Dynamics of lyotropic ferronematic liquid crystals submitted to magnetic fields

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The dynamical behavior of lyotropic ferronematic liquid crystals of potassium laurate, decanol (or decilamonium chloride), water, and ferrofluid is studied by means of optical techniques, under the influence of magnetic fields. Making use of interferometric measurements, three different processes, with typical characteristic times, were identified. The usual rotational viscosity of lyotropic liquid crystals (~ 1 P) is obtained associated with the collective behavior of the magnetic particles in the nematic matrix.

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I. INTRODUCTION

Ferronematic liquid crystals [1] are obtained by doping usual nematic liquid crystals [2] with ferrofluids [3,4]. Ferrofluids are colloidal suspensions of small magnetic grains, with typical dimensions of 100 Å, dispersed in a liquid carrier. Ionic ferrofluids [5] are synthesized by alkaline condensation of Fe ions in colloidal magnetic grains. The grains are electrically charged and dispersed in an aqueous solution.

It was theoretically predicted [1] and experimentally verified [6–8] that the immersion of ferrofluid in liquid crystals reduces the magnetic field's strength (H), by a factor of 10^3, necessary to orient them. This doping makes the ferronematics' magneto-optical properties very interesting. In particular, the dynamics of such systems has not been well understood yet. The response of the ferronematic to small magnetic fields and the relaxation times involved can be useful tools to study the dynamics of these systems.

In this paper we report interferometric measurements of the optical birefringence of the lyotropic systems, potassium laurate (LK) decanol (DeOH)–water and potassium laurate/decilamonium chloride (DaCl)–water, doped with ionic ferrofluids. The measurements are done as a function of the time and H.

II. EXPERIMENT

The lyotropic systems used in this experiment have the following concentrations (in weight percent) in their compounds:

Sample 1 (S1): LK (27.7)–DeOH (6.2)–water (66.1),
Sample 2 (S2): LK (37.3)–DaCl (4.2)–water (58.5).

Such mixtures present a large calamitic nematic (N_c) phase near the room temperature (~24 °C, which is the experiment's temperature). The samples are encapsulated inside microslides (Vitro Dynamics) 200 μm (thick), 20 mm (length), and 2.5 mm (width). The ionic ferrofluid used is composed of grains of γ-Fe_2O_3 with typical dimensions of 100 Å (electrically charged) and dispersed in water [9]. The concentration of magnetic grains used is over the minimum concentration required to present a collective behavior of the nematic matrix [1]. It is estimated in about 10^{12} grains/cm^3 which corresponds to a volume fraction of magnetic material in the solution $\phi \sim 10^{-5}$%. The sample is placed on a platform between the poles of an electromagnet, which can apply the field $0 < H_1 \leq 6000$ G along the microslide's length. The microslide's flat surface is placed in the horizontal plane. Another magnetic field, $0 < H_2 \leq 1200$ G, perpendicular to $\vec{H}_1$ (in the horizontal plane), can also be applied in the sample by two coils in Helmholtz geometry. The laboratory frame axes are defined as follows: the x axis is parallel to $\vec{H}_1$, the y axis is parallel to $\vec{H}_2$, and the polarized laser light beam (HeNe) is directed vertically, parallel to the z axis. The polarizing direction of the beam is parallel to the x axis. The light emerging from the sample is analyzed by a linear polarizer, with the polarizing direction perpendicular to the incident laser polarizing direction and detected by a photodiode. The transmittance I is registered in a computer. Two softwares were developed for this experiment: one reaches 2000 points in 2.5 s and the other 2000 points in 600 s.

The sample is initially oriented in a planar geometry with the director $\vec{n}$ parallel to $\vec{H}_1$ (~ 6000 G, $H_2 = 0$) for about 2 h. The alignment's quality can be followed by measuring I versus time, also optically removing the photodiode and placing an ocular at its position. After a perfect orientation of the sample in the magnetic field H_1, the angles of polarizer and analyzer are turned up in order to obtain a true minimum of the transmittance at

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the geometry of crossed polarizers. Then, H_2 is applied during the inverval Δt_0, and after that, it is turned off. The amplitude ratio of the fields H_2/H_1 defines an angle of rotation of the magnetic field of 0.2 rad. The experimental setup has rough accuracy to detect rotation a hundred times smaller than 0.1 rad. The transmittance I is registered during the whole orienting and relaxation processes. Special care was taken to avoid the sample's heating (larger than about 1 °C) due to the electromagnet poles and the coils. The magnet was refrigerated by cold water and H_2 was applied during a short interval.

III. RELATION BETWEEN τ AND THE DECAY TIME OF THE TRANSMITTANCE

Experimentalists usually measure the sample's transmittance I as a function of time. It can easily be shown [10,11] that

$$I \propto \sin^2 2\theta \,,$$

where θ is the angle between $\vec{H}_1$ and $\vec{m}_s$, the magnetization of the grain, and for small θ, $I \propto \theta^2 \propto \exp(-2t/\tau)$, taking into account an exponential decay in θ with the time (see Sec. V). Therefore $I \propto \exp(-t/\tau')$, where

$$\tau' = \frac{\tau}{2} \quad . \tag{1}$$

IV. RESULTS

Two types of experiment have been performed with a constant field H_1, short pulse in H_2 with $\Delta t_0 \cong 1.5$ s, and long pulse $\Delta t_0 \cong 60$ s. The ratio H_1/H_2 is kept constant and equal to 5 whatever is the field H_1. It means a rotation of the magnetic field direction of 0.2 rad.

Figures 1 and 2 show, respectively, typical transmittance as a function of time for the samples S1 and S2 for short pulse. Figures 3 and 4 show, respectively, the transmittance as a function of time for the samples S1 and S2 for long pulse.

The maximum transmittance (I_0) for the short pulse experiment is 7500 and 4000 times smaller than I_0 for the long pulse in samples S_1 and S_2, respectively. For the long pulse, the transmittance is roughly saturated; it means that the director has the time to orientate parallel to the magnetic field ($\theta \simeq 0.2$ rad). For short pulse, the angle calculated following $I \propto \theta^2$ is about a hundred times smaller. It means that the physics can be different.

We have verified that in samples without ferrofluid, for the experiment times used ($\Delta t_0 < 75$ s) and $H \leq 3000$ G, the transmittance variation as a function of the time is negligible.

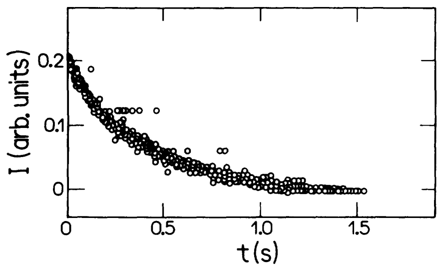

FIG. 2. Transmittance (I) as a function of time, sample S2. $H_1 = 2000$ G, $H_2 = 400$ G, and $\Delta t_0 \sim 1.5$ s.

V. DYNAMICAL MODEL

In ferronematic liquid crystal, a critical concentration ϕ^* in magnetic particle exists. For $\phi < \phi^*$ individual behavior of magnetic grain appears. For $\phi > \phi^*$ collective behavior takes place. These facts have been theoretically shown [1] and experimentally proved [8,12].

Collective behavior ($\phi > \phi^*$)

If one considers a ferronematic [1] with magnetic grains of typical dimensions D_3, elastic constant [2] K, and magnetization at saturation m_s, when in the presence of $\vec{H}$, the grain tends to align $\vec{m}_s$ parallel to $\vec{H}$.

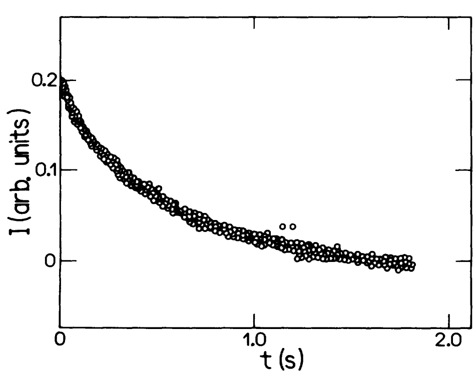

FIG. 1. Transmittance (I) as a function of time, sample S1. $H_1 = 2000$ G, $H_2 = 400$ G, and $\Delta t_0 \sim 1.5$ s.

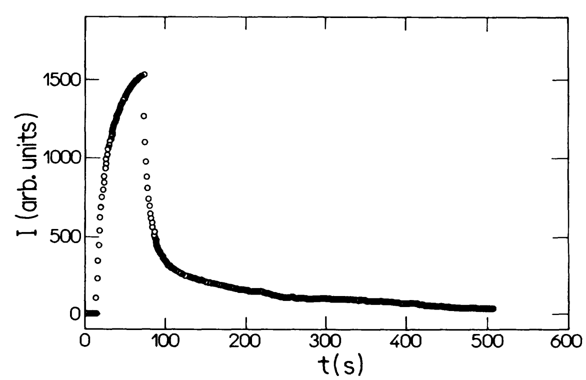

FIG. 3. Transmittance (I) as a function of time, sample S1. $H_1 = 3000$ G, $H_2 = 600$ G, $\Delta t_0 \sim 74$ s.

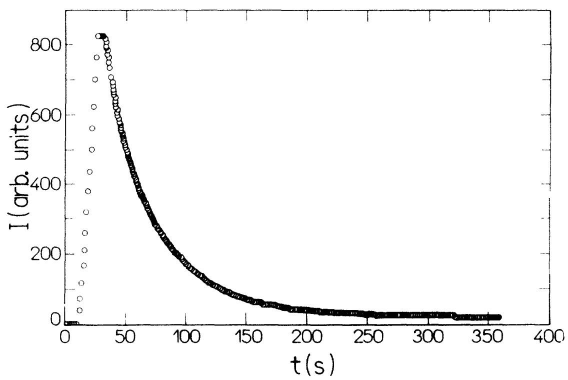

FIG. 4. Transmittance (I) as a function of time, sample S2. $H_1 = 3000$ G, $H_2 = 600$ G, $\Delta t_0 \sim 32$ s.

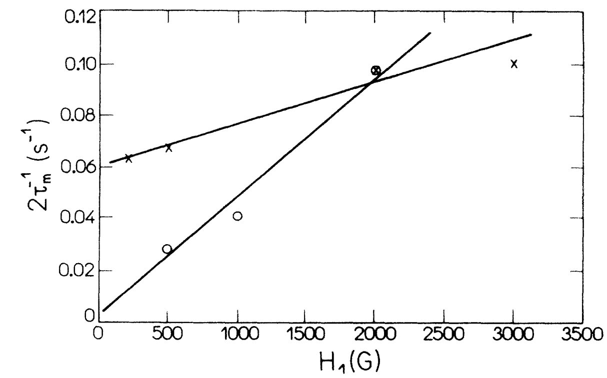

FIG. 5. Medium relaxation time τ_m^{-1} as a function of the magnetic field H$_1$. The solid lines are linear fits: ×, sample S1; ○, sample S2.

With $\theta(t)$ an angle between $\vec{m}_s$ and $\vec{H}$ as a function of time, the torque balance equation per unit area can be written as

$$\gamma D_1 \dot{\theta} = -\frac{K}{D_2}\theta - D_1\, m_s\, H\,\theta\,\phi \quad , \tag{2}$$

where γ is a viscosity, and D_1 and D_2 are the typical length in rotation and distortion, respectively.

The solution for Eq. (2) is

$$\theta(t) = \theta_0 \, \exp\,(-t/\tau) \quad , \tag{3}$$

where θ_0 is a constant and

$$\tau^{-1} = \frac{K}{\gamma D_1 D_2} + \frac{m_s}{\gamma}\,\phi\, H \; . \tag{4}$$

The distortion length D_2 is strongly dependent on the shape of the grain, the local director's boundary conditions, and the grain's surface [13]. At this point we assume that $D_1 \sim D_2$ and Eq. (4) can be rewritten as

$$\tau^{-1} = \frac{K}{\gamma}\,\frac{1}{D_1^2} + \frac{m_s}{\gamma}\,\phi\, H \quad , \tag{5}$$

or, schematically,

$$\tau^{-1} = \tau_0^{-1} + \alpha H \quad . \tag{6}$$

Whatever the nematic samples are without magnetic grains, the behavior of the characteristic time is proportional to $1/H^2$ [2,14]; with magnetic grains the model always shows a relaxation time proportional to $1/H$.

VI. DISCUSSION

In our experimental condition $\phi > \phi^*$ [12] leads only to a collective behavior.

A. Long pulse experiment

On analyzing all our results, we have found that for the long pulse experiment, we obtain two relaxation times: τ_m (medium time) and τ_ℓ (long time).

In the long pulse experiments, the inverse of the medium time is plotted versus the magnetic field for the two samples S1 and S2 (Fig. 5). The values of τ_{0m} and α_m are given in Table I. Figure 6 presents the result for the long time, for sample S2. The long time τ_ℓ for sample S1 is independent of the magnetic field.

In conclusion, all these different characteristic times (when they are the dependent field), follow with a good accuracy the law of Eq. (6).

D_1^2 represents the surface size of a domain which is characterized by a solid rotation of the ferronematic. The viscosity values deduced from τ_0 and α are in good agreement with the macroscopic ones in the case of the medium time (Table I). The mean sizes of these domains for samples S1 and S2 (about 26 μm and 260 μm, respectively) are in good agreement with optical microscopic observations.

The long time has already been measured in lyotropic nematics without ferrofluid [14], being related to the gliding anchoring effect. For sample S1 τ_ℓ is constant, i.e., field independent. This result seems to indicate that the director can freely rotate at the glass boundaries by the action of the magnetic grain rotation. If $\tau_{0\ell} = \frac{\gamma D^2}{K}$ where D is the half thickness of the cell; with $\gamma = 4.6$ P,

TABLE I. Experimental values of τ_0 and α and the calculated values of D_1 and γ of short, medium, and long processes, with samples S1 and S2.

Sample	Process →	Short	Medium	Long
S1	τ_0 (s)	1.7	3.2×10	3.0×10^2
	α ($s^{-1}G^{-1}$)	1.9×10^{-4}	7.5×10^{-6}	
	D_1 (cm)	2.3×10^{-4}	2.6×10^{-3}	
	γ (P)	18.4	4.6	
S2	τ_0 (s)	1.7	10^3	2.7×10^2
	α ($s^{-1}G^{-1}$)	2.6×10^{-4}	2.3×10^{-5}	3.0×10^{-6}
	D_1 (cm)	2.7×10^{-4}	2.6×10^{-2}	4.8×10^{-3}
	γ (P)	13.5	1.5	11.7

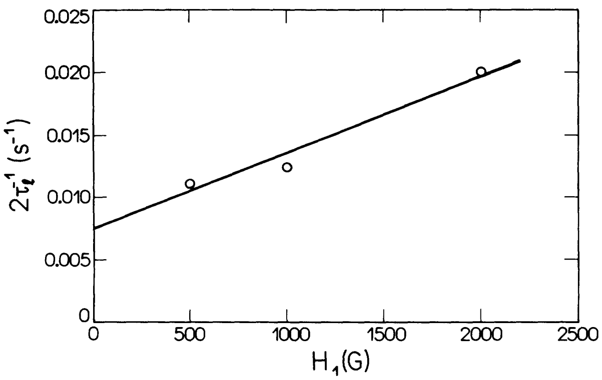

FIG. 6. Long relaxation time τ_l^{-1} as a function of the field H_1, sample S2. The solid line is a linear fit.

$K = 10^{-6}$ dyn and $D = 200$ μm, $\tau_{0\ell} = 460$ s, which is the same order of magnitude as the experimental value $\tau_{0\ell} = 300$ s.

For sample S2, the long time is field dependent. This anchorage energy gives a characteristic length D_1 of 50 μm; the viscosity involved in that process is eight times larger than in the medium time process.

B. Short pulse experiment

We analyze now the short time experiments where these samples do not achieve the uniform orientation with $\vec{n}$ parallel to $\vec{H}$ as in the case of the long time experiments. Figure 7 shows the behavior of τ_c^{-1} as a function of H_1 with samples S1 [Fig. 7(a)] and S2 [Fig. 7(b)]. The mean rotation of the director is very small (10^{-2} rad). The magnetic grains can only disturb a small volume of the nematic; for $\phi = 10^{-5}$%, the mean distance between two particles is 50 times the diameter of the magnetic particle. In that case the characteristic length is, respectively, 2.3×10^{-4} cm and 2.7×10^{-4} cm for samples S1 and S2 and the viscosities deduced from the experimental results are 18.4 and 13.5 P, respectively.

For the short time experiments, the results show that the typical dimension D_1 of the distorted volume is roughly ten and 100 times (samples S1 and S2, respectively) smaller than for the saturated pulse experiments. The large value of the viscosity (respectively, 18.4 P and 13.5 P for S1 and S2) can be explained by small angular rotation of the domain, and these experiments probe the viscoelasticity behavior of the nematic at very low shear rate (10^{-2} s). These results seem to indicate that the nematic is non-Newtonian at this scale.

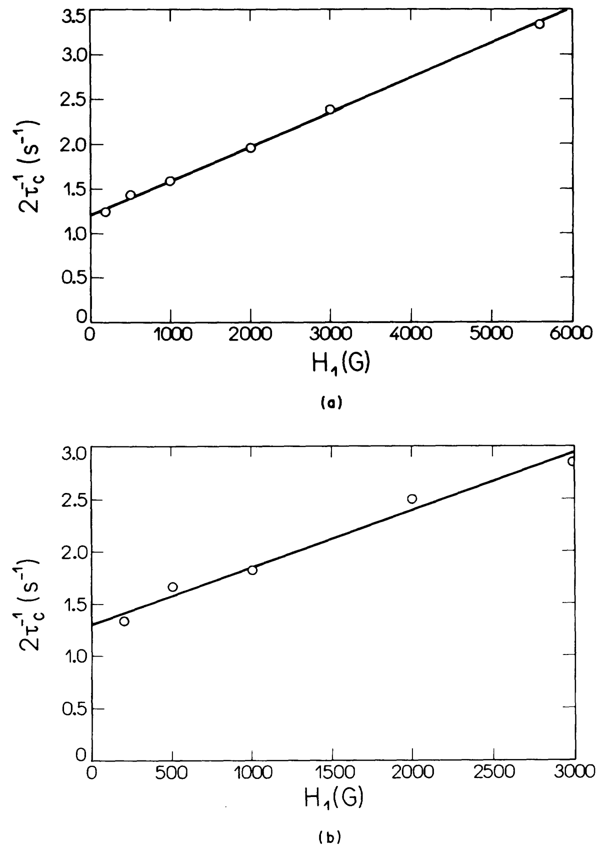

FIG. 7. Behavior of the relaxation time τ_c^{-1} as a function of the magnetic field H_1: (a) sample S1, (b) sample S2.

VII. CONCLUSIONS

The dynamical behavior of the lyotropic ferronematic studied by means of optical techniques under magnetic fields shows the existence of three different times. The characteristic times τ^{-1} follow the law $\tau^{-1} = \tau_0^{-1} + \alpha H$, which is different from the usual H^2 dependence for non-doped nematics. The analysis of τ_m gives the usual value of viscosity of lyotropics. τ_ℓ gives access to the anchoring properties of lyotropics and the gliding anchoring effect. The short time experiment probes the viscoelasticity behavior of the nematic at very low shear rate (10^{-2} s). The large values of the viscosities found seems to indicate that the nematic is a non-Newtonian fluid at this shear rate scale.

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