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## Magnetic transient birefringence of ferrofluids : particle size determination

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**Résumé.** — Le temps de relaxation de la biréfringence magnétique de solutions de ferrofluide est mesurée pour des échantillons de polydispersité variée. Un diamètre hydrodynamique,  $d_H$ , des particules est déduit de l'expérience et est comparé à un calcul numérique avec une distribution log-normale. On en déduit que la relaxation de la biréfringence magnétique est une bonne technique pour sonder dans la distribution de taille des échantillons les particules les plus grandes. Lorsque cette distribution est étroite ( $\sigma \approx 0,25$ ), l'expérience est en bon accord avec le modèle :  $d_H$  est deux fois plus grand que le diamètre le plus probable.

**Abstract.** — Relaxation time measurements of magnetically induced birefringence of ferrofluid solutions are performed with samples of various polydispersities.  $d_H$ , the hydrodynamic diameter of particles deduced from experiments, is compared to a numerical computation with a log-normal distribution. Dynamic magnetic birefringence appears to be a good test of the tail of the sample size distribution. For a narrow distribution ( $\sigma \approx 0.25$ ), the experiment is in good agreement with the model:  $d_H$  is two times larger than the most probable diameter and corresponds to the largest particles in the sample.

### 1. Introduction.

Among experimental tools available for the study of colloidal solutions, transient birefringence measurement is a simple, fruitful and often used technique. Transient electric birefringence is presently well known through both theoretical and experimental studies [1-4]. If the studied colloidal solution is polydisperse, it is possible to perform different measurements in different and well defined asymptotic regimes where the signal decay is related to given order moments of the size distribution [3], allowing a complete characterization of the solution.

Transient magnetic birefringence, for its part, is a method of analysis of ferrofluid solutions. Ferrofluids are colloidal suspensions of monodomain magnetic grains of typical size 100 Å. Immersed in a constant magnetic field  $H$ , the magnetic moment of these grains tends to align along  $H$  through two different processes: Brownian rotation or Neel relaxation [5]. If Brownian relaxation is pre-

dominant, the solutions may exhibit an optical birefringence which saturates for magnetic fields ca.  $10^4$  Oe. In contrast with transient electric birefringence, the high-field asymptotic regime is quite inaccessible: for aqueous ferrofluids, a pulsed magnetic field of  $10^4$  Oe with a time cut-off of  $10^2$  ns would be required. It is then impossible to use this technique to determine the whole size distribution of particles. However the experiment in low and intermediate fields is relatively simple to set up and is frequently used as a characterization of ferrofluids [6-11]. The purpose of this paper is, with respect to previous studies on electric birefringence [3], to clarify the hydrodynamic size determined in the zero concentration limit, from transient magnetic birefringence. The hydrodynamic size deduced from these measurements is always much larger than sizes determined from electron microscopy or magnetization measurements, whatever the particle stabilization (electrostatic stabilization for ionic ferrofluids or polymeric one for surfacted ferrofluids). The disparity in diameter may vary by factors of 2 to 10. This difference is frequently ascribed to bound water surrounding ionic ferrofluid particles or to the poly-

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mer layer coating on surfacted ones. We show here that the low field range of experiments and polydispersity of ferrofluid particles, even for samples of narrow size distribution, give a much greater weight to large particles than to small ones. This kind of measurements appears to be a good test of the largest particles in the sample.

## 2. Ferrofluid characterizations.

Ferrofluid samples are never monodisperse and their size distribution is analysed using electron micrographs. Typical pictures usually show roughly spherical particles and lead to size histograms (cf. Fig. 1).

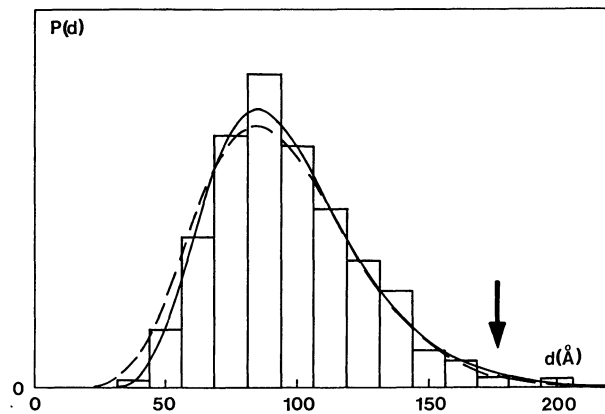


Fig. 1. — Histogram of the size distribution of particles from electron microscopy. The full line corresponds to a best fit of log-normal distribution  $P(d)$  ( $d_{mp} = 85 \text{ \AA}$ ,  $\sigma = 0.3$ ) and the dashed line to a gamma-distribution [3] of same  $d_{mp}$  and same width ( $\alpha = 10$ ). Both of these distributions are equivalent in the whole paper. The arrow points to the calculated  $d_H$  value ( $d_H = 177 \text{ \AA}$ ) using  $P(d)$  (cf. Sect. 4).

It is convenient to use an analytical distribution function in which the width and the position of maximum are characterized by two adjustable parameters. For ferrofluid samples, and whatever the way of preparation of these fine particles, a log-normal distribution of diameters  $P(d)$  is frequently assumed [12]:

$$\frac{P(d)}{P(d_{mp})} = \exp\left(-\frac{1}{2\sigma^2} \ln^2\left(\frac{d}{d_{mp}}\right)\right) \quad (1)$$

where  $d_{mp}$  is the most probable value of the particle diameter  $d$  and  $\sigma$  is the standard deviation of  $\ln(d)$ . The maximum value of  $P(d)$  is

$$P(d_{mp}) = (d_{mp} \sigma \sqrt{2\pi} \exp(\sigma^2/2))^{-1}$$

and

$$\int_0^{+\infty} P(d) \cdot dd = 1.$$

This size distribution may be tested through other measurements, such as variations *versus* magnetic field  $H$  of magnetization  $M(H)$  or static birefringence  $\delta n(H)$  [13-16]. Ferrofluid particles are magnetic monodomain grains. They bear a magnetic moment  $\mu$ , the magnitude of which is:

$$\mu(d) = m_s \frac{\pi d^3}{6} \quad (2)$$

where  $m_s$  is the saturation magnetization of the grain material. Each ferrofluid particle has an optical anisotropy  $\delta\alpha$  arising from either a crystalline or a shape anisotropy. For a dilute enough solution, the influence of polydispersity on the magnetization curve and static birefringence may be taken into account by the following averages:

$$\begin{cases} M(H) = \int_0^{+\infty} M(d, H) P(d) dd \\ \delta n(H) = \int_0^{+\infty} \delta n(d, H) P(d) dd \end{cases} \quad (3)$$

with

$$\begin{cases} M(d, H) = m_s \phi(d) \left(\operatorname{ctgh} x - \frac{1}{x}\right) \\ \delta n(d, H) \propto \delta\alpha \phi(d) \left(1 - \frac{3}{x} \operatorname{ctgh} x + \frac{1}{x^2}\right) \end{cases} \quad (4)$$

where

$$x = \frac{\mu(d) H}{k_B T} \quad (5)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the temperature.  $\phi(d)$  is the volume of a particle, of diameter  $d$ , times the total number of particles per unit volume.  $\phi(d)$  is dependent on the particle size,  $\phi(d) \propto d^3$ , and the ferrofluid volumic fraction  $\phi$  is equal to

$$\int_0^{+\infty} \phi(d) P(d) dd.$$

A fit between calculated and experimental curves allows the determinations of the parameters  $d_{mp}$  and  $\sigma$  [13-16] (\*). For the ionic ferrofluid samples used in this study, magnetization and static birefringence measurements lead to comparable  $\sigma$  values. As both methods take into account all the small aggregates of the ferrofluid solution, this distribution width  $\sigma$  is slightly larger than that deduced from electron microscopy [13]. On the contrary  $d_{mp}$  values determined from static birefringence are approximately

(\*) If in [14], as in [17], the size dependence of  $\phi(d)$  is taken into account, it is frequently omitted [13, 15, 16]: it does not affect  $\sigma$  determinations but the deduced  $d_{mp}$  values have to be modified by a multiplying factor:  $\exp(-3\sigma^2)$  (see Appendix I).

35 % larger than those determined from the magnetization curve [13, 16]. This may be explained by the details of particle rotation (cf. Sect. 4).

Now if a square pulse of magnetic field  $H$  is applied to the ferrofluid solution [10, 11], magnetic particles first tend to align along the field leading to birefringence  $\delta n(H)$  (cf. Exprs. (3) and (4)), and, as the field is switched off, they thermally relax to random directions; birefringence exponentially decreases according to Perrin's law [18]. The signal has the following time dependence :

$$\delta n(t) = \delta n(d, H) e^{-t/\tau(d)} \quad (6)$$

with a characteristic time  $\tau(d)$  equal to

$$\tau(d) = \frac{\pi}{6} d^3 \frac{\eta}{k_B T} \quad (7)$$

where  $\eta$  is the viscosity experienced by the particles in the fluid.  $\tau(d)$  is related to  $D$ , the rotational diffusion coefficient of the particles through the relation :  $\tau(d) = (12 D)^{-1}$ . In the quantity  $\delta n(t)$ , the polydispersity of the samples modifies both

$\delta n(d, H)$  and  $\tau(d)$ . Taking into account this polydispersity, the time dependence of the birefringent pulse becomes :

$$\Delta n(t) = \int_0^{+\infty} \delta n(d, H) e^{-t/\tau(d)} P(d) dd . \quad (8)$$

Owing to the size distribution,  $\Delta n(t)$  is not a simple exponential function of time. Anyway, in order to characterize  $\Delta n(t)$ , one can use the shortest time  $\tau_H$  deduced from the initial slope of the function  $\ln(\Delta n(t))$  versus  $t$  [4.a], an average being made on the first 60 % of the variations (cf. Fig. 2). The determination of  $\tau_H$  leads to the diameter  $d_H$  deduced according to (7) :

$$\tau_H = \frac{\pi}{6} \frac{\eta}{k_B T} d_H^3 . \quad (9)$$

These experimental determinations of hydrodynamic diameters deduced from magnetic birefringence relaxation, from the literature, are presented in table I. Till now the large difference between  $d_H$  and the physical, or magnetic diameter of particles, sometimes up to a factor of 10, has not been satisfactorily accounted for. The disparity is never less than a factor of 2 (see for example [11]).

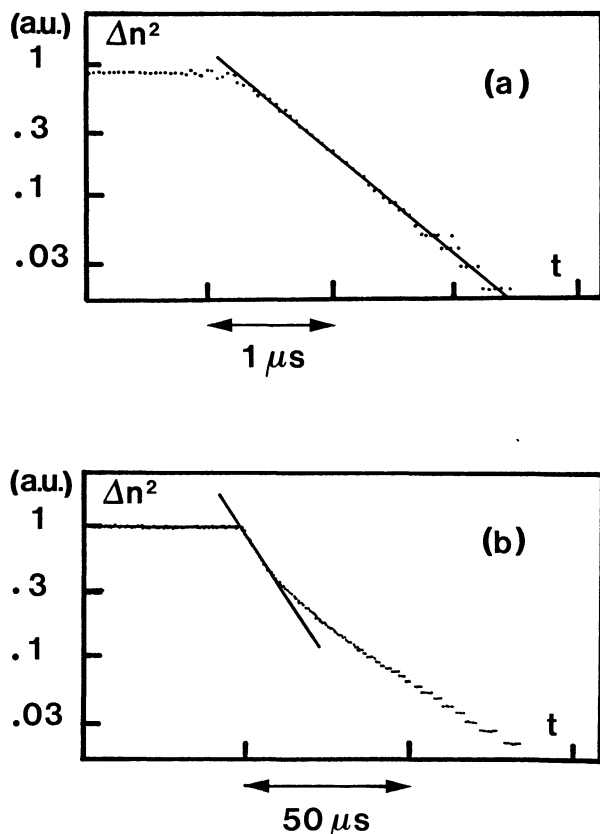


Fig. 2. — Semi-logarithmic plot of the birefringence decay versus  $t$ .  $\tau_H$  is deduced from the initial slope (full line); with the experimental device used the signal is proportional to  $(\Delta n)^2$  and the relaxation time is  $\tau_H/2$  (see [11]). (a)  $d_{mp} = 85 \text{ \AA}$ ;  $\sigma = 0.25$ ;  $\tau_H = 1.14 \text{ \mu s}$ . (b)  $d_{mp} = 75 \text{ \AA}$ ;  $\sigma = 0.4$ ;  $\tau_H = 23 \text{ \mu s}$ .

Table I. — Comparison between experimental  $d_H$  and  $d_{mp}$  measurements in the literature.  $d_{mp}$  are determined from magnetic measurements. Ratios in brackets correspond to the  $d_{mp}$  determination from electron microscopy.

Ref.	Solvent	$d_H/d_{mp}$
[7] (**)	kerosene	15
[8] (**)	min. oil	11
[9] (**)	water	1.7
[6]	diester	3.1
[10]	toluene + polym. (*)	2.1 (1.6)
[10]	water	1.8 (3)
[11]	water	2.4 (2.3)

(\*) In [10] the viscosity used in the  $d_H$  derivation is the macroscopic viscosity of the polymeric solution. There is no evidence that the ferrofluid probes experience this macroscopic viscosity and not a local viscosity close to the solvent one. This would enhance even more the ratio  $d_H/d_{mp}$ .  
 (\*\*) Values from Table II of [6].

In order to clarify the effect of sample polydispersity on the dynamic magnetic birefringence, systematic hydrodynamic measurements are performed on ionic ferrofluids of various size distributions.

### 3. Experiments.

The samples are aqueous  $\gamma\text{-Fe}_2\text{O}_3$  ferrofluids obtained using a chemical synthesis described in [19-21]. Their size distribution is tested using various techniques: electron microscopy, magnetization and, for a few samples, static birefringence measurements as in [13]. The saturation magnetization of the particles is found to be equal to  $4\pi m_s = (3.4 \pm 0.5) 10^3 \text{ G}$ . Remanent magnetization measurements on frozen solutions at low temperatures show [13] that the anisotropy constant of isolated particles is the same as in bulk material without any shape anisotropy contribution. The experimental apparatus used for hydrodynamic measurements is the short time set-up fully described in [11]. The magnetic pulse is of order 100 Oe and its duration is large enough in order that the equilibrium birefringence  $\delta n(H)$  is reached before the relaxation measurement.  $\tau_H$  is deduced from the initial slope of  $\ln(\Delta n(t))$  versus  $t$  (cf. Exprs. (8) and (9) and Fig. 2). The sample volume fraction is always less than 2%. In this concentration range no interaction effect is detected on  $\tau_H$  within the error bar of the experiment:  $\Delta\tau_H/\tau_H \approx 10\%$ .

An extensive study is performed for samples of different  $\sigma$  and different  $d_{mp}$  (cf. Tab. II). In figure 3, experimental determinations of  $\tau_H$  are plotted versus  $d_{mp}$  on a log-log scale.  $d_{mp}$  and  $\sigma$  are determined from the analysis of the magnetization curve of the samples. For comparison a measurement made with a surfacted ferrofluid ((O):  $d_{mp} = 73 \text{ \AA}$ ;  $\sigma = 0.3$ ) is plotted in the same figure. This experiment is performed in decaline and the value of  $\tau_H: 2.2 \mu\text{s}$ , in figure 3, is equivalent to that of the water relaxation time taking into account the viscosity ratio between water and decaline. This shows that measurements on ionic aqueous ferrofluids are very similar to those on surfacted ferrofluids.

Qualitatively the values of  $d_H$  are much larger

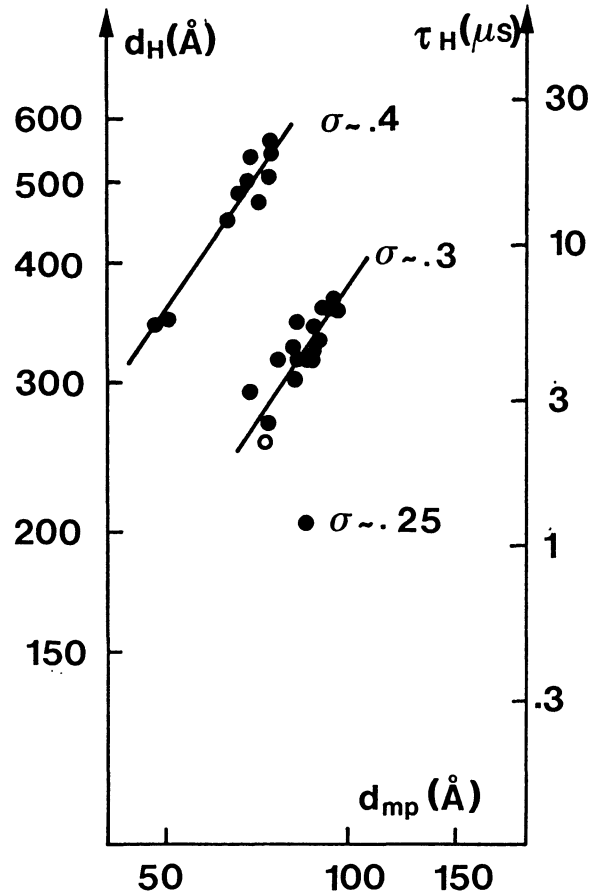


Fig. 3. — Experimental variation of  $\tau_H$  (and  $d_H$ ) versus  $d_{mp}$  for ionic ferrofluids ( $\bullet$ ) of different  $\sigma$ .  $d_{mp}$  and  $\sigma$  are determined through magnetization measurements; ( $\circ$ ): surfacted ferrofluid in decaline, a viscosity correction is performed in order to obtain an equivalent water relaxation time. The full lines are guides for the eye corresponding to  $d_H/d_{mp} = \text{cte}$ .

than those of  $d_{mp}$ . Samples of the same  $d_{mp}$  have very different experimental relaxation times  $\tau_H$  if their

Table II. — Comparison between experimental  $d_H$  and  $d_{mp}$  measurements for ionic ferrofluid samples.

$\sigma = 0.25$ (*)		$\sigma = 0.3$		$\sigma = 0.4$	
$d_H/d_{mp} = 2.4$		$d_H/d_{mp} = 3.8$		$d_H/d_{mp} = 7.2$	
$d_{mp}$ ( $\text{\AA}$ )	$\tau_H$ ( $\mu\text{s}$ )	$d_{mp}$ ( $\text{\AA}$ )	$\tau_H$ ( $\mu\text{s}$ )	$d_{mp}$ ( $\text{\AA}$ )	$\tau_H$ ( $\mu\text{s}$ )
85	1.14	95	6	75	20
		90	5	70	16
		85	4.3	65	13
		75	3	50	5.5

(\*) Measurements of [11].

The accuracy on  $d_{mp}$  and  $\tau_H$  measurements is 10%. A given value of  $\sigma$  corresponds to a given value of ratio  $d_H/d_{mp}$ , as experimentally (cf. Fig. 3)  $d_H$  is roughly proportional to  $d_{mp}$ ,  $\sigma$  being constant.

Samples of standard deviation  $\sigma \approx 0.5$  lead to experimental values of  $\tau_H$  very close to these of  $\sigma \approx 0.4$  samples: log-normal distribution does not account correctly for the tail of the distribution for large  $\sigma$ .

distribution widths are different. The experimental ratio  $d_H/d_{mp}$  varies from 2.4 for  $\sigma = 0.25$  to 7.2 for  $\sigma = 0.4$ .

4. Discussion.

From expressions (8) and (9), the relaxation time  $\tau_H$  may be computed. In a very similar way as in [3] for transient electric birefringence, one obtains that if  $t/\tau(d) \ll 1$  for any  $d$ ,  $\tau_H$  does not depend on the magnetic field  $H$  except in the two limits  $x \ll 1$  and  $x \gg 1$  where  $d_H = kd_{mp}$ ,  $k$  being a numerical constant which is only a function of the size distribution width :

— if  $x \ll 1$ , then  $\delta n(d, H) = \delta n_0 \phi(d) \frac{x^2}{15}$  and  $k = \exp(25.5 \sigma^2/3)$   
 — if  $x \gg 1$ , then  $\delta n(d, H) = \delta n_0 \phi(d)$  and  $k = \exp(7.5 \sigma^2/3)$ .

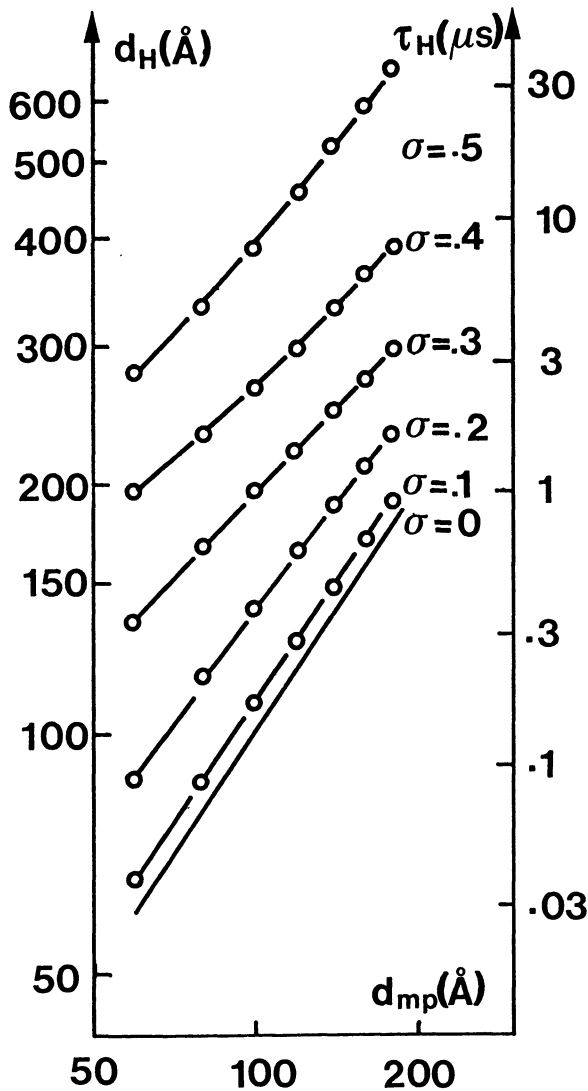


Fig. 4. — Calculated variations of  $\tau_H$  and  $d_H$  (cf. formulae (8) and (9)) versus  $d_{mp}$  using a log-normal distribution  $P(d)$  with various  $\sigma$  values.

Unfortunately, in usual experiments, the situation is in between, moreover  $t/\tau(d) \sim 1$  for some  $d$ . Thus a complete calculation has to be performed, the result of which is given on a log-log scale in figure 4 with the following parameters :  $4 \pi m_S = 3400 \text{ G}$  ;  $H = 100 \text{ Oe}$  ;  $\eta = 10^{-2} \text{ Po}$  ;  $T = 295 \text{ K}$ .  $d_H$  is no more strictly proportional to  $d_{mp}$  and depends on the magnetic pulse intensity. However this influence is relatively weak in this range as lowering  $H$  by a factor of 2 only induces a 10% increase of  $d_H$ . The disparity between  $d_H$  and  $d_{mp}$  varies by upto a factor of 4 as the distribution broadens. Practically, for a ferrofluid sample,  $\sigma$  may vary from 0.2 to 0.5 :  $\sigma = 0.1$  is unrealistic,  $\sigma = 0.2$  corresponds to a very narrow distribution and is quite rare,  $\sigma = 0.5$  on the contrary corresponds to an extremely broad distribution. If an external layer of water or polymer with a thickness  $e = 5 \text{ \AA}$  is introduced in the relaxation time calculation, replacing  $\tau(d)$  by  $\tau(d + 2e)$  in expression (8), it only produces an increase of  $d_H$  of the order of less than  $2e/d_H$  ; that is a 10% increase for  $d_{mp} = 100 \text{ \AA}$  and an ideal sample of  $\sigma = 0$ , but only a 2% increase if  $\sigma = 0.5$ . The influence on  $d_H$  of such an external layer is thus much lower than the polydispersity effect as calculated from expression (8).

This birefringence relaxation leads to a determination of the particle diameter  $d_H$  much larger than  $d_{mp}$ , the most probable diameter of the size distribution. In figure 1, the arrow corresponds to the calculated  $d_H$  value using the log-normal distribution found from electron microscopy measurements ; this shows that  $d_H$ , or identically  $\tau_H$ , determinations mainly probe the tail of the size distribution. The pulse of the magnetic field, due to its low intensity, only induces a birefringent signal from the largest particles.

Measurements on figure 3 and calculations of figure 4 qualitatively exhibit the same behaviour leading to values of  $d_H$  much larger than those of  $d_{mp}$ . Samples of the same  $d_{mp}$  have very different experimental relaxation times  $\tau_H$  if their distribution widths are different. However a direct comparison does not work quantitatively ; two reasons may be put forward :

- (a) the details of the particle rotation in a magnetic birefringence experiment.
- (b) the validity of a log-normal distribution for the tail of the largest particles in the samples.

a) When immersed in a constant magnetic field  $H$ , the magnetic moments of ferrofluid particles tend to align along the field. They may achieve thermal equilibrium through two different processes [5] : Brownian rotation or Néel relaxation, leading respectively to extrinsic and intrinsic superparamagnetism :

— for Brownian rotation, moment alignments are achieved by a rotation of the whole particle in the carrier liquid ; the magnetic moment is locked in an easy direction of magnetization.

— Néel relaxation is a rotation of the magnetic moment away from the easy direction within the particle. This rotation is hindered by an energy barrier of  $KV$ ,  $K$  and  $V$  ( $V = \pi d^3/6$ ) being respectively the anisotropy constant and the volume of a particle. A characteristic time of the Néel process is  $\tau_N \sim \tau_0 \exp(KV/k_B T)$  with  $\tau_0 \sim 10^{-9}$  s.

In a liquid solution both mechanisms occur, the dominant process being determined by the shortest characteristic time. For large values of  $KV/k_B T$ , the Brownian rotation of the whole particle is the dominant behaviour and for low values of  $KV/k_B T$ , the Néel relaxation of the magnetic moment is the dominant one, the boundary between these two ranges being dependent on the time scale of the experiment [22].

If the particles are trapped in a tight polymeric array, Brownian rotation is locked and Néel relaxation only subsists. A typical ionic ferrofluid solution of  $d_{mp} \approx 100$  Å immersed in a magnetic field exhibits a magnetization and becomes birefringent. If these same ferrofluid particles are prevented from moving by being quenched in a gel network (gelatine of a mesh size smaller than the particles), the system does not exhibit a birefringent signal any more but still exhibits magnetization [13]. Birefringence is thus only due to the mechanical rotation of the grains and has a dielectric physical origin (as far as magnetic particles are roughly spherical).

In liquid solutions, the particles contributing to the birefringent signal are only those for which the Brownian rotation is the dominant behaviour : the particles with a diameter larger than  $d_S$ , the so-called Shliomis diameter [22]. Thus in expressions (3) and (8), the lower limits of the birefringence integral should be taken equal to  $d_S$ . In expression (3) it is usually not done and this explains why the maximum  $d'_{mp}$  of the particle size distribution deduced from static birefringence is found to be 1.35 times larger than  $d_{mp}$ , the one deduced from the magnetization measurements : the dominant process of the smaller particles is the Néel relaxation ; thus they contribute to the magnetization but not to the birefringent signal. So a better representation of figure 3 would be obtained using birefringence  $d'_{mp}$  values. This change applied to the ionic samples of  $\sigma = 0.25$  and  $d'_{mp} = 115$  Å leads to a better agreement between calculation ( $d_H = 190$  Å) and experiment ( $d_H = 205$  Å). The difference in  $d_H$  is close to the error bar ( $\sim 10$  Å) and may be explained by the existence of a water layer bounded to the grain.

b) The previous remark leads to an agreement between experiments and calculations for less polydisperse samples, but it is not sufficient to

explain the discrepancy for larger values of  $\sigma$ . Thus a log-normal law may not be a good enough description for the tail of sample distribution which is essentially probed in these dynamic birefringence measurements (in opposition to electron microscopy measurements, for example, which test the more numerous particles (cf. Fig. 1)). A slight deviation in the tail of the log-normal distribution, imperceptible in a magnetization curve, can strongly modify the dynamic birefringence.

Thus for samples of very narrow distribution, the experimental determinations of  $d_H$ , which is twice larger than  $d_{mp}$ , are well explained with the size distribution of expression (1). On the contrary, the samples of very broad distribution exhibit a tail of larger particles ill-described by a log-normal law. This tail may contain small aggregates [13] which cannot be distinguished from single particles in a birefringence relaxation measurement. As these small aggregates frequently adopt chain conformations [23, 24], they may exhibit a shape anisotropy which could explain the large  $d_H$  values of the more polydisperse samples.

As dynamic birefringence relaxation is very sensitive to the largest particles in solution, it appears to be a powerful technique to establish the tail of a sample size distribution. It may be important, for example, in the analysis of the onset of remanent magnetization of frozen ferrofluids [13] or in the study of phase separation induced, for ionic ferrofluids, by an excess of counterions in solution [25].

## 5. Conclusion.

Experimental measurements of ferrofluid birefringence relaxation have been performed with samples of various polydispersities. Due to this sample polydispersity and to the small magnetic pulse intensity, the deduced particles diameter  $d_H$  is always much larger than  $d_{mp}$ , the most probable diameter. Even with a sample of size distribution as narrow as  $\sigma = 0.25$ , the difference between  $d_H$  and  $d_{mp}$  is as large as a factor of 2 : this is well explained by calculations and the details of the particle rotation.

Birefringence relaxation allows a determination of the hydrodynamic size of the largest particles in solution, these being either isolated grains or small aggregates of a few grains. With respect to the classical size determinations, through electron microscopy or magnetization measurements, this determination leads to additional information on the samples as it probes the tail of the size distribution.

## Acknowledgment.

We are greatly indebted to V. Cabuil and R. Massart for providing us with the ionic ferrofluid samples and to K. Raj (Ferrofluidic Co.) for the surfactant sample.

**Appendix 1.**

Variations of magnetization  $M(H)$  and static birefringence  $\delta n(H)$  versus magnetic field may be calculated using expressions (3) and (4). If a log-normal distribution  $P(d)$  (cf. formula (1)) is assumed for the ferrofluid sample, ratios of  $M(H)$  and  $\delta n(H)$  to their saturation values are equal to

$$\frac{M(H)}{m_s \int_0^{+\infty} \Phi(d) P(d) dd} = f\left(m_s \frac{d_{mp}^3 H}{k_B T}, \sigma\right)$$

$$\frac{\delta n(H)}{\delta \alpha \int_0^{+\infty} \Phi(d) P(d) dd} = g\left(m_s \frac{d_{mp}^3 H}{k_B T}, \sigma\right) \quad \text{i)}$$

where  $f$  and  $g$  are function of the two same variables. If, as in [11], the size dependence of  $\phi(d)$  is omitted, expressions i) may be written as :

$$\frac{M(H)}{m_s \phi} = f\left(m_s \frac{d_1^3 H}{k_B T}, \sigma\right)$$

$$\frac{\delta n(H)}{\delta \alpha \phi} = g\left(m_s \frac{d_1^3 H}{k_B T}, \sigma\right) \quad \text{ii)}$$

where functions  $f$  and  $g$  are the same as in expressions i) with  $d_{mp} = d_1 e^{3\sigma^2}$ .  $\sigma$  determinations are thus not affected by a fit of experimental curves to expressions ii) instead of expressions i). On the contrary, the deduced  $d_{mp}$  values are too large by a factor of  $\exp(3\sigma^2)$ .

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