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Yield stress and wall effects in magnetic colloidal suspensions

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Abstract. The static yield stress of magnetic colloidal suspensions is measured as a function of the applied magnetic field in a controlled stress rheometer. The experimental results are analysed with the help of the magnetization curve for different volume fractions.

The experimental yield stress scales as the square of the magnetization but its magnitude is always lower than the one predicted on the basis of interparticle forces.

The nature of the material used for the plates of the rheometer cell, as well as the surface roughness, is shown to have a large effect on the measured yield stress.

1. Introduction

Magnetic dispersions are used in several industrial processes, for example, the coating of flexible substrates to make magnetic tape and floppy computer disks, or to stabilize fluidized beds. The rheological behaviour of these dispersions in the presence of a magnetic field is rather difficult to interpret, both experimentally and theoretically [1–4]. On its own the system is already complicated, since it is composed of magnetic particles (very often Fe_2O_3) which are more or less rod-like and have a broad size distribution. Furthermore the clumping of particles in the presence of a magnetic field enhances the sedimentation rate of the particles or the radial flux in the presence of centrifugal forces. At low shear rates the rheological behaviour of these suspensions is dominated by the existence of a static yield stress which comes from the attractive interactions between the magnetic moments induced on each particle by the applied field. This situation is equivalent to that of electrorheological fluids where the polarization of the particles is induced by an electrical field [5]. In this case the measured yield stress grows proportionally with the square of the electrical field and the rheological behaviour is fairly well represented by a Bingham model. Recently Klingenberg and Zukoski [6] have derived a theoretical expression for the yield stress on the basis of the force induced by an electrical field on two spheres characterized by an internal permittivity different from that of the surrounding medium. This derivation does not take into account the interactions between the ionic clouds of each particle whose contribution to the polarization can be dominant, resulting in extra forces which should be modelled on a basis other than the use of a difference in permittivity between the particles and the solvent. In the case of magnetic particles we can characterize the particles by an internal magnetic permeability and apply the same results as in the electrostatic case as long as no currents are involved [7].

In this paper we study a colloidal suspension of polystyrene particles containing Fe_3O_4 inclusions. In section 2 we present the experimental results for the static yield stress as a function of the magnetization obtained in a plate–plate configuration, and for discs made of different materials. In section 3 we compare the theoretical predictions based on an effective medium theory combined with the known results for the interactions between two dielectric spheres.

2. Experimental

The magnetic polystyrene particles, designed by Rhône–Poulenc, are spherical. They contain 60% (weight ratio) of magnetite and their average size is centred around 0.8 μ. Previous rheological experiments on these suspensions using a capillary viscometer have shown the existence of yield stresses depending on the intensity of the magnetic field [7] but the interpretation of the flow curves did not allow us to obtain reliable values. Actually the fibre structure, which forms under the action of a magnetic field (cf figure 1), has a finite hydrodynamic permeability, so we always observe a flow which is that of water through the fibres acting as a porous medium. In these new experiments we measure the static yield stress between two discs (cf figure 2) on a Carrimed rheometer. The magnetic field is perpendicular to the surfaces of the discs and the fibre structure, resulting from the dipolar forces which tend

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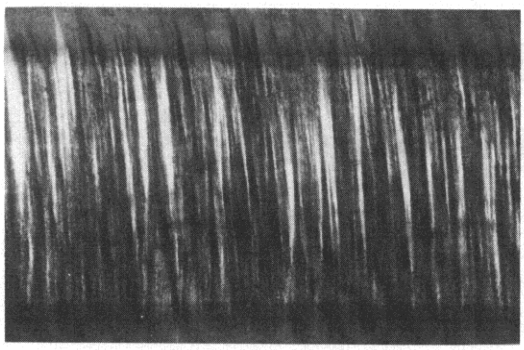

Figure 1. Fibrillation induced by a magnetic field of 100 Oersted.

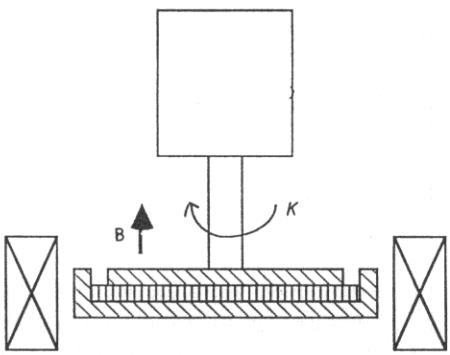

Figure 2. Schematic representation of the experiment.

to align the particles, adhere the two discs together. When the applied couple overcomes a given value, K_m, necessary to break all the links, the upper disc begins to rotate and we deduce the yield stress τ_m by writing:

$$K_m = \int_0^R (r\tau_m)\, 2\pi r\, \mathrm{d}r = \frac{2\pi R^3}{3}\tau_m.$$

This relation assumes that the force necessary to break a link, for instance at the outer radius, has to be maintained continuously in order to break the reforming links. The measurements have been carried out as a function of the magnetic field for three different volume fractions: $\varphi = 10\%$, 20%, 30% with either stainless steel or iron discs, and also with glass for $\varphi = 10\%$, In each case the magnetic field in the empty cell, is measured as a function of the current in the coil. As an example of the change obtained with these different materials we have plotted in figure 3 the measured yield stress, τ_m, as a function of H_0, for a volume fraction $\varphi = 10\%$. We note that for the same field, H_0, measured in the empty cell, the nature (ferromagnetic or paramagnetic) of the disks has a large effect on the measured yield stress, the larger yield stress (for the same field in the empty cell) being obtained with the ferromagnetic material. Furthermore if we remove the surface roughness by using glass discs we get very small yield stresses. These observations are obviously connected to the slipping of the fibres on the

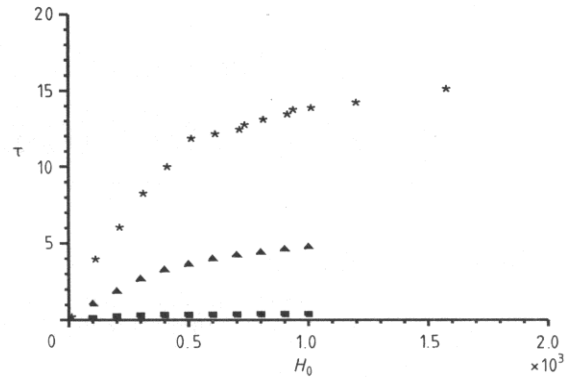

Figure 3. Measured yield stress τ_m as a function of the magnetic field, for a volume fraction $\varphi = 10\%$. ▲: Stainless steel discs; ∗: iron discs; ■: glass discs.

surface which will depend both on the surface roughness and on the force pressing the particles on the discs. The force between a particle and the wall can be approximated by the interaction between the magnetic moment of the particle, m, and its image in the wall whose amplitude m_{im} is equal to [8]:

$$m_{im} = m(\mu_w - \mu_e)/(\mu_w + \mu_e)$$

where μ_w is the magnetic permeability of the disc and μ_e the permeability of the suspending liquid. The suspending liquid has a permeability very close to unity as has stainless steel which is paramagnetic, so in that case there is no force between one particle and the wall; multiparticle interactions can induce such a force but it will always be far smaller than the interaction between a particle and a ferromagnetic wall whose permeability is very large compared to unity. In this last case the magnetic dipole induced by the field and its image are parallel resulting in an attractive force. So even if the roughnesses of iron or stainless steel discs are quite identical (about 10 microns depth), in the first case the particles are pushed against the defects of the wall where they become trapped whereas in the other case they can roll more easily over small bumps. For the two paramagnetic materials (glass and steel) there is no attractive force between the particles and the wall; the difference just comes from the roughness of the wall. For the glass disc the roughness is smaller than the size of the particles so that they can slip tangentially without any force to retain them, which explains the very low values of the yield stress.

Figure 4 shows, for the stainless steel plates, the evolution of the yield stress with the concentration. Rather surprisingly it appears that increasing the concentration from 20% to 30% results in a decrease of the yield stress. Actually we must keep in mind that the force between the particles does not depend directly on the applied field but rather on the effective field in the suspension. For two infinite plates with the field

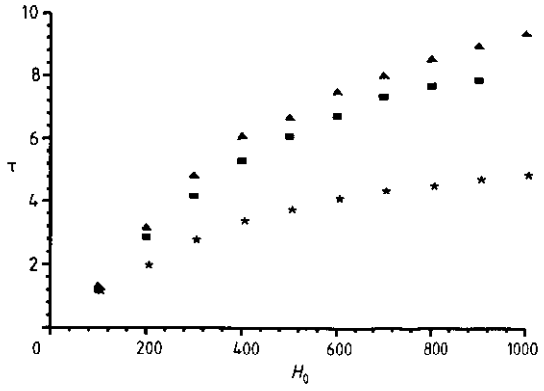

Figure 4. Measured yield stress τ_m as a function of the magnetic field, H_0, for different volume fractions, and with the stainless steel discs: ∗: $\varphi = 10\%$; ▲: $\varphi = 20\%$; ■: $\varphi = 30\%$.

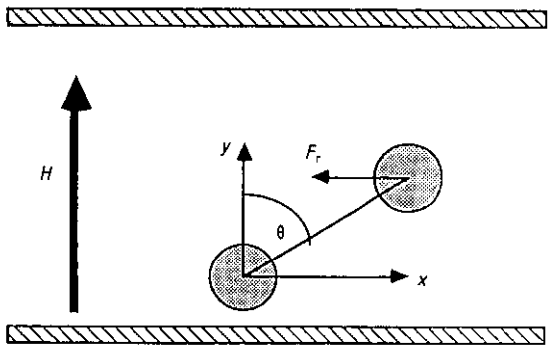

Figure 5. Restoring force F_r induced by the magnetic field H. μ_i: internal permeability of the particle; μ: permeability of the suspension.

perpendicular to them the effective field, H, is given by

$$H = H_0 - 4\pi M \tag{1}$$

where M is the magnetization or with

$$M = \chi H \tag{2}$$

$$H = H_0/\mu(H) \tag{3}$$

where $\mu(H) = 1 + 4\pi\chi(H)$ is the permeability of the suspension. As this permeability increases with the concentration, the force between the particles will decrease. On the other hand, raising the concentration increases the number of links between the discs; it is the competition between these two effects which explains the existence of an optimum concentration (for the yield stress) which can be rather low.

3. Comparison with the theory

In order to predict the yield stress behaviour we use the model proposed by Klingenberg and Zukoski [6–9] who calculate the restoring force, F_r, between two particles in an electric field (cf figure 5). This force, which is zero when the two spheres are aligned with the field, increases with the angle θ up to a maximum, f_m, for an angle, θ_m, which depends on the ratio of the internal and external permittivities: $\varepsilon_i/\varepsilon_e$ and then decreases. Using magnetostatic instead of electrostatic we get for the restoring force between two particles of radius a (in cgs units):

$$F_r = 3\mu a^2 H^2 \beta^2 f \tag{4a}$$

with

$$\beta = (\mu_i - \mu)/(\mu_i + 2\mu) \tag{4b}$$

and

$$f = (a/r)^4[(2f_\parallel + 2f_\Gamma)\sin\theta\cos^2\theta - f_\perp \sin^3\theta]. \tag{4c}$$

The coefficients for $f_\parallel$, f_Γ and $f_\perp$ are all equal to one in the point dipole approximation. In this approximation the function, f, reaches a maximum: $f_m = 5.71 \times 10^{-2}$ for $\theta_m = 21.3°$. For two spheres the values of f_m and θ_m calculated in [6] are listed in table 1.

The relations (4) apply uniquely to two spheres in an external field. For a concentrated suspension we can use an effective medium picture where two spheres of permeability μ_i are immersed inside a continuous medium having the average permeability μ of the suspension with the average field, H, given by (1).

Now if we consider the case where all the spheres contribute to the formation of chains which link the two discs, the force needed to break N_c chains by unit surface will give the yield stress τ_m:

$$\tau_m = \frac{N_c}{S} F_r = \frac{\varphi}{\frac{2}{3}\pi a^2} F_r. \tag{5}$$

In order to calculate F_r we need to know the average permeability μ of the suspension and the internal permittivity μ_i of the particle. We can obtain these by measuring the magnetization curve. The experimental results are not well represented by a Langevin function. A best fit is obtained with a modified Langevin equation:

$$M(H_0) = M_r + (M_S - M_r)(\coth(aH_0) - 1/aH_0) \tag{6}$$

where $a = \mu/kT$.

The parameters, M_r, M_S, and a are listed in table 2 for the three concentrations used. The permeability is then obtained by writing:

$$H = H_0 - 4\pi n\chi(H)H$$

$$\mu(H) = 1 + 4\pi M(H_0)/H$$

where n is the depolarization factor of the cylindrical cell used for the determination of the magnetization.

Then the internal permeability of the particles, μ_i, can be estimated using an effective medium theory for

Table 1. Values of f_m and θ_m for two spheres (from [7]).

μ_i/μ	1	2	3	4	5	6	7	8
f_m	0.05714	0.06817	0.07748	0.08556	0.09271	0.09914	0.10500	0.11038
θ_m	21.27	20.09	18.96	17.98	17.10	16.34	15.64	15.01
μ_i/μ	9	10	11	12	13	14	15	
f_m	0.11536	0.12001	0.12438	0.12850	0.13240	0.13612	0.13967	
θ_m	14.44	13.91	13.43	12.95	12.52	12.12	11.75	

Table 2. Values of the parameters for the fit of the magnetization curves (6).

φ	$M_r(G)$	$M_S(G)$	$a(Oe^{-1})$
0.1	2.97	4.92	4.40×10^{-3}
0.2	3.95	9.27	3.56×10^{-3}
0.3	4.34	15.53	5.42×10^{-3}

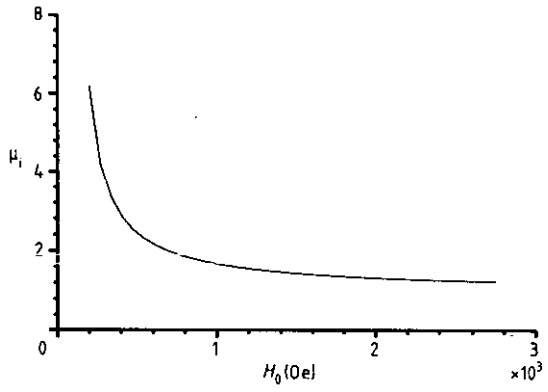

Figure 6. Internal permittivity deduced from the magnetization curve using equation (7).

a composite material. For instance in the Maxwell-Garnet theory [10] we have:

$$(\mu - 1)/(\mu + 2) = \varphi(\mu_i - 1)/(\mu_i + 2) \qquad (7)$$

and in the Bruggeman theory [11]:

$$\varphi \frac{\mu_i - \mu}{2\mu + \mu_i} + (1 - \varphi)\frac{1 - \mu}{2\mu + 1} = 0. \qquad (8)$$

The permeability obtained for the different concentrations either from (7) or from (8) does not differ by more than a few per cent, for internal field H larger than 300 Oersted. A typical curve is drawn in figure 6 and corresponds to the Maxwell-Garnett theory.

Knowing the functions $\mu(H)$ and $\mu_i(H)$ we can calculate the theoretical yield stress. For a given external field, H_0, the effective field, H, inside the suspension, between the discs, is found from the root of (3) and we take the values of μ_i and μ corresponding to this effective field in order to calculate the restoring force (4). If we assume that with the iron discs the structured suspension does not slip along the wall, we can compare these experimental results with the theoretical predictions.

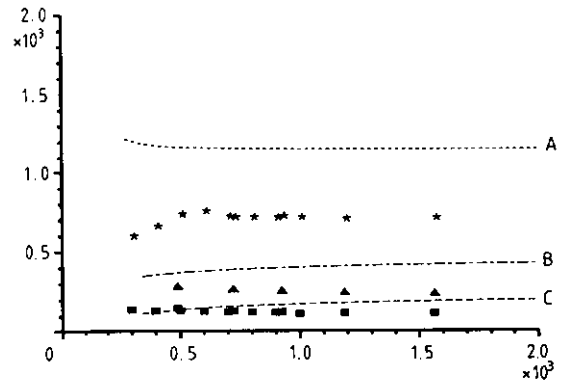

Figure 7. Yield stress normalized by the square of the magnetization against magnetic field for iron discs. Theory: curve A: φ = 10%; curve B: φ = 20%; curve C: φ = 30%. Experimental: *: φ = 10%; ▲: φ = 20%; ■: φ = 30%.

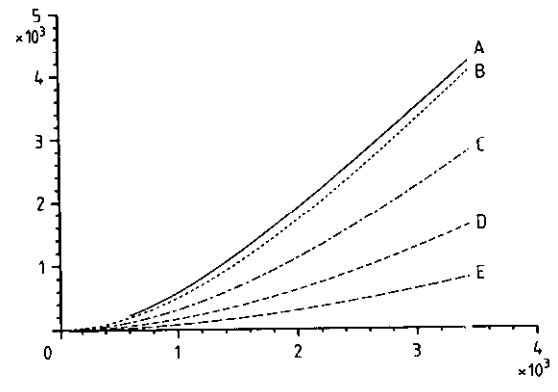

Figure 8. Theoretical yield stress against magnetic field for a suspension whose internal permeability of the particles would be equal to that of steel. A: φ = 10%; B: φ = 20%; C: φ = 30%: D: φ = 40%; E: φ = 50%.

The comparison is made in figure 7 for the three concentrations with the yield stress normalized by the square of the magnetization. We first note that for external fields larger than approximately 300 Oersted the yield stress scales as the square of the magnetization. This can be understood quite easily since in the simplest dipolar approximation we can write that the restoring force F_r between two particles is proportional to the square of the magnetic moment of each particle which is itself proportional to the magnetization divided by the density. The theory overestimates the yield stress by about sixty per cent. It is

noticeable that we get this same ratio between theory and experiment for the three concentrations. Actually it is not surprising that such a crude model without any parameters does not give the right value. A possible explanation could be that a rather important fraction of the particles does not contribute to the strength of the fibres (in our case the useful volume fraction would be $\varphi_u = \varphi/1.6$). For instance we can imagine that in our polydisperse suspensions the smaller spheres are positioned randomly along a chain constituted of the larger spheres and so do not contribute a great deal to the solidity of the chain.

4. Discussion

It appears that the experimental yield stress of a magnetic suspension is proportional to the square of the magnetization but that its value greatly depends on the interaction between the particles and the walls. In the case of iron walls the magnetic interaction between the particles and the walls together with the roughness of the surface prevents the fibres slipping on the wall. Nevertheless the experimental yield stress is still 60% lower than the one predicted by a model of a monodisperse suspension with equally spaced chains of spheres. If we compare these systems with electrorheological fluids where the yield stress can attain 3000 Pascals for electric fields of approximately 30 kV/cm, the values we get are two orders of magnitude lower. Actually the yield stress depends strongly on the permeability of the particles we use; figure 8 shows the theoretical yield stress obtained from equations (4) and (5) with the internal permeability corresponding to that of steel. We get yield stress of about 3000 Pascals for an applied magnetic field of about 3000 Oersteds which is not difficult to obtain in practice. Furthermore the optimum concentration is rather low ($\approx$10%) which would correspond to a viscosity in the absence of a magnetic field which is still close to that of the suspending fluid. This is important for potential applications where we need that, without applied field, the heat dissipation remains low.

Another interesting question is the influence of the polydispersal of the suspension. We can try to reduce it by some size separation processes, but another possibility is to use calibrated polystyrene particles inside a ferrofluid. In that case, even if the permeability of the ferrofluid is smaller than the one of magnetic particles, we have the same kind of interactions between magnetic holes as that between magnetic particles in water, but with the possibility of mastering the size distribution of the particles. In this way we can hope for a better understanding of the effect of polydispersal on rheological behaviour of magnetic suspensions.

Acknowledgments

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