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Rheological properties of dense ferrofluids. Effect of chain-like aggregates

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Abstract

Rheological properties of dense ferrofluid are studied both experimentally and theoretically. Experimental dependence of the fluid effective viscosity on magnetic field is much more than predicted by known theories. New theoretical model is suggested to explain and describe these results. This model is based on assumption that linear chain-like aggregates appear in the ferrofluid; these chains induce strong magnetoviscous effect. The results of the theoretical calculations are in good agreement with the experiments.

Keywords: Ferrofluids; Microstructures; Effective viscosity

1. Introduction

Real magnetic fluids are practically always polydisperse and often contain ferromagnetic particles that are large enough to agglomerate, under dipole–dipole interaction, into soft heterogeneous aggregates. The important portion of these large particles are so-called primary agglomerates appearing during ferrofluid preparation as a result of van der Walls interaction. These soft and hard aggregates can influence macroscopical properties of ferrofluids strongly. That is why the properties of the real systems can be far from predictions of theories of magnetic colloids consisting only of separate particles.

2. Experimental results

In order to study general peculiarities of the rheological properties of dense magnetic fluids, we have carried out a series of experiments with typical commercial ferrofluid APG 513 A by FERROFLUIDS. These polydisperse colloids contain magnetic particles with a mean diameter of the magnetic corn about 10 nm. The particles are covered with a surfactant layer of about 3 nm thickness. The total volume concentration of magnetic phase is about 6.7%, hydrodynamical volume concentration is about 27%. Diagram of the particle size distribution is given [1]. To study the influence of magnetic field on rheological properties of the ferrofluid we have used a specially designed rheometer, described in details in Refs. [2,3]. The experimental results of the field dependence of reduced parameter $S(H) = (\eta(H) - \eta(0))/\eta(0)$ of stationary magnetoviscous effect, where $\eta(H)$ is effective viscosity under the field H, are shown in Figs. 1 and 2 for various values of shear rate $\dot{\gamma}\cdot$ For $\dot{\gamma} = 0.1\,\mathrm{s}^{-1}$ the magnitude S increases up to 14 times under weak fields that are far from saturation of the magnetoviscous effect. Calculations, based on known models of ferrofluids with separate particles, give the increase of S up to several percent only. This significant discrepancy between theoretical and experimental results leads to the assumption that a new physical situation, absent in dilute ferrofluids, takes place when the concentration and size of ferroparticles are large enough.

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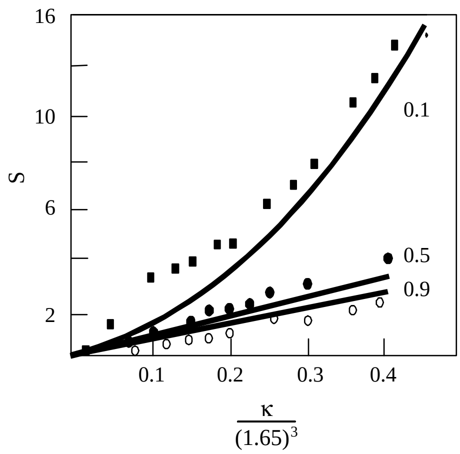

Fig. 1. Experimantal (dots) and theoretical (lines) dependences of parameter S of magnetoviscous effect on dimensionless magnetic field κ· Figures—shear rate in s^{-1}.

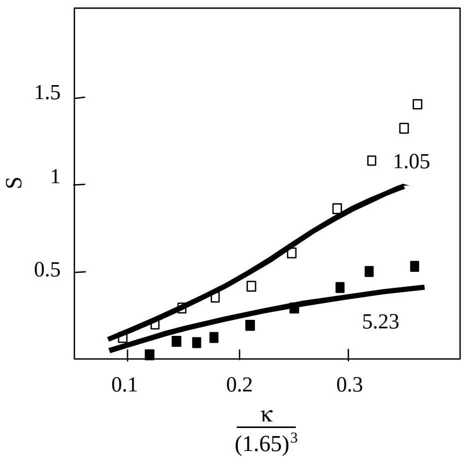

Fig. 2. Same as in Fig. 1.

3. Theoretical model

To explain the strong magnetoviscous effect observed in the experiments, new theoretical model is suggested. To simplify calculations, instead of real many-fraction ferrocolloid, we consider a bidisperse model of particles with significantly different diameters. The size of the "small" particles and their volume concentration are assumed near the mean values for the suspension. The size of the "large" particles and their volume concentration, assumed small, are to be estimated. We also assume that the large particles can unite into linear chain-like aggregates. As in the model [4], the chains are treated as straight and rigid rod-like aggregates. The borders of validity of this approximation are estimated in Ref. [4]. We restrict our analysis by a situation when magnetic interaction of the nearest particles in the chain is much more than interaction between the particle and magnetic field. Next, any interaction between the particles from different chains is neglected.

Let g_n be number of the n-particle chains per unit volume. We assume that this function provides a minimum of free energy F of this unit volume; the last can be represented as [4]

$$F = kT\sum_n \left(g_n \ln\frac{g_n}{e} + g_n f_n\right), \tag{1}$$

where f_n is dimensionless "internal" free energy of the chain. Taking into account interaction between the nearest-neighboring particles in the chain, we come to the following approximation:

$$f_n = -\varepsilon(n-1) + f_{nH}(\kappa), \tag{2}$$

where

$$\boldsymbol{\kappa} = \mu_0\frac{m\mathbf{H}}{kT}, \quad \varepsilon = \frac{m^2}{2\pi\mu_0 d^3 kT}.$$

Here m is magnetic moment of the "big" particle, d is its hydrodynamical diameter. The energy of f_{nH} of the chain interaction with magnetic field can be represented as

$$f_{nH} = \int \phi_n \ln\frac{\phi_n}{2.72}\,d\mathbf{e} - \int (\mathbf{e}\boldsymbol{\kappa})\phi_n\,\mathrm{d}\boldsymbol{\kappa}, \tag{3}$$

where $\mathbf{e}$ is unit vector aligned along the chain axis, $\phi_n(\mathbf{e})$ is normalized distribution function. The condition of minimum of F as functional of g_n for equilibrium states is usual thermodynamical condition. For steady states (for example, for stationary shear flow), this condition can be considered as an approximation for estimation g_n.

To determine $\phi_n(\mathbf{e})$, one needs to solve appropriate Fokker–Planck equation for the rod-like magnetic particles placed in shear flowing fluids and magnetic field. We have found approximate solution of this equation and determined g_n both for equilibrium and steady states. Then, using the well-known results of statistical hydrodynamics of suspensions of rod-like particles, we represented hydrodynamical stress tensor $\boldsymbol{\sigma}_n$, induced by n-particle chains through moments of the nonequilibrium distribution function ϕ_n. The explicit form of $\boldsymbol{\sigma}_n$ is given, for example, in Ref. [4]. It should be noted that $\boldsymbol{\sigma}_n$ increases very fast with the number n. The mean (measurement) stress tensor is

$$\boldsymbol{\sigma} = \sum_{n=1}^{n_c} \boldsymbol{\sigma}_n g_n. \tag{4}$$

We take into account that there is a maximal value n_1 so that when $n > n_1$, the hydrodynamical forces destroy the chain. That is why the sum in Eq. (4) is restricted by n_1. The magnitude of n_1 is estimated in Ref. [2].

Effective viscosity η of the suspension can be determined as

$$\eta = \frac{\sigma}{2\dot{\gamma}}. \tag{5}$$

Using this approach, we have calculated $\eta(H)$ for vanishing $\dot{\gamma}$ and fitted the parameters d and hydrodynamical volume concentration of the big particles comparing the results of calculations with the experiments shown in Fig. 1 for minimal $\dot{\gamma}$, namely $\dot{\gamma} = 0.1\,\mathrm{s}^{-1}$. We have got $d = 22.5\,\mathrm{nm}$ (that corresponds to diameter of magnetic corn 16.5 nm) and $\varphi = 0.015$. These magnitudes seem to be reasonable. Then, using these values of d and φ, we have calculated $\eta(H)$ for several $\dot{\gamma}$, used in the experiments. The results are shown in Figs. 1 and 2. One can see that the theory is in agreement with the experiments. The strong magnetoviscous effect for small shear rates has a physical origin in strong hydrodynamical perturbations that appear in the shear flowing ferrofluid due to the chains. When shear rate increases, the chains are destroyed and magnetoviscous effect decreases fast.

This analysis allows us to make the following conclusion. The biggest particles in real ferrofluids can play a principal role in formation of rheological properties of these systems in spite of their small concentration. The origin of this strong effect lies in the formation of elongated heterogeneous structures (for example, chains) consisting of the big particles. The small particles with sizes near typical mean sizes in real magnetic fluids are too small to unite into heterostructures. Therefore, they cannot provide a significant magnetoviscous effect.

Acknowledgements

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References

[1] S. Odenbach, Gilly, J. Magn. Magn. Mater. 152 (1996) 123.
[2] S. Odenbach, H. Stork, J. Magn. Magn. Mater. 183 (1998) 188.
[3] S. Odenbach, T. Rylewicz, M. Heyen, J. Magn. Magn. Mater. 201 (1998) 155.
[4] A.Yu. Zubarev, L.Yu. Iskakova, Phys. Rev. E 61 (2000) 5415.