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Rheological properties of ferrofluids with microstructures

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Abstract
This paper presents results of a theoretical study of the effects of linear chain-like as well as bulk drop-like heterogeneous aggregates on the rheological properties and behaviour of ferrofluids. The results demonstrate that the appearance of both these internal structures leads to a strong (one–two orders of magnitude) increase of the ferrofluid effective viscosity under the action of the magnetic field applied parallel to the gradient of the ferrofluid flow. When the ferrofluid fills a thin channel (gap) placed into a normal magnetic field, the drop-like structures can overlap with the channel. In the case of a rigid connection between the drop-like domains and the channel walls, the appearance of elastic and yield stress effects on the ferrofluid is expected.

1. Introduction

Experiments carried out in recent years with various commercial ferrofluids demonstrate more than an order of magnitude increase of the fluid viscosity under the action of quite moderate magnetic fields (10–100 kA m^{-1}) [1]. The magnetoviscous effect is especially strong when the shear rate $\dot{\gamma}$ of the fluid flow is weak (<1 s^{-1}) and decreases quickly with increasing $\dot{\gamma}$. These experimental results are in a disagreement with the classical models [2] which consider ferrofluid as a system of non-interacting magnetic particles and predict for the system studied in experiments [1] a maximal, saturated increase of viscosity of several per cent.

The strong difference between the magnetoviscous effects predicted from the models of isolated particles (several per cent) and those observed in the experiments (two orders of magnitude) leads to the assumption that in real systems these effects occur due to heterogeneous aggregates which appear because of magnetodipole interactions between the particles. Analysis shows (see the discussion below) that a magnetic field stimulates the appearance of these internal heterogeneous structures and elongates them along the field force lines. These structures, aligned along the fluid gradient flow, can provide the strong rheological effects observed in the experiments.

There are two types of the internal heterogeneous structures in ferrofluids known from experiments and computer simulations. The first are the linear chain-like clusters. Because the size of typical particles in ferrofluids is less than the wavelength of visible light, the chains cannot be directly observed in optical experiments. However, they have been detected in many computer simulations of ferrofluids (see, for example, [3]). The second type of internal structure is bulk dense drop-like aggregates. These drops have been directly observed in many experiments with usual microscopes (see, for example, [4]).

In the present paper we discuss the macroscopical rheological phenomena which can appear due to both types of internal structures in ferrofluids. In sections 2 and 3 we consider the influence of respectively linear chains and bulk drops on the magnetoviscous effects in these systems. Then we discuss the elastic and yield stress effects in the case when the drops overlap with the channel (gap) filled by the ferrofluid.

2. Chains in ferrofluids and their influence on magnetoviscous effects in these systems

Possibly the first theoretical model of the chain-like structures in a system of magnetic particles was suggested in [5]. However, the analysis in [5] was performed by using the methods of the thermodynamical theory of homogeneous fluctuations in a gas-like system of dipole particles. That is why the structures considered in this work are homogeneous fluctuations of density (clouds) rather than heterogeneous chains in the usual sense of the words. Statistical models of the heterogeneous clusters have been developed in [6] on the basis of methods of the theory of reaction kinetics.

Another approach, based on minimization of the free energy of the ensemble of heterogeneous chains, has been proposed in [7]. For maximal simplification of the analysis, any fluctuations of positions and orientations of magnetic particles in these chains have been neglected in the model of [7]. In other words, chains have been considered as rigid straight rods; the magnetic moments of all chain particles have been assumed to be aligned along the rod axis. The fluctuations of positions of particles in the chains have been taken into account in [8] in the approximations of zero and infinitely strong applied magnetic fields. The model of the fluctuating chains placed into a finite magnetic field has been developed in [9].

In the works [1, 10] and [11] theoretical results of the model [7] have been compared with the results of measurements of the magnetoviscous effects in various commercial ferrofluids. The theoretical and experimental results are in reasonable agreement; at least they are of the same order of magnitude (see below, figures 1, 2). The agreement between the theory and experiments demonstrates that, in spite of the strong approximations, this simple model reflects important features of microscopical formation of the macroscopical rheological effects in ferrofluids. Below we will briefly discuss the main points of the model [7].

We consider a ferrofluid as a system of identical magnetic spheres of radius a and permanent magnetic moment m. The particles are covered with surface layers of thickness s. We assume that the hydrodynamical (defined with the surface layers) volume concentration φ of the particles is small and, therefore, any interaction between the chains may be neglected. We also suppose that any other heterogeneous aggregates (for example, drops) are absent in the ferrofluid.

In the framework of the model of the chains as rigid rod-like non-interacting clusters, the free energy F of a unit volume of the system can be presented as

$$F = kT \sum_{n=1}^{n_c} \left(g_n \ln \frac{g_n v}{e} + g_n f_n \right). \qquad (1)$$

Here g_n is the number of n-particle chains in the unit volume, $e = 2.72\ldots$, n_c is the maximal number of particles in the chain, estimated below, $v = 4\pi(a+s)^3/3$ is the hydrodynamical vol-

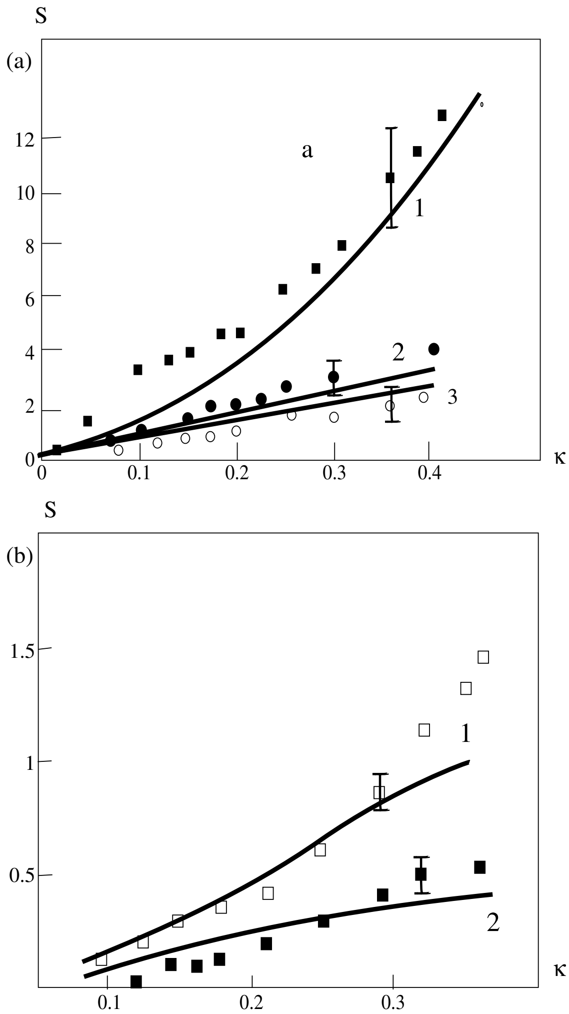

Figure 1. The dependence of the reduced magnetic effective viscosity on the dimensionless magnetic field κ inside the sample ($\kappa = \mu_0 mH/kT$ where m is the magnetic moment of particles with magnetic core diameter $\langle 2a \rangle = 10$ nm). Dots are experiments with the magnetite ferrofluid APG 513A; lines are calculations. (a) Squares correspond to a shear rate of $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$, line 1 to $\dot{\gamma} \to 0$; black circles and line 2 to $\dot{\gamma} = 0.5\ \mathrm{s}^{-1}$, white circles and line 3 to $\dot{\gamma} = 0.9\ \mathrm{s}^{-1}$. (b) Light squares and line 1 correspond to $\dot{\gamma} = 1.05\ \mathrm{s}^{-1}$, black squares and line 2 to $\dot{\gamma} = 5.23\ \mathrm{s}^{-1}$ (after [11]).

ume of the particle. The first term in the brackets of the right part of (1) represents the entropy of the ideal gas of the chains, f_n is the free self-energy of the chain due to magnetic interaction between the particles in the chain and due to their interaction with the local magnetic field H.

In the framework of the approximation of the chains as rigid rods, with account of interactions only between the nearest particles in the chain, we get (see details in [7])

$$f_n = -\left[\varepsilon(n-1) + \ln\frac{\sinh(\kappa n)}{\kappa n}\right]$$
$$\varepsilon = \frac{m^2}{4\,(a+s)^3\,kT}, \qquad \kappa = \frac{mH}{kT}. \tag{2}$$

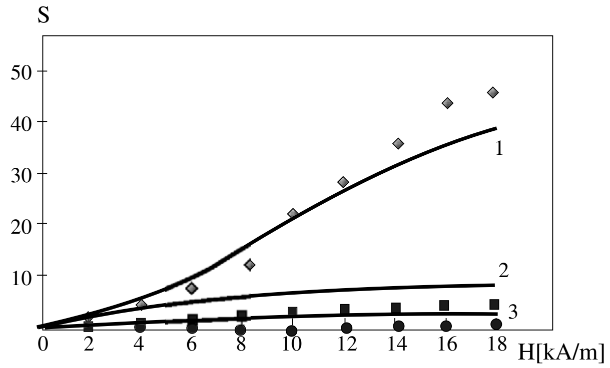

Figure 2. The reduced magnetic effective viscosity versus dimensional field H inside the sample for the magnetite ferrofluid TTR (after [10]). Dots are experiments; lines are results from the chain model. Diamonds and line 1 correspond to $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$, squares and 2 to $\dot{\gamma} = 1\ \mathrm{s}^{-1}$, circles and 3 to $\dot{\gamma} = 10\ \mathrm{s}^{-1}$.

Here ε is the dimensionless parameter of dipole–dipole interaction between the particles, κ is the dimensionless energy of the particle interaction with the magnetic field H. We use here and below the Gaussian system of magnetic units, most convenient for calculations.

The simple approximation (2), obtained with neglect of the chain fluctuations, of course, overestimates the absolute magnitude of the chain free energy; nevertheless it allows us to get the results correct at least to the order of magnitude. One needs to note that this estimate is approximately valid only when the dimensionless parameter ε of magnetic interaction between particles is far in excess of unity and the inequality $\varepsilon > \kappa$ holds. The point is that only in this case the chain can be approximately considered as a rod-like particle with the magnetic moment parallel to its axis. In the case $\kappa > \varepsilon$, every particle in the chain interacts with the field independently of the other particles of the chain. Generally speaking, in this case the direction of the chain magnetic moment does not coincide with the chain axis direction. When $\varepsilon \sim 1$ or less, the chains, as heterogeneous clusters, cannot appear. In this part of the paper we will suppose that the inequalities $\varepsilon > 1$, $\varepsilon > \kappa$ hold true.

Estimates [7] show that in the shear flowing ferrofluids the deviations of the chain orientation distribution from the equilibrium distribution are weak for all real magnitudes of the shear rate. That is why in the first approximation we can determine the distribution function g_n over the number of particles in the chain as for the equilibrium system by using the thermodynamical condition of the minimum of the system free energy.

The equilibrium distribution function provides the minimum of the free energy (1) under the following obvious normalization condition:

$$\sum_{n=1}^{n_c} g_n n = \frac{\varphi}{v}. \tag{3}$$

After standard minimization of (1) one can obtain

$$g_n = \frac{1}{v} X^n \exp(-f_n) \tag{4}$$

where X is the Lagrange multiplier. In order to determine X, we substitute (4) into (3) which leads to a transcendental equation for X. For the equilibrium systems one can put $n_c = \infty$. In this case we get the following analytical expression (see calculations in [7]):

$$X = \frac{2y\cosh\kappa - \sinh\kappa - \sqrt{(2y\cosh\kappa - \sinh\kappa)^2 - 4y^2}}{2y}$$
$$y = \kappa\varphi\exp\varepsilon. \tag{5}$$

When the ferrofluid is involved in shear flow with a rate $\dot{\gamma}$, the hydrodynamical viscous forces destroy too long chains. The finite magnitude of the maximal number n_c of the particles in the chain has been estimated in [1] as

$$n_c \sim \sqrt{\varepsilon\frac{D_r}{\dot{\gamma}}} \tag{6}$$

where $D_r = kT/6v\eta_0$ is the rotational coefficient of the single particle, η_0 is the viscosity of the carrier liquid.

It is well known, since Einstein's classical work [12], that the difference between effective viscosity of a suspension and viscosity of its carrier liquid is a result of hydrodynamical perturbations created by the suspension particles in the mean flow of the fluid. It is practically impossible to calculate these perturbations produced by the chains because of the too complex shape of these aggregates. In order to get reasonable estimates, the model of the n-particle chains as prolate ellipsoids of revolution with the minor semiaxis $a + s$ and major semiaxis $n(a + s)$ has been used in [7] and [11]. It is of principal importance that the volume of this spheroid is equal to the total volume nv of the particles in the chain. Therefore, the volume concentration of the model ellipsoids coincides with the concentration φ of the particles in the ferrofluid.

Using the well-known results of the statistical hydromechanics of suspensions of rigid ellipsoids [13], one can get the following expression for the mean (measured) stress σ in the suspension:

$$\sigma = 2\eta_0\left[\dot{\gamma} + \sum_{n=1}^{n_c}\Phi_n(\dot{\gamma}, \langle e_i\rangle, \langle e_i e_j\rangle, \langle e_i, e_j, e_k\rangle, \langle e_i e_j e_k e_l\rangle)g_n\right]$$
$$\langle\cdots\rangle = \int\cdots\phi(\mathbf{e})\mathrm{d}\mathbf{e}. \tag{7}$$

Here $\mathbf{e}$ is the unit vector aligned along the ellipsoid axis, $i, j, k, l = x, y, z$ are the Cartesian coordinates, the angle brackets $\langle\cdots\rangle$ denote the statistical moments of the non-equilibrium distribution function $\phi(\mathbf{e})$ over orientations of the ellipsoid, Φ_n is some function of the statistical moments $\langle\cdots\rangle$, defined in the work [13] (see also [7, 11]).

The distribution function $\phi(\mathbf{e})$ can be determined from a solution of a special Fokker–Planck equation. This equation can be found in [7, 11, 13]. The strict solution of this equation is unknown. An approximate way of solving this problem is suggested in [7, 11].

Once the approximate solution has been found, we can determine the statistical moments $\langle\cdots\rangle$ in equation (7) and, therefore, the effective viscosity of the ferrofluid $\eta(H) = \sigma/\dot{\gamma}$.

Some results of calculations of the magnetoviscosity parameter $S(H) = (\eta(H) - \eta(0))/\eta(0)$ and results of measurements of this parameter for two ferrofluids with magnetite particles are shown in figures 1 and 2. It should be noted that both ferrofluids are polydisperse systems with wide distributions (see [1]) over particle sizes. The magnetic diameter $2a$ of the majority of ferrofluid particles is about 8–10 nm. Simple estimates show that these particles are too small and the magnetic interaction between them is too weak to provide the formation of any heterogeneous aggregate. However in both these ferrofluids there are particles of diameter $2a = 16$–20 nm. The energy of magnetic interaction between these relatively large particles is several times over kT and, therefore, they are able to form the heterogeneous aggregates.

It is very difficult to develop a constructive statistical model of a real polydisperse ferrofluid. That is why we use a simplest bidisperse model, assuming that the system consists of two fractions of magnetic particles. The first fraction consists of 'small' particles with the magnetic diameter near the mean diameter 8–10 nm and volume concentration of about the total volume concentration of magnetic particles in the system. The second fraction consists of relatively large particles with magnetic diameter $2a_l$ and hydrodynamical volume concentration φ_l. We suppose that the chains consist of the 'large' particles only. The unknown parameters $2a_l$ and φ_l were fitted by comparing the results of calculations of the curve $S(H)$ for vanishing shear rate $\dot{\gamma}$ with the experimental data obtained for minimal shear rate 0.1 s^{-1}. For the APG ferrofluid we got $2a_l \approx 16$ nm, $\varphi_l \approx 0.017$, for the TTR $2a_l \approx 17$ nm, $\varphi_l \approx 0.014$ respectively. These estimates look quite reasonable. Then the same magnitudes of $2a_l$ and φ were used for calculations of the curves $S(H)$ for other, higher, magnitudes of the shear rate.

In spite of the strong approximations (bidisperse model of polydisperse ferrofluid, approximation of non-interacting rigid rod-like chains, the estimate (6) for the maximal number of the particles in the chain, neglect of the influence of the 'small' particles on the chain structure), quite good agreement between the theory and experiments is achieved for wide regions of the magnetic field and shear rate. This agreement shows that the model is adequate, at least in its main points, for the physical situation which appears in ferrofluids under the action of an applied magnetic field. Analysis of effects of fluctuations of the chain shape, magnetic and hydrodynamical interactions between the chains, interactions between the chains and ensembles of the non-aggregated 'small' particles can be considered as a development and generalization of this simple model. In this context we would like to note that the influence of the small particles on the chain structure in the framework of the bidisperse model has been studied in the works [14] and in computer simulations [15]. The general conclusion of these investigations is that the small particles can have significant influence on the typical length of the chains. The magnetic interaction of the chains with these particles reduces the mean length of the chains, whereas the steric interaction increases this length. The magnetic effects dominate when the chains, consisting of the magnetite particles with the magnetic diameter $2a_l \approx 15$–17 nm, interact with the particles of diameter 10–12 nm, whereas the steric effects dominate when the chains interact with the particles of diameter about 5 nm and less. Thus the total effect of the influence of the 'small' particles on the chains consisting of 'big' particles is determined by the size distribution of the particles in the concrete ferrofluid. Moreover, one needs to take into account that the carrier media in many modern ferrofluids present quite complex fluids with polymer and other non-magnetic admixtures. The steric interactions between the 'big' magnetic particles and non-magnetic admixtures can also markedly affect the internal structure of the ferrofluids and, therefore, the macroscopic rheological effects in these systems.

3. Influence of drop-like aggregates on magnetoviscous effects in ferrofluids

The bulk drop-like aggregates have been observed in many experiments with various ferrofluids (see [4]). That is why their appearance may be considered as a quite common and fundamental phenomenon for ensembles of magnetic particles.

The typical size of the drops observed in experiments varies from several microns to several tens of microns. Simple estimates show that the dense bulk clusters of these sizes consist of millions of magnetic nanoparticles. The tremendous number of particles in the drops allows one to consider their appearance as a specific condensation phase transition in ensembles of the particles, and the drops as domains of the new dense phase.

The first theoretical models of the condensation phase transitions in ensembles of ferroparticles have been developed in [16]. In spite of the quite different approaches used in

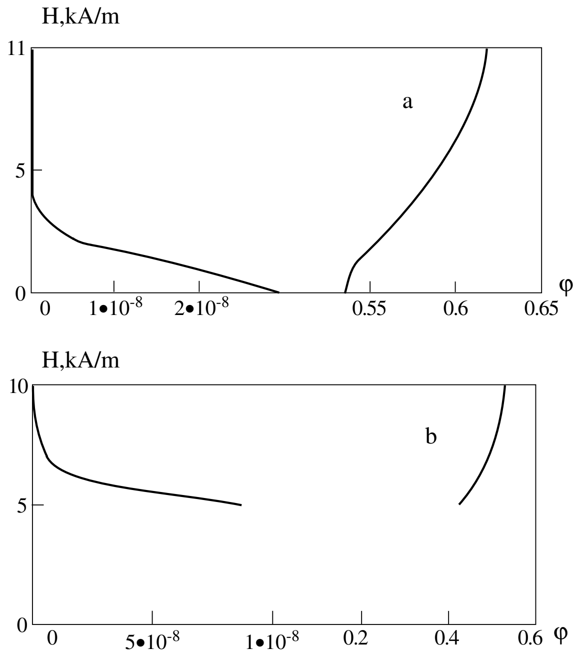

Figure 3. Phase diagrams of the magnetite ferrofluid separation into dense and dilute phases for room temperature. (a) The particle diameter is 18 nm, thickness of the surface shell is 2.5 nm; therefore, $\varepsilon = 7.76$. (b) The same for the particle diameter 17 nm, $\varepsilon = 6.3$.

these works, they have a common point—the appearance of drops is treated as the classical van der Waals 'gas–liquid' phase transition in an ensemble of single magnetic particles. Any heterogeneous aggregates are ignored in these models. However, the computer [3] and analytical [17, 18] investigations indicate that the appearance of the linear chains in ferrofluids precedes the particle condensation into bulk dense phases. This result has been taken into account in [19] where the following scenario of the condensation phase transition has been suggested. When the system inverse temperature $1/kT$ and/or applied magnetic field H increase, the thermodynamically stable ensemble of the linear chains first appears in the ferrofluid. When $1/kT$ and/or H exceed some threshold magnitudes, the longest chains transform into compact dense globules, which play the part of nuclei of the new dense phase. In this scenario the classical critical point of the 'gas–liquid' phase transition, where the gas and liquid densities coincide, is absent. At the threshold magnitudes of $1/kT$ and H, the system separates into phases with quite different concentrations of the particles.

The equilibrium volume concentrations φ of the particles in the coexisting phases can be determined from the condition of equalities of the particle chemical potentials and osmotic pressures in the phases. These thermodynamical functions for the dilute and dense phases have been estimated in [18, 19]. The results of calculations of the concentrations in the coexisting phases are shown in figure 3 in the form of standard phase diagrams—any horizontal line, corresponding to a given magnitude of the field H, crosses the diagram branches at the points corresponding to the concentrations in these phases. These results, in agreement with all known experiments, demonstrate that the applied field stimulates the phase transition. Indeed, according to figure 3, the coexistence of the dilute and dense phases is possible only when the field exceeds a certain threshold magnitude. In the opposite case the system is in a macroscopically homogeneous state, possibly with the chain-like aggregates.

Analysis shows that there are two factors which play the main part in the formation of macroscopical rheological properties of a ferrofluid with the drops. They are the shape and volume concentration Φ of these aggregates.

The volume concentration of the drops can be determined from the obvious condition of conservation of total number of particles after the phase separation, which gives directly

$$\Phi = \frac{\varphi_0 - \varphi_{\text{dilute}}}{\varphi_{\text{dense}} - \varphi_{\text{dilute}}} \tag{8}$$

where φ_0 is the total volume concentration of the particles in the ferrofluid. Estimates show that the effect of the shear flow on the thermodynamical functions of the particles in ferrofluid is weak. Thus, in the first approximation, the concentrations $\varphi_{\text{dilute}}, \varphi_{\text{dense}}$ in the shear flowing ferrofluid can be estimated in the same way as for the equilibrium system. In other words, one can use the magnitudes of $\varphi_{\text{dilute}}, \varphi_{\text{dense}}$ determined by using the diagrams of figure 3.

The shape of the drop is determined by the balance between the surface tension effects on the drop boundary and effects of the drop demagnetizing field. The first effect tends to transform the drop into a ball-like aggregate, the second one into a very thin and long 'needle'. Since the capillary energy is proportional to the drop surface Σ, whereas the demagnetizing energy is to the volume V, the elongation of the drop increases with its volume V.

In the approximation of the drop as an ellipsoid of revolution the shape factor c, which is equal to the ratio of the ellipsoid minor axis to its major axis, has been estimated in [19–21] in the form of a function of the drop volume V. According to these results, for all magnitudes of the applied magnetic field, interesting from the viewpoint of the magnetorheological effects in ferrofluids, the viable drops are always highly elongated ($c \ll 1$).

It is well known from the classical theories of the condensation phase transitions that during the phase separations the nuclei of new phase amalgamate into one, theoretically infinite volume. This amalgamation is a consequence of the tendency of a system to minimize its phase interface. For the ferrofluids placed into an external magnetic field a similar conclusion has been drawn in [22]. However, in the case of shear flow the situation with drop growth is quite different from the situation in motionless systems.

Indeed, under the condition of the shear flow, the hydrodynamical forces make the drop axis deviate from the magnetic field direction. Obviously, for highly elongated large drops this deviation is more than for the relatively short small drops. However this deviation is thermodynamically unprofitable for the drops. Therefore this effect restricts the drop growth and establishes some maximal volume of the drop. Below we explain briefly the estimation of the maximal drop volume V_{m} and corresponding shape factor c_{m}. In more detail the results will be published further.

The free energy of a drop placed into magnetic field H can be presented as

$$F = F_{\text{m}} + F_s,$$
$$F_{\text{m}} = -V \int_0^H M_z(H_{\text{i}})\,\text{d}H, \qquad F_s = \alpha\Sigma. \tag{9}$$

Here α is the surface tension, H_{i} is the field inside the drop, M_z is the component of the drop magnetization along the applied field H. This component can be estimated by using the classical results for the magnetostatics of a continuum [23]:

$$M_z = \chi_{\text{m}}(H_{\text{i}})H\left[\frac{\cos^2\theta}{1 + 4\pi\chi_{\text{m}}(H_{\text{i}})N(c)} + \frac{\sin^2\theta}{1 + 2\pi\chi_{\text{m}}(H_{\text{i}})\,(1 - N(c))}\right], \tag{10}$$

where θ is the angle of deviation of the drop axis from the applied field H, χ_{m} is the drop susceptibility, which, in general, depends on the internal field H_{i}, $N(c)$ is the drop demagnetizing factor determined, for example, in [23]. For highly elongated drops ($c \ll 1$)

$$N(c) \approx -c^2 \ln c. \tag{11}$$

A quite accurate and simple estimate for the susceptibility χ_m of dense ferrofluids has been obtained in [24] in the framework of a semiempirical mean field model.

The internal field H_i can be found by using the results of [23] as

$$H_i = \sqrt{H_{i\|}^2 + H_{i\perp}^2}$$
$$H_{i\|} = \frac{\cos\theta}{1 + 4\pi\chi_m(H_i)N(c)}H, \qquad H_{i\perp} = \frac{2\sin\theta}{2 + 4\pi\chi_m(H_i)\,(1 - N(c))}H. \tag{12}$$

Here indices $\|$ and $\perp$ mark the components of the internal field parallel and perpendicular to the drop axis.

The drop surface Σ can be calculated by using the well-known formula for the surface of ellipsoid of the volume V. When $c \ll 1$, we get approximately

$$\Sigma = \pi^2\left(\frac{3}{4\pi}\right)^{2/3} V^{2/3}c^{-1/3}. \tag{13}$$

Combining formulae (9)–(13) and assuming that θ and c are small, after some calculations we get

$$F = F_0 + V\left(2\pi M^2 N + \pi\frac{M^2}{1 + 2\pi\chi_m}\theta^2\right) + V^{2/3}\tilde{\alpha}\left(-\frac{\ln N}{N}\right)^{-1/6} \tag{14}$$

where

$$\tilde{\alpha} = \pi^2\left(\frac{3}{4\pi}\right)^{2/3} 2^{-1/6}\alpha, \qquad F_0 = -Vf_0, \qquad f_0 = \int_0^H \chi_m(H)H\,\mathrm{d}H,$$
$$M = \chi_m(H)H.$$

The free energy F_0 corresponds to an infinitely elongated drop parallel to the applied field H.

Assuming that the angle θ is small, in the first approximation we can estimate the shape factor N in the same way as for the drop aligned along the field H (i.e. for $\theta = 0$.) Minimizing (14) with respect to the demagnetizing shape factor N and neglecting the angle θ, we come to the following equation for N:

$$N^7 = -\left(\frac{V_0}{V}\right)^2 \ln N \tag{15}$$

where

$$V_0^2 = \left(\frac{\tilde{\alpha}}{12}\right)^6 M^{-12}.$$

The angle θ can be found from the balance between the magnetic Γ_m and hydrodynamical Γ_h torques acting on the drop. The magnetic torque by definition is

$$\Gamma_m = \frac{\partial F_m}{\partial\theta}. \tag{16}$$

The hydrodynamical torque, acting on the rigid ellipsoid, can be found as (see [13])

$$\Gamma_h = \frac{2\eta_0 V\dot{\gamma}}{c^2\,(1 - N)\,/2 + N}\left[\cos^2\theta + c^2\sin^2\theta\right]. \tag{17}$$

Equating (16) and (17), we find the angle θ. When this angle is small and c, $N \ll 1$, we have approximately

$$\theta = \frac{1 + 2\pi\chi_m}{\pi M^2 N}\eta_0\dot{\gamma}. \tag{18}$$

Combining this result for θ and equations (10), (12), (15) with (9), we get the drop free energy in the following form:

$$F = Vf(V) \tag{19}$$

where

$$f(V) = -f_0 + 2\pi M^2 N(V) + \frac{1}{\pi}\frac{1+2\pi\chi_m}{M^2 N(V)^2}(\eta_0\dot{\gamma})^2 + \tilde{\alpha}N(V)^{-1/6}(-\ln N(V))^{1/6}V^{-1/3}.$$

The total free energy of the ensemble of the drops is

$$F_{tot} = N_d F = W\Phi f(V) \tag{20}$$

where N_d and W are the number of drops in the ferrofluid and the total volume of the system respectively.

Analysis shows that the energy F_{tot} as a function of the drop volume V has a minimum at a certain volume V_m which decreases with the shear rate $\dot{\gamma}$. Although the principle of the free energy minimum, strictly speaking, is not valid for the shear flowing suspension, in the first approximation we can associate the steady stable volume of the drop in the shear flowing ferrofluid with V_m. Indeed, let us assume that some potential torque, which depends on the angle θ and the factor N in the same way as the hydrodynamical torque Γ_h, acts on the drops instead of Γ_h. In this case the drop stable volume must correspond to the minimum of the suspension free energy. This volume is approximately equal to V_m.

Once the equation $\partial f(V)/\partial V$ is solved, i.e. the volume V_m is determined, then, by using equation (15), we can estimate the corresponding demagnetizing shape factor N. After calculations we get

$$N^{-1} \approx \left(7\pi^2\right)^{1/3}\frac{M^{4/3}}{(1+2\pi\chi_m)^{1/3}}(\eta_0\dot{\gamma})^{-2/3}. \tag{21}$$

Combining equations (21) with (11), we can find the factor c for the steady stable drops.

Let us estimate now the angle θ corresponding to the steady stable drop. Combining equations (18) and (21), to order of magnitude we get

$$\theta \sim \frac{(\eta_0\dot{\gamma})^{1/3}}{M^{2/3}}.$$

In the region of moderate and strong magnetic fields (which is especially interesting from the point of view of study of the magnetorheological effects), to order of magnitude $M \sim \varphi_{dense}m/v$ and $\varphi_{dense} \sim 0.5$–0.7, where φ_{dense} is the hydrodynamical volume concentration of the particles in the drop. Taking into account these estimates, after simple transformations we come to the following:

$$\theta \sim \left(\frac{\pi}{6\varphi}\right)^{2/3}\left(\frac{s}{\varepsilon}\right)^{2/3}, \qquad s = \frac{\eta_0\dot{\gamma}d^3}{kT}$$

where ε is the same as in equation (2), $d = 2(a+s)$ is the hydrodynamical diameter of the particle.

For the particles able to aggregate, $\varepsilon > 6$ (see diagrams in figure 3). Estimates show that for all realistic magnitudes of the shear rate $\dot{\gamma}$ the dimensionless parameter s is several orders of magnitude less than unity. Therefore, the approximation $\theta \ll 1$ holds true, at least for moderate and strong fields H. When the field is weak, the magnetization M in denominator of the estimate for θ can be small and, as a result, the angle θ can be about unity or more. In this case the approximation (21) is not quite accurate. However the case of the weak fields is not interesting from the viewpoint of the magnetorheological effects.

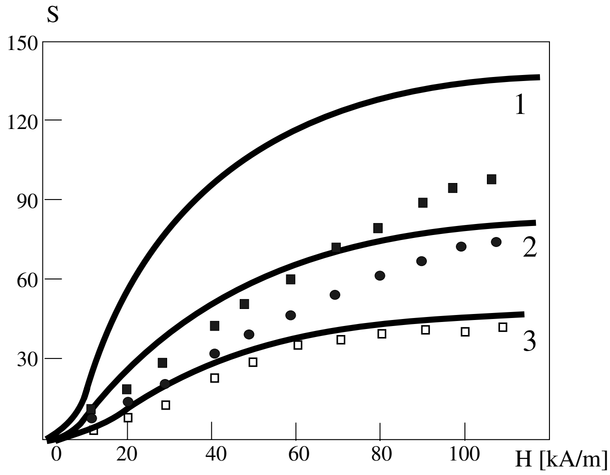

Figure 4. Experimental results for the magnetoviscous parameter S for the monodisperse ferrofluid with cobalt particles 11 nm in diameter, magnetic volume concentration 0.0035, hydrodynamical volume concentration $\varphi = 0.011$. Dots are experiments [25], lines calculations. Black squares and line 1—$\dot{\gamma} = 1\ \mathrm{s}^{-1}$, circles and line 2—$\dot{\gamma} = 3\ \mathrm{s}^{-1}$, light squares and line 3—$\dot{\gamma} = 10\ \mathrm{s}^{-1}$.

Now we are in a position to estimate the effective viscosity of the ferrofluid with the drops. Considering the ferrofluid as a suspension of the quasi-rigid ellipsoids with the found volume concentration Φ and the shape factor c, by using the results of hydromechanics of suspensions of non-spherical particles [13], after some calculations we come to the following estimate for the ferrofluid effective viscosity η, which is valid when the ellipsoids are highly elongated ($c \ll 1$):

$$\eta = \eta_0(1 + S) \tag{22}$$

where

$$S = \Phi\left[\beta(c)\cos^2\theta + (\chi(c) - \beta(c))\sin^2\theta + \frac{1}{s}q\frac{\kappa^2}{\varepsilon}\sin\theta\cos\theta\right] \tag{23}$$

Here $s = \dot{\gamma}\eta_0 d^3/kT$ is the dimensionless shear rate,

$$q = \frac{1}{8\pi}\frac{(4\pi\chi_{\mathrm{m}})^2(1 - 3N))}{(1 + 4\pi\chi_{\mathrm{m}}N)(1 + 4\pi\chi_{\mathrm{m}}(1 - N)/2)}.$$

Parameters $\beta(c)$ and $\chi(c)$ are the shape factors of the drop. They can be found in [13] and [11]. When $H = 0$, parameter $S = 0$; it increases quickly with the field. That is why S can be considered as the parameter of the magnetoviscous effect in the ferrofluid.

It is important to note that the estimate (23) has been obtained for the monodisperse systems of magnetic particles neglecting any interactions between the ellipsoids. Some results of [25] of measurements of the effective viscosity of nearly monodisperse ferrofluid with cobalt particles are shown in figure 4 (dots). Calculations of the magnetoviscous parameter $S = \Delta\eta(H)/\eta(0)$ performed by using equation (23) lead to the results which are about an order of magnitude greater than the experimental ones. The physical reason for the strong difference between the theoretical and experimental results may lie in the fact that the approximation (23) has been obtained neglecting any interactions between the drops.

The strict theory of the rheological properties of suspensions of hydrodynamically interacting particles (drops) has not been developed. In order to get approximation valid at least to order of magnitude, we use here the following simple approach, well known in the theory of various disperse systems. In the framework of this approximation, first, we calculate the effective viscosity η_1 of the non-interacting ellipsoids by using equation (23). In the second step the ellipsoids are considered as placed into homogeneous fluid with the effective viscosity η_1. This means that the final magnetoviscous parameter S is calculated by using equation (23); however in the definition of s in (23) and in equations (17), (18), (21) the carrier liquid viscosity η_0 is replaced by the effective viscosity η_1. Some results of calculations of the parameter S, performed by using this approximation of the effects of the hydrodynamical interaction between the drops and approximation [24] for χ_m, are shown in figure 4. Comparing them with the experimental results, one can see that the maximal difference between the experimental and theoretical results is several tens per cent. Taking into account the series of strong approximations and that no fitting parameters have been used in these calculations, the agreement between the theory and experiments can be considered as reasonable. It should be noted that we tried to apply the chain-like model described in the previous part of this work, and various modifications of the model to get results close to the experimental ones in figure 4, but failed. In all situations the theoretical results were much more than the results of the measurements.

Our estimates show that in the region of the magnetic field shown in figure 4 the drop length can achieve several tens and even hundreds of microns, their diameter several microns. One needs to admit that the dense bulk clusters of these sizes have not been detected in the small angle neutron scattering experiments, performed in [25]. However, possibly, these relatively large aggregates simply cannot be detected in the experiments adopted to detect the structures with sizes of several diameters of the magnetic particles. On the other hand, aggregates of the micron sizes, if they appear, can be observed by using ordinary optical microscopes. That is why the direct optical observations could give an answer to the question of the microscopical nature of the macroscopical rheological effects in ferrofluids.

Let us discuss, briefly, rheological effects which are expected in ferrofluids filling channels (gaps) with finite thickness, placed into a perpendicular magnetic field. It is well known from many experiments that in these systems the bulk dense drops form thermodynamically stable ensembles of the cylinder-like domains, spanning the channel (gap) [4]. Theoretically the domain systems in the thin gaps have been studied in [26]. It was shown that the appearance of these domains is a result of the condensation phase transition in an ensemble of the magnetic particles. The physical cause of the formation of the system of the discrete domains, instead of massive simply connected phases, is a competition between the surface tension effects on the domain boundaries, which tend to amalgamate the drops into one phase, and the drop demagnetizing effects, which tend to transform the drops into very thin needles.

The appearance of the domains linking the gap boundaries can induce elastic and yield stress effects in these systems, similar to those in the magnetorheological (MRS) and electrorheological suspensions. Analysis of these effects in ferrofluids has been performed in [27] under the assumption that rigid connection between the domains and the gap boundaries is provided. The results show that for the scenario of the transition from the elastic to the flow rheological behaviour, magnitudes of the yield stress τ_y as well as the yield stress dependences on the applied field H and the gap thickness L in ferrofluids are quite different from those in MRS. For example the scaling relation $\tau_y \sim H^2$ is well known for the magnetorheological suspensions, whereas the relation $\tau_y \sim H^{4/3}$ is expected, according to [27], for ferrofluids. The yield stress dependence on the gap thickness L in MRS is weak, whereas for ferrofluids the results [27] give $\tau_y \sim L^{-2/3}$.

One needs to stress that the elastic and yield stress effects in ferrofluids can be observed only in the case when the rigid connection between the gap walls and the domains is provided.

The results of [27] show that under this condition the yield stress of typical ferrofluid, filling a flat gap with the thickness L of several millimetres, can achieve quite measurable magnitudes around several pascals.

4. Conclusion

The results discussed show that internal structures of both types (linear chains and dense bulk drops) can provide significant growth of magnetoviscous effects in ferrofluids. The estimated values of these effects are comparable with those observed in experiments with various ferrofluids. The achieved level of theoretical knowledge about internal structures in ferrofluids and their influence on macroscopical properties of these systems does not allow us to answer with certainty the question of a concrete internal mechanism of the macroscopical rheological effects in a concrete ferrofluid. Possibly, in some systems these effects are provided by the linear chains, in others by the bulk dense drops. Since a mathematically strict statistical theory of the internal structures in ferrofluids is absent and hardly likely to be developed in the near future, only purposeful experiments in combination with relevant theoretical models can give the final answer to the question of the internal mechanism of the rheological effects. It should be noted that determination of the non-equilibrium steady stable size distribution of the chains as well as of the steady stable drop volume (shape) under conditions of shear flow is one of the main and most difficult problems of the theory of ferrofluids with microstructures. The chain size distribution and drop stable volume, obtained here from the free energy minimum, can be considered only as a first, perhaps rough approximation. However, general theorems, similar to the theorems of the thermodynamical potential minimum in equilibrium systems, which could allow us to determine the internal structure of a non-equilibrium system, are absent. The achieved agreement between the theoretical and experimental results indicates that in the situations under study the principle of the free energy minimum leads to quite a reasonable approximation.

The typical size (several microns or several tens of microns) of the drops in ferrofluids allows us to observe them directly by using ordinary optical microscopes. Direct observation of the linear chains is more sophisticated because of the small size of the magnetic particles in ferrofluids. Recently the chains in two-dimensional ferrofluid layers, with thickness about the diameter of the magnetic particle, were observed in [28]. This direct observation of the chains can be considered as an undoubted experimental success. However one needs to take into account that the conditions of the chain and drop appearance in the two-dimensional monolayers are quite different from those for the three-dimensional samples. Estimates show that formation of the chains is significantly easier in the layers than in the three-dimensional samples, whereas formation of the drops is easier in the three-dimensional ferrofluids.

In the case of thin (however with the thickness much greater than the particle diameter) channels (gaps) with ferrofluids, placed into a perpendicular magnetic field, the drop-like structures can appear and span the channel. Providing the rigid connection between the drop and the channel boundaries, one can observe quite measurable elastic and yield stress effects in these systems.

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