Colloidal Stability and Transport Properties of Ferrofluids

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Rheological properties of ferrofluid solutions variously stabilized, are investigated as a function of experimental parameters, such as volume fraction of particles, external magnetic field and ionic strength of the carrier. Colloidal stability of the magnetic fluid systematically leads to Newtonian behaviours in presence of an external magnetic field. On the contrary, in phase separated samples, non Newtonian effects are clearly observed.

I. Introduction

Transport properties of a suspension are strongly dependent on its microscopic structure. In regards to their technological applications for servo-dampers or clutches, electrorheological and magnetorheological fluids are widely studied^[1,2]. These fluids are important because a convenient external parameter enriches the system: for example with Magnetic Fluids^[3], also called ferrofluids, a magnetic field applied to the flowing system, introduces an anisotropy inside the fluid, which is different of the anisotropy of the shear flow and which then leads to specific effects.

We are here concerned with colloidal solutions containing magnetic particles of typical mean diameter 10nm bearing a magnetic moment of a few 10" Bohr magnetons. Rheological behaviour, as most of physical properties of ferrofluids is related to a major problem: the colloidal stability of the magnetic fluid. In order to counterbalance van der Waals attraction and attractive - through a steric hindrance, coating the particles with surfactant chains,

- through an electrostatic repulsion, magnetic particles being also macro-ions, all of the same sign.

Anyway, whatever the nature of interparticle repulsion, some failures of stability are variously reported^[4-9] leading either to a pliase separation into two liquids of different particle concentrations^[7]: droplets of concentrated phase growing among the more dilute phase, either to a flocculation of some particles in a solid precipitate.

As magnetic fluids experiencing the first process still flow, the phenomenon is sometimes difficult to identify. First experimental observations were microscopic views of elongated liquid droplets, a few hundred $\mu m \log$, being formed parallely to an externally applied magnetic

part of magnetic dipolar interaction, colloidal stahility of magnetic liquids require an additional repulsion between the grains. This may be realized in two different ways:

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field^[4-9]. Many factors are able to induce such a phase separation, for example:

- a temperature lowering,

- for sterically stabilized particles, some variations of free surfactant concentration or addition of extra polymeric chains,

- for electrostatically stabilized particles, an increase of ionic strength.

It may lead to very surprising experimental observations: for example, the observation of several propagating sound waves in the solution or large light scattering patterns. Macroscopic structurations^[4,9] then appear inside the fluid leading to large apparent viscosities, usually going with non-Newtonian behaviours^[2,10,11]. To some extents, rheology of such diphasic solutions may be compared to non-colloidal suspensions of a few μ m-sized magnetic grains^[12].

First section deals with viscosity of monophasic ferrofluids, described as a function of various experimental parameters. The second section shows how these rheological properties are modified with ferrofluids undergoing a phase separation.

II. - Viscosity of rnonophasic magnetic liquids

In this section properties of magnetic liquids monophasic and stable from a colloidal point of view are first studied. In zero magnetic field, and because of Brownian motion of magnetic particles, a ferrofluid is an isotropic liquid. Its viscosity is greater than that of the fluid carrier: there is an extra energy dissipation due to the suspended particles. After a brief summary of shear rate, temperature and particle volume fraction dependences in zero fields, we shall investigate the effect on ferrofluid viscosity of an external magnetic field: providing that the ferrofluid remains monophasic, it remains a Newtonian liquid in the usual ranges of shear rates.

II.1. Zero magnetic field properties

Rheology of suspensions^[13] is a complex hydrodynamic question. If the very dilute regime is now well understood from a theoretical point of view, the concentrated regime still raises many questions. In his pioneering works Einstein^[14] proposed a powerful model, derived from the flow field of pure strain perturbed by the presence of a sphere, which correctly accounts for viscosity of suspensions in the limit of low concentrations of suspended particles, taking in account hydrodynamic interactions, Batchelor^[15] then calculated the second order in concentration contribution to viscosity. Many other laws, semi-phenomenological^[16], are proposed to describe the whole viscosity dependence on concentration. Viscosity of colloids^[17] is an even more difficult problem, because thermodynamical interactions between particles such as van der Waals or electrostatic interactions, have to be encountered together with Brownian motion and hydrodynamic interactions. In magnetic colloids^[3,18,19], in addition to dipolar-magnetic interactions, magnetic field is an external parameter which enriches the system.

a) Shear rate effect

In a laminar shear flow, with a Newtonian fluid, the shear stress **r** is proportional to the shear rate $\dot{\gamma}$ and dynamic viscosity η is defined as the ratio $\tau/\dot{\gamma}$. In a ferrofluid undergoing a homogeneous shear flow, the stream lines are perturbed by the particles and because of the velocity differences of liquid layers inside the flow, a rotation of the particles is induced. Increasing shear rate $\dot{\gamma}$, the liquid remains Newtonian, up to a limit of the order of the characteristic frequency of rotation of a particle suspended in the solvent^[18]: $kT/\eta_0 V_k$ Boltzman constant, T temperature, η_0 solvent viscosity, V_h hydrodynamic volume of a particle. This characteristic time can be measured experimentally for example through transient birefringence measurements and is typically of the order of 1 to 10 μ s in water^[20]. Usual experiments are performed with $\dot{\gamma} < 10^5 \text{ s}^{-1}$ and are thus always in the low shear rate limit: in this $\dot{\gamma}$ range, monophasic ferrofluids, in zero magnetic field, are Newtonian fluids.

b) Temperature influence

Viscosity of the liquid carrier exponentially depends on temperature: in the same way temperature leads to wide variations of the ferrofluid viscosity. On the other hand this parameter also influences the ferrofluid viscosity through the Brownian motion of particles^[18]: kTarises as a normalizing coefficient in all the reduced parameters of interaction (particle-particle interactions or particle-field interaction). At least, temperature variations can also lead to severe chemical modifications inside the fluid such as a desorption of surfactant chains, miscellisation of free surfactant or change in solvent quality with respect to the surfactant, any of these modifications being ahle to destabilize the colloid.

c) Volume fraction dependence

Because of the addition of rnagnetic particles, the viscosity η of a ferrofluid is greater than the solvent viscosity η_0 ancl at a given temperature, it is an increasing function of the volume fraction of particles Φ . Fig. 1 presents variations of reduced viscosity $(\eta - \eta_0)/\eta_0$ versus Φ . Variously stabilized ferrofluid samples are presented^[21,22]: η is measured with a capillary viscometer^[11,23]. Two ranges may be distinguished in η variations, a low concentration regime ancl a high concentration one, the boundary heing around a few percent in volume fraction.

Low concentration regime

In this regime^[24], η is a linear function of Φ and its variations are well described by Einstein model^[14]:

$$\eta = \eta_0 [1 + (5/2)\Phi_h] \tag{1}$$

with Φ_h , the hyclroclynamic volume fraction of particles. The Einstein model supposes that the solution is a suspension of monodispersed hard spheres without interactions, this description is thus only valid for $\Phi_h \ll 1$. Coefficient 5/2 is enlarged^[25,26] for elongated particles (instead of spherical). However two experimental difficulties are encountered in determining this coefficient: - polydispersity of ferrofluid particles^[27] ancl - a precise measurement of Φ_h . The whole solvation layer surrounding the magnetic particles enters in their hydrodynamic volume. Usual Φ determinations are nonhydrodynamic ones. For example in fig. 1, Φ is deterrnined through chemical titration of iron, ancl in^[24], variations of density ρ feature Φ variations; from magnetic measurements a magnetic volume fraction Φ_m can also be determined; none of these three determinations accounts for the solvation layer. The more frequent Φ_h determinations suppose that a given law $\eta = f(\Phi_h)$ is valid and Φ_h is deduced from a best fit to experimental data^[24,28]. An independent Φ_h determination would

be much preferable but surely much more difficult to develop.



Figure 1: Log-Log plot of $(\eta - \eta_0)/\eta_0$ versus Φ for various ferrofluid samples prepared through Massart's synthesis^[21,22]. Measurements are performed in zero field with a capillary viscometer and Φ is deduced from chemical titration of iron. Full circles: maghemite aqueous samples (T = 22°C); open circles: cobalt ferrite aqueous samples^[23] (T = 22°C); stars: magliemite surfacted samples in a commercial oil based on dibutyl phtalate (T = 25°C and 45°C); crosses: maghemite ionic samples in ethylene-glycol^[11] (T = 20°C and 25°C). Figures 2 and 3 correspond to the more concentrated of these samples (T = 25°C, $\Phi = 16\%$, ionic strength c, < 10⁻² mole/l).

- High concentration regime

For Φ greater than 3 to 4%, reduced viscosity deviates substantially from the linear behaviour of Einstein law. In this regime, the interactions hetween particles are dominant, both hydrodynamic and thermodynamic interactions being important, and the Einstein model is no longer valid. A large number of empirical and theoretical equations have heen used to describe viscosity at high concentrations^[16,17]. It is not to the purpose here to give a detailed list of these expressions. From Fig. 1, it seems possible to extract a general behaviour at different temperatiires and for various kinds of ferrofluids. These samples cliffer from:

- the magnetic material of particles (γ -Fe₂O₃, Fe₂CoO₄),

- the nature of the solvent: polar (aqueous medium, Ethylene-glycol) or non-polar (oil based on dibutylphtalate)

- the particle stabilization (surfactant coating, various surface ligands)

However detailed studies are still necessary in order to point out the influence on viscosity of the particle size distribution, the magnetic material of particles, and the thickness of the solvation layer through interactions and hydrodynamic fraction. Some intermediate situations are experimentally possible: magnetic particles coated with a very thick surfactant layer can exhibit a dilute regime behaviour from the point of view of thermodynamic interactions and a concentrated regime behaviour from the hydrodynamic point of view.

II.2 Behaviour in a uniform magnetic field

In presence of a magnetic field, in the same way as in zero field, two concentration regimes can be distinguished. A very dilute one, where magnetic particles, under both flow and field, exhibit an isolated particle behaviour. This regime is explored by Shliomis^[29], taking in account particle alignment along the field together with Brownian desorientation and flow induced rotation. This work is performed in the rigid dipole approximation. This condition is only fulfilled for particles of large anisotropy energy KV with respect to both magnetic energy μH and thermal energy kT (K being anisotropy constant, V volume of particle and μ its magnetic moment): in low fields, if KV < kT, magnetic moment μ is free to rotate with respect to particle crystalline axes and moment alignment occurs through thermal fluctuations (Néel relaxation process) without mechanical rotation of particle. On the contrary if KV >> kT, magnetic moment is locked in an easy direction of magnetization inside the particle and the moment alignment process involves a mechanical rotation of the whole particle which can strongly interact with the flow.

a) Rigid dipoles in dilute regime

Application of a magnetic field **H** introduces a torque $\mu \times \mathbf{H}$ which hinders the particle rotation about axes perpendicular to the field. Thus an additional frictional coupling between fluid layers is introduced

which increases viscosity. The orienting effect of magnetic field is balanced by hydrodynamic forces and rotational Brownian motion^[29]. The increase of viscosity is greater if magnetic field is perpendicular to vorticity: in these conditions, the magnetic torque is more efficient in hindering the shear induced rotation.

Shliomis calculates in reference^[29] the viscosity dependence on magnetic field in a Couette flow. In the dilute regime without particle interactions and in the low shear rate regime, he obtains:

$$\eta(H) = \eta(H=0) \left[1 + (3\Phi_h/2)sin^2 \alpha \frac{(\xi - tanh\xi)}{(\xi + tanh\xi)} \right]$$
(2)

with $\eta(H = 0)$ given by Einstein law (equation (1)), α being the angle between magnetic field and vorticity of the flow, and $\xi = \mu/kT$ the reduced parameter of the Langevin function. Exactly as in zero magnetic field, the liquid remains Newtonian up to a shear rate of the order of the characteristic frequency of particle rotation which is much greater than usual experimental shear rates.

b) Experiments in concentrated solutions

Several experiments in moderately concentrated solutions are well explained by Shliomis model^[24,30]. In the same way, viscosity measurements from reference^[26] performed in a capillary viscometer with increasing hydrodynamic volume fractions from 6% to 17% show that Shliomis model correctly accounts for viscosity of a sample of $\Phi_h = 6\%$. On the contrary, deviations become more and more important as Φ_h increases. To fit the data, the authors propose to introduce an effective volume fraction which takes in account the interactions. With the more concentrated samples and for ξ larger than an experimental value ξ^* which is a decreasing function of Φ_h , this effective volume fraction becomes magnetic field dependent due to magnetic interactions.

If concentration is further increased, expression (2) become unable to explain experimental results: ξ , becomes larger than ξ^* even in low fields. This is shown^[11], with a ferrofluid sample of γ -Fe₂O₃ particles suspended in ethylene-glycol; mean size of particles is 7 nm; volume fraction from iron titration is 16%. The viscosity is measured in a Couette viscometer with a radial magnetic field. It is experimentally verified that

magnetic field does not perturb the linear relation between shear stress and shear rate (see Fig. 2): the liquid remains Newtonian even in high field at least till $\dot{\gamma} = 200 \text{ s}^{-1}$. Reduced variations $\eta(H)/\eta(H = 0)$ as a function of magnetic field are presented in Fig. 3.



Figure 2: Linear behaviour of shear stress τ versus shear rate $\dot{\gamma}$ at H = 400 Oe (lower curve) and H = 4600 Oe (upper curve). See caption of figure I for sample characteristics.



Figure 3: $\eta(H)/\eta(H=0)$ versus magnetic field (same sample as in figure 2). In low fields (full symbols), $\eta(H)/\eta(H=0)$ is deduced from a measurement of $\tau(H)/\tau(H=0)$ at $\dot{\gamma} = 100 \text{ s}^{-1}$.

Thus a general rheological property of monophasic ferrofluids is that they remains Newtonian liquids in the usual range of shear rates ($\dot{\gamma} \leq 10^3 \text{ s}^{-1}$), both in zero magnetic field and in presence of an external magnetic field. In this range of $\dot{\gamma}$, a shear stress non-proportional to shear rate marks the occurence of macroscopic structurations inside the liquid, signature of a phase separation^[2,10].

III. Rheology of diphasic magnetic fluids

It is not always easy to know a priori if a sample is monophasic or not, especially if the volume fraction of particles is large. This point explains many former controversies about viscosity of ferrofiuids. Coupling viscosity measurements to colloidal stability studies on ionic ferrofluids, two main effects are observed: drastic viscosity increases and non-Newtonian behaviour in conditions where optical tests reveal a phase separation inside the sample. Two examples are given in Figs. 4 and 5. In Fig. 4, phase separation is induced in zero magnetic field through an increase of ionic strength^[7] (i.e. a decrease of electrostatic repulsion between particles). Viscosity is measured in a capillary viscometer. For ionic strengths larger than the threshold of phase separation, the measured apparent viscosity increases abruptly^[11]. In Fig. 5, the ferrofluid viscosity is determined with an acoustic viscometer^[31] measuring the velocity of a falling ball. Experiment is performed with two comparable samples one stable on the whole range of magnetic field and the second one undergoing a field induced phase separation for H = 750 Oe. A large increase of the measured quantity is observed here also. However such viscometers involve complicated flows, simple shear flows are necessary to clear up the question. Samples of Fig. 4 are tested under radial magnetic field in a Couette viscometer. In the phase separated sample of Fig. 6, non-Newtonian effects clearly occur whatever the magnetic field.



Figure 4: $\eta(c_s)/\eta(c_s = 0)$ versus ionic strength c,, in zero magnetic field. Full line: liquid carrier behaviour as ionic strength is increased; dotted iine: ferrofluid sample; initial point corresponds to sample of figure 2 for which c, $< 10^{-2}$ mole/l.



Figure 5: Apparent viscosity versus magnetic field for two comparable ferrofluid samples in dibutylphtalate (apparent $\dot{\gamma} \simeq 20 \text{ s}^{-1}$), $\Phi = 5\%$ (open circles: sample stable in the experimental range of magnetic fields; filled circles: sample exhibiting an optically-tested phase-separation around 750 Oe). In the monophasic state expected viscosity variations, as a function of field H are smaller than detection accuracy.



Figure 6: Shear stress r versus shear rate $\dot{\tau}$ at H = 400 Oe (lower curve) and H = 4600 Oe (upper curve). The sample is the same as in figure 2 with an increased ionic strength: $c_r = 0.3 \text{ mole/l}$. (see figure 4).

The appearance of macroscopic structures inside the fluid, here thin droplets elongated along the magnetic field (a few μ m thick and a few 100 μ m long) leads to a rheofluidizing (or pseudo-plastic) effect^[2]. It is most probable that the visco-plastic (Bimgham body) behaviour which is sometimes observed^[28] with some magnetic fluids is related to the range of shear rate **j** which is experimentally explored. Although behaviour in high shear rate implies the existence of a shear stress threshold, experiments performed in the same $\dot{\gamma}$ range as in Fig. 6, could exhibit the characteristic behavior of pseudo-plastic fluids.

In this diphasic regime, one can try representations of $\eta_{app}(H)/\eta_{app}(H=0)$ versus $\dot{\gamma}$. Fig. 7 gives such variations at a constant field **as** ionic strength is increaseù for a given sample. The same representation performed in lower fields gives similar trends, the effects being of lower amplitude. Large ionic strengths lead to large apparent viscosities in low shear rates, related to the structurations inside the fluid. As shear rate is increased, apparent viscosity decreases towards the Newtonian behaviour of low ionic strength samples. The structurations are progressively broken by the flow as $\dot{\gamma}$ increases: elongated drops separate in small droplets which even could be dissolved in the fluid under some conditions.



Figure 7: Reduced apparent viscosity $\eta_{app}(H)/\eta_{app}(H=0)$ in a constant and high magnetic field (4600 Oe) versus $\dot{\gamma}$ for samples of increasing ionic strength (squares: $c_{,} < 10^{-2}$ mole/l; filled circles: $c_{,} = 0.2$ mole/l; open circles: $c_{,} = 0.3$ mole/l). $\eta_{app}(H) = \tau/\dot{\gamma}$ is deduced from plots such as figures 2 and 6 (T = 25°C).

IV. Conclusion

As a conclusion, magnetic fluids may be separated in two classes depending on their Newtonian or non-Newtonian rheological behaviours. Some magnetic fluids remain Newtonian fluids in the usual range of shear rates ($j < 10^3 s^{-1}$) whatever volume fraction of particles and even in presence of magnetic fields. These magnetic liquids are stable and monophasic colloids. Their low concentration behaviour is well described through combined Einstein and Shliomis formalisms, some approximations being sometimes necessary. For higher concentrations, particle interactions become significant

and must be taken in account, however the liquid remains Newtonian. Such magnetic colloids are required in devices where invariance of magnetic and fluid properties is required, for example in seals, printing inks or heat exchangers. Nevertheless, it is clear that diphasic magnetic liquids are full of potentialities: for weak $\dot{\gamma}$ values, viscosity can be multiplied by a factor of 10 to 20 if a magnetic field is applied! This could enlarge widely the range of work of many servo-rheological devices such as dampers or car-springs. On the other hand, Bimgham fluids exlibiting an important shear stress threshold τ_0 at $\dot{\gamma} = 0$, could be useful in magnetic clutches. The next objectives are thus to control hoth appearence and organization of structurations inside the initial magnetic fluid, and to control phase separation dynamics.

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