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STRESS RELAXATION FUNCTION RESPONSE OF FERROFLUIDS IN THE PRESENCE OF A MAGNETIC FIELD TO TRANSIENT SHEAR FLOWS: STEP STRAIN AND OSCILLATORY SHEAR.

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Abstract. *In this article, the rheological response of two commercial ferrofluids to transient shearing flows is experimentally evaluated using a parallel disc rheometer device equipped with a magnetic cell. The basic difference between the ferrofluids is their volume fraction of magnetic particles. The ferrofluids are composed of magnetic magnetite nanoparticles with a high magnetization of saturation. Samples of both ferrofluids are tested according to two experimental protocols of the Laboratory of Microhydrodynamics and Rheology of the University of Brasília. The first transient shear flow explored is a step-strain under the influence of a magnetic field, from which the stress relaxation functions for both magnetic fluids tested are determined in terms of the magnetic field strength and the intensity of the step strain. The relaxation times of the fluids are calculated. For both ferrofluids, the main relaxation times present a nonlinear increase as the intensity of the magnetic field heightens. We also observed that the shear stress relaxes to a residual stress which is strongly dependent on both field strength and strain strength. This uncommon residual stress increases as the intensity of the magnetic field rises. In terms of strain strength, the residual stress is found to present two interesting behaviors. First, for small values of strain, the residual stress increases linearly until a maximum is reached. Further increases in the strain strength led to a nonlinear decrease in the residual stress. The linear regime was associated with a predominance of elastic deformation of the fluid microstructure while the nonlinear one to its plastic deformation or even to the break-up. The second procedure refers to tests under the condition of oscillatory shear in a linear viscoelastic regime and in the presence of an applied magnetic field. The main viscoelastic modulus of the ferrofluids as functions of the frequency and the magnetic field intensity is presented. Besides, it is also shown, for both ferrofluids, that viscous and elastic characteristics are severely increased when the applied magnetic field intensity is enhanced. Compatibility checks between the viscous modulus and the apparent shear viscosity under conditions of the same frequency and shear rate are performed and the first normal stress difference is calculated using Laun's rule. The presence of normal stresses indicates that the microstructure of the fluid may drastically change to a configuration of strongly anisotropic structures (chain-like) in the presence of an external magnetic field and under the condition of weak flows.*

Keywords: *Ferrofluids, Stress relaxation, Residual stress, Linear viscoelasticity, First normal stress difference.*

1. INTRODUCTION

Ferrofluids are suspensions of magnetic nanoparticles dispersed in a carrier fluid medium. The magnetic nanoparticles are commonly made of magnetite Fe_3O_4, but a mix of ferrites and cobalt are used (Odenbach, 2000). Odenbach and Thurm (2002) state that ferrofluids used in technical applications and for experiments in research usually contain a volume fraction of magnetic nanoparticles (magnetite) in the order of 7-10 vol%, that is, they are relatively concentrated suspensions. The main rheological effect observed on ferrofluids is the severe increase of its viscosity measured when the fluid is sheared in the presence of an external magnetic field, this effect is denominated in the literature as the magnetoviscous effect. This effect arises from a hindrance of rotation perpetrated by the suspended magnetic particles due to the action of the magnetic field (Rosensweig, 2013). That is, the particles are no longer free to rotate by the action of the flow-induced mechanical torque. This results from the fact that when an external magnetic field, whose intensity is H, is applied, the magnetic moment $\boldsymbol{m}$ of the particles will try to align with the magnetic field direction by the action of the magnetic torque, that arises from the misalignment between $\boldsymbol{m}$ and $\boldsymbol{H}$ promoted by the mechanical torque. Such competition between mechanic and magnetic torque increases the local viscous dissipation of energy in each particle, which is translated into an increase of the suspension's viscosity.

Another important effect of the application of an external magnetic field on a ferrofluid is the formation of a microstructure of chains and clusters of particles as discussed in (Odenbach, 2003). The presence of these structures results in elastic effects in the dynamical system corresponding to the ferrofluid. Thus, the fluid is observed to present a viscoelastic behavior. The viscoelastic response of ferrofluids is explored experimentally by the application of transient shearing flows. The most commonly used are the small amplitude oscillatory shear (SAOS) and the step-strain. SAOS experiments are excellent to verify the viscoelastic response of a ferrofluid when in the presence of an external magnetic field. It permits, by the variation of the frequency of the applied oscillating shearing flow, to collect directly the viscoelastic moduli of the fluid. It is well-known that the imaginary part of the complex viscosity η'' is observed to increase with the strengthening of the applied magnetic field in ferrofluids, which indicates viscoelastic effects in the fluid (Odenbach, 2003).

Step-strain experiments are deeply important in the analysis of the viscoelastic behavior of complex fluids. They allow the capture of the fluid stress relaxation function. From this material function, the spectrum of the relaxation times of the fluid can be determined and also can be verified how complex the material memory is. This memory is entirely related to the elastic response of the fluid. Besides that, this type of experiment can also portrait a panorama of the general complexity of the fluid, because it allows the determination of not only the main relaxation time of the fluid but also the secondary ones. In the case of ferrofluids, it is interesting to study the dependence of the fluid's relaxation time and of the residual stress on the intensity of the applied magnetic field. Borin *et al.* (2014), through a set of experiments in the regime of step-strain in the presence of an external magnetic field, has observed that the stress relaxation strongly depends on the magnetic field magnitude and that the stress decreases over time in a close exponential fashion. The authors relate the fact that higher magnitudes of stress occurring for higher magnetic field strengths conditions to the formation of more stable aggregate structures with an overall larger size in the fluid. It is also observed that the residual stress decreases from values typically in the order of the yield stress when in the presence of an external magnetic field, tending to a constant value for higher shear rates. The decrease is associated with the break-up of the agglomerates by the shearing-flow intensity.

In this article, it is presented and discussed the results concerning an experimental investigation of the rheological behavior of two ferrofluids, which differ only by their volume fraction of magnetic nanoparticles (magnetite). The experimental studies are carried out using transient shearing flows, specifically step-strain and small amplitude oscillatory shear, both in the absence and in the presence of an external magnetic field. Using step-strain experiments, it shall be determined the stress relaxation functions for both magnetic fluids regarding the magnetic field strength and the intensity of the applied strain. In addition, the spectrum of relaxation time of the fluids shall be determined and the main relaxation time of the fluid identified. It will be also examined the residual stress in the fluid and its dependence on both field strength and strain intensity. Using SAOS, it will be obtained the main viscoelastic modulus of the ferrofluids as functions of the frequency and the magnetic field intensity. As the experiments will be conducted in the regime of linear viscoelasticity, Laun's rule (Bird *et al.*, 1987a) is going to be applied in order to calculate the first normal stress difference from $G'(\omega)$ and the ratio $G''(\omega)/G'(\omega)$.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

In this article, the rheological behavior of two ferrofluids is investigated: EFH1 and EFH3. The fluids EFH1 and EFH3 are produced by the Ferrotec Corporation (USA) and the same are examples of the EFH product series. They correspond to a class of ferrofluids designed to be used on educational applications. Regarding this context, they feature strong magnetic properties, such as the magnetization of saturation (M_s), in order to make easy the visualization of magnetic patterns that result from the interaction between the fluid and an external magnetic field. These ferrofluids are suspensions of nanoparticles of magnetite (Fe_3O_4) dispersed on a base fluid composed of synthetic hydrocarbons that present very low volatility and high thermal stability. The average particle diameter on both ferrofluids is typically equal to 10nm. Their unique difference is on the volume fraction of magnetite (ϕ).

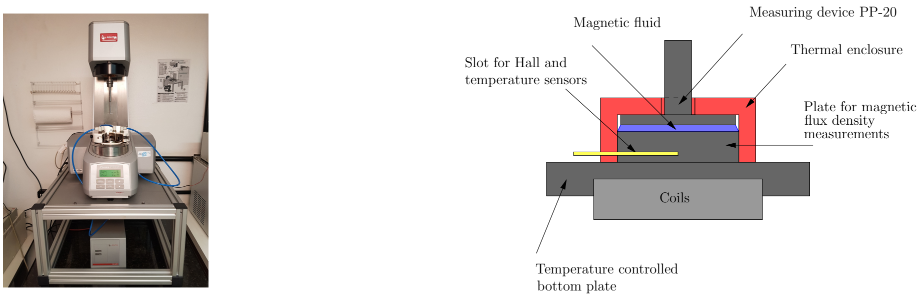
The characteristics regarding the ferrofluids EFH1 and EFH3, according to technical data obtained from the manufacturer, are summarized in table 1.

Table 1: Properties of the ferrofluids EFH1 and EFH3.

Ferrofluid	M_s (kA/m)	ϕ	η_0(cP) (27°C)	ρ (g/ml) (25°C)	Base fluid
EFH-1	35.0	7.9%	6.0	1.21	hydrocarbons
EFH-3	52.5	11.8%	12.0	1.42	hydrocarbons

2.2 Apparatus

The rheological properties of the fluids under analysis are obtained using a high-performance Physica Modular Compact Rheometer - MCR 301 (Anton Paar GmbH, Germany) equipped with a magnetic cell. The measuring system is powered by a permanent magnet synchronous drive motor placed on the measuring head, which is able to apply torques from 0.1μN.m to 200 mN.m with a resolution of 0.001 μN.m and accuracy of 0.2 μN.m. The capability of the device to apply a wide range of torques is the key factor that allows the measurement of several rheological properties of a considerable variety of fluids. The motor can also apply oscillations in a range from 0.0001 to 100 Hz. The device can set gaps between the two disks with micrometric precision. The magnetic cell is designed in order to provide a constant homogeneous magnetic field, which intensity can be actively controlled by the operator.



(a) (b)

Figure 1: (a) Parallel disk rheometer Anton Paar, model Physica MCR 301 with an automatic control of fluid-gap and a magnetic cell. (b) Schematics of the rheometer's magnetic cell.

2.3 Methods

Three experimental procedures were designed to test the rheological response of the ferrofluids under analysis. Two of them correspond to experiments on step-strain flow regime and one to an experiment on small amplitude oscillatory shearing flow regime. It is important to notice that each kind of experiment is conceived to be carried out both in the absence and in the presence of an external magnetic field. All the experimental procedures start by setting the temperature of the measuring cell at 25°C and by completing a previously calibrated gap between the disks of the rheometer with the fluid to be tested. In our device, the process of gap calibration depends mainly on the viscosity of the fluid to be tested.

The first methodology is used to study the influence of an external magnetic field on the stress relaxation process of the ferrofluids and also on their spectrum of relaxation times. This experimental method consists of a step-strain experiment that is used to obtain the stress relaxation function. Consequently, the spectrum of relaxation times of the fluids is determined in the presence of an uniform magnetic field intensity. To this end, after the fluid is placed in the measuring gap, a constant magnetic field is applied to the fluid for 4 min, with the fluid at rest. After this procedure, a step-strain with a constant angular strain of 0.5 is applied to the fluid sample. The resulting stress relaxation function is measured as a function of time every 0.01s. The process is repeated ten times for five distinct conditions of magnetic field intensities. These conditions correspond to the intensities of the magnetic fields induced by electrical currents of 0, 1, 2, 3, and 4A.

The second methodology also corresponds to a step-strain experiment, but in this case, the aim is to observe the influence of varying the amplitude of the applied angular strain on the stress relaxation process of the ferrofluids when in the presence of an external magnetic field with uniform magnitude. The experiments are carried out considering two conditions of constant magnetic field intensity, the ones induced in coils (under the bottom plate) by currents of 2 and 4A. For each condition of magnetic field intensity, a sequence of step-strains is applied to the sample. The data concerning the stress relaxation function, for each value of step-strain applied, is acquired as a function of time. The frequency of data acquisition was 1 point every 0.01s. The experiment was repeated over ten independent realizations for each value of angular strain.

The third experimental procedure is designed to directly measure the viscoelastic moduli of the ferrofluid in the presence of an external magnetic field. The experimental protocol is composed of two steps. A preliminary, which is essential for determining the appropriate parameters to be used in the second step. The second step is effectively the one in which the viscoelastic moduli are measured. The two steps are carried out for both ferrofluids at four different conditions of magnetic field intensity, induced by the currents: 1, 2, 3, and 4A. In the preliminary step, it is the determined the angular strain, which must be used to ensure that the test will be performed under the regime of linear viscoelasticity. This process was carried out according to the following experimental protocol: the magnetic field is applied and an oscillatory shear is programmed by setting in the software of the rheometer a fixed value of angular frequency ω. This value is the maximum frequency that shall be achieved in the frequency sweep experiments. This value was set to be 100 rad/s for all the cases treated in this experimental work. Besides that, the angular strain is set to vary from 1×10^{-5} to 1. It is measured the dependence of the storage modulus on the angular strain for the fixed value of angular frequency prescribed at each fixed condition of external magnetic field intensity. The optimal angular strain, that is, the one that will guaranty that the experiments of frequency sweep will be carried out in a regime of linear viscoelasticity, is chosen between the range of angular strains for which the storage modulus is verified to be independent of the angular strain.

From this initial analysis, it has been verified that an angular strain of 0.01 was sufficient to ensure the linear viscoelastic regime, for both ferrofluids, in all conditions of magnetic field intensity analyzed in this work. After determining this essential parameter, the second part of the experiments, which is focused on the measurement of the viscoelastic moduli as functions of frequency, for fixed conditions of magnetic field intensities, could be carried out. The frequency sweep experiments were executed, for each condition of magnetic field intensity, through the following protocol. In the software of the rheometer, it is programmed a variation of the applied angular frequency from 0.1 to 100 rad/s, according to a logarithmic ramp, with a rate of increase of 8 points per decade. During this process, the amplitude of angular strain was held constant at 0.01. The software collects data for viscoelastic modules as functions of the angular frequency and, indirectly, of the magnetic field intensity. The process is repeated ten times for each value of magnetic field intensity.

The results obtained from the three experimental procedures undergo a statistical analysis, which is performed over the experimental realizations. This process results in the computation of the average values and error bars for the rheological quantities under analysis.

3. RESULTS AND DISCUSSIONS

The results obtained for the ferrofluids are going to be discussed in terms of nondimensional parameters. Regarding this context, the intensity of the effective applied magnetic field is expressed by the magnetic parameter α, defined as:

$$\alpha = \frac{\mu_0 v_p M_d H}{k_B T}, \tag{1}$$

where μ_0 is the vacuum magnetic permeability, $v_p = 4\pi a^3/3$ is the volume of a magnetic particle of radius a, M_d is the magnetization of the material that the particles are made of, H is the modulus of the effective magnetic field, k_B is the Boltzmann constant and T is the absolute temperature. It is important to remark that this parameter measures the relative importance between the magnetic and the Brownian forces acting upon the particles.

Other important parameter is the ratio between the magnetic dipolar force and the Brownian force, named parameter of dipolar interaction,

$$\lambda = \frac{\mu_0 \pi v_p M_d^2}{24 k_B T}. \tag{2}$$

It should be important to note that this parameter is intrinsically related to the formation of particles chains. Large values of λ indicate that the magnetic force dominates the Brownian one so that the aggregative structure could be formed. The particles which compose the ferrofluids used in the experiments have the same average diameter (10nm) and are made of the same material, magnetite, whose magnetization M_d is 440 kA/m. Besides that, the experiments were carried out at a constant temperature of 300 K. Regarding this context, the parameter of dipolar interactions is constant for both ferrofluids and equals to 1.3.

3.1 Stress relaxation I: magnetic field influence

Step-strain experiments were carried out in this work to evaluate the dependence of the stress relaxation function Φ of both ferrofluids on the intensity of the applied magnetic field. Based on the time behavior of the referred material function, it was determined the spectrum of relaxation times for each fluid at different values of field intensity. Besides that, the residual stress relaxation parameter Φ_R was also obtained as a function of the magnetic field intensity for both ferrofluids.

The results are presented here in a nondimensional form. The nondimensional magnetic intensity is represented here by the magnetic parameter α. Regarding this context, the stress relaxation function, for a fixed intensity of the external magnetic field, $\Phi(s)|_\alpha$ was made nondimensional using the following time and viscosity characteristic scales: $t^* \sim \tau_m$ and $\eta^* \sim \eta_0$. τ_m is the principal relaxation time of the fluid evaluated in the presence of the lowest magnetic field intensity applied, η_0 is the viscosity of the ferrofluid at 25°C, in the absence of external magnetic field. Using those scales, the typical scale of the stress relaxation function, which has the unit of stress is given by: $[\Phi|_\alpha]^* \sim \eta_0/\tau_m$.

Besides that, the time shift, $s = t - t'$, has the following typical scale: $s^* \sim t^* \sim \tau_m$. Therefore, the nondimensional form of the stress relaxation function, at a fixed value of α, is given by:

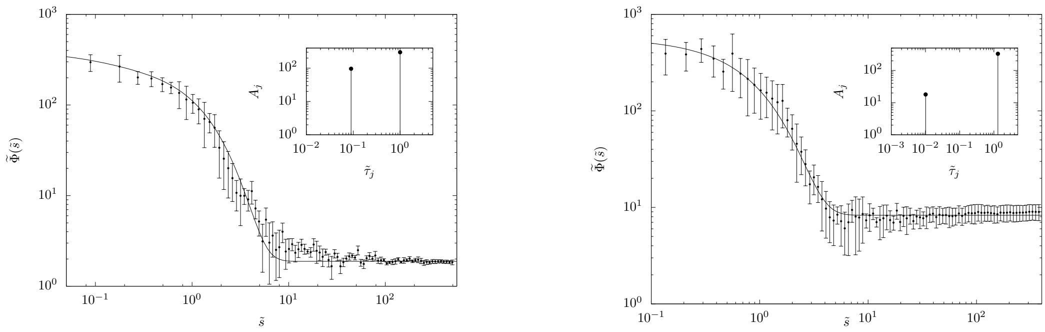
$$\widetilde{\Phi}(\tilde{s})|_\alpha = \frac{\Phi(s/s^*)|_\alpha}{[\Phi|_\alpha]^*} = \frac{\Phi(s/\tau_m)\tau_m}{\eta_0} = \frac{\Phi(\tilde{s})\tau_m}{\eta_0}, \tag{3}$$

where $\tilde{s}$ is the nondimensional time shift.

Analyzing the graphs presented in figs. 2 and 3, it is seen that both ferrofluids presented a long-time stress relaxation process after the application of the step-strain, which was done under the permanent action of a sequence of external magnetic field intensities. The fact that those fluids are non-instantaneous, in the presence of an external magnetic field, indicates that their rheology changed towards a viscoelastic behavior. Bird *et al.* (1987b) suggest that the time retardation on the stress relaxation of complex fluids is intimately related to elastic effects arising from its microstructure. This context strongly requires the use of a viscoelastic constitutive model for describing the relaxation of the shear stress on these fluids. We propose here a Maxwell's generalized viscoelastic model slightly modified by a new term that computes the fact that the shear stress does not relaxes to zero for long times. In contrast, the stress relaxation function goes to a constant value at very long times, which we denoted here as being the stress relaxation parameter $\tilde{\Phi}_R|_\alpha$. Under these conditions, the resulting constitutive equation takes the following nondimensional form:

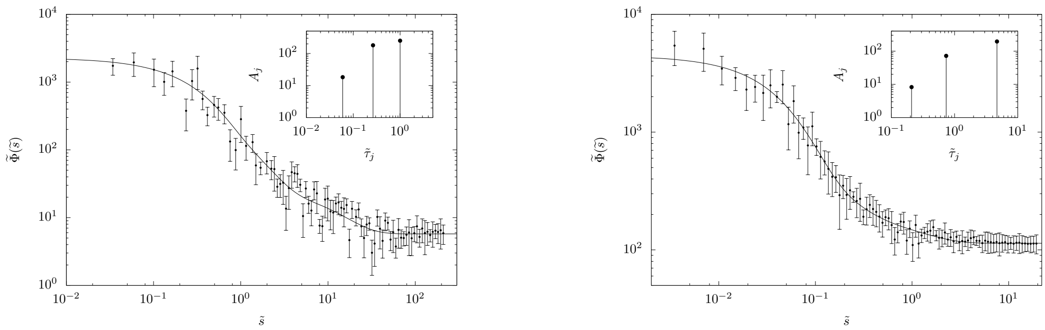
$$\widetilde{\Phi}(\tilde{s})|_\alpha = \tilde{\Phi}_R|_\alpha + \sum_{j=1}^{N} A_j \exp\left(\tilde{s}/\tilde{\tau}_j\right). \tag{4}$$

Using eq. 4 to fit the experimental data obtained for each ferrofluid, at four different conditions of magnetic field intensity α, we obtain the nondimensional relaxations times $\tilde{\tau}_j$ and the nondimensional shear stress amplitudes A_j.



(a) $\alpha = 4.85 \times 10^0$.   (b) $\alpha = 1.36 \times 10^1$.

Figure 2: Ferrofluid EFH1: Nondimensional stress relaxation function $\tilde{\Phi}$ in terms of the nondimensional time shift $\tilde{s}$ for different values of α. The curves are fits of the experimental data by an adaptation of the generalized Maxwell's model, given by eq. 4. In the inserts, it is shown a plot of the amplitude of the stress A_j as a function of the characteristic times $\tilde{\tau}_j$ involved in the process of stress relaxation at each condition of magnetic field strength α (i.e. the spectrum of relaxation time of the complex fluid).



(a) $\alpha = 4.84 \times 10^0$.   (b) $\alpha = 1.35 \times 10^1$.

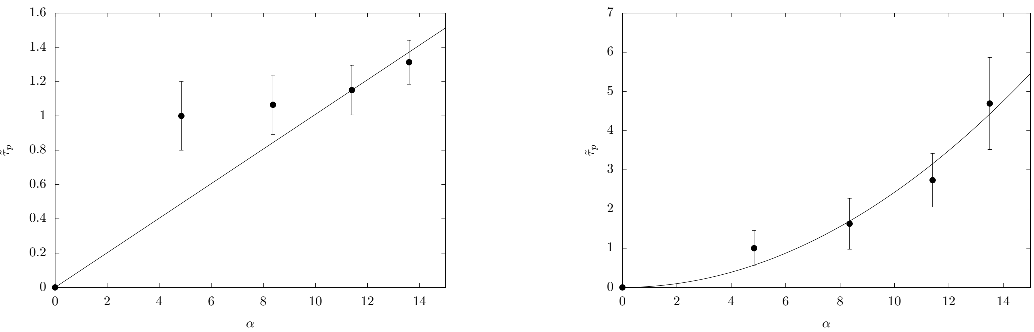
Figure 3: Ferrofluid EFH3: Nondimensional stress relaxation function $\tilde{\Phi}$ in terms of the nondimensional time shift $\tilde{s}$ for different values of α. The curves are fits of the experimental data by an adaptation of the generalized Maxwell's model, given by eq. 4. In the inserts, it is shown a plot of the amplitude of the stress A_j as a function of the characteristic times $\tilde{\tau}_j$ involved in the process of stress relaxation at each condition of magnetic field strength α (i.e. the spectrum of relaxation time of the complex fluid).

According to Borin *et al.* (2011, 2014), the total stress achieved by the magnetic fluid just after the cessation of the flow is determined by the presence of linear chains and dense aggregates (clusters) due to the action of dipolar interactions between the particles. It is important to remark that structures like chains of particles can be formed even in conditions in which α tends to zero. This happens since the formation mechanism of structures is governed by dipolar interactions.

Regarding this context, it should be important to note that the volumetric fraction of magnetic particles plays an important role in stress relaxation because it influences directly the complexity of the microstructure formed when a magnetic field is applied. Ferrofluids with higher ϕ produce bigger and stiffer linear chains and clusters, that form the field-induced microstructure when a given α is applied. According to Borin *et al.* (2014), the linear chains are responsible for the stress relaxation at short time scales, whereas the dense clusters are involved in the final long part of the process. This mechanism of magnetic effect inducing structure formation in the suspension produces a complex and nonlinear rheological response of the ferrofluids under shear.

From the inserts of figs. 2 and 3, we can see that for the fluid EFH1, it has been possible to describe its stress relaxation function, for every condition of α applied, using two Maxwell's elements. On the other hand, for the ferrofluid EFH3, it was necessary to use three elements. The results show that the fluid EFH3 presents a more complex memory than the fluid EFH1 since it involves at least three relaxation times. It can be argued, that probably the microstructure of the fluids evolves with different mechanisms related to orientation and deformation of the individual chains and aggregate-like structures. In addition, these structures can interact magnetically and hydrodynamically inside the suspension producing fluctuations in these trajectories. The rapid relaxation times can be associated with internal mechanisms inside the agglomerates, involving fluid redistribution and particle interactions. The results indicate that the mechanisms of structure relaxation due to orientation and deformation, particle and structures interactions, and fluid redistribution inside a cluster occur in a more complex way in the fluid EFH3. Indeed, Bird *et al.* (1987a) emphasize that each time scale of a spectrum of relaxation times represents a different physical mechanism.

The main relaxation time of both ferrofluids depends on the strength of the applied magnetic field. This dependence is shown respectively for the ferrofluids EFH1 and EFH3 in the figs. 4a and 4b. Regarding this context, one can see that, when α increases from its lower to its higher value (an increase of almost 180%), the time of relaxation of EFH1 increases 31%, while in the case of the ferrofluid EFH3, this increase is of approximately 370%. This big difference in the growth of the main time of relaxation is also because EFH3 has a larger volume fraction of magnetic particles than EFH1. Therefore, the magnetic field induces the formation of larger and more complex structures like long chains and aggregates inside the magnetic suspension EFH3. So, this more complex particle size distribution (i.e. involving more anisotropic and heterogeneous large structures) in EFH3 leading to a more substantial increase in the fluid memory and consequently the overall elastic response of this fluid as compared to EFH1.



(a) EFH1 (b) EFH3

Figure 4: Nondimensional time of relaxation $\tilde{\tau}_p$ as a function of the magnetic field intensity parameter α. The curves are fits of the experimental data to eq. $\tilde{\tau}_p(\alpha) = c_1\alpha^n$. The fitting parameters for EFH1 are $c_1 = 1.01 \times 10^{-1} \pm 1.25 \times 10^{-2}$ and $n = 1$. The parameters for EFH3 are:$c_1 = 2.43 \times 10^{-2} \pm 1.62 \times 10^{-3}$ and $n = 2$.

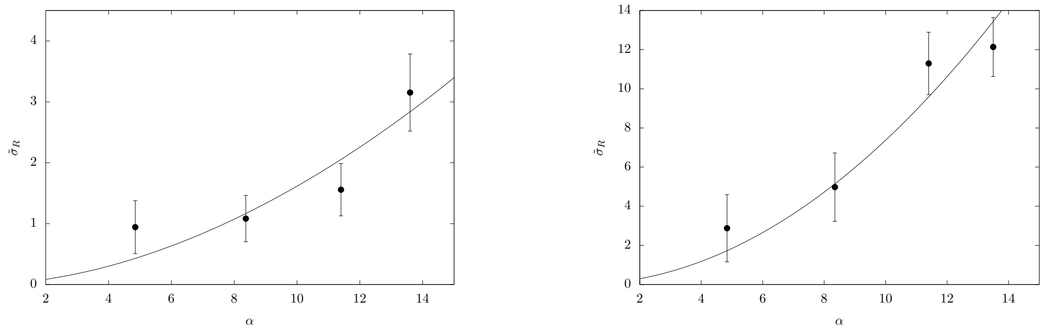
Note that, from the constant value towards the stress relaxation function tends, that is, the residual stress relaxation parameter $\tilde{\Phi}_R$, it can be defined a nondimensional residual stress $\tilde{\sigma}_R$ as

$$\tilde{\sigma}_R = \tilde{\Phi}_R \gamma_0, \tag{5}$$

where, γ_0 is the angular strain. Therefore, regarding the results displayed in figs. 2 and 3, we can see a residual stress $\tilde{\sigma}_R$ associated with both fluids tested at each constant strength of magnetic field applied. For the two ferrofluids, the residual stress increased as the intensity of the magnetic field strengthened. According to Borin *et al.* (2014), this increase can be related to the enhancement of the size of the magnetic field-induced aggregates as the intensity of the magnetic field rises. This effect is stronger on EFH3 than on EFH1, owing to its larger volume fraction of magnetic particles. Figures 5a and 5b show the dependence of the residual stress $\tilde{\sigma}_R$ as a function of the nondimensional magnetic field α.

3.2 Stress relaxation II: effects of the magnitude of the applied strain

As in the previous section, step-strain experiments were used to examine the dependence of the stress relaxation function $\widetilde{\Phi}(\tilde{s})$, of both ferrofluids, on the intensity of the applied shear-flow, here denoted by Péclet number, Pe (i.e. the

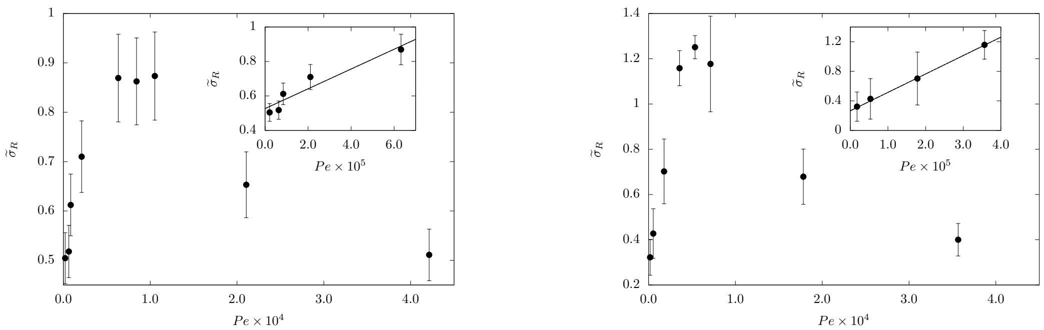


(a) EFH1 (b) EFH3

Figure 5: Dimensionless residual stress $\tilde{\sigma}_R$ as a function of the non-dimensional magnetic field α. The curves are fits of the experimental data to eq. $\tilde{\sigma}_R = c_2\alpha^n$. The fitting parameter for EFH1 is $c_2 = 2.38 \times 10^{-2} \pm 4.84 \times 10^{-3}$ and $n = 1.83 \times 10^0 \pm 8.12 \times 10^{-1}$. For EFH3, the parameters are: $c_2 = 2.23 \times 10^{-1} \pm 2.13 \times 10^{-2}$ and $n = 1.56 \times 10^0 \pm 3.84 \times 10^{-1}$.

nondimensional shear rate). The main goal is to evaluate the dependence of the residual stress, defined by eq. 5, on Pe.

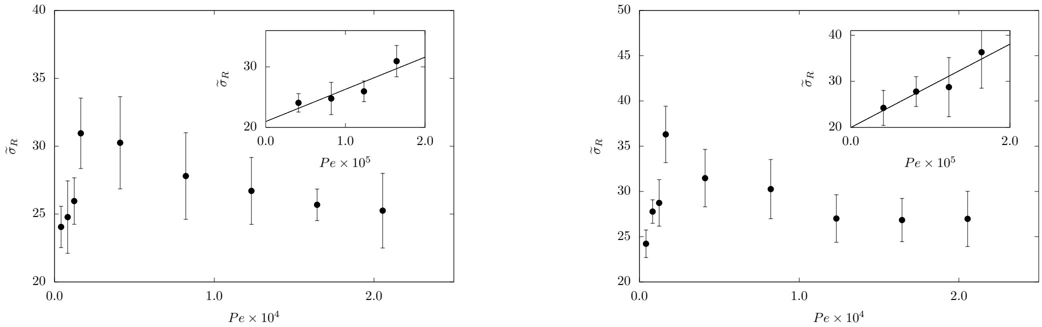
For the ferrofluid EFH1, the dependence of its $\tilde{\sigma}_R$ on Pe is shown, for the two conditions of external magnetic field intensities, in the plots of fig. 6. The same is depicted for the ferrofluid EFH3 in the plots of fig. 7. The data displayed on fig. 6a and 7a are obtained by keeping a constant value of magnetic field intensity, $H = 1.18 \times 10^5$ A/m, whereas the ones displayed on fig. 6b and 7b are for $H = 1.92 \times 10^5$ A/m. There are two distinct behaviors of the residual stress as a function of Pe. For small values of Pe, the residual stress is found to increase as Pe enhances until a critical value of Pe is achieved, from which, the residual stress starts to decrease when Pe is further increased. The second behavior, that is, the decrease of the residual stress as the flow gets more intense is in qualitative agreement with the results presented on Borin *et al.* (2014). According to those authors, this rheological behavior is motivated by the fact that an increase in the shear rate in this regime leads to a break-up process of the field-induced structures, resulting in lower values of $\tilde{\sigma}_R$. The authors punctuate that their methodology did not permit the application of much lower flow intensities, however, they argue that it would be expected that the value of the residual stress stayed saturated and constant on this regime. Nonetheless, the results obtained in this work strongly disagree with the last assumption. As stated previously, the experiments carried out in this work showed that, in regimes of very small Pe, the residual stress increases following increments on Pe.



(a) (b)

Figure 6: EFH1: nondimensional residual stress $\tilde{\sigma}_R$ as a function of Pe for two intensities of the external magnetic field: (a) $\alpha = 8.37 \times 10^0$ and (b) $\alpha = 1.14 \times 10^1$. In the inserts is shown a detailed view of the experimental data in the range of small Pe. The lines are fits of experimental data concerning the range of small Pe to $\tilde{\sigma}_r = c_1$Pe The constant is, for (a), $c_1 = 5.74 \times 10^3$ and, for (b), $c_1 = 2.49 \times 10^4$.

The ascending behavior of the residual stress, in the regime of low values of Pe, indicates that the flow is not strong enough to promote plastic deformations or, even, to break up magnetic field-induced structures. That is, the shear stress is inferior to the yield stress of the microstructure, which results from the action of the dipolar interactions between the magnetic particles. As a result, in this regime, the effect of the flow is resumed to promote elastic deformations of the elements that compose the microstructure. The magnetic dipolar interactions are the main restoration mechanism. However, when the flow reaches an intensity in which it produces shear stresses strong enough to surpass the yield stress, the microstructure starts to experience plastic deformations and, as a result, the residual stress is observed to start decreasing. Further increments on Pe lead to the break up of structures, followed by a strong decrease on $\tilde{\sigma}_R$. In a limit where Pe$\rightarrow \infty$, the residual stress would become zero, as the field-induced microstructure would vanish, due to the high intensity of the shearing flow.



(a) (b)

Figure 7: EFH3: nondimensional residual stress $\tilde{\sigma}_R$ as a function of Pe for two intensities of the external magnetic field: (a) $\alpha = 8.37 \times 10^0$ and (b) $\alpha = 1.14 \times 10^1$. In the inserts is shown a detailed view of the experimental data in the range of small Pe. The lines is are fit of experimental data concerning the range of small Pe to $\tilde{\sigma}_r = c_1\text{Pe}$. The constant is, for (a), $c_1 = 5.32 \times 10^5$ and, for (b), $c_1 = 9.06 \times 10^5$.

3.3 Small amplitude oscillatory shear

The oscillatory experiments allow us to observe the changes in the rheological response of a given complex fluid as a consequence of elastic effects arising from its microstructure, orientation, flow-induced deformation, and effects of the application of the magnetic field. In the experiments, it has been measured, as functions of the frequency of excitation ω and of the intensity of the magnetic field, the complex shear modulus $G_c(\omega, H)$, with its storage $G'(\omega, H)$ and loss $G''(\omega, H)$ components. Also, it has been measured the complex viscous modulus $\eta_c(\omega, H)$, with its viscous $\eta'(\omega, H)$ and its complex $\eta''(\omega, H)$ components. These quantities were made nondimensional by using the following characteristic time and viscosity scales: $t^* \sim \tau_m$ and $\eta^* \sim \eta_0$, where τ_m is the main relaxation time for the condition obtained in the presence of the lowest magnetic field intensity applied and η_0 is the viscosity of the ferrofluid, at 25°C, evaluated in a condition of no external magnetic field applied. Therefore, the nondimensional form of those material functions are, respectively: $\widetilde{G}_c = G_c\tau_m/\eta_0$ and $\widetilde{\eta}_c = \eta_c/\eta_0$.

It is immediate that the nondimensional form of the material function $\widetilde{G}'$and $\widetilde{G}''$ is the same of $\widetilde{G}_c$, what is also true for the functions $\widetilde{\eta}'$ and $\widetilde{\eta}''$ in relation to $\widetilde{\eta}_c$. In order to make the frequency nondimensional, one defines its characteristic scale as: $\omega^* \sim 1/\tau_m$. Hence, the nondimensional frequency, also known as the Deborah number De, is given by:

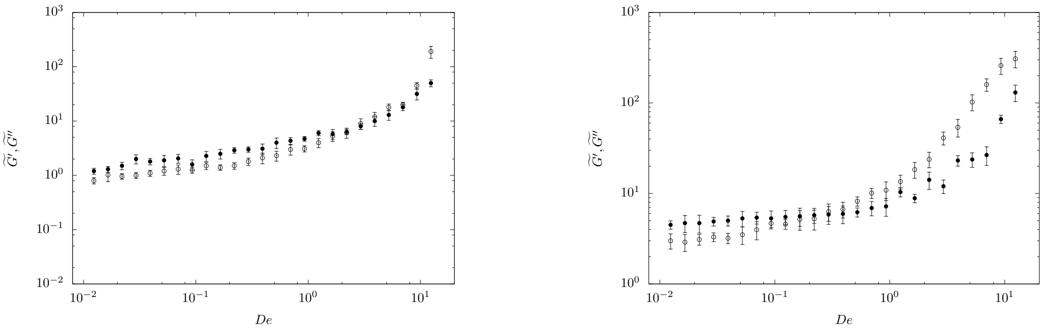
$$De = \widetilde{\omega} = \omega/\omega^* = \omega\tau_m. \tag{6}$$

It should be important to mention that for the ferrofluid EFH1, $\eta_0 = 0.94 \times 10^{-2}$ Pa.s and $\tau_m = 1.24 \times 10^{-1}$ s, while, for EFH3, $\eta_0 = 0.18 \times 10^{-1}$ Pa.s and $\tau_m = 6.73 \times 10^{-1}$ s.

Figures 8 and 9 present, for the fluids EFH1 and EFH3, the behavior of the storage and the loss modulus as a function of De. Figures 8a and 9a present results for a condition of weak magnetic field and figs. 8a and 9a for a condition of strong magnetic field intensity. Comparing the figs. 8a and 8b and, also, the figs. 9a and 9b, which are, respectively, representatives of the viscoelastic behavior of the ferrofluid EFH1 and of EFH3, one can observe two slightly different regions at each plot. There is a critic value of De below which, $G' < G''$ and above which, $G' > G''$. Such observation confirms the fact that, at a range of low De, the viscoelastic response has a more dissipative character, behaving, predominantly, like a viscous liquid. Similarly, for frequencies above the critical value of De, the opposite is true, indicating that the behavior of the solution is mostly elastic, but the dissipative effect should not be neglected, since the values of $\widetilde{G}''$ and $\widetilde{G}'$ are very near. Another important remark is that below the critical De, $\widetilde{G}'$ and $\widetilde{G}''$ seem to present only a slight variation with De. They are approximately constant. However, for higher De, the behavior changes drastically with $\widetilde{G}''$ and $\widetilde{G}'$ systematically increasing as De increases. The dependence seems to be nonlinear mainly for the case of larger α where the structures like chains are formed ($\text{De}_{\text{critical}}$ >1 for smaller α and $\text{De}_{\text{critical}}$ <1 for α =13.6). The effect of a higher magnetic field intensity is to increase the range of the elastic response of the fluid, which dominates the viscous one.

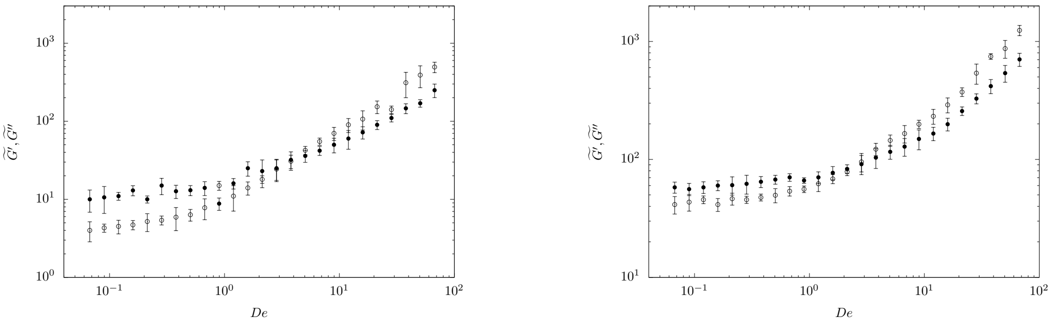
As commented previously, the formation of chains and agglomerates of particles by the action of the magnetic field is the key factor for the appearance of elastic effects on ferrofluids. Regarding this context, fig. 10 displays the influence of the magnetic field intensity on the nondimensional storage modulus of both ferrofluids. In order to allow comparison, for each α, $\widetilde{G}'$ was evaluated for De=1. It is immediate that, for both ferrofluids, the elastic component has increased as α heightened. This can be explained, according to Borin *et al.* (2014), by the fact that a strong magnetic field induces the formation of larger structures in the fluid, which, collaterally, means an intenser injection of elasticity in the fluid. The effect is more pronounced in the ferrofluid EFH3 due to its higher particle volume fraction.

Experiments in the regime of small amplitude oscillatory shear (linear viscoelasticity) allows the indirect determina-



(a) $\alpha = 4.85$ (b) $\alpha = 13.6$

Figure 8: EFH1: Nondimensional storage modulus $\tilde{G}'$ (○) and nondimensional loss modulus $\tilde{G}''$ (●) as a function of De, for (a) $\alpha = 4.89$ and (b) $\alpha = 13.5$.



(a) $\alpha = 4.89$ (b) $\alpha = 13.5$

Figure 9: EFH3: Nondimensional storage modulus $\tilde{G}'$ (○) and dimensionless loss modulus $\tilde{G}''$ (●) as a function of De, for (a) $\alpha = 4.89$ and (b) $\alpha = 13.5$.

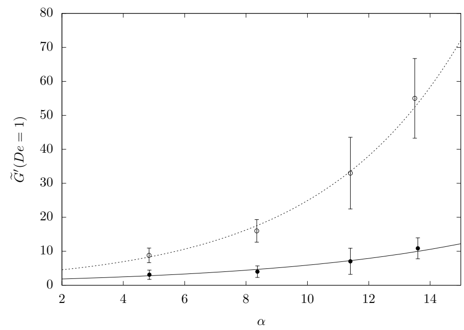
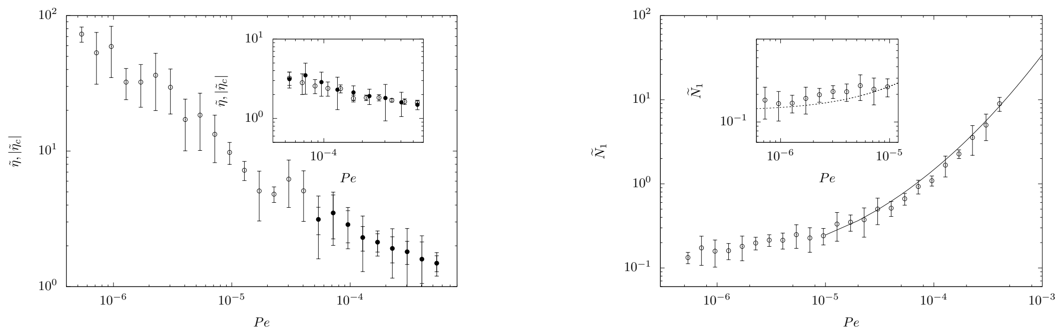


Figure 10: Nondimensional storage modulus $\widetilde{G}'$ evaluated at $De = 1$ for different values of α for the ferrofluids EFH1 (●) and EFH3 (○). The curves are fits to the experimental data to $\widetilde{G}'(De = 1, \alpha) = c_1 \exp(c_2 \alpha)$. The constants for the dashed curve are $c_1 = 2.97$ and $c_2 = 0.21$. For the continuous curve, they are $c_1 = 1.39$ and $c_2 = 0.15$.

tion of the fluid first normal stress difference. To measure this rheological quantity (N_1), one can apply the empirical correlation of Cox and Merz (1959) or the more general one of Laun (1986). Both experimental correlations provide a link between the description of the fluid's material functions obtained by oscillatory experiments and those measured on permanent shear experiments. A way to guarantee that the referred agreement is representative of the reality is to verify if the modulus of the complex viscosity $|\eta_c(\omega)|$ and the apparent viscosity $\eta(\dot{\gamma})$ are equal for correspondent values of ω and $\dot{\gamma}$. To use the correlation by Laun (1986), the validation has been carried out for both ferrofluids at all the applied magnetic field intensities α. However, it was found to apply only for the ferrofluid EFH1, at the lowest value of magnetic field intensity, which is shown in fig. 11a.

Figure 11b shows a variation of several orders on $\widetilde{N}_1$ as Pe heightens. This is a confirmation of the fact that, under an influence of an external magnetic field, the stresses in the fluid become anisotropic. This fact was first punctuated as a possibility in the theoretical work of Zubarev (1992) and has been first observed experimentally by Odenbach *et al.* (1999). In the insert of fig. 11b, it is also depicted that $\widetilde{N}_1$ has two different functional dependencies on Pe. In the range of low Pe, the first difference of normal stresses displays a linear dependence on Pe, whereas, in a regime of moderate and high Pe, this dependence becomes quadratic. The linear behavior is possibly explained by collisional effects between the magnetic field-induced chains and agglomerates, which leads to an initial anisotropy of the microstructure and, as a result, to the appearance of normal stresses. The quadratic dependence is generated by a collective alignment of the field-induced chains and structures within the fluid with the direction of the shear flow.



(a) (b)

Figure 11: (a) - EFH1: Nondimensional apparent viscosity $\tilde{\eta}$ ($\bullet$) and nondimensional absolute value of the complex viscosity $|\tilde{\eta}_c|$ ($\circ$) as functions of Pe (calculated considering $\omega = \dot{\gamma}$) at $\alpha = 4.85$. In the insert is shown a detailed view of the zone of agreement between the $\tilde{\eta}$ and $|\tilde{\eta}_c|$. (b) - Nondimensional first normal stress difference $\tilde{N}_1$ as a function of Pe obtained by applying Laun's rule to the measured values of $G'(\omega)$ and $G''(\omega)$. The dashed curve, in the insert, is a fit of the experimental data for the range of small Pe to $\tilde{N}_1 = c_1 + c_2\text{Pe}$, with $c_1 = 1.33 \times 10^{-1}$ and $c_2 = 1.11 \times 10^4$. The continuous curve is a fit of the experimental data for the complete range of Pe to $\tilde{N}_1 = c_1 + c_2\text{Pe}+c_3\text{Pe}^2$, with c_1 and c_2 equals to the one determined for the dashed line and $c_3 = 2.30 \times 10^7$.

4. CONCLUSION

It was observed that in the presence of a magnetic field, the ferrofluids EFH1 and EFH3 become viscoelastic liquids. This was first verified in the experiments of step-strain, conducted with a small angular strain, for increasing values of magnetic field intensity. In all field conditions, the fluids presented a delay in their process of stress relaxation, which is a direct sign of the presence of elastic behavior. These elastic properties arise from the formation of a microstructure, due to the action of the magnetic field. The relaxation process of the ferrofluids in the analysis was found to be highly complex, characterized by more than one time of relaxation and by the relaxation of the shear stress for a non-zero value after the cessation of the flow. The residual stress can be understood as the yield stress of the fluid because it represents the minimum stress to which the stress relaxes. This process of relaxation was found to be well modeled by an adaptation of Maxwell's viscoelastic constitutive model. The main time of relaxation of both fluids, as well as their residual stresses, were found to be strongly dependent on the intensity of the magnetic field.

The dependence of the residual stress on the shear flow intensity was analyzed. The results showed two very distinct behaviors, depending on the range of the applied flow intensity. For very low flow intensities, the residual stress was found to increase linearly with the flow intensity, until it reaches a maximum and starts to decrease rapidly as the flow strengthens. The first effect has not yet been covered in the specific literature on the rheology of ferrofluids. This work suggests that this behavior is associated with the fact that, for the low regime of flow intensities, the shear rate is not strong enough to produce plastic deformations or even breakups of the field-induced structures, being characterized by a regime dominated by elastic (reversible) deformations, that are not able to change permanently the overall topology of the microstructure. This behavior shifts when the yielding point is reached and the flow starts to provoke plastic deformations, even leading to the breakup of the magnetic field-induced structures. For extremely high values of flow intensity, the structures are supposed to break down completely leading to a vanish of the residual stress.

It was verified, from the results obtained from the experiments of small amplitude oscillatory shear, that both ferrofluids have a storage modulus and a loss modulus different from zero in the complete range of frequencies applied when they are in the presence of an external magnetic field. This is another strong confirmation that both fluids are viscoelastic. A comparison between the complex viscosity and the apparent viscosity for compatible values of frequency and shear rate has been carried out for both ferrofluids in all conditions of the magnetic field studied. However, the agreement between the two sets of data was just verified for the ferrofluid EFH1 at the lowest magnetic field intensity applied. This compatibility validated the use of Laun's rule to calculate, from the storage and the loss modulus, the first normal stresses difference. The fact that the fluid, when subjected to a magnetic field, presents a first normal stress difference is a solid indication that the fluid becomes anisotropic. This material function presented two kinds of functional dependencies on the shear rate. For weak flows, the first normal stresses difference displayed a linear dependence on the shear rate. This is related to collisional effects between the chains and particles of the magnetic field-induced microstructure. For medium-high flow intensities, the first normal stresses difference was observed to depend quadratically on the shear rate, which is a straightforward consequence of the alignment of the field-induced microstructure of the fluid with the direction of the shearing flow.

5. ACKNOWLEDGMENTS

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