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Rheological properties of magnetic suspensions

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Abstract
We present results of a theoretical study of the magnetorheological viscosity η of a suspension versus the applied magnetic field H and shear rate $\dot{\gamma}$. It is supposed that the macroscopic rheological effects are provided by linear chain-like aggregates. Unlike in traditional models, the natural statistical distribution of the chains over the number of particles in them is taken into account. The results obtained explain important features of the rheological η versus $H, \dot{\gamma}$ law, which has been detected in experiments but qualitatively contradicts known theories of rheological properties of magnetic suspensions.

1. Introduction

Many experiments (see, for example, [1–5]) with magnetic suspensions demonstrate the following rheological power law: $\eta/\eta_0 = 1 + \varphi Mn^{-\Delta}$, where η and η_0 are the effective viscosities of the suspension and carrier liquid respectively, φ is the volume concentration of the particles, $Mn \sim \dot{\gamma}/H^2$ is the dimensionless Mason number, equal to the ratio of the hydrodynamical force, destroying links between particles, to the force of magnetic attraction between them, Δ is some exponent, $\dot{\gamma}$ and H are, as usual, the shear rate and magnetic field. There are two kinds of theoretical derivations of this power law. The first approach, presented in [1–3, 6], is based on a model of linear chain-like aggregates, consisting of the magnetic particles. All chains are supposed to have identical length, equal to the maximal length of undestroyed chain at given H and $\dot{\gamma}$. These models give $\Delta = 1$. Another approach, developed in [4, 5], is based on a model of dense bulk drop-like ellipsoidal aggregates, consisting of an enormous number of particles. Depending on the supposed mechanism of the destruction of drops under hydrodynamical shear forces, these models give either $\Delta = 2/3$ [4] or $\Delta = 1$ [5].

It should be stressed that in all known models the magnitudes of Δ are fixed and depend neither on the applied field, nor on the particle volume concentration φ. However the magnitudes 2/3 or 1 have never been measured in experiments, where various intermediate values of Δ have been detected. Moreover, in experiments [1, 2, 4], carried out with quite different magnetic suspensions, increase of Δ with H and φ from, approximately, 2/3 to, approximately, 1 has been observed. Pronounced deviations of the function $\eta(Mn)$ from the power law have been detected in [2] when Mn was either very small or about unity. These dependences of η and Δ on H, φ and $\dot{\gamma}$ are in qualitative disagreement with the known theories. Since the magnitude of Δ as well as the forms of the dependences of η on H and $\dot{\gamma}$ reflect the internal microscopic nature of the macroscopic rheological phenomena, the lack of understanding of the behaviour of the functions $\eta(H, \dot{\gamma})$ and $\Delta(H, \dot{\gamma})$ means a qualitative misunderstanding of the physical cause of the observed phenomena. Moreover, the condition $Mn \ll 1$ is quite typical for experiments and many technologies with magnetic suspensions. Thus, small errors in predictions of the exponent Δ lead to very bad errors in predictions of the rheological properties of these systems.

In the work presented we suggest a model of rheological properties of magnetic suspensions with chain-like aggregates. Unlike the previous theories, our work takes into account the natural statistical distribution of the chains over the number of particles in them. It is shown that this model explains the above discussed dependences of η and Δ on H and $\dot{\gamma}$, which cannot be explained in the framework of the traditional models.

2. Main approximation and mathematical model

In a short paper we cannot describe all mathematical details of the model. That is why here we will restrict ourselves to discussion of its main physical points.

We consider a suspension of identical magnetizable particles typical for the magnetorheological suspensions and inverse ferrofluids. The suspension is involved in shear flow with gradient velocity parallel to the applied magnetic field. We ignore the effect of interaction between particles on their magnetic moments. According to all known photos of chains in MRS and inverse ferrofluids, we assume that thermal fluctuations of the chains are weak and consider the chains as nearly straight rod-like aggregates. Next, we take into account interactions only between nearest particles in the chains and ignore any interactions between the chains.

In order to determine the suspension's effective viscosity, first, we estimate the angle θ_n of deviation of the n-particle chain from the field H (see figure 1).

To this end we estimate the magnetic Γ_n^{m} and hydrodynamical Γ_n^{h} torques, acting on the chains. The explicit forms of these torques, determined in [1, 4, 8], can be presented as

$$\Gamma_n^{\mathrm{m}} = -(n-1)\,kT\lambda_* 6\sin\theta\cos\theta$$

$$\Gamma_n^{\mathrm{h}} = \tfrac{1}{3}\dot{\gamma}\beta d^2\cos^2\theta\,\nu\left(2\nu^2+3\nu+1\right)$$

where $\nu = (n-1)/2$, m is the magnetic moment of the particle, and

$$\lambda_* = \lambda - \ln(3\lambda), \qquad \lambda = \frac{\mu_0}{4\pi}\frac{m^2}{d^3kT}.$$

Here μ_0 is the vacuum permeability, m is the particle magnetic moment. Neglecting the mutual induction of the particles, we estimated m in the same way as for a single paramagnetic sphere placed into a field H. The magnitude λ is the traditional dimensionless parameter of the dipole–dipole interaction between two closely situated particles; the logarithmic term in the expression for λ_* appears due to the particle fluctuations in the chain.

Equating the Γ_n^{m} and Γ_n^{h}, we get

$$\tan\theta_n = \frac{\pi}{12}\frac{s}{\lambda_*}\left(2\nu^2+3\nu+1\right) \qquad s = \dot{\gamma}\frac{\eta_0 d^3}{kT}.$$

Then we estimate the radial, along the chain axis, components of the magnetic $F_n^{\mathrm{m}}(\theta_n)$ and hydrodynamical $F_n^{\mathrm{h}}(\theta_n)$ forces, acting on the particles in the chain. The first one is the force of attraction between the particles; the second force tends to destroy the chain. The result is

$$F_{\mathrm{r}}^{\mathrm{m}} = -3\lambda_*\frac{kT}{d}\left(3\cos^2\theta - 1\right)$$

$$F_{\mathrm{r}}^{\mathrm{h}} = \dot{\gamma}\beta d\frac{\nu(\nu+1)}{2}\cos\theta\sin\theta, \qquad \beta = 3\pi\eta_0 d.$$

Balancing the magnetic $F_{\mathrm{r}}^{\mathrm{m}}$ and hydrodynamical $F_{\mathrm{r}}^{\mathrm{h}}$ radial forces, we obtain the following condition of chain destruction:

$$\frac{2-tg^2\theta_n}{\tan\theta_n} = \frac{\pi}{2}\frac{s}{\lambda_*}\nu(\nu+1).$$

Analysis shows that when the number n of particles in the chain exceeds the magnitude determined from the last relation, the inequality $F_{\mathrm{r}}^{\mathrm{h}} > F_{\mathrm{r}}^{\mathrm{m}}$ holds. This means that the hydrodynamical forces destroy the chain. Thus the solution of this equation gives us the maximal number $n_{\max}$ of particles in the undestroyed chain.

Let g_n denote the number of n-particle chains in unit volume of the system. For the equilibrium suspension the distribution function g_n can be determined from the condition of the minimum of the system free energy with respect to g_n [7]. In the framework of the approximations discussed, this approach leads to the following Boltzmann-like form:

$$g_n = \frac{1}{v}X^n\exp\left(-(n-1)w(\theta_n)\right) \tag{1}$$

where v is the particle volume, X is the Lagrange multiplier, which can be determined by substituting equation (1) into the following normalization condition:

$$\sum_{n=1}^{n_{\max}} ng_n = \frac{\varphi}{v}. \tag{2}$$

The magnitude $w(\theta_n)$ is the dimensionless (relatively to kT) energy of bonds between the nearest particles in the chain. We calculate this energy taking into account weak fluctuations of the mutual positions of the particles near the ground state of the doublet (pole to pole position with both magnetic moments parallel to the field H). Taking into account estimates obtained in [7], we get

$$w(\theta) = -\lambda_*\left(3\cos^2\theta - 1\right).$$

Strictly speaking, the theorem of the free energy minimum is not valid for the system under shear flow. However, analysis shows that when the Peclet number constructed for the particle diameter d is not much greater than unity, this condition can be used, at least as a first approximation. It gives a background for estimating g_n from equations (1), (2) taking into account the chain deviation from the field under action of the shear flow.

Having estimated g_n, we can consider the suspension as an ensemble of the rod-like chains with the size distribution g_n determined. It is well known that the macroscopic hydrodynamical stress tensor σ in a polar liquid can be presented as $\sigma = \sigma^{\mathrm{s}} + \sigma^{\mathrm{a}}$ where σ^{s} and σ^{a} are the symmetrical and antisymmetrical parts of σ. By using the well-known results for hydrodynamics of polar suspensions [8] we get

$$\sigma^{\mathrm{a}} = \tfrac{1}{2}\sum_{n=2}^{n_{\max}}\Gamma_n^{\mathrm{m}}(\theta_n)g_n = \tfrac{1}{2}\sum_{n=2}^{n_{\max}}\Gamma_n^{\mathrm{h}}(\theta_n)g_n. \tag{3}$$

Combining equation (3) with the expressions for the magnetic Γ_n^{m} and hydrodynamical Γ_n^{h} torques we estimate the antisymmetrical part σ^{a} of the stress tensor σ.

The symmetrical part of the tensor can be presented as [8]

$$\sigma^{\mathrm{s}} = \eta_0\left(1 + \sum_{n=1}^{n_{\max}}\Phi_n(\theta_n)ng_n\right)\dot{\gamma}. \tag{4}$$

The explicit form of the function Φ_n is cumbersome; that is why we omit it here. This form can be found in [8].

Combining equations (1), (3) and (4), we estimate the total stress tensor σ. The effective viscosity of suspension by

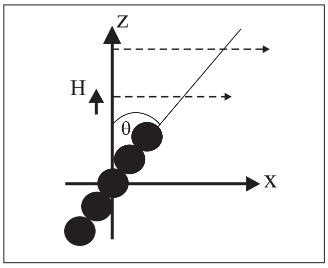

Figure 1. Sketch of the chain, deviating via the flow from the applied field. Dashed lines present the flow velocity.

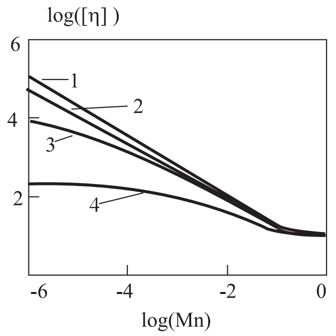

Figure 2. Calculations of the reduced effective viscosity $[\eta]$ as a function of the Mason number. Lines—1: $\lambda_* = 15$; 2: $\lambda_* = 8$; 3: $\lambda_* = 6$; 4: $\lambda_* = 4$. Particle volume concentration $\varphi = 0.01$.

definition is $\eta = \sigma/\dot{\gamma}$. One needs to note that the symmetrical part σ^{s} of the stress tensor has not been taken into account in the models of [1–6]; however its magnitude is not less than the magnitude of the antisymmetrical tensor σ^{a}, and thus σ^{s} cannot be ignored.

3. Results of calculations

Figure 2 demonstrates some results of calculations of the reduced effective viscosity $[\eta] = (\eta - \eta_0)/\eta_0$ versus the Mason number $Mn = \pi s/(2\lambda_*)$.

On the intermediate parts these curves are nearly linear, which indicates the power dependence of the reduced effective viscosity $[\eta]$ on Mn. Unlike the models of [1–6] which give either $\Delta = 2/3$ or $\Delta = 1$, in our calculations the exponent Δ is always between 2/3 and 1. For line 1 this exponent is about 0.7, which ties up with experiments [3]. For $Mn \to 0$ and $Mn \to 1$ our calculations lead to quasi-horizontal dependences of $[\eta]$ on Mn. Similar quasi-horizontal parts are seen in the experimental curves [2] shown in figure 3 (especially well in figure 3(b)).

These horizontal plateau-like regions cannot be explained by the traditional models [1–6]; however the physical reasons for their appearance are quite clear. Indeed, when the applied magnetic field is relatively weak, the absolute majority of the chains are short; the number n of particles in them is much less than n_{max}. Thus, the weak shear flow can neither destroy the chains nor cause them to deviate from the field. This means that the effect of the shear rate on the suspension effective viscosity is weak. Therefore the suspension viscosity here is approximately the same as that for the vanishing shear rate. The quasi-horizontal right parts of the graphs in figure 2 correspond to the situation of almost completely destroyed chains ($n_{\mathrm{max}} \approx 1$) when the Mason number is relatively large. At this state the suspension consists, mainly, of single particles; that is why its viscosity depends on the shear rate (i.e. on Mn) very weakly. We have just mentioned that the tendency of the reduced viscosity to the horizontal plateau, when the Mason number decreases, has been detected in experiments [2] shown in figure 3. In these experiments the relation between $\log([\eta])$ and $\log(Mn)$ was almost linear for the systems with relatively large particles which provide high magnitudes of λ_*; the plateau-like shape of the graphs was observed for the case of smaller particles, corresponding to low magnitudes of λ_*.

The agreement between experimental and theoretical results, shown in figure 3, is quite reasonable, especially taking into account that no free fitted parameters have been used in the calculations. It should be noted that neither the plateau in the left parts of the plots of $\log([\eta])$, nor the horizontal right parts of these plots, observed in the experiments, can be explained in the framework of the traditional theories which lead to the linear dependences between $\log([\eta])$ and $\log(Mn)$, whereas in our model these horizontal parts appear automatically.

Experimental [2] and theoretical dependences of the exponent Δ on the applied magnetic field are shown in figure 4.

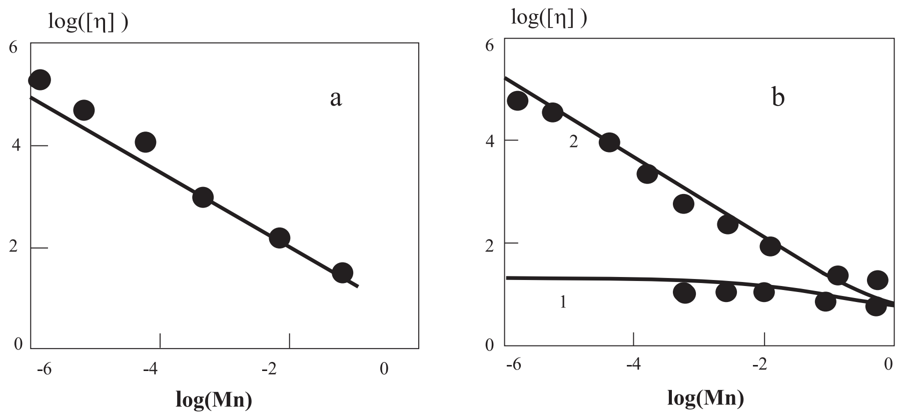

Figure 3. Theoretical (lines) and experimental (dots) results for the reduced viscosity $[\eta]$ versus the Mason number. (a) $\lambda_* = 15$, $\varphi = 0.01$, experiments [1]; (b) 1, $\lambda_* = 1.3$, 2, $\lambda_* = 258$, $\varphi = 0.18$, experiments [2].

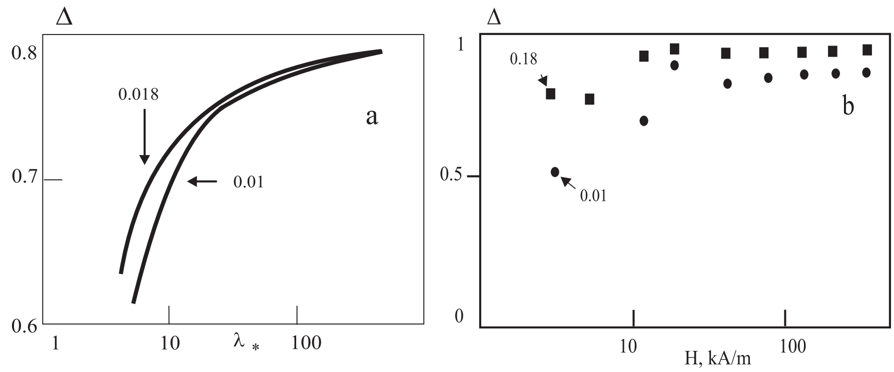

Figure 4. Calculated (a) and experimental [2] (b) dependences of the exponent Δ from the dimensionless parameter λ_* (a) and from the applied magnetic field (b) for two different volume concentrations φ of the particles (figures near the plots).

Unfortunately, important data necessary for transformation of the field H to the dimensionless parameter λ are not given in [2]; that is why we cannot compare the theoretical and experimental results directly. However, figure 4 shows that the theoretical and experimental curves vary in the same region—from approximately 2/3 to (approximately) 0.8–0.9 and slowly go up with increasing concentration φ. The qualitative and quantitative agreement between the theoretical and experimental results shows that the model is adequate at least in its main points.

4. Conclusion

We present results of a theoretical study of the rheological effects for magnetic suspensions placed into magnetic fields parallel to the gradient of the suspension flow. We suppose that these phenomena are produced by the linear chain-like aggregates, consisting of suspended particles. Unlike the previous works on this theme, in which the internal aggregates in the suspension are assumed to be identical, our work takes into account that the chains, being specific fluctuations of density, cannot be identical and must obey a certain law of distribution over the number of particles in the chain. Our results show that the relation between the suspension effective viscosity η and the Mason number Mn can be presented in the experimentally observed power form $\eta/\eta_0 - 1 \sim \varphi Mn^{-\Delta}$ when the energy of magnetic interaction between particles in the chain is high as compared with the thermal energy kT. The known (from the literature) models of the rheological properties of magnetic suspensions lead to fixed magnitudes of the exponent Δ, equal either to 2/3 or to 1, depending on the model. However, in experiments Δ varies with applied magnetic field in the region from (approximately) 2/3 to 1 and slowly increases with the particle volume concentration. The same behaviour of this exponent has been obtained in our model. This allows us to conclude that the experimentally detected rheological properties of magnetic suspensions are produced by polydisperse ensembles of internal structures; the chain polydispersity should be taken into account for an understanding of the physical mechanisms of the rheological phenomena in these systems.

Acknowledgments

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