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Ferrofluid viscometer

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Résumé. — L'alignement de particules colloïdales magnétiques suivant un champ magnétique induit une biréfringence de la solution. Lorsque ce champ est coupé, le niveau de biréfringence décroît exponentiellement avec un temps de relaxation proportionnel à la viscosité de la solution. La mesure de ce temps caractéristique conduit à une détermination de la viscosité avec une précision relative de 5 % et ce, sur environ sept décades de variation de viscosité.

Abstract. — The alignment of magnetic colloidal particles along a magnetic field induces a birefringence of the solution. As the magnetic field is switched off, this birefringence level relaxes to zero with a characteristic time proportional to the viscosity of the solution. The measurement of this relaxation time gives the value of the viscosity with a relative accuracy of 5 % and over a viscosity range of seven decades.

We describe here a new method to measure the local viscosity of a liquid. The principle is founded upon the determination of the relaxation time of small magnetic particles in suspension in the studied medium. In a constant magnetic field these ferrofluid particles behave as magnetic dipoles and experience a couple which tends to align these along the field. Then the suspension exhibits an optical birefringence. As the magnetic field is removed, the dipoles randomly relax by Brownian motion and the suspension birefringence decays to zero with a characteristic time proportional to the viscosity of the carrier liquid.

This method turns a viscosity measurement into an optical birefringence measurement with many advantages :

- i) no mechanical movement is needed [1];
- ii) the use of a laser beam for the birefringence measurement allows a viscosity determination in a small volume : the few mm³ of the laser beam in the liquid ;
- iii) as the size of the magnetic probe is of order 100 Å, the measured viscosity is a local one.

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1. Ferrofluid.

The most important part of the method is to add the ferrofluid to the liquid to be studied.

A ferrofluid (or magnetic colloid) is a colloidal suspension of magnetic monodomain particles dispersed in a carrier liquid. We use aqueous ionic ferrofluids synthesized in a simple chemical way [2]. Coprecipitation in an alkaline medium of a Fe^{2+} - Fe^{3+} mixture leads to ferrimagnetic macroions of $\gamma\text{-Fe}_2\text{O}_3$. If the electrostatic interactions between the polar solvent and the solute [3] are strong enough, these macroions stay in solution. This kind of ferrofluid may be obtained in alkaline medium as a macroanion suspension or in acidic medium as a macrocation suspension and is suitable for measurements in aqueous media. In order to solubilize the magnetic particles in organic media, they are usually coated with a layer of surfactant, oleic acid. This is possible with ionic ferrofluids [4] which may be obtained in most organic liquids.

The ferrofluids always present a certain polydispersity with a particle size distribution. Usually a log normal distribution of spherical grain diameters d is used to describe the samples :

$$P(d) = \frac{1}{\sqrt{2} \pi \sigma d} \exp\left(-\frac{1}{2 \sigma^2} \ln^2\left(\frac{d}{d_0}\right)\right). \quad (1)$$

The maximum of the distribution corresponds to a diameter $d_0 e^{-\sigma^2}$ and σ is the standard deviation. As a characterization of the sample a determination of these two parameters may be realized by electron microscopy and magnetization measurements [5]. The chemical synthesis allows a control of these characteristics [6] : the mean magnetic diameter may vary from $\sim 30 \text{ \AA}$ to $\sim 150 \text{ \AA}$ and also the width of the distribution from $\sigma \simeq 0.5$ to $\sigma \simeq 0.25$.

2. Relaxation time of the optical birefringence.

The method of viscosity study, which is described here, is a relaxation time measurement of the optical birefringence induced by the magnetic grains dispersed in the analysed medium. The volumic fraction of particles lays between 10^{-3} and 10^{-4} and does not modify the macroscopic viscosity of the liquid : from Einstein law [7] the relative viscosity variations would be much less (2.5×10^{-3} to 2.5×10^{-4}) than the measurement accuracy.

As a constant magnetic field $\mathbf{H}$ is applied, the ferrofluid particles tend to align along the field, following a paramagnetic Langevin behaviour ; the medium is then birefringent with a level of birefringence $\Delta n_0(H)$. If the magnetic field is removed, the ferrofluid particles thermally relax towards random directions and the birefringence Δn decreases according to Perrin's law [8] :

$$\Delta n = \Delta n_0 \exp(-6 D t) \quad (2)$$

where Δn_0 depends on H and on the magnetic probes, and where D is the diffusion coefficient of Brownian rotation of a ferrofluid particle.

$$D = k_B T / 8 \pi \eta R_H^3 \quad (3)$$

η is the viscosity of the carrier liquid, k_B the Boltzmann constant, T the temperature, and R_H the hydrodynamic radius of a ferrofluid particle. The relaxation time of birefringence is defined as $\tau_R^{-1} = 6 D$:

$$\tau_R = \frac{4}{3} \pi R_H^3 \cdot \frac{\eta}{k_B T}. \quad (4)$$

For a typical hydrodynamic radius $R_H = 100 \text{ \AA}$, τ_R may vary from a microsecond for a carrier liquid viscosity close to water-viscosity ($\sim 10^{-2} \text{ Po}$) till times as long as a few minutes for very viscous liquids ($\sim 10^5 \text{ Po}$).

e being the sample thickness. For sample thicknesses thin enough in order that $\varphi/2 \ll 1$, it is experimentally verified by a dichroism measurement that for our ferrofluids the dichroism factor [term (a) in formula (5)] is negligible with respect to the birefringence factor [term (b) in formula (5)]. Then formulae (2), (4), (5) and (6) simplify and give :

$$I \propto (E_0 e \Delta n_0)^2 e^{-2t/\tau_R}. \quad (7)$$

Thus, in this experiment, the characteristic time of the intensity decay is equal to $\tau_R/2$. We have to notice that the pulse duration must be large enough in order that the equilibrium value Δn_0 is reached. As the larger characteristic time of the rising up signal is $3 \tau_R$ [9], a duration larger than $10 \tau_R$ is required. This experimental set up allows measurements of birefringence relaxation times τ_R from $0.5 \mu\text{s}$ to 1 ms . In figure 2 the intensity pulse and its decay analysis are presented for a ferrofluid sample of thickness $e = 1 \text{ cm}$ and of concentration 0.06% in volume, in water at 20°C . The exponential relaxation of the signal is sensitive to the sample polydispersity ($\tau_R \propto R_H^3$). For this ferrofluid of narrow size distribution ($\sigma \simeq 0.25$), the intensity relaxation may be analysed with a single relaxation time within two orders of magnitude of the signal. The characteristic time deduced $\tau_R = 1.14 \pm 0.06 \mu\text{s}$ leads, taking into account the accuracy of viscosity measurements, to an hydrodynamic radius $R_H = 103 \pm 3 \text{ \AA}$. This R_H value is compatible with quasielastic light scattering measurements realized on the same sample (¹).

4. Long time experimental set up ($\tau \gtrsim 100 \mu\text{s}$) and birefringence measurement.

The experimental set-up is schematized in figure 1c. The optical system is now composed of a polarizer (P), a photoelastic modulator (PEM), which modulates at 50 kHz the phase of the

Fig. 2. — Intensity pulse *versus* time as recorded by the boxcar (a) and decay analysis of the pulse (b) on a semi-logarithmic scale. For this sample (see text) the decay is exponential with a single relaxation time $\tau_R/2 = 0.57 \pm 0.03 \mu\text{s}$ (straight line).

(¹) In a quasielastic light scattering experiment a translational diffusion coefficient is measured which is proportional to R_H^{-1} . It is, as a matter of fact, less sensitive to polydispersity than the rotational diffusion coefficient measured in the birefringence experiment and which is proportional to R_H^{-3} .

signal between two perpendicular directions, and then the sample (S), the analyser (A) and the photocell (PC).

The lock in amplifier (LA) compares the electric signal from the photocell to the reference signal from the modulator. As the magnetic field is switched off, the output of the lock-in amplifier is recorded through a transient analyser.

A possible optical set-up with the axes of magnetic field $\mathbf{H}(=\mathbf{u}_{\parallel})$, polarizer $\mathbf{\Pi}_p(=\mathbf{u}_{\perp})$, analyser $\mathbf{\Pi}_A$ and photoelastic modulator ($\mathbf{X} = \mathbf{\Pi}_A$, $\mathbf{Y}$) is sketched in figure 1d; the electric field $\mathbf{E}$ at the output of the modulator is :

$$\mathbf{E} = \frac{E_0}{\sqrt{2}}(\mathbf{X} + \mathbf{Y} e^{i\delta}) \quad (8)$$

with $\delta = a \sin \omega t$ and $\omega/2\pi = 50$ kHz. After crossing the sample, the electric field is then :

$$\mathbf{E}_1 = \frac{E_0}{2}(\sqrt{t_{\parallel}}(e^{i\delta} - 1)\mathbf{u}_{\parallel} + \sqrt{t_{\perp}}(e^{i\delta} + 1)e^{i\varphi}\mathbf{u}_{\perp}).$$

At the analyser output $\mathbf{E}_1$ becomes :

$$\mathbf{E}_2 = \frac{E_0}{2\sqrt{2}}(\sqrt{t_{\parallel}}(1 - e^{i\delta}) + \sqrt{t_{\perp}}(1 + e^{i\delta})e^{i\varphi})\mathbf{X}.$$

The light intensity I collected by the photocell is :

$$I = \frac{E_0^2}{4} (t_{\parallel}(1 - \cos \delta) + t_{\perp}(1 + \cos \delta) - 2\sqrt{t_{\parallel}t_{\perp}} \sin \varphi \sin \delta).$$

Expanding $\cos \delta$ and $\sin \delta$ in terms of Bessel functions :

$$I = \frac{E_0^2}{4} \left(\{ (t_{\perp} + t_{\parallel}) + (t_{\perp} - t_{\parallel}) J_0(a) \} - 4\sqrt{t_{\parallel}t_{\perp}} J_1(a) \sin \varphi \sin \omega t + 2(t_{\perp} - t_{\parallel}) J_2(a) \cos 2\omega t \right). \quad (9)$$

Thus intensity component I_2 at pulsation 2ω is proportional to the sample dichroism whereas the intensity component I_1 at pulsation ω is related to the sample birefringence ($\varphi \propto \Delta n$, cf. (6)). For a modulation $a = \pi/2$, $J_1(a) = 0.56$ is close to its maximum and the I_1 component is optimized. As for our ferrofluids $|\sqrt{t_{\parallel}} - \sqrt{t_{\perp}}| \ll \sqrt{t_{\parallel}} \approx \sqrt{t_{\perp}}$, I_1 is proportional to $\sin \varphi$. For thin enough samples $\varphi \ll 1$, formulae (2), (4) and (6) simplify into :

$$I_1 \propto e \Delta n_0 e^{-t/\tau_R}.$$

This experimental set-up allows measurements of birefringence relaxation times τ_R from 100 μ s to several minutes.

5. Efficiency of the measurements.

To test our technique we perform a measurement of glycerol viscosity *versus* temperature. Glycerol exhibits a vitreous transition at $T_g = -88$ °C. As temperature T decreases, glycerol viscosity η drastically increases from 6.3 Poises at 30 °C to 6.7×10^4 Poises at -42 °C [10]. So these four decade variations of viscosity are a good test of the method. In figure 3 our measurements of τ_R , as well as the experimental values of glycerol viscosity from reference [11], are plotted *versus* T .

Fig. 3. — Semi-logarithmic plot of relaxation time τ_R (vertical left axis) and of viscosity η (vertical right axis) versus temperature T for glycerol. (O : our measurements, full line represents the experimental values of η from Ref. [11].)

The accordance between the two sets of experimental values, over the whole range of measurements is simply obtained, in this semilogarithmic plot, with a vertical translation. This corresponds to the proportional relationship between τ_R and η through the hydrodynamic radius R_H of the probe (expressions (3) and (4)). From these measurements in glycerol, we get a value $R_H = (100 \pm 5) \text{ \AA}$ in accordance with the one we get with the same probe in water (short time experiment). This allows to say that the method works from short times ($\tau_R \sim 1 \mu\text{s}$, $\eta \sim 10^{-2}$ Poises) to long ones ($\tau_R \sim 1 \text{ mm}$, $\eta \sim 10^5$ Poises), i.e. on a viscosity range of seven decades.

We have to notice that an extension of this method has already been used to measure weak elastic constants (from 1 dyne/cm^3 to 10^3 dynes/cm^3) in the study of the sol-gel transition in gelatin [12]. At a given magnetic field, the birefringence level is related to a competition between magnetic energy of grains and elastic energy of the polymeric gel array.

6. Conclusion.

This method allows viscosity measurements from 10^{-2} Poise to 10^5 Poises. Relative measurements are obtained with an accuracy $\Delta\eta/\eta \simeq \pm 5\%$ using a ferrofluid probe of $\sigma = 0.25$. For absolute measurements, the accuracy is related to the knowledge of the hydrodynamic radius which can be measured using a viscosity standard.

One of the main limitations of the method is the chemical compatibility between the studied medium and the ferrofluid probes. It must be noted that polydispersity of the magnetic grains drastically influences the shape of the birefringence relaxation and that a sample of at least $\sigma \simeq 0.3$ must be used in order to get an exponential relaxation with only one characteristic time.

On the other hand, the advantages of this method are numerous :

- local viscosity measurement in a few mm^3 volume;
- use of a 100 Å probe;
- no mechanical system necessary;
- a simple extension to measurements of weak elastic constants.

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