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EFFECT OF POLYDISPERSITY ON MAGNETOVISCOUS PROPERTIES OF FERROFLUIDS

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The paper deals with a theoretical study of the magnetoviscous effect in polydisperse ferrofluids. A two-fractional model of colloid consisting of relatively large and small particles is studied. The model is based on the idea that the magnetoviscous effect is determined by chain-like aggregates formed by large particles. The effect of the small particle fraction is determined by two factors: (i) the magnetic interaction between large and small particles, which leads to a reduction of the chain length and weakening of the fluid magnetoviscosity, (ii) the steric interaction between small and large particles, which enlarges the chain length, therefore, enhances this effect. The resulting effect is determined by the ratio of the sizes of large and small particles.

Introduction.

Ferrofluids are colloidal suspensions of single-domain ferromagnetic or ferrimagnetic nanoparticles. Special surface layers on the particles inhibit their colloidal irreversible aggregation. The intensive Brownian motion of the particles prevents their gravitational sedimentation. The unique combination of good fluidity with high reaction to the applied magnetic field and the ability to control the position, shape and physical properties of these system using the magnetic field offer a wide range of engineering [1] and bio-medical [2, 3] applications of these systems.

One of the interesting features of ferrofluids is the increase of viscosity under the magnetic field effect. This phenomenon, called the magnetoviscous effect [4], was demonstrated experimentally in [5, 6] and explained theoretically in [7, 8] in the frames of the model of isolated non-interacting magnetic ferroparticles (ideal gas of particles). Note that any Brownian effects in the system of the particles were neglected in [7]; these effects were considered in theory [8].

Experiments [4] (see also references therein) show that in commercial ferrofluids the magnetoviscous effect can exceed the prediction of the model [8] by two orders of magnitude. In [4], this strong effect has been qualitatively explained by the appearance of linear chain-like aggregates in fluids, whose length is limited by the global shear rate of the fluid flow. A quantitative theoretical model of the chains influence on the magnetoviscous effect was proposed in [9].

All real ferrofluids are polydisperse systems, often with a wide range of particles sizes. The chains can be formed by relatively large particles, which interact magnetically strongly enough with each other. In the model [9], small particles are considered rather as a background, weakly affecting the macroscopic rheological effects. However, the experiments [10] with specially prepared two-fractional ferrofluids have demonstrated that the influence of small particles can be very significant and, even with a small concentration of small particles, assist in enhancing the magnetoviscous effect up to several times. It should be noted that the effect of small particles on the chains consisting of large particles has been studied theoretically in [11]. The results [11] indicate that the small particles make the chains shorter and, therefore, must weaken the macroscopic magnetoviscous effect.

This study is aimed at theoretical explanation of the internal mechanisms of enhancement of the magnetoviscous effect due to the small particle fraction.

1. General model and main approximations.

We consider a two-fractional ferrofluid consisting of large and small single-domain spherical nanoparticles with the magnetic core diameters $d_{\rm ml}$ and $d_{\rm ms}$, respectively. All particles are synthesized of the same magnetic material with a saturated magnetization $M_{\rm p}$. Each particle is covered with a stabilizing layer preventing their colloidal aggregation (s is the thickness of the layer). Note that usually the values $s \approx 2-2.5$ nm can be used [4]. The hydrodynamic diameters (the magnetic core and the shell) of the particles are, respectively, $d_{\rm l} = d_{\rm ml} + 2s$ and $d_{\rm s} = d_{\rm ms} + 2s$.

The energy of the dipole-dipole interaction between the particles can be characterized by the dimensionless parameters

$$\lambda_{\rm ll} = \frac{\mu_0}{4\pi}\frac{M_{\rm p}^2 v_{\rm ml}^2}{d_{\rm l}^3 {\rm kT}}, \quad \lambda_{\rm ss} = \frac{\mu_0}{4\pi}\frac{M_{\rm p}^2 v_{\rm ms}^2}{d_{\rm s}^3 {\rm kT}}, \quad \lambda_{\rm ls} = \frac{2\mu_0}{\pi}\frac{M_{\rm p}^2 v_{\rm ml} v_{\rm ms}}{(d_{\rm l}+d_{\rm s})^3\,{\rm kT}}; \qquad (1)$$
$$v_{\rm ml} = \frac{\pi}{6} d_{\rm ml}^3, \quad v_{\rm ms} = \frac{\pi}{6} d_{\rm ms}^3.$$

Here μ_0 is the vacuum magnetic permeability; kT is the absolute temperature in energy units; the indices 'll', 'ss' and 'ls' indicate the parameters of the interaction between two large, two small and large-small particles, respectively. It is assumed that $\lambda_{\rm ll}$ is significantly larger that unity, therefore, the magnetic interaction between large particles can initiate their aggregation into chains; $\lambda_{\rm ss}$ does not exceed unity or is less. This means that the interaction between small particles is weak and can be ignored. The parameter $\lambda_{\rm ls}$ can have some intermediate values.

We consider a simple shear fluid flow with a macroscopic shear rate $\dot{\gamma}$. The flow velocity is perpendicular to the applied field $\mathbf{H}$, with its gradient directed along this field. Note that this is quite a typical geometry of the flow in experiments.

The rheological properties of ferrofluids with chain aggregates are determined by the length of the chains. In its turn, the chain length is determined by the combination of the following factors: (i) the magnetic particle interaction; (ii) the thermal motion of particles, and (iii) the chain breakup due to hydrodynamic forces acting in the flowing fluid.

Our first aim is to determine the function g_n of the distribution over the particle number n in the chain, i.e. the number of chains consisting of large particles per unit volume of the fluid. Meticulous determination of this function in the macroscopically flowing ferrofluid is mathematically a very difficult problem. However, the results in [9] demonstrate that the following method can be used, at least, to get first approximations for g_n and the fluid rheological characteristics. Namely, we consider the chains as straight rigid aggregates and neglect the thermal fluctuations of their shape and the orientation of the particles moments. Next, we neglect any interaction of the chains with each other. Usually this is justified when the volume concentration of the large particles and, therefore, chains does not exceed several percent. Third, we take into account that very long chains are ruptured by the hydrodynamic forces. This means that the number n of the particles in the chain cannot exceed some critical value $n_{\rm c}$ estimated, for example, in [4]. Then we consider that the shear flow deflects the chain from the applied field. The angle of deviation is determined by the balance between the magnetic and the hydrodynamic torque acting on the chain. Next, we introduce a free energy F of the unit volume of the chain ensemble as a functional of the function g_n and determine g_n by minimizing F provided that the large particles maintain,

$$\sum_{n=1}^{n_c} n g_n = \frac{\varphi_l}{v_l}, \quad v_l = \frac{\pi}{6} d_l^3 \tag{2}$$

Here ϕ_l is the hydrodynamic (with the surface layers) volume concentration of large particles, ϕ_l/v_l is their number in a unit volume. Following [4], we evaluate the maximum number n_c of the particles in the chains as

$$n_c \sim \sqrt{\frac{\mu_0}{18\eta_0\dot{\gamma}}} M_p \tag{3}$$

where η_0 is the viscosity of the carrier liquid, $\dot{\gamma}$ is the macroscopic shear rate.

In the frame of the used approximations, the system free energy F is presented as

$$F = kT \sum_{n=1}^{n_c} g_n \left[\ln \frac{g_n v_l}{e} + U_n + W_n(\varphi_s)\right] \tag{4}$$

Here U_n is an internal dimensionless (with respect to kT) energy of the n-particle chain due to its particles' interaction with each other and with the applied magnetic field $\mathbf{H}$, $W_n(\phi_s)$ is the energy of the interaction between the chain and the small particles. We omit here the term of gas entropy of small particles because it does not play a role in the further consideration.

Minimizing Eq. (4) and taking into account Eqs. (2) yield the relation

$$g_n = \frac{1}{v_l} \exp\left(-U_n - W_n(\varphi_s) - \Lambda n\right) \tag{5}$$

were Λ is the Lagrange multiplier to be determined by substituting Eq. (5) into Eqs. (2) that leads to an equation with respect to Λ.

Because the energy of the dipole-dipole interaction between the particles decays with the distance r between them as r^{-3}, in the first approximation, we consider the interaction only between the nearest particles in the chain. In the frame of the model of rod-like chains, this yields (see details in [9]):

$$U_n = -2\lambda_{ll}(n-1) - \ln \frac{\mathrm{sh}(h_l n)}{4\pi h_l n}, \quad h_l = \mu_0 \frac{M_p v_{ml}}{\mathrm{kT}} H. \tag{6}$$

Here h_l is the ratio of the Zeeman energy of a large particle in the field $\mathbf{H}$ to the thermal energy of the system.

The dimensionless energy $W_n(\phi_s)$ of the chain interaction with small particles is the sum of the magnetic W_{nm} and steric W_{ns} parts.

$$W_n = W_{nm} + W_{ns} \tag{7}$$

We determine W_{nm} in the frame of the classical, mathematically regular method of virial expansion which is productive at small concentrations of the interacting particles. Using this approach in the second virial approximation (see, for example, [12]) yields:

$$\begin{gathered} W_{ns} = \frac{\varphi_s}{v_s} \int f_c(\mathbf{e}_c) f_s(\mathbf{e}_s) \left[1 - \exp\left(-w_n(\mathbf{e}_c, \mathbf{e}_s, \mathbf{r})\right)\right] \mathrm{d}\mathbf{e}_c \mathrm{d}\mathbf{e}_s \mathrm{d}\mathbf{r}, \\ w_n(\mathbf{e}_c, \mathbf{e}_s, \mathbf{r}) = -\lambda_{ls} \left(\frac{d_s + d_l}{2}\right)^3 \sum_{i=1}^{n} \frac{3\left(\mathbf{e}_c(\mathbf{r} - \mathbf{r}_i)\right)\left(\mathbf{e}_s(\mathbf{r} - \mathbf{r}_i)\right) - (\mathbf{e}_c \mathbf{e}_s)(\mathbf{r} - \mathbf{r}_i)^2}{|\mathbf{r} - \mathbf{r}_i|^5}. \end{gathered} \tag{8}$$

Here $\mathbf{c}_{\mathrm{c}}$ and $\mathbf{e}_{\mathrm{s}}$ are the unit vectors aligned with the chain axis and magnetic moment of the small particle, respectively; $\mathbf{r}$ is the radius-vector of the small particle; $\mathbf{r}_i$ is the radius-vector of the i-th large particle in the chain; w_n is the dimensionless energy of the dipole-dipole interaction between the n-particle chain and the small particle; $f_{\mathrm{c}}(\mathbf{e}_{\mathrm{c}})$ and $f_{\mathrm{s}}(\mathbf{e}_{\mathrm{s}})$ are the orientational distribution functions of a single chain and a small particle. These functions are determined by the combination of the thermal rotational motion of the chain and a small particle, respectively, and by the chain and the particle Zeeman interaction with the applied field, and by the effect of hydrodynamic forces which tend to deflect the chain axis (the particle magnetic moment) from the field $\mathbf{H}$.

Note that $W_{n\mathrm{m}}$ and $W_{n\mathrm{s}}$ are statistically average values of the free energies of the magnetic and steric interaction between the chain and the small particles; w_n denotes the exact potential of the dipole-dipole interaction between the chain with the orientation $\mathbf{e}_{\mathrm{c}}$ and the small particle with the vector $\mathbf{e}_{\mathrm{s}}$ of the moment orientation of the particle situated at the point r.

Strictly speaking, the functions $f_{\mathrm{c}}(\mathbf{e}_{\mathrm{c}})$ and $f_{\mathrm{s}}(\mathbf{e}_{\mathrm{s}})$ can be found from the solution of the corresponding Fokker–Plank equations. However, estimations show that in realistic situations the characteristic angles of deviation of the chains axes from the field are small and, in the first approximation, can be neglected. The mean angle of deviation of the single small particle magnetic moment is much smaller than that for the chain. It allows to simplify the consideration and assume the functions $f_{\mathrm{c}}(\mathbf{e}_{\mathrm{c}})$ and $f_{\mathrm{s}}(\mathbf{e}_{\mathrm{s}})$ as equilibrium ones, neglecting the shear flow effect. Under this approximation,

$$f_{\mathrm{c}}\left(\mathbf{e}_{\mathrm{c}}\right)=\frac{h_{\mathrm{l}}n}{4\pi\mathrm{sh}\left(h_{\mathrm{l}}n\right)}\exp\left(n\left(\mathbf{e}_{\mathrm{c}}h_{\mathrm{l}}\right)\right),\quad f_{\mathrm{s}}\left(\mathbf{e}_{\mathrm{s}}\right)=\left(\frac{h_{\mathrm{s}}}{4\pi\mathrm{sh}h_{\mathrm{s}}}\exp\left(\mathbf{e}_{\mathrm{s}}h_{\mathrm{s}}\right)\right),$$
$$h_{\mathrm{s}}=\mu_0\frac{M_{\mathrm{p}}v_{\mathrm{ms}}}{\mathrm{kT}}H. \tag{9}$$

In the general case, the integral in Eqs. (8) cannot be calculated analytically; the numerical calculations take too much time. Here, because the parameter λ_{sl} of the dipole-dipole interaction between small and large particles is about unity or less, we can expand the exponent in Eqs. (8) in the power series with respect to w_n and to restrict ourselves to the linear approximation

$$W_{n\mathrm{s}}=\frac{\varphi_{\mathrm{s}}}{v_{\mathrm{s}}}\int f_{\mathrm{c}}\left(\mathbf{e}_{\mathrm{c}}\right)f_{\mathrm{s}}(\mathbf{e}_{\mathrm{s}})w_n\left(\mathbf{e}_{\mathrm{c}},\mathbf{e}_{\mathrm{s}},\mathbf{r}\right)\mathrm{d}\mathbf{e}_{\mathrm{c}}\mathrm{d}\mathbf{e}_{\mathrm{s}}\mathrm{d}\mathbf{r}. \tag{10}$$

Because of the slow decay of the potential of the dipole-dipole interaction with the distance $|\mathbf{r}-\mathbf{r}_i|$ between the particles, the integrals (8) over $\mathbf{r}$ converge conditionally. The result depends on the shape of the volume of integration and on the order of integration over the components of this vector [13]. A correct way of this integration has been proposed in [12]. The main idea of this method is to integrate in Eq. (10) over an infinite cylinder aligned with the field $\mathbf{H}$. This choice of the volume of integration provides the equality to zero of the demagnetizing factor of the volume of integration and, therefore, the equality of $\mathbf{H}$ in Eqs. (9), (10) to the mean (Maxwell) magnetic field at the place, where the particles are situated. This method has been used in [12] for ferrofluids with identical spherical particles. However, in the case of the chain, it leads to very cumbersome calculations, and the final results for $W_{n\mathrm{m}}$ are very difficult to be used. In order to obtain physically reasonable results in a transparent form, we consider the chain as oriented along the field $\mathbf{H}$ and assume that the component of the vector $\mathbf{e}_{\mathrm{c}}$

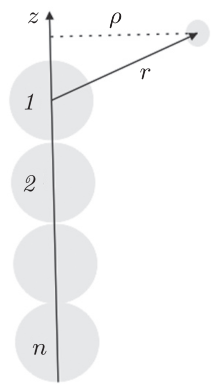

Fig. 1. Schematic view of the cylindrical coordinate system, and enumeration of particles in the chain.

along the field **H** is equal to the mean value of this component:

$$e_{cz} = L(nh_l), \quad e_{cx,y} = 0. \tag{11}$$

Here we use the Cartesian coordinate system with the z-axis along the field **H**. According to the main idea of [12] and considering Eq. (11), Eq. (10) can be written as

$$\begin{aligned} W_{ns} = &- 2\pi\lambda_{ls}\frac{\varphi_s}{v_s}\left(\frac{d_s+d_l}{2}\right)^3 \\ &\left[2\int\limits_0^{\frac{d_s+d_l}{2}}\int\limits_{z_{\min}}^{\infty} f_s(\mathbf{e}_s)e_{sz}\sum_{i=1}^{n}\frac{2(z-z_i)^2-\rho^2}{\left[(z-z_i)^2+\rho^2\right]^{5/2}}\rho\mathrm{d}\mathbf{e}_s\mathrm{d}z\mathrm{d}\rho\ + \right. \\ &\left.\int\limits_{\frac{d_s+d_l}{2}}^{\infty}\int\limits_{-\infty}^{\infty} f_s(\mathbf{e}_s)e_{sz}\sum_{i=1}^{n}\frac{2(z-z_i)^2-\rho^2}{\left[(z-z_i)^2+\rho^2\right]^{5/2}}\rho\mathrm{d}\mathbf{e}_s\mathrm{d}z\mathrm{d}\rho\right] L(nh_l), \\ z_{\min} = &\sqrt{\left(\frac{d_s+d_l}{2}\right)^2-\rho^2}. \end{aligned} \tag{12}$$

In Eqs. (12), z and ρ are the cylindrical coordinates of the small particle in the system illustrated in Fig. 1; $z_i = -(i-1)\,d_l$ is the vertical coordinate of the i-th large particle in the chain. The equality

$$\int e_{x,y} f_s\left(\mathbf{e}_s\right)\mathrm{d}\mathbf{e}_s = 0$$

is accounted for. The order of integration in Eqs. (12) is first over z, only then over ρ, which is principally important in Eqs. (12).

The direct calculations show that the second integral in the brackets in Eqs. (12) is equal to zero. Integrating the first one over $\mathbf{e}_s$ yields the following equation:

$$W_{ns} = -4\pi\lambda_{ls}\frac{\varphi_s}{v_s}\left(\frac{d_s+d_l}{2}\right)^3 L(nh_l)L(h_s)\sum_{i=1}^{n}\int\limits_0^{\frac{d_s+d_l}{2}}\int\limits_{z_{\min}}^{\infty}\frac{2(z-z_i)^2-\rho^2}{\left[(z-z_i)^2+\rho^2\right]^{5/2}}\rho\mathrm{d}z\mathrm{d}\rho.$$

The direct integration leads to the relations:

$$
\begin{aligned}
W_{ns} &= -2\pi\lambda_{\mathrm{ls}}\frac{\varphi_{\mathrm{s}}}{v_{\mathrm{s}}}\left(\frac{d_{\mathrm{s}}+d_{\mathrm{l}}}{2}\right)^3 L(nh_{\mathrm{l}})L(h_{\mathrm{s}})\sum_{i=1}^{n}\int_0^{D^2}\frac{\sqrt{D^2-x}-z_i}{\left[(\sqrt{D^2-x}-z_i)^2+x\right]^{3/2}}\mathrm{d}x,\\
W_{ns} &= -2\pi\lambda_{\mathrm{ls}}\frac{\varphi_{\mathrm{s}}}{v_{\mathrm{s}}}\left(\frac{d_{\mathrm{s}}+d_{\mathrm{l}}}{2}\right)^3 L(nh_{\mathrm{l}})L(h_{\mathrm{s}})\sum_{i=1}^{n}\left[J(z_i,\theta_2)-J(z_i,\theta_1)\right],\\
J(z,\theta) &= \frac{1}{2z}\left[\left(z^4-D^4\right)\theta^{-1/2}-2D^2\theta^{1/2}+\frac{1}{3}\theta^{3/2}\right],\\
\theta_2 &= D^2+z^2,\quad \theta_1=(D-z)^2,\quad D=\frac{d_{\mathrm{s}}+d_{\mathrm{l}}}{2}.
\end{aligned}
\tag{13}
$$

The dimensionless free energy of the steric interaction between the chain and the gas of small particles, in the second virial approximation, has been estimated in [14] as

$$
\begin{aligned}
W_{ns} &= \frac{\varphi_{\mathrm{s}}}{v_{\mathrm{s}}}\left[n\left(V_1-V_2\right)+V_2\right],\\
V_1 &= \frac{\pi}{6}\left(d_{\mathrm{l}}+d_{\mathrm{s}}\right)^3,\quad V_2=2\pi\left(\frac{d_{\mathrm{s}}}{2}\right)^2\left(\frac{1}{2}d_{\mathrm{l}}+\frac{2}{3}d_{\mathrm{s}}\right).
\end{aligned}
\tag{14}
$$

Combining Eqs. (5), (13) and (14) yields

$$
g_n = \frac{1}{v_{\mathrm{l}}}X^n\exp\left(-2\lambda_{ll}-\frac{\varphi_{\mathrm{s}}}{v_{\mathrm{s}}}V_2-W_{ns}\right). \tag{15}
$$

By substituting Eq. (15) into Eqs. (2) we derive the equation for a new Lagrange multiplier X:

$$
\sum_{n=1}^{n_{\mathrm{c}}} nX^n\exp\left(-W_{ns}\right)=\varphi_{\mathrm{l}}\exp\left(2\lambda_{\mathrm{ls}}+\frac{\varphi_{\mathrm{s}}}{v_{\mathrm{s}}}V_2\right). \tag{16}
$$

This equation can be solved numerically. Having found X and substituting it into Eq. (15), we determine the distribution function g_n.

2. Magnetoviscous effect.

We consider a bidisperse ferrofluid involved in a simple shear flow with the velocity perpendicular to the applied field **H** and the gradient velocity parallel to **H**. Let us introduce the Cartesian coordinate system (x, y, z) with the Oz-axis parallel to **H** and the Ox-axis parallel to the flow velocity.

The macroscopic (measured) stress tensor can be presented as

$$
\sigma = \sigma^{\mathrm{s}} + \sigma^{\mathrm{a}} \tag{17}
$$

where σ^{s} is the symmetric part of the tensor corresponding to the viscous friction inside the carrier liquid, with account of deformations of the simple shear flow caused by the chains. In the approximation of small angles of the chain deviation from the field, it can be estimated as [9, 15]

$$\sigma^{\mathrm{s}} = \eta^{\mathrm{s}}\dot{\gamma},$$

$$\eta^{\mathrm{s}} = \eta_0 \left[1 + \sum_{n=1}^{n_{\mathrm{c}}} n g_n \left[\alpha_n + \frac{1}{2}\left((\zeta_n + \beta_n\lambda_n)\left(\langle e_{\mathrm{c}x}^2\rangle_n^0 + \langle e_{\mathrm{c}z}^2\rangle_n^0\right) + \beta_n\left(\langle e_{\mathrm{c}x}^2\rangle_n^0 - \langle e_{\mathrm{c}z}^2\rangle_n^0\right) + 2\left(\chi_n - 2\lambda_n\right)\langle e_{\mathrm{c}x}^2 e_{\mathrm{c}z}^2\rangle_n^0\right)\right] v_{\mathrm{l}}\right], \tag{18}$$

where α_n, ..., χ_n are the shape-factors of the n-particle chain; their explicit forms are given in the [15], and

$$\langle \ldots \rangle_n^0 = \int \ldots f_n\left(\mathbf{e}_{\mathrm{c}}\right) \mathrm{d}\mathbf{e}_{\mathrm{c}} \tag{19}$$

where $f_n^0(\mathbf{e}_{\mathrm{c}})$ is the equilibrium distribution function over the chain orientation defined in (7). Combining Eq. (7) and Eqs. (18), (19) yields

$$\begin{aligned}
\langle e_{\mathrm{c}z}^2\rangle_n^0 &= 1 + 2\left(\frac{1}{(nh_{\mathrm{l}})^2} - \frac{1}{nh_{\mathrm{l}}}\mathrm{cth}\left(nh_{\mathrm{l}}\right)\right), \\
\langle e_{\mathrm{c}x}^2\rangle_n^0 &= \frac{1}{nh_{\mathrm{l}}}\left(\mathrm{cth}\left(nh_{\mathrm{l}}\right) - \frac{1}{nh_{\mathrm{l}}}\right) = \frac{1}{nh_{\mathrm{l}}} L(nh_{\mathrm{l}}), \\
\langle e_{\mathrm{c}x}^2 e_{\mathrm{c}z}^2\rangle_n^0 &= \frac{1}{nh_{\mathrm{l}}}\left[L(nh_{\mathrm{l}})\left(1 + \frac{12}{(nh_{\mathrm{l}})^2}\right) - \frac{1}{nh_{\mathrm{l}}}\right]
\end{aligned} \tag{20}$$

The antisymmetric component of the stress tensor is [8, 15]

$$\sigma^{\mathrm{a}} = \frac{\mu_0}{2} M_{\mathrm{p}} H \sum_{n=1}^{n_{\mathrm{c}}} n g_n \langle e_{\mathrm{c}x}\rangle_n. \tag{21}$$

The finite (non-zero) components $\langle e_{\mathrm{c}x}\rangle$ of the chain orientation vector $\langle \mathbf{e}_{\mathrm{c}}\rangle_n$ appear because of the chain deviation from the field direction under the shear flow. For the rod-like chains, these components have been estimated in [11] by using the effective field method [4]. For the stationary flow and small angles of this deviation, this estimate reads

$$\begin{aligned}
\sigma^{\mathrm{s}} &= \eta^{\mathrm{s}}\dot{\gamma}, \\
\eta^{\mathrm{a}} &= \frac{3}{2}\eta_0 h_{\mathrm{l}} v_{\mathrm{l}} \sum_{n=1}^{n_{\mathrm{c}}} n g_n \langle e_{\mathrm{c}x}^2\rangle_n^0 \frac{\lambda_n\left(\langle e_{\mathrm{c}z}\rangle_n^0 - 2\langle e_{\mathrm{c}x}^2 e_{\mathrm{c}z}\rangle_n^0\right) + \langle e_{\mathrm{c}z}\rangle_n^0}{2\langle e_{\mathrm{c}x}^2\rangle_n^0 + nh_{\mathrm{l}}\langle e_{\mathrm{c}x}^2 e_{\mathrm{c}z}\rangle_n^0}\delta_n, \\
\langle e_{\mathrm{c}z}\rangle_n^0 &= L(nh_{\mathrm{l}}), \quad \langle e_{\mathrm{c}x}^2 e_{\mathrm{c}z}\rangle_n^0 = \frac{3}{(nh_{\mathrm{l}})^2}\left(\frac{nh_{\mathrm{l}}}{3} - L(nh_{\mathrm{l}})\right).
\end{aligned} \tag{22}$$

Here δ_n is the chain shape factor; its explicit form is given in the [15]. Note that $\delta_1 = 1$. After simple transformations, one gets from Eqs. (22)

$$\eta^{\mathrm{a}} = \frac{3}{2}\eta_0 v_{\mathrm{l}} \sum_{n=1}^{n_{\mathrm{c}}} g_n \frac{\lambda_n\left(nh_{\mathrm{l}} L\left(nh_{\mathrm{l}}\right) + 3\right) L(nh_{\mathrm{l}}) + h_{\mathrm{l}} L^2\left(nh_{\mathrm{l}}\right)}{nh_{\mathrm{l}} - L\left(nh_{\mathrm{l}}\right)}\delta_n. \tag{23}$$

If all large particles are in the single state ($g_{\mathrm{l}} = \varphi_{\mathrm{l}}/\nu_{\mathrm{l}}$) all others $g_n = 0$, and relation (22) coincides with the corresponding result in [4].

The effective viscosity of the ferrofluid is

$$\eta = \eta^{\mathrm{s}} + \eta^{\mathrm{a}}. \tag{24}$$

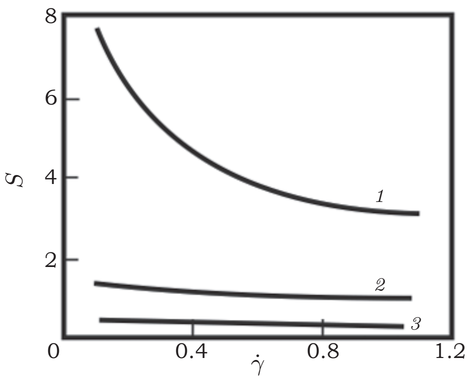

Fig. 2. Calculation results of magnetoviscous effect S vs shear rate $\dot{\gamma}$. Particle saturated magnetization $M_{\mathrm{p}} = 400$ kA/m, magnetic field $H = 35$ kA/m. *1, 3* – diameters of small particle magnetic cores $d_{\mathrm{ms}} = 5$ nm and 10 nm, respectively, their hydrodynamic volume concentration $\phi_{\mathrm{s}} = 10\%$; 2 – $\phi_{\mathrm{s}} = 0$ (no small particles).

3. Results and discussion.

Let us consider a fluid consisting of magnetite particles. It is assumed that the diameter of the magnetic core of the large particle is $d_{\mathrm{lm}} = 19$ nm, their volume concentration is $\phi_{\mathrm{l}} = 1\%$, the surface layer thickness $s = 2.5$ nm. Some results of the calculations of the magnetoviscosity parameter $S = (\eta(H) - \eta(0))/\eta(0)$ as a function of the shear rate $\dot{\gamma}$ are shown in Fig. 2 for the systems with small particles of two sizes.

The results demonstrate that the presence of the smallest particles with the core diameter 5 nm, like that in experiments [10], enhances the magnetoviscous effect because the steric depletion interaction of the small particles with the chains dominate over the magnetic interaction. For the particles with the diameter $\phi_{\mathrm{s}} = 10$ nm, the opposite effect takes place, i.e. these particles decrease the magnetoviscosity because their magnetic interaction with the chains dominates over the steric one.

Conclusions.

The magnetoviscous effect in a bidisperse ferrofluid consisting of relatively large and small particles is considered theoretically. It is suggested that this effect is provided by chains consisting of the largest particles, whereas the small particles form a "cloud" around the chains. The magnetic interaction between the small and large particles decreases the characteristic chain length, therewith, weakens the macroscopic magnetoviscous effect. In contrast, the steric depletion interaction increases the chain length, therefore, enhances this effect.

If the size of small particles is four times less than the size of large particles, their steric effects dominate over the magnetic ones, and the presence of small particles enhances magnetoviscosity. The results qualitatively explain the experiments in [10]. If the small particles are approximately twice smaller than the large particles, their magnetic interaction with the chains dominates over the steric one; this reduces the chains length and weakens the magnetoviscous effect.

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