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Effect of chainlike aggregates on dynamical properties of magnetic liquids

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The effect of chain-shaped aggregates on the dynamic properties of magnetic liquids is studied under the assumption that the chains can be modeled as straight and rigid. On the basis of microscopical analysis the macroscopical expression for average stress tensor is obtained. The effective viscosity and viscoelastic characteristics are estimated.

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I. INTRODUCTION

One of the fundamental problems of the physics of magnetic fluids is the determination of their macroscopical characteristics (functions of magnetic response, effective viscosity, etc.) as functions of the microscopical characteristics of the system (shape, size, physical properties, and concentration of ferroparticles, properties of a solvent).

The known consistent theories of dynamic properties of ferroliquids [1–3] deal with the very dilute systems for which any interparticle interactions are negligible. However, these interactions may play an important, and often principal, role in the formation of macroscopical properties of ferrocolloids. They lead to the occurence of long-range correlations between positions and orientations of the particles and to a rise of droplike, chainlike and other heterogeneous aggregates consisting of the particles.

The general statistical theory of nondilute ferrocolloids is not developed, and hence it is impossible to study the properties of magnetic fluids with all types of inner structures on the basis of one theoretical model. Therefore, it is reasonable to construct models for the systems with different structures individually. Such ''ideal'' models must help us to understand, first, what inner structures can be expected in the given ferrocolloid for given external conditions; second, how these structures can affect macroscopical properties of the system.

The effect of long-range interparticle correlations on macroscopical dynamic properties of homogeneous, moderately concentrated magnetic liquids was studied in [4]. The effective viscosity of a ferroliquid with droplike aggregates has been estimated in Ref. [5]. The works [6–8] are devoted to the analysis of the effect of chainlike aggregates on the stationary effective viscosity of ferrocolloids in linear approximation in gradient of flow velocity.

The primary aim of our work is to study the influence of chain aggregates on macroscopical rheological properties of ferrofluids. In order to focus our attention specifically on the chains, we adopt the following assumptions. First, we treat ferromagnetic particles as identical spheres. The magnetic moment of the particle is frozen to its body. The magnitude of this moment m is given and is constant. Second, we assume the chains to be straight and rigid. The validity of this assumption will be established below. Third, the interparticle interaction is taken into account only for the particles placed in one chain, the interaction between particles in different chains is neglected. It should be noted that for the real systems this approximation can be too strong and the interchain interactions can be significant. Fourth, we restrict our analysis to the systems in which the energy of a magnetodipole interaction between neighboring particles in a chain is much larger than that of the interaction of the particle with a magnetic field. For this reason, the magnetic moments of all particles in one chain are aligned along the chain axis.

II. SIZE DISTRIBUTION OF A CHAIN

Let us find the distribution function g_n of the chains with respect to the number n of particles in them. For this purpose we use the same ideas as in Ref. [8].

The chains may be treated as heterogeneous fluctuations. Using the well-known Frenkel's theory of heterofluctuations, we can write the free energy per unit volume of the ferrocolloid as follows:

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

Here T is the absolute temperature in energy units, the left term in square brackets in Eq. (1) is the entropy of a gas of n-particle chains due to their translation motion, f_n is a dimensionless ''internal'' free energy of a chain of n particles, a is radius of the particle.

Similar to [6–8] we suggest that the neighboring particles in a straight chain are close to each other. As it is shown in Ref. [8], in the boards of this approximation the following estimation is valid:

$$f_n \approx -\left(\varepsilon(n-1) + \ln\frac{\sinh(\kappa n)}{\kappa n}\right), \tag{2}$$

$$\kappa = \frac{mH}{T}, \quad \varepsilon = 2\frac{m^2}{8a^3 T}.$$

Here H is the magnetic field, the dimensionless parameter κ is the ratio of the energy of interaction of a particle with the magnetic field to a thermal energy, and the dimensionless parameter ε is the energy of interaction of two neighboring particles with each other divided by a thermal energy.

Substituting (2) into (1), we obtain

$$F = T\sum_{i=1}^{\infty}\left[g_n \ln\frac{g_n v}{e} - \left(\varepsilon(n-1) + \ln\frac{\sinh(\kappa n)}{\kappa n}\right)\right]. \tag{3}$$

In an equilibrium state, the distribution function g_n should minimize F under the normalization condition

$$\sum_{n=1}^{\infty} n g_n = \frac{\varphi}{v}, \tag{4}$$

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

Minimizing (3) under (4), and carrying out some standard manipulations, we find

$$g_n = \frac{x^n}{v}\frac{\sinh(\kappa n)}{\kappa n}\exp(-\varepsilon), \quad x = \exp(\varepsilon + \lambda), \tag{5}$$

where λ is the Lagrange coefficient. To find it we substitute Eq. (5) into (4). As a result, we get an equation for x:

$$\sum_{n=1}^{\infty} x^n \sinh(\kappa n) = y, \quad y = \kappa\varphi\exp(\varepsilon). \tag{6}$$

After some transformations we obtain the solution of this equation:

$$x = [2y\cosh\kappa + \sinh\kappa - \sqrt{(2y\cosh\kappa + \sinh\kappa)^2 - 4y^2}] \times (2y)^{-1}. \tag{7}$$

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

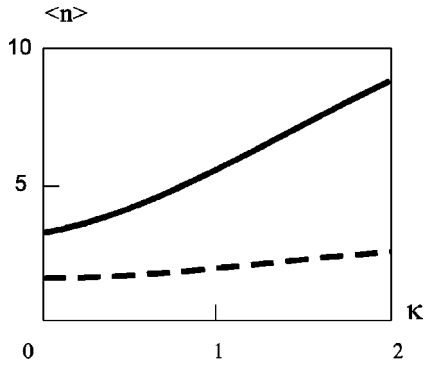

FIG. 1. The mean number of particles in a chain vs the dimensionless magnetic field for $\varphi = 0.05$. Solid line corresponds to $\varepsilon = 5$, dashed line to $\varepsilon = 3$.

$$\langle n\rangle = \frac{\sum_n n g_n}{\sum_n g_n} = \frac{\kappa\varphi\exp(\varepsilon)}{\sum_n x^n \sinh(\kappa n) n^{-1}}. \tag{8}$$

In the absence of the field ($\kappa = 0$)

$$\langle n\rangle = \varphi\frac{1 - x_0}{x_0}\exp(\varepsilon), \tag{9}$$

$$x_0 = x(\kappa = 0) = \frac{1 + 2\varphi\exp(\varepsilon) - \sqrt{1 + 4\varphi\exp(\varepsilon)}}{2\varphi\exp(\varepsilon)}.$$

Figure 1 illustrates the dependencies of $\langle n\rangle$ on κ for given φ and different values of ε.

Using standard reasonings of the theory of polymer chains, one can show that deviation of the aggregate shape from a straight line is small if the number of the particles in the chain is less than ε (see details in Ref. [8]). For this reason, the condition of the validity of the model is the following inequality: $\langle n\rangle < \varepsilon$.

Let φ_c be the value of the volume concentration corresponding to $\langle n\rangle = \varepsilon$. The plot of φ_c as a function of œ for ε is shown on Fig. 2. If at a given ε the concentration $\varphi < \varphi_c$, then the model of straight aggregates may be used.

It should be noted that the similar model of a ferrocolloid with chainlike aggregates was suggested in the work of [9].

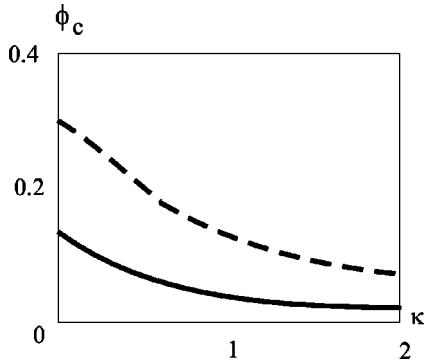

FIG. 2. The critical volume concentration of particles for the model of straight aggregates vs the dimensionless magnetic field. Solid and dashed lines correspond to $\varepsilon = 5$ and $\varepsilon = 3$, respectively.

The model [9] is based on a chemical kinetics approach and the prime difference between this theory and ours is in the method of estimating our free energy f_n of the chain. One may say, that our approximation (2) is the upper estimation of the absolute value of f_n; the approximation of [9] is a lower one. At the same time it seems to us that the relation (2) is more convenient than the same one from [9] for calculations in arbitrary magnetic fields.

III. MATHEMATICAL MODEL

The effect of chain aggregates on rheological properties of polar suspensions (magnetic liquids, magneto- and electrorheological suspensions) was studied in many works (see, for example Refs. [6–10]). Numerical methods were used in Refs. [6,10]. The length of all of the chains was assumed to be identical and known. Our aim is the analytical calculation of the effective functions of viscoelasticity of a ferrocolloid with chainlike aggregates, taking into account the statistical character of the chain length. We assume that the shear rate is weak enough to neglect the effect of deviation from equilibrium on the dimensions and shape of the chains. A condition for the validity of this approximation can be easily derived comparing the hydrodynamic force F_h, which tends to decouple two particles, with the magnetic adhesion force of the particles, F_m. By the order of magnitude $F_h \sim \eta_0 d^2 E$ and $F_m \sim \theta T\varepsilon/d$, where $d=2a$, E is the shear rate, η_0 is the viscosity of a pure solvent, θ is an average angle between the line, connecting the centers of two neighboring particles in a chain, and the direction of their magnetic moments (in the equilibrium state $\theta=0$). The condition under which the chain cannot be broken up is $F_h << F_m$; the condition under which the chain is undeformed, is $\theta\langle n\rangle \ll 1$. The condition we are seeking is, therefore,

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

It can be shown that substituting in this strong inequality well-known estimations of the physical parameters of known magnetic fluids preserves it for many real situations.

To incorporate the hydrodynamic interaction of the chain with a surrounding medium we model the n-particle chain as a prolate spheroid with a semiminor axis a and semimajor na. It is of principal importance that the volume of this spheroid is equal to the total volume of all particles in the chain.

Using the known results of statistical hydrodynamics of dilute suspensions of rigid spheroids (see, for example, [11]), we write expressions for the Cartesian components of the average viscous stress tensor σ as follows:

$$\sigma_{ik} = \sigma^s_{ik} + \sigma^a_{ik}, \tag{10}$$

$$\sigma^s_{ik} = 2\eta_0\gamma_{ik} + \eta_0 \times \left\langle\left\langle \left[(2\alpha_n\gamma_{ik} - \rho_n\langle e_j e_s\rangle_n \delta_{ik}\gamma_{js}) + (\zeta_n + \beta_n\lambda_n) \times (\langle e_i e_j\rangle_n \gamma_{jk} + \langle e_k e_j\rangle_n \gamma_{ji}) + \beta_n(\omega_{ij}\langle e_j e_k\rangle_n + \omega_{kj}\langle e_j e_i\rangle_n) + (\chi_n - 2\lambda_n\beta_n)\langle e_i e_k e_j e_s\rangle_n \gamma_{js} - \beta_n \frac{d}{dt}\langle e_i e_k\rangle_n \right] \right\rangle\right\rangle,$$

$$\sigma^a_{ik} = \frac{\kappa T}{2v}\langle\langle \langle e_i\rangle h_k - \langle e_k\rangle h_i\rangle\rangle, \quad h_i = \frac{H_i}{H},$$

$$\gamma_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right), \quad \omega_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} - \frac{\partial u_k}{\partial x_i}\right).$$

Here and below

$$\langle\langle \cdots \rangle\rangle = \sum_n \cdots n v g_n,$$

$$\langle \cdots \rangle = \int \cdots \mathbf{e}\varphi_n(\mathbf{e}) d\mathbf{e}, \quad \langle \cdots \rangle^o = \int \cdots \mathbf{e}\varphi^o_n(\mathbf{e}) d\mathbf{e},$$

$$i, \ldots, k = x, y, z,$$

$\mathbf{u}$ is average velocity of the colloid.

The unit vector $\mathbf{e}$ is aligned along the chain axis, φ_n is normalized to the unity distribution function over $\mathbf{e}$, $\varphi^o_n(\mathbf{e})$ is φ_n in an equilibrium state. Parameters $\alpha_n \cdots \zeta_n$ are determined in Ref. [11] and given in the Appendix.

In the assumptions $\varepsilon >> 1$, and $\varepsilon >> \kappa$, the magnetic moments of all particles in the chain are aligned along the chain axis. Hence, the equilibrium distribution function $\varphi^o_n(\mathbf{e})$ coincides with that for the rigid particle with the magnetic moment mn. Using the well-known results, we write

$$\varphi^o_n(\mathbf{e}) = \frac{\kappa n}{4\pi \sinh(\kappa n)} \exp[\kappa n(\mathbf{eh})]. \tag{11}$$

In order to determine the nonequilibrium function φ_n, one needs to write and solve a corresponding Fokker-Plank equation. Using our model of the chains as rigid spheroids and the well-known form of this equation for such particles (see, for example, Ref. [11]), we have

$$\frac{\partial\varphi_n}{\partial t} + \lambda_n(e_s\gamma_{sl} - e_m e_s e_l \gamma_{ms})\frac{\partial\varphi_n}{\partial e_l} + \omega_{ls} e_s \frac{\partial\varphi_n}{\partial e_l} - 3\lambda_n e_l e_s \gamma_{ls}\varphi_n - D_n\kappa n\left[(e_j e_m h_m - h_j)\frac{\partial\varphi_n}{\partial e_j} + 2e_j h_j \varphi_n\right] = D_n\left(\frac{\partial^2\varphi_n}{\partial e_j^2} - 2e_s\frac{\partial\varphi_n}{\partial e_s} - e_j e_s \frac{\partial^2\varphi_n}{\partial e_j \partial e_s}\right). \tag{12}$$

where

$$D_n = \frac{T}{8\pi\eta_0 a^3 n \delta_n}, \quad \delta_n = \frac{\beta_n}{3\lambda_n}.$$

The exact solution of this equation for arbitrary κn is unknown. To find its approximation solution we use the method of trial function. Let us write the distribution function in the following form:

$$\varphi_n = \varphi^o_n[1 + a_i(e_i - \langle e_i\rangle^o_n) + b_{ik}(e_i e_k - \langle e_i e_k\rangle^o_n)]. \tag{13}$$

Here a_i and b_{ik} are components of unknown vector and tensor, to be determined.

For these purposes let us multiply both parts of Eq. (12) on the components of vector **e** and tensor $e_i e_m$ and then integrate the obtained relation over all orientations of **e**. As a result, in linear approximation in the flow velocity gradient, we obtain the following moment equations (see, for example, Ref. [11]):

$$\frac{d\langle e_k\rangle_n}{dt}=-\frac{1}{\tau_{1n}}\langle e_k\rangle_n+\lambda_n(\langle e_j\rangle_n^o\gamma_{jk}-\langle e_k e_j e_s\rangle_n^o\gamma_{js}) +\omega_{kj}\langle e_j\rangle_n^o+D_n\kappa n(h_k-\langle e_k e_j\rangle_n h_j) \tag{14}$$

and

$$\frac{d\langle e_i e_k\rangle_n}{dt}=-\frac{1}{\tau_{2n}}\left(\langle e_i e_k\rangle_n-\frac{1}{3}\delta_{ik}\right)+\lambda_n(\langle e_i e_s\rangle_n^o\gamma_{sk} +\langle e_k e_s\rangle_n^o\gamma_{si})+\omega_{ij}\langle e_j e_k\rangle_n^o+\omega_{kj}\langle e_j e_i\rangle_n^o -2\lambda_n\langle e_i e_k e_s e_j\rangle_n^o\gamma_{sj}+D_n\kappa n(\langle e_k\rangle_n h_i -2\langle e_j e_i e_k\rangle_n h_j+\langle e_i\rangle_n h_k), \tag{15}$$

where

$$\tau_{1n}=\frac{1}{2D_n},\quad \tau_{2n}=\frac{1}{6D_n}.$$

Substituting Eq. (13) into (14) and (15), we come to a system of differential equations for functions $a_i(t)$ and $b_{ik}(t)$ corresponding to given n. After solving this system, we can use function (13) to determine the nonequilibrium moments derived in Eq. (10). Note that the linear approximation in γ_{ij},ω_{ij} corresponds to the linear approximation in a_i, b_{ij}.

IV. VISCOELASTIC PROPERTIES OF A FERROCOLLOID

In general, the problem of calculating a_i and b_{ij} is not difficult, however, it is very cumbersome. Here we consider separately some typical examples of the ferrofluid flow in the linear approximation in the gradient of velocity. Let us introduce the Cartesian coordinate system (x,y,z) and suppose that the axis Oz is parallel to the external magnetic field $(H_z=H=\text{const},\ H_x=H_y=0)$.

A. Stationary flow

We consider now two actual situations. In the first of them we consider the colloid with the velocity aligned along the axis Ox, and its gradient directed along the axis Oz (i.e., along the external field **H**). In the second one the velocity is aligned along Oz, and its gradient along Ox.

Let $\nu=\gamma_{xz}=\gamma_{zx}=-(-1)^p\omega_{xz}=(-1)^p\omega_{zx}$ (here and below $p=1$ for the first above mentioned situation, $p=2$ for the second one). For these stationary types of flow the equations (13)–(15) in the linear approximation in γ_{ij} and ω_{ij} lead to the following system of equations with respect to a_x and b_{xz} (the other components a_i and b_{ij} are now equal to zero):

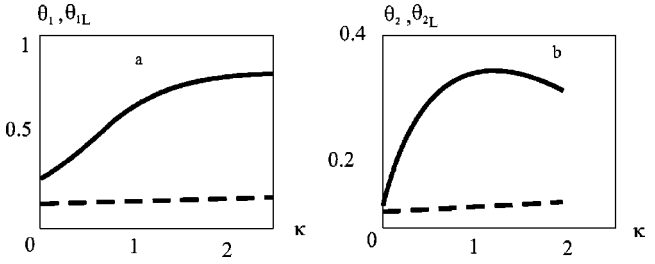

FIG. 3. Dimensionless stationary effective viscosities as functions of external magnetic field for $\varepsilon=3$, $\varphi=0.05$. Solid lines correspond to θ_p, dashed curves to θ_{pL}. (a) The field is aligned along the gradient of the flow velocity; (b) along the flow velocity.

$$\left[\left(\frac{1}{\tau_{1n}}\right)\langle e_x^2\rangle_n^o+D_n\kappa n\langle e_x^2 e_z\rangle_n^o\right]a_x+\left[\left(\frac{1}{\tau_{1n}}\right)\langle e_x^2 e_z\rangle_n^o +D_n\kappa n\langle e_x^2 e_z^2\rangle_n^o\right]2b_{xz} =[\lambda_n(\langle e_z^2\rangle_n^o-2\langle e_x^2 e_z\rangle_n^o)-(-1)^p\langle e_z\rangle_n^o]\nu \tag{16}$$

and

$$\left[\left(\frac{1}{\tau_{2n}}\right)\langle e_x^2 e_z\rangle_n^o+D_n\kappa n(2\langle e_x^2 e_z^2\rangle_n^o-\langle e_x^2\rangle_n^o)\right]a_x+\left[\left(\frac{1}{\tau_{2n}}\right) \times\langle e_x^2 e_z^2\rangle_n^o+D_n\kappa n(2\langle e_x^2 e_z^3\rangle_n^o-\langle e_x^2 e_z\rangle_n^o)\right]2b_{xz} =[\lambda_n(\langle e_x^2\rangle_n^o-4\langle e_x^2 e_z^2\rangle_n^o+\langle e_z^2\rangle_n^o)-(-1)^p(\langle e_z^2\rangle_n^o -\langle e_x^2\rangle_n^o)]\nu. \tag{17}$$

Substituting Eq. (13) into Eq. (10), we have

$$\sigma_{xz}=2\eta_1\nu \tag{18}$$

for the first type of flow and

$$\sigma_{zx}=2\eta_2\nu \tag{19}$$

for the second one. The corresponding effective viscosities η_p are

$$\eta_p=\eta_0\left[1+\left\langle\left\langle \alpha_n+\frac{1}{2}[(\zeta_n+\beta_n\lambda_n)(\langle e_x^2\rangle_n^o+\langle e_z^2\rangle_n^o) -(-1)^p\beta_n(\langle e_z^2\rangle_n^o-\langle e_x^2\rangle_n^o)+2(\chi_n-2\lambda_n\beta_n)\langle e_x^2 e_z^2\rangle_n^o] -(-1)^p\frac{1}{2v}\frac{T\kappa}{\eta_0}(A_1\langle e_x^2\rangle_n^o+B_1\langle e_x^2 e_z\rangle_n^o)\right\rangle\right\rangle\right], \tag{20}$$

$$A_1=\frac{a_x}{2\nu},\quad B_1=2\frac{b_{xz}}{2\nu},\quad p=1,2.$$

Let us introduce the dimensionless effective viscosities $\theta_p=(\eta_p-\eta_0)/\eta_0$ and the same quantities θ_{pL} for the colloid containing only single particles (without chains). The dependencies of θ_p as well as θ_{pL} on the dimensionless field κ are given in Fig. 3. The main conclusion following from these results is that even short chains (see Fig. 1) increase the effective viscosities significantly. The magnetoviscous ef-

fects in nondilute ferrofluids have been observed in many experiments (see, for example, Ref. [12]). Our results show that the chainlike aggregates can be physical in nature in these phenomena.

The nonmonotonic dependence of η_2 on κ is explained as follows. When the order of the chain orientation is weak, an increase in their concentration with the external field increases the effective viscosity of the system. However, when elongated particles (for example, chains) are oriented strongly along the velocity of the suspension, their hydrodynamic resistance is less than the same for the single spherical particles with the same summing volume. For this reason, when the field is strong enough and the chains with a high accuracy are oriented along the suspension velocity, the increase of the field leads to a decrease of the concentration of single particles and, as a result, to a decrease of the viscosity η_2.

B. Nonstationary flow

For example, let us consider the colloid flow when its velocity is parallel to the axis Ox, and its gradient is aligned along Oz. Using the Fourier transformations over time of Eqs. (10), (14), and (15) and using for the Fourier components of physical values with the same notations as for their originals, we come to the following system for a_x and b_{xz}:

$$\left[\left(i\Omega+\frac{1}{\tau_{1n}}\right)\langle e_x^2\rangle_n^o+D_n\kappa n\langle e_x^2e_z\rangle_n^o\right]a_x+\left[\left(i\Omega+\frac{1}{\tau_{1n}}\right)\times\langle e_x^2e_z\rangle_n^o+D_n\kappa n\langle e_x^2e_z^2\rangle_n^o\right]2b_{xz}=[\lambda_n(\langle e_z^2\rangle_n^o-2\langle e_x^2e_z\rangle_n^o)+\langle e_z\rangle_n^o]\nu, \tag{21}$$

$$\left[\left(i\Omega+\frac{1}{\tau_{2n}}\right)\langle e_x^2e_z\rangle_n^o+D_n\kappa n(2\langle e_x^2e_z^2\rangle_n^o-\langle e_x^2\rangle_n^o)\right]a_x+\left[\left(i\Omega+\frac{1}{\tau_{2n}}\right)\langle e_x^2e_z^2\rangle_n^o+D_n\kappa n(2\langle e_x^2e_z^3\rangle_n^o-\langle e_x^2e_z\rangle_n^o)\right]2b_{xz}=[\lambda_n(\langle e_x^2\rangle_n^o-4\langle e_x^2e_z^2\rangle_n^o+\langle e_z^2\rangle_n^o)(\langle e_z^2\rangle_n^o-\langle e_x^2\rangle_n^o)]\nu \tag{22}$$

and the following expression for the hydrodynamic stress

$$\sigma_{xz}=2\eta_{1\Omega}\nu, \tag{23}$$

$$\eta_{1\Omega}=\eta_0\left[1+\left\langle\left\langle\alpha_n+\frac{1}{2}[(\zeta_n+\beta_n\lambda_n)(\langle e_x^2\rangle_n^o+\langle e_z^2\rangle_n^o)+\beta_n(\langle e_z^2\rangle_n^o-\langle e_x^2\rangle_n^o)+2(\chi_n-2\lambda_n\beta_n)\langle e_x^2e_z^2\rangle_n^o]+\frac{1}{2v}\frac{T\kappa}{\eta_0}(A_1\langle e_x^2\rangle_n^o+B_1\langle e_x^2e_z\rangle_n^o)-i\Omega\beta_n(A_1\langle e_x^2e_z\rangle_n^o+B_1\langle e_x^2e_z^2\rangle_n^o)\right\rangle\right\rangle\right].$$

$$A_1=\frac{a_x}{2\nu},\quad B_1=2\frac{b_{xz}}{2\nu}.$$

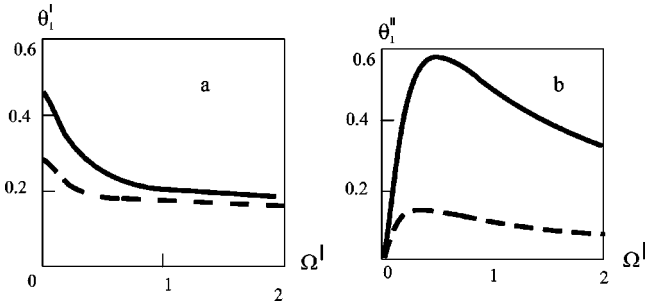

FIG. 4. (a) Real and (b) imaginary parts of the dimensionless complex effective viscosity vs the dimensionless flow frequency $\Omega'=\Omega/D_1$. The external field is aligned along the gradient of the flow velocity, $\varepsilon=3$, $\varphi=0.05$. Solid and dashed lines correspond to $\kappa=1$ and $\kappa=0.5$, respectively.

Here Ω is the Fourier frequency. Let $\eta'_{1\Omega}=\mathrm{Re}\,\eta_{1\Omega}$ and $\eta''_{1\Omega}=-\mathrm{Im}\,\eta_{1\Omega}$ be the real and imaginary parts of the effective complex viscosity of the colloid, respectively, $\theta'_1=(\eta'_{1\Omega}-\eta_0)/\eta_0$, $\theta''_1=(\eta''_{1\Omega}-\eta_0)/\eta_0$ and $\theta'_{1L},\theta''_{1L}$ are the same as for the colloid with the single particles.

The dependences of θ'_1 and θ''_1 on Ω are presented in Fig. 4. The same results for $\theta'_{1L},\theta''_{1L}$ are given in Fig. 5.

The comparison of the results on these figures shows that chainlike aggregates increase both the real and imaginary parts of the effective viscosity and significantly decrease the flow frequency corresponding to a maximum of θ''_1. We would like to emphasize that the mean number $\langle n\rangle$ of the particles in aggregates for situations corresponding to Fig. 4 is not large (see Fig. 1). Consequently, even the short chains are able to increase greatly the characteristic time of hydrodynamic relaxation.

For zero magnetic field one can obtain the following short expression for the complex effective viscosity:

$$\eta_{1\Omega}=\eta_0\left[1+\left\langle\left\langle\alpha_n+\frac{1}{2}\left(\frac{2}{3}(\zeta_n+\beta_n\lambda_n)+\frac{2}{15}(\chi_n-2\lambda_n\beta_n)\right)-\frac{4}{15}\beta_n\lambda_n\frac{\Omega\tau_{2n}}{1+(\Omega\tau_{2n})^2}(\Omega\tau_{2n}+i)\right\rangle\right\rangle\right]. \tag{24}$$

It should be noted that the rheological equation of state for the colloids containing only single ferroparticles (without chains) has no relaxation character.

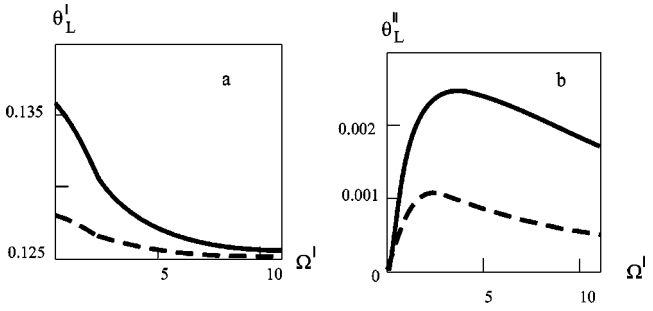

FIG. 5. The same curves as in Fig. 4 for a single-particle colloid.

V. NORMAL STRESSES

Using the above mentioned method, one can estimate the normal components of the stress tensor at the shear flow of the colloid. For example, let the field **H** be aligned along the axis $0z$, the stationary velocity **u** of the colloid along Ox, and its gradient along Oy. By definition we note

$$\nu=\frac{1}{2}\frac{\partial u_x}{\partial y}=\text{const.}$$

Substituting Eq. (13) into Eqs. (16) and (17), for stationary flow in the linear approximation in ν, one obtains

$$b_{xy}=B_n\frac{\nu}{D_1},\quad b_{i\neq x,j\neq y}=a_k=0, \tag{25}$$

$$B_n=\lambda_n\frac{\langle e_y^2\rangle_n^o-2\langle e_x^2e_y^2\rangle_n^o}{3\langle e_x^2e_y^2\rangle_n^o+\kappa n\langle e_x^2e_y^2e_z\rangle_n^o}\frac{D_1}{D_n},$$

$$D_1=\frac{T}{8\pi a^3\eta_0}.$$

Using Eqs. (13) and (22) in Eq. (10), after simple calculations we have

$$\sigma_{ii}=F_i\eta_0\frac{\nu^2}{D_1},\quad i=x,y,z, \tag{26}$$

$$F_z=\sum_n\left[-\rho_n\langle e_x^2e_y^2\rangle_n^o+2(\chi_n-2\beta_n\lambda_n)\langle e_x^2e_y^2e_z^2\rangle_n^o\right]B_n n g_n,$$

$$F_x=\sum_n\left\{\left[-\rho_n+2(\zeta_n+\beta_n\lambda_n)+2\beta_n\right]\langle e_x^2e_y^2\rangle_n^o+2(\chi_n-2\beta_n\lambda_n)\langle e_x^4e_y^2\rangle_n^o\right\}B_n n g_n,$$

$$F_y=\sum_n\left\{\left[-\rho_n+2(\zeta_n+\beta_n\lambda_n)-2\beta_n\right]\langle e_x^2e_y^2\rangle_n^o+2(\chi_n-2\beta_n\lambda_n)\langle e_x^2e_y^4\rangle_n^o\right\}B_n n g_n.$$

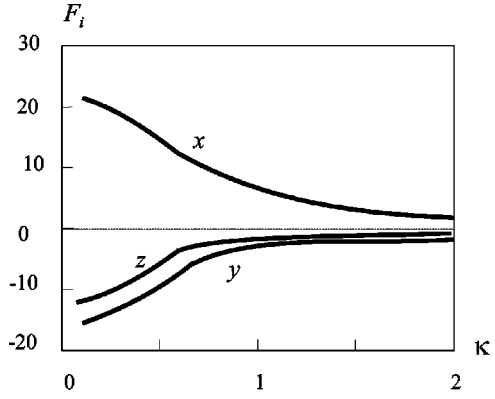

FIG. 6. The parameters F_i calculated from Eq. (26) as functions of the external magnetic field when $\varepsilon=3$. (b) Solid line corresponds to F_x, dashed line to F_y.

The results of calculations of parameters F_i are given in Fig. 6. One can see that for this geometry of flow $|F_{x,y}|>F_z$. Let us note that for colloids with only separate particles $F_i=0$.

The normal stresses in ferrocolloids may be the cause of the Weissenberg effect recently observed in the experiments of Ref. [13]. It should be noted that the individual spherical particles as well as spherical (without field) droplike aggregates cannot induce appearance of the normal stresses and, therefore, the Weissenberg effect. Hence, the results of Ref. [13] show that nonspherical, i.e., possibly, chainlike aggregates can occur in nondilute ferrofluids.

VI. CONCLUSIONS

We have studied the effect of short, straight chains on the effective rheological properties of ferrocolloids as well as the characteristic time of hydrodynamic relaxation. If the external magnetic field is parallel to the gradient of velocity, the presence of the chains leads to a significant increase of both the effective viscosity and time of hydrodynamical relaxation.

Due to the chains, the normal stresses can arise in a shear flowing ferrocolloid. The magnitudes of these stresses increase significantly in the weak or moderate magnetic field; in a very strong field the stresses equal zero. The normal stresses can induce the Weissenberg effect in ferrocolloids, observed in experiments of Ref. [13]. In the condition of normal gravitation this phenomena is too weak. However it is significant under conditions of low gravitation.

It should be noted that in the real ferrocolloids the shape of chains is not exactly straight due to the action of thermal fluctuations. For this reason, our calculations can be considered as an upper estimation for both the length of the chains and for their effect on macroscopical properties of ferrocolloids. This is not a rough estimation when inequality $\langle n\rangle<\varepsilon$ is held (see Figs. 1, 2). At the same time, while interpreting experimental results on the ferrofluid rheology it is necessary to take into account that not only chainlike aggregates can take place in these systems. For example, these aggregates can be droplike, fractal, circlelike, etc. Besides that, the real ferrocolloids, unlike our model, are polydisperse. Next, in the real ferrofluids interactions between the chains, neglected here, can play a significant role in formation of the macroscopical properties. However, we believe that it is reasonable to analyze the influence of different types of heterostructures and the influence of polydispersity on macroscopical properties of ferrofluids separately. This work can be considered as an example of such model analysis.

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APPENDIX

The calculations lead to the following values of the equilibrium moments:

$$\langle e_i\rangle_n^o=h_iL_1,$$

$$\langle e_i e_k \rangle_n^o = \frac{1}{2}(1-L_2)\delta_{ik} + \frac{1}{2}(3L_2-1)h_i h_k,$$

$$\langle e_i e_k e_j \rangle_n^o = \frac{1}{2}(L_1-L_3)(\delta_{ik}h_j + \delta_{ij}h_k + \delta_{kj}h_i) + \frac{1}{2}(5L_3-3L_1)h_i h_j h_k,$$

$$\langle e_i e_k e_l e_m \rangle = \frac{1}{8}(1-2L_2+L_4)(\delta_{ik}\delta_{lm}+\delta_{im}\delta_{kl}+\delta_{ik}\delta_{lm}) + \frac{1}{8}(6L_2-5L_4-1)(h_i h_k \delta_{lm} + h_i h_m \delta_l + h_i h_l \delta_{km} + h_l h_m \delta_{ik} + h_l h_k \delta_{im} + h_m h_k \delta_{li}) + \frac{1}{8}(3-30L_2+35L_4)h_i h_k h_l h_m,$$

$$L_J = L_J(\kappa n), \quad J = 1,2,3,4,$$

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

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

The parameters $\alpha_n \cdots \zeta_n$ are given in Ref. [10]:

$$\alpha_n = \frac{1}{n\alpha_0'},$$

$$\beta_n = \frac{2(n^2-1)}{n(n^2\alpha_0+\beta_0)},$$

$$\zeta_n = \frac{4}{(n^2+1)n\beta_0'} - \frac{2}{n\alpha_0'},$$

$$\chi_n = \frac{2\alpha_0''}{n\alpha_0\beta_0''} - \frac{8}{n(n^2+1)\beta_0'} + \frac{2}{n\alpha_0'},$$

$$\rho_n = \frac{1}{3n\alpha_0'\beta_0''}[2(\alpha_0''-\beta_0'') + 3n(\alpha_0\alpha_0''-\beta_0\beta_0'')],$$

$$\chi_n = \frac{2\alpha_0''}{n^4\alpha_0\beta_0''} - \frac{8}{n^2(1+n^2)\beta_0'} + \frac{2}{n^4\alpha_0'},$$

$$\lambda_n = \frac{n^2-1}{n^2+1}.$$

Here

$$\alpha_0 = \int_0^\infty \frac{ds}{(n^2+s)Q}, \quad \beta_0 = \int_0^\infty \frac{ds}{(1+s)Q},$$

$$\alpha_0' = \int_0^\infty \frac{ds}{(1+s)^2 Q}, \quad \beta_0' = \int_0^\infty \frac{ds}{(n^2+s)(1+s)Q},$$

$$\alpha_0'' = \int_0^\infty \frac{sds}{(1+s)^2 Q}, \quad \beta_0'' = \int_0^\infty \frac{sds}{(n^2+s)(1+s)Q},$$

$$Q = (1+s)\sqrt{n^2+s}.$$

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