl} + \delta_{il}\delta_{km}) \\ & + \tfrac{1}{8}(6L_{2n} - 5L_{4n} - 1)(h_i h_k \delta_{lm} + h_i h_m \delta_{kl} \\ & + h_i h_l \delta_{km} + h_l h_m \delta_{ik} + h_k h_l \delta_{im} + h_k h_m \delta_{il}) \\ & + \tfrac{1}{8}(3 - 30L_{2n} + 35L_{4n})h_i h_k h_l h_m,\end{aligned}$$

$$L_{Jn} = L_J(\alpha n), \quad J = 1,2,3,4,$$

$$L_1(x) = \coth(x) - \frac{1}{x}, \quad L_2(x) = 1 - \frac{2}{x}L_1(x), \tag{43}$$

$$L_3(x) = \frac{1}{x} - L_1(x) - \frac{3}{x}L_2(x), \quad L_4(x) = 1 - \frac{4}{x}L_3(x).$$

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