Dynamic optical probing of the magnetic anisotropy of nickel-ferrite nanoparticles

Yu. L. Raikher and V. I. Stepanov
Institute of Continuous Media Mechanics, Ural Division of the Russian Academy of Sciences, 1 Korolyev St., Perm, 614013, Russia

J. Depeyrot
Complex Fluids Group, Instituto de Física-Universidade de Brasília, Caixa Postal 04455, 70919-900 Brasília (DF), Brazil

M. H. Sousa
Complex Fluids Group, Instituto de Química-Universidade de Brasília, Caixa Postal 04478, 70919-970 Brasília (DF), Brazil and Laboratoire des Milieux Désordonnés et Hétérogènes, associated with the Centre National de la Recherche Scientifique, UMR 7603, Université Pierre et Marie Curie (Paris 6), Case 78, Site de Boucicaut, 140 rue de Lourmel, 75015, Paris, France

F. A. Tourinho
Complex Fluids Group, Instituto de Química-Universidade de Brasília, Caixa Postal 04478, 70919-970 Brasília (DF), Brazil

E. Hasmonay and R. Perzynski
Laboratoire des Milieux Désordonnés et Hétérogènes, UMR 7603, Université Pierre et Marie Curie (Paris 6), Case 78, Site de Boucicaut, 140 rue de Lourmel, 75015, Paris, France

(Received 29 March 2004; accepted 19 July 2004)

Field dependence of dynamic magneto-orientational birefringence in a ferrocolloid based on the nickel-ferrite nanoparticles is examined. The nanoparticles are electrostatically stabilized and suspended in glycerin at low-volume fractions \( \Phi \leq 0.75 \%). The colloids are tested under crossed magnetic fields: an alternating weak (probing) and a constant strong (bias) one. By comparison to a theoretical model of the birefringence relaxation, an evaluation of the mean nanoparticle magnetic anisotropy energy, \( E_a \), is done. We get \( \sigma = E_a / kT \sim 10 \), given that the particles are rather polydisperse: a log-normal distribution with \( \ln \langle d_i \rangle = 6.5 \text{ nm} \) and the width \( s = 0.55 \). With the parameter \( \sigma \) in such a range, the NiFe\(_2\)O\(_4\) grains make a first example of a nanodisperse material (ferrofluid) whose anisotropy properties differ substantially from both magnetically soft (e.g., maghemite with \( \sigma < 2 \)) and magnetically hard (e.g., cobalt ferrite with \( \sigma > 50 \)) nanosubstances of the same grain size. © 2004 American Institute of Physics. [DOI: 10.1063/1.1790574]

I. INTRODUCTION

The colloidal systems studied herein are based on the nanoparticles made of nickel ferrite (NiFe\(_2\)O\(_4\)). Those particles are manufactured with a long-range perspective for biological applications.\(^{1,2}\) Being dispersed in an aqueous carrier, they could be specifically coupled either to antibodies and then used for the *in vitro* antigen/antibody titration or coupled to a medical agent and employed as the *in vivo* drug carriers.\(^{3,4}\) Another potential application is the *in vivo* determining of biodistributions of such nanoparticles by nickel titration of blood probes. The nanoparticles in question are developed in Universidade de Brasília\(^{5}\) following the core/shell strategy: a magnetically ordered core of nickel ferrite protected by a more disordered external shell of iron oxide. The tests of static magnetic and magneto-optical properties of the aqueous dispersions of these nanoparticles are reported in Refs. 6 and 7. They confirm the core/shell internal magnetic structure and evidence a strong effect, stemming from the magnetic disorder of the surface spins.

The objective of the present work is to study and characterize the anisotropy energy of these new nanoparticles by dynamical magneto-optical measurements at room temperature, under crossed magnetic fields. This determination is initiated by comparison of the data on the optical probing of nickel-ferrite nanograins with the recent experimental and theoretical works,\(^{8,9}\) performed with more standard (and, thus, better known) ferrite nanoparticles of rather weak (\( \gamma -\text{Fe}_2\text{O}_3 \)) and rather strong (\( \text{CoFe}_2\text{O}_4 \)) anisotropy.

The paper is structured as follows: the first part presents the experimental system and recalls the previous static characterizations. In the second part, we describe the magneto-optical method, the setup realizing it, and present the experimental results. The theoretical background is detailed in the third part, and in the final fourth part, a discussion of the experimental results is given.

II. EXPERIMENTAL SYSTEM

The preparation of magnetic fluids (frequently called ferrofluids) is carried out in two steps. First, the ferrite particles are synthesized, and secondly, they are dispersed in a liquid carrier. To synthesize the nanosize particles, a method\(^{10}\) based on the Massart polycondensation technique\(^{11}\) is used.
Cocoprecipitation of an aqueous solution of NiCl₂ and FeCl₃ in an alkaline medium, yields nanoparticles of NiFe₂O₄. As shown in Ref. 12, surface stabilization is performed by an alkaline medium, yields nanoparticles of NiFe₂O₄. As presented in Fig. 1 by empty symbols were interpreted in terms of field-induced orientation of individual particles with a disordered spin structure.

Static probing of the magnetic properties of these colloids has revealed the complex internal structure of nanoparticles. It is surmised as a combination of a magnetic core with a uniform magnetization \( m_r \approx 270 \text{ kA/m} \), a large polydispersity, and a surface layer of thickness \( \sim 0.9 \text{ nm} \) with a disordered spin structure.

Static measurements of magneto-optical birefringence presented in Fig. 1 by empty symbols were interpreted in terms of field-induced orientation of individual particles with a log-normal distribution of diameters

\[
P(d) = \frac{1}{\sqrt{2\pi sd}} \exp \left[ -\frac{\ln^2(d/d_0)}{2s^2} \right].
\]  

The parameters \( d_0 = \exp((\ln d)) = 6.5 \text{ nm} \) and standard deviation \( s = 0.55 \) were found from fitting the data of Fig. 1 (empty symbols) with a superposition of Langevin functions.

The parameters \( \rho = 2.3 \) and \( 7.5\% \). The viscosity of pure glycerin at 27°C is 0.85 Pa·s. The concentration is determined by gravimetric analysis. Two volume fractions of nanoparticles are used here, namely \( \Phi = 2.3 \) and 7.5%. The viscosity of pure glycerin at 27°C is \( \eta = 0.85 \text{ Pa·s} \).

Static probing of the magnetic properties of these colloids revealed the complex internal structure of nanoparticles. It is surmised as a combination of a magnetic core with a uniform magnetization \( m_r \approx 270 \text{ kA/m} \), a large polydispersity, and a surface layer of thickness \( \sim 0.9 \text{ nm} \) with a disordered spin structure.

Static measurements of magneto-optical birefringence presented in Fig. 1 by empty symbols were interpreted in terms of field-induced orientation of individual particles with a log-normal distribution of diameters

\[
P(d) = \frac{1}{\sqrt{2\pi sd}} \exp \left[ -\frac{\ln^2(d/d_0)}{2s^2} \right].
\]  

The parameters \( d_0 = \exp((\ln d)) = 6.5 \text{ nm} \) and standard deviation \( s = 0.55 \) were found from fitting the data of Fig. 1 (empty symbols) with a superposition of Langevin functions.

III. DYNAMIC MAGNETO-OPTICAL BIREFRINGENCE UNDER CROSSSED FIELDS

A. Experimental setup

The experimental setup with crossed magnetic fields is presented in Fig. 2. A He-Ne nonpolarized laser beam of wavelength \( \lambda_0 = 632.8 \text{ nm} \) and of weak power (1 mW) first passes a polarizer (P). After that, it goes through a nonbirefringent silica glass cell of thickness \( l \), which contains the probed ferrofluid sample. The optical cells of two thicknesses are used in the present work: 0.2 and 1.0 mm. A cell is positioned between the polar pieces of an electromagnet that produces a horizontal static magnetic field \( H_c \) (bias field), which maximally can reach 240 kA/m. Two coils (B₁ and B₂) in Helmholtz’s position generate a uniform magnetic alternating field, \( H_A \) (probing field) oriented vertically. Its amplitude ranges from 1.6 to 5.6 kA/m. All the experiments are performed under condition that the ratio of the field amplitudes is small: \( H_A/H_c \ll 0.1 \).

With a field on, the cell filled with a ferrofluid behaves as an anisotropic plate and produces a phase lag \( \varphi \) between the two components of the electric field of the light wave (one along and the other across \( H_c \)). Due to that, the laser beam arriving at the analyzer \( A \) is polarized elliptically. The intensity of the light after analyzer is measured with a photodiode (PD) connected to a lock-in amplifier (LIA). This device also generates an oscillating voltage of frequency \( \omega \). This voltage through another amplifier (AMP) is fed to the coils B, creating the alternating field \( H_A \). The temperature of the sample is continuously measured with a platinum probe (R) linked to a voltmeter (V) and is maintained constant at 27±0.2°C with the aid of a Peltier device.

If \( H_A = 0 \), the static bias field \( H_C \) aligns the magnetic particles on the average along its direction. Therefore, the optical axis of the sample coincides with the direction of \( H_C \). As the axis of the polarizer is set parallel to \( H_C \), the beam enters the sample with a plane polarization and preserves it until it meets the analyzer. As the latter is normal to \( H_C \), just the background current of the photodiode is registered, i.e., the setup does not detect any signal.

At \( H_A \neq 0 \), this ac magnetic field, normal to \( H_C \), induces a time-dependent modulation \( \theta(t) \) of the direction of the optical axis (here, \( \theta \) is the angle between the bias field and the instantaneous optical axis of the ferrofluid). The occurring

FIG. 1. Field dependence of the reduced birefringence (Δn scaled with the pertinent saturation values); open symbols: static measurements; and full symbols: measurements at 1 Hz obtained with the setup of Fig. 2. Solid line is the fit by the formulas for birefringence in the static case with the histogram (1).

FIG. 2. Scheme of the experimental setup. The inset shows the configuration of the magnetic fields and the component of the electric vector of the light beam with respect to the instantaneous field \( H_s = H_c + H_A \).
modulated birefringence $\Delta n(t)$ results from the modulation of $\theta(t)$, which in turn is caused by the time dependence of the effective acting field, $\mathbf{H}_e = \mathbf{H}_c + \mathbf{H}_s(t)$.

We assume here that dichroism of the ferrofluid is weak compared to its birefringence, as it is for CoFe$_2$O$_4$ and $\gamma$-Fe$_2$O$_3$. The intensity registered by the present setup is produced by the modulation of birefringence and thus the main response signal is registered at the frequency $2\omega$ (see Ref. 8). The collected light intensity, we denote as $I_{2\omega}$; provided $\varphi \ll 1$, it writes

$$I_{2\omega}(\omega) \propto (\Delta n)^2 \tilde{\theta}^2,$$

with $\tilde{\theta} = \theta e^{i\omega t}$. (2)

As the Brownian relaxation time, $\tau_B$, of rotational diffusion of a nanoparticle in glycerin is about a millisecond, the condition $\omega \tau_B \approx 1$ then corresponds to a frequency about $f_0 = 200$ Hz. The experiment for each pair of fields ($H_A$ and $H_C$) is performed by sweeping the frequency $f = \omega/2\pi$ from 1 Hz up to 10 kHz.

B. Experimental results

We present the measured optical signal as

$$I_{2\omega} = A \exp[i(2\omega t - \psi)],$$

where $A$ is the amplitude and the phase lag $\psi$ is measured with respect to the reference oscillation of the doubled frequency. Both $A$ and $\psi$, as it follows from Eq. (2), are directly related to $\tilde{\theta}$. Two ferrofluid samples ($\Phi = 2.3$ and 7.5‰) are both investigated using the cells of two thicknesses: 0.2 and 1 mm.

The lowest frequency of the experiment is $f_0 = 1$ Hz, which lies well below the Brownian frequency $f_B = (2\pi \tau_B)^{-1}$ of the samples. Making use of this, with good accuracy, we set $A(f_0) = \lim_{f \to 0} A(f)$ and $\psi(f_0) = \lim_{f \to 0} \psi(f)$. The validity of these approximations is proven by Fig. 1, where the birefringence $\Delta n$ obtained with the crossed-fields setup at $f_0$ is compared with the measurements obtained by a static device for the several volume fractions and the previously mentioned thicknesses. Note that at $f_0 = 1$ Hz, one has $\tilde{\theta} = \psi_0 = \arctan(|H_A|/|H_C|)$ that entails $\psi(f_0) = 0$ and $\Delta n(f_0) \approx \sqrt{A(f_0)}$. In the latter relationship, the proportionality factor depends on the light beam intensity and on the sample absorption. Further on, we denote $A(f_0)$ as $A_0$.

The experimental signal $I_{2\omega}$ being proportional to $\tilde{\theta}^2$, in the framework of a simple Debye model, for example, will scale as $(1 - i\omega \tau)^{-2}$ so that the following relations for the amplitude and the phase lag will hold:

$$\frac{A}{A_0} = \frac{1}{1 + \omega^2 \tau^2},$$

$$\psi = \arctan \frac{2\omega}{1 - \omega^2 \tau^2}. \quad (4)$$

For $\omega \tau = 1$ Eq. (4) render $A/A_0 = 1/2$ and $\psi = \pi/2$. We use these relations to define the experimental relaxation time $\tau_{exp}$ and do that, as in Ref. 8, by means of the requirement

$$A(\omega \tau_{exp}) = A_0 / 2.$$

Graphic solution of Eq. (5) is illustrated in Fig. 3. The characteristic time, $\tau_{exp}$, is derived for each experiment, that is, for each volume fraction, each cell thickness, and for each pair of values ($H_A$ and $H_C$). As an example, we find $\tau_{exp} = 2.0$ ms for the experimental conditions of Fig. 3, which are the following: $\Phi = 2.3$‰, $l = 0.2$ mm, $H_C = 48$ kA/m, and $H_A = 4.8$ kA/m.

The specific convenience of the cross-fields method is the possibility to diagnose the mechanism of orientational relaxation in a ferrofluid by analyzing the dependence of the characteristic time, $\tau_{exp}$, on the magnitude of the bias field $H_C$. As shown in Ref. 8, for magnetically soft particles, $\tau_{exp}$ does not depend on the bias field, whereas for magnetically hard grains, the scaling law is close to $\tau_{exp} \propto 1/H_C$ (forced rotary relaxation). To characterize the relaxation mechanism of birefringence in the NiFe$_2$O$_4$ colloids in Fig. 4, the measurements of $\tau_{exp}$ are plotted in a log-log representation for two samples with the NiFe$_2$O$_4$ volumetric content of 7.5 and 2.3‰, respectively, at cell thicknesses 0.2 and 1 mm. Taken in this form, the observed field dependence data group

![Figure 4](image-url)
around the power law \((H_0)^{0.26}\) indicated in Fig. 4 by a straight line. Thus, as a specific feature of the nickel-ferrite ferrofluids, we remark that the effective power exponent differs considerably from both the magnetoisotropic case (exponent equals zero) and the hard-dipole limit with its \(-1\) exponent. 8, 9

### IV. TREATMENT WITH THE JOINT-DIFFUSION MODEL

#### A. Reference times

Apparently, rather simple models of Ref. 8 cannot account for the “fractional” scaling law \(\tau_{\text{exp}} \propto (H_0)^{0.26}\). To obtain an explanation, we employ a much more realistic, and thus, powerful approach proposed recently in Ref. 9. Here, we adapt this treatment for the nickel-ferrite ferrofluids. Specifically, the model explicitly takes into account the fact that in their orientational motion the particles of a ferrofluid are capable of two ways of response to the exerted magnetic field. One is the internal mode: the magnetic moment rotates inside the particle body. The other mode is external (mechanical), and when following it, the magnetic moment turns around together with the particle. Those motions are coupled to each other by means of two physical mechanisms of different origins. One is the internal magnetic anisotropy that makes the easy axis of the particle to be sensitive to the orientation of the magnetic moment and vice versa. The presence and the nature of this interaction are apparent from the expression of the orientation-dependent energy of a particle subjected to a magnetic field \(\mathbf{H} = H\mathbf{h}\)

\[
U = - \mu_0 m_V H (\mathbf{e} \cdot \mathbf{h}) - E_a (\mathbf{e} \cdot \mathbf{n})^2,
\]

where \(m_v\) is the magnetization of the particle substance and \(\mathbf{e}\) is the unit vector of the magnetic moment whose modulus is \(\mu = m_v V_m\), with \(V_m\) being the volume of the ferromagnetic core of the particle. In the highly dispersed systems, like ferrofluids, due to the surface effects, \(V_m\) may be considerably smaller than the entire physical volume, \(V\), of the grain.

In Eq. (6), a positive parameter, \(E_a\), renders the energy of uniaxial magnetic anisotropy, and the easy axis of the latter is determined by the unit vector \(\mathbf{n}\), “imprinted” in the particle body. There exist at least three well-known sources of \(E_a\): bulk (crystallographic), shape, and surface anisotropies.

The second type of interaction between the internal and external motions of the particle is of kinetic origin. This mechanism is due to the internal “magnetic viscosity,” or, in other words, to the finite rate of the establishment of magnetic equilibrium in the particle. This means that it equally exists even if the coupling between \(\mathbf{e}\) and \(\mathbf{n}\) via the anisotropy energy is “switched off” by setting: \(E_a = 0\) in Eq. (6), i.e., in the case of a completely magnetoisotropic object.

To clarify the magnetoviscous coupling of \(\mathbf{e}\) and \(\mathbf{n}\), we recall the Landau-Lifshitz equation, which describes a ferromagnet as a gyrotropic medium. For a particle, it takes the form

\[
\frac{d}{dt} \mathbf{e} = - \gamma (\mathbf{e} \times \mathbf{H}_{\text{eff}}) - \alpha \gamma (\mathbf{e} \times (\mathbf{e} \times \mathbf{H}_{\text{eff}})),
\]

where \(\gamma\) is the gyromagnetic ratio for electrons and \(\alpha\) is a dimensionless damping parameter. In equilibrium, the magnetic moment settles parallel to the effective magnetic field that is expressed by the condition \((\mathbf{e} \times \mathbf{H}_{\text{eff}}) = 0\). On a perturbation, vector \(\mathbf{e}\) does not turn by the shortest way to its equilibrium position but starts to precess about the direction of the effective field \(\mathbf{H}_{\text{eff}}\) with the reference (Larmor) frequency \(\omega_L = \gamma |\mathbf{H}_{\text{eff}}|\). The decay of this gyration is determined by the last term in Eq. (7). Consider the behavior of a perturbed magnetic moment in a spherical coordinate framework rotating about the polar axis \(\mathbf{H}_{\text{eff}}\) with the angular velocity \(\omega_L\). There, Eq. (7) has only the meridional projection, which upon linearization writes

\[
d\theta/dt = - a \gamma |\mathbf{H}_{\text{eff}}| \theta,
\]

where \(\theta\) is the angular deviation of \(\mathbf{e}\) from its equilibrium orientation. Taking into account that \(\mu_0 \mu |\mathbf{H}_{\text{eff}}|\) is the magnitude of the torque that induces the relaxation motion, one finds, according to the usual rules that the coefficient

\[
b = \alpha \gamma / \mu_0 \mu
\]

is the rotary mobility of the magnetic moment. Then, for a system in a thermostat of a temperature \(T\), the use of the Einstein relationship yields

\[
D = b kT,
\]

\[
\tau_D = 1/2D = \mu_0 \mu/2 \alpha \gamma kT,
\]

where \(D\) is the rotary diffusion coefficient of the magnetic moment and \(\tau_D\) is the corresponding rotary diffusion time. For the inner magnetic motions of the particle, this time plays a role analogous to that played by the time \(\tau_B\) of the Brownian rotary motion for a hard-dipole particle. Namely, \(\tau_D\) determines the reference interval after which the magnetic moment “forgets” its direction. With regard to the fact that for a spherical particle, the customary form of the external time is

\[
\tau_B = 3 \eta V/kT,
\]

where \(\eta\) is the viscosity of the suspending liquid and \(V\) is the “hydrodynamic” volume of the particle; the time of internal diffusion may be written in the form resembling that of Eq. (11) as, \(17\)

\[
\tau_D = 3 \eta_m V_m / kT,
\]

\[
\eta_m = \mu_0 m_z / 6 \alpha \gamma
\]

thus introducing the “magnetic viscosity” that has the dimensionality of the usual viscosity but is constructed of the solid-state material parameters. Here, with \(m_z = 270\) kA/m, the bulk magnetization of nickel ferrite (see Sec. II), using \(\alpha = 0.1\) (a typical reference value for ferrites) and \(\gamma \approx 2.3 \times 10^5\) rad-m/(s·A), it becomes \(\eta_m \approx 3 \times 10^{-6}\) Pa·s.

As any viscosity, the magnetic viscosity implies the entrainment effect. Rotating a solid particle in a viscous liquid, one entrains the liquid in motion. A similar situation occurs in the magnetic case: once set out to rotation, the magnetic
moment (spin) experiences the resisting torques on the part of the lattice. This means that by the third Newton law, the particle body, whose angular position in the laboratory frame is described by the vector $\mathbf{n}$, is entrained to follow $\mathbf{e}$. Note that the effect is always of the transient (nonequilibrium) nature, the crucial condition of its existence is the gyrotropy, that is the precessional character of the magnetic-moment motion. Had the precession damped in zero time, i.e., had $\eta_m$ been negligible, there would have been no entrainment of the said kind. Using a conventional language, one may call this case the adiabatic limit with respect to the magnetic degrees of freedom of the particle. Indeed, at $\alpha \to \infty$, its magnetic moment permanently maintains the equilibrium orientation, remaining parallel to the effective field that is the vector sum of the external and internal (anisotropy) ones.

### B. Theoretical analog of $\tau_{\text{exp}}$

The theory of birefringence in crossed fields given in Ref. 9 is based on the solution of the generalized Fokker-Planck equation in the extended configuration space. One of the main results of Ref. 9 is a procedure, which "convolutes" the solution of the kinetic equation into a single reference time. The main steps to that are as follows: First, the pertinent Fokker-Planck equation for the orientation distribution function $W(\mathbf{e}, \mathbf{n}, t)$ of an assembly of magnetic nanoparticles in the cross-field geometry of Fig. 2 is transformed to the set of moment equations. Then, by means of the effective-field method, this infinite set is reduced to just two equations coupling the vector (magnetization) and second-rank tensor (order parameter) modes; for further use, we denote them as $Q_1$ and $Q_2$, respectively. The obtained set on the basis of minimal sufficiency describes an interplay between the external and internal degrees of freedom of the particle, and accordingly incorporates both relaxation times, $\tau_B$ and $\tau_T$, as defined by Eqs. (11) and (12), respectively. Being completely reliable at low fields ($\mu_0 m_s V_m H_C \ll E_D$), the effective-field description becomes inaccurate in the range of $\mu_0 m_s V_m H_C \sim E_D$ as the latter falls beyond the validity limit of the model. On the other hand, the situation where the bias field is comparable with the internal anisotropy, is essential for the experiments of Sec. III.

An adequate improvement of the effective-field approach, which at the same time does not complicate the theory too much, is achieved by renormalizing the internal diffusion time $\tau_D$. Namely, as proposed in Ref. 9, it is changed for an effective value

$$\tilde{\tau}_D = \tau_D(\xi_0, \alpha),$$

$$\xi_0 = \mu_0 m_s V_m H_C / kT,$$

$$\sigma = E_D / kT.$$  \hspace{1cm} (13)

The function $g(\xi_0, \sigma)$ does not have an analytical representation, it is determined from the results of numerical evaluation of the integral time for the vector magnetic relaxation mode in a mechanically trapped particle. Being \textit{a priori} not exact, thus, modified relaxation time $\tilde{\tau}_D$ nevertheless fairly well renders the dependence of the internal relaxation time on the static (bias) field at any value of the anisotropy parameter $\sigma$. Equation (13) is our way to deal with the major problem, whereas the function $g(0, \alpha)$ is known rather well, including the exact solution, a reliable interpolation, and a full function $g(\xi_0, \sigma)$, which until now did not have any convenient approximate representation.

The theoretical dependencies valid for comparison with the optical measurements described in Sec. III are derived in the following way. According to a single-particle concept of field-induced birefringence in ferrofluids (see Ref. 9, for example), the orientational order parameter of the particle assembly in direct proportion determines the optical anisotropy $\Delta n$. The latter, in turn, by the relation $(\Delta n)^2 \approx I$ [see Eq. (2)], is connected to the light intensity $I$, which is recorded experimentally. To obtain a theoretical analog of Eq. (5), we first solve the two-equation set coupling $Q_1$ and $Q_2$. In the result, one gets $Q_2$ as a finite expression incorporating all the kinetic coefficients of the set: the diagonal and cross-relaxation ones; in particular, the explicit frequency dependence is determined. At the next step, in the function $Q_2(\omega)$, the plain internal relaxation time, $\tau_D$, is replaced by $\tilde{\tau}_D$. Then, the equation

$$[Q_2(\omega)]^2 = \frac{1}{2} [Q_2(0)]^2,$$  \hspace{1cm} (14)

is constructed. The quantity $Q_2(0)$ is the static, i.e. maximal, value of the order parameter for a given sample. Equation (14) is the theoretical analog of Eq. (5), which defines the experimental time $\tau_{\text{exp}}$. Resolving this transcendental equation with respect to frequency, one gets the root $\omega_*$, which depends parametrically on the dimensionless bias field strength $\xi_0$, the anisotropy parameter $\sigma$, and on the modified ratio $\tilde{e} = \tilde{\tau}_D / \tau_B$ of the relaxation times of the system. The quantity $1 / \omega_*$ is then taken as a reference time for the light intensity relaxation and is denoted as $\tau_{1/2}$. As it follows from the previously described procedure, in the framework of our theory, $\tau_{1/2}(\xi_0, \sigma, \tilde{e})$ is the closest analog of the experimental time $\tau_{\text{exp}}$. Except for limiting cases, finding $\tau_{1/2}(\xi_0, \sigma, \tilde{e})$ is a numerical operation. For further use, we remark the value that $\tau_{1/2}$ assumes at $\xi_0 \to 0$ and $\sigma = \infty$, i.e., in the hard-dipole case. This number may be found analytically and writes

$$\tau_{1/2}(0, \infty) / \tau_B = 2 / \sqrt{265 - 11} = 0.8705.$$  \hspace{1cm} (15)

Note that setting $\sigma = \infty$ is equivalent to the statement that in the hard-dipole limit $\tilde{e}$ is infinite. We remark that the number given by Eq. (15) is close to the same (i.e., hard dipole) asymptotic value of the conventional effective relaxation time, $\tau_{\text{eff}} = 5 \tau_B / 6 = 0.8333 \tau_B$ (see Refs. 9 and 20), but does not equal it. This absence of coincidence is quite natural as those two times, although both of them are integral ones and both describe the relaxation of birefringence in a suspension of hard-dipole particles, are evaluated by different procedures.

We write $\tau_{1/2}$ as a function of the modified ratio $\tilde{e}$, despite the fact that the function $g$ depends on the same arguments: $\xi_0$ and $\sigma$. This is done to emphasize the essential role, which $\tilde{e}$ plays in our considerations. Meanwhile, the absolute value of the "seeding" parameter is typically quite small. Taking the ratio of the relaxation times in Eqs. (11) and (12) one gets
Taking \( \eta_0 \approx 3 \times 10^{-6} \) Pa·s [see Eq. (12)], \( \eta = 0.85 \) Pa·s (glycerin), and \( V_m/V \approx 0.1 \), one finds \( \varepsilon \approx 3 \times 10^{-7} \). This does not mean, however, that \( \varepsilon \) may be neglected. Indeed, due to the renormalization \( \tau_0 \Rightarrow \bar{\tau}_D \), the equations contain not \( \varepsilon \) itself but the effective parameter \( \bar{\varepsilon} \). The latter incorporates the function \( g(\xi_0, \sigma) \), which at large \( \sigma \) becomes exponential. Consequently, at any nonzero \( \varepsilon \), whatever small, the parameter \( \bar{\varepsilon} \) becomes relevant. The range where neglecting \( \varepsilon \) is essentially incorrect, i.e., the potential barrier is high enough, may be approximately written as \( \sigma \gg \xi_0 \gg 1 \). This condition is not trivial. The appropriate estimation was derived in Ref. 21 (for extended discussion see Refs. 19 and 22), where it was shown that the lowest eigenvalue (the inverse of the longest reference relaxation time) of the appropriate micromagnetic Fokker-Planck equation ceases to be exponential in \( \sigma \) as soon as \( \xi_0/\sigma \gg 0.17 \). This establishes the range within which the particle magnetic moment overcoming the anisotropy energy barrier becomes quite feasible. In other words, the hard-dipole approximation is no longer valid.

Using the previously written condition for the qualitative renormalization of the superparamagnetic relaxation time, one arrives at the Néel-like expression \( \bar{\varepsilon} = \varepsilon \exp(\sigma - 6\xi_0) \). Substituting it in the estimation \( \bar{\varepsilon} \sim 1 \), one defines the reference value \( \xi_0^* = (\sigma + \ln\sigma)/6 \). Apparently, this criterion applies only to the cases where \( \xi_0^* \) comes out positive. Then, its role is shown as follows: At \( \xi_0 \ll \xi_0^* \), the particle behaves similar to a hard magnetic dipole, whereas at \( \xi_0 \ll \xi_0^* \), the times \( \tau_0 \) and \( \tau_D \) are comparable. Accordingly, the interaction between the modes is strong and cannot be reduced to any limiting cases. At \( \xi_0 \gg \xi_0^* \), the orientational potential is dominated by the external field, one may neglect \( \bar{\varepsilon} \), and thus \( \bar{\tau}_D \). In this case, the particle behaves as a magnetically soft one.

V. DISCUSSION OF THE RESULTS

On the basis of the model developed in Ref. 9, we perform a detailed comparison between the measured dependence \( \tau_{exp}(H_C) \) given in Fig. 4 and the integral time \( \tau_{1/2} \). However, before describing the fitting procedure, it is instructive to discuss the situation in the qualitative aspect. First, we recall that in the high-field range \( \xi_0 \gg \xi_0^* \) setting \( \varepsilon = 0 \) is justifiable, one may write down the approximate relationship \( \tau_{1/2} \approx \tau_B \approx g_1(\sigma) / \xi_0^* \) with the limiting behaviors

\[
g_1 = \begin{cases} 
\frac{1}{3} + \frac{1}{\sigma} - \frac{5}{441} \sigma^2 + \cdots & \text{for } \sigma \ll 1, \\
\frac{1}{\sigma} + \frac{1}{\sigma^2} - \frac{1}{\sigma^3} + \cdots & \text{for } \sigma \gg 1,
\end{cases}
\]

Estimating these relationships with respect to the same double logarithmic scale as used in Fig. 4, one sees that, depending on the relative magnitudes of the coefficients \( g_1 \) and \( g_2 \), the log-log trend may have two limiting regimes. The first occurs for perfectly isotropic magnetic particles: \( \sigma = g_2 = 0 \), hence \( \tau_{1/2} = \tau_B / \xi_0^* \), and the slope is zero. The second regime takes place for the particles with an infinite magnetic rigidity: \( 1/\sigma = g_1 = 0 \), so that at \( \xi_0 \gg 1 \), one has \( \tau_{1/2} \approx \tau_B / \xi_0^* \) and the slope equals -1. For intermediate situations, Eq. (17) yields a behavior in which a double logarithmic plot will be confined in between the two previously mentioned lines. The slope -0.26 characteristic of Fig. 4 definitely falls inside this range.

In order to quantitatively interpret the data of Fig. 4 in terms of the time \( \tau_{1/2}(H_C) \), the experimental parameters should be converted in the dimensionless forms used as the input for the model. We do that for the bias field \( H_C \) and the seeding relaxation times [see Eq. (16)], keeping the anisotropy parameter \( \sigma \) as an adjustable quantity.

With respect to the bias field, it is necessary to estimate the ratio \( \xi_0/H_C = \mu_0 m V_m / kT \). According to the log-normal size distribution given by Eq. (1) in Sec. II, we define the magnetic volume of a particle as

\[
V_m = \frac{\pi}{6} d^3 = \frac{\pi}{6} d^3 \exp \left( \frac{9\xi_0^2}{2} \right) = 5.6 \times 10^{-25} \text{ m}^3,
\]

where, the current diameter \( d \) refers to the magnetic core of the particle. Taking for the equilibrium magnetization of the core, the value \( m_s = 270 \) kA/m, as for the bulk NiFe\(_2\)O\(_4\), we obtain

\[
\xi_0 = \frac{\mu_0 m_s V_m}{kT} H_C = 4.7 \times 10^{-2} H_C
\]

with \( H_C \) in kA/m; reading this relation in an inverse direction, one gets \( H_C = 21.3 \xi_0 \) in kA/m.

The second input parameter is \( \varepsilon \) introduced by Eq. (16), and for the reference material parameters, its numerical value is

\[
\varepsilon \approx 3 \times 10^{-7}.
\]

As already mentioned, in the fitting process, we have to find the value of the anisotropy parameter \( \sigma \) at which the theoretical curve \( \tau_{1/2}(\xi_0) \) in the best way follows the experimental points. We perform nonlinear fitting using the
As it follows from the theory, the extent of coupling of the relaxation processes directly affects the value, which the curve \( \tau_{1/2}(H_C) \) tends to at zero bias fields. Visually, in Fig. 5, the theoretical relaxation time (solid curve) “hits” the vertical axis close to 3 ms. In the hard-dipole approximation, this level equals 0.87 \( \tau_B \) [see Eq. (15)], which for the set of parameters shown in Eq. (22), makes about 4.3 ms. The behavior of \( \tau_{1/2}(H_C) \) in the hard-dipole case is shown in Fig. 5 by the upper dashed curve. On the other hand, for a perfectly magnetically soft particle \( (\sigma=0) \), the limit at \( H_C \to 0 \) is \( \tau_{1/2} = \tau_B/3 \approx 1.6 \) ms. The corresponding contour is shown by the lower dashed curve in Fig. 5. One sees that both dashed curves differ considerably from the solid one. Grouping of the measured data around the latter curve clearly proves that the orientational relaxation of nanoparticles in the nickel-ferrite ferrofluids is a process where the internal and external rotary degrees of freedom are strongly coupled.

For NiFe\(_2\)O\(_4\) particles, there exists enough evidence to associate their magnetic anisotropy mostly with the surface. In this case, the dimensionless parameter we use may be presented as \( \sigma = \pi a^2 K_S/kT \), where \( K_S \) is the density of the surface anisotropy energy, which we associate with the anisotropy of the Aharonian type.\(^{24}\) Such a structure of the anisotropy gets nowadays more and more justifications; we note Ref. 25, where this phenomenology has been given a new advance. With the log-normal distribution of diameters (1), one has \( d^2 = d_0^2 \exp(2s^2) = 7.5 \times 10^{-17} \) m\(^2\). Then, a preliminary estimate is \( \sigma = 6 \times 10^4 K_S \), where \( K_S \) is expressed in Joule per square meter, and the result is dimensionless.

Concerning the numerical value of \( K_S \), we remark the following: In Ref. 26, we have derived the value of this parameter for maghemite nanoparticles from the FMR measurements on the frozen ferrofluids and found \( K_S \approx 3 \times 10^{-3} \) J/m\(^2\). In Ref. 27, the authors did a numerical simulation of the structure of fine particles of both maghemite and nickel ferrite. To match the experimental evidence, they had to assign to nickel ferrite the value of the surface anisotropy four times higher than that for the maghemite. We adopt the mentioned proportion and take for nickel ferrite \( K_S \approx 1.2 \times 10^{-3} \) J/m\(^2\). Substituting this in our estimation, we get \( \sigma = 6 \times 10^4 K_S \approx 7 \). The latter value plays the role of an independent estimation for \( K_S \) in the nanodisperse NiFe\(_2\)O\(_4\) and is to be compared to \( \sigma \approx 20 \) obtained from fitting in Fig. 5. Recalculating the latter to the surface anisotropy constant, one finds \( K_S \approx 3 \times 10^{-1} \) J/m\(^2\). With allowance for a strong polydispersity of the NiFe\(_2\)O\(_4\) ferrofluids under study, one should take this mostly by the order of magnitude. As such, it is consistent with the value \( K_S \approx 1.2 \times 10^{-3} \) J/m\(^2\) adopted in Ref. 27 to describe the experimental hysteresis loops of solid samples containing the nanosize NiFe\(_2\)O\(_4\) particles.

On the subject of \( K_S \) values for NiFe\(_2\)O\(_4\), we remark also Ref. 28, where an example demonstrating the ability of the nickel-ferrite nanoparticles to considerably enhance their surface anisotropy in response to stresses is given. There, the NiFe\(_2\)O\(_4\) grains of the size about 8 nm in a silica matrix were studied. The strong surface magnetic anisotropy had been encountered and attributed to the stress accumulated at the particle-matrix interface. Recalling that the particles under

Levenberg-Marquardt method implemented in the MRQMIN routine.\(^{23}\) Keeping constant only the “seeding” ratio of the relaxation times, the values of \( \sigma, \xi_0/H_C \), and \( \tau_0 \) as the normalizing parameters we determine from fitting. The result is as follows:

\[
\sigma = 19.7, \quad \xi_0/H_C = 0.033 \text{ m/kA}, \quad \tau_B = 4.9 \text{ ms}. \tag{22}
\]

We note that the obtained value of the coefficient \( \xi_0/H_C \) is close enough to that obtained as a simple estimate [see Eq. (20)]. The full theoretical calculation of \( \tau_{1/2}(\xi_0) \) with the parameters shown in Eqs. (19) and (22) is presented in Fig. 5; the graph is plotted in exactly the same scale as the one shown in Fig. 4. The comparison of those figures shows that the theoretical model curve fairly well accounts for the experimental points.

To test the consistency of the fitting results, let us first estimate the mean “hydrodynamic” volume of the particle corresponding to \( \tau_B = 5 \) ms. Equation (11) gives \( V \approx 8 \times 10^{-24} \) m\(^3\). Comparing this with Eq. (19), we find \( V_m/V = 0.1 \). The last result yields a justification for the numerical value of the volume ratio, which in Eq. (16), we have chosen as an \textit{a priori} one.

Combining the found value of the anisotropy parameter \( \sigma \approx 20 \) with \( \epsilon \) from Eq. (20), we get an estimate for the reference parameter \( \xi_0 \approx 1 \). On the other hand, the maximal bias field used in the experiment ranges \( H_C = 240 \) kA/m, which with allowance for the coefficient from Eq. (22), recalculates to \( \xi_0 \approx 8 \). Thus, one sees that the range of bias fields shown in Fig. 5 corresponds to the situation \( \xi_0 \approx \xi_0^* \), which means closeness of the relaxation times and, consequently, strong coupling of the internal and external magnetono-orientational modes. This means that despite obvious smallness of the “seeding” \( \epsilon \) shown in Eq. (21), it ought to be taken into account for a correct calculation of the relaxation time.

As it follows from the theory, the extent of coupling of the relaxation processes directly affects the value, which the curve \( \tau_{1/2}(H_C) \) tends to at zero bias fields. Visually, in Fig. 5, the theoretical relaxation time (solid curve) “hits” the vertical axis close to 3 ms. In the hard-dipole approximation, this level equals 0.87 \( \tau_B \) [see Eq. (15)], which for the set of parameters shown in Eq. (22), makes about 4.3 ms. The behavior of \( \tau_{1/2}(H_C) \) in the hard-dipole case is shown in Fig. 5 by the upper dashed curve. On the other hand, for a perfectly magnetically soft particle \( (\sigma=0) \), the limit at \( H_C \to 0 \) is \( \tau_{1/2} = \tau_B/3 \approx 1.6 \) ms. The corresponding contour is shown by the lower dashed curve in Fig. 5. One sees that both dashed curves differ considerably from the solid one. Grouping of the measured data around the latter curve clearly proves that the orientational relaxation of nanoparticles in the nickel-ferrite ferrofluids is a process where the internal and external rotary degrees of freedom are strongly coupled.

For NiFe\(_2\)O\(_4\) particles, there exists enough evidence to associate their magnetic anisotropy mostly with the surface. In this case, the dimensionless parameter we use may be presented as \( \sigma = \pi a^2 K_S/kT \), where \( K_S \) is the density of the surface anisotropy energy, which we associate with the anisotropy of the Aharonian type.\(^{24}\) Such a structure of the anisotropy gets nowadays more and more justifications; we note Ref. 25, where this phenomenology has been given a new advance. With the log-normal distribution of diameters (1), one has \( d^2 = d_0^2 \exp(2s^2) = 7.5 \times 10^{-17} \) m\(^2\). Then, a preliminary estimate is \( \sigma = 6 \times 10^4 K_S \), where \( K_S \) is expressed in Joule per square meter, and the result is dimensionless.

Concerning the numerical value of \( K_S \), we remark the following: In Ref. 26, we have derived the value of this parameter for maghemite nanoparticles from the FMR measurements on the frozen ferrofluids and found \( K_S \approx 3 \times 10^{-3} \) J/m\(^2\). In Ref. 27, the authors did a numerical simulation of the structure of fine particles of both maghemite and nickel ferrite. To match the experimental evidence, they had to assign to nickel ferrite the value of the surface anisotropy four times higher than that for the maghemite. We adopt the mentioned proportion and take for nickel ferrite \( K_S \approx 1.2 \times 10^{-3} \) J/m\(^2\). Substituting this in our estimation, we get \( \sigma \approx 6 \times 10^4 K_S \approx 7 \). The latter value plays the role of an independent estimation for \( K_S \) in the nanodisperse NiFe\(_2\)O\(_4\) and is to be compared to \( \sigma \approx 20 \) obtained from fitting in Fig. 5. Recalculating the latter to the surface anisotropy constant, one finds \( K_S \approx 3 \times 10^{-1} \) J/m\(^2\). With allowance for a strong polydispersity of the NiFe\(_2\)O\(_4\) ferrofluids under study, one should take this mostly by the order of magnitude. As such, it is consistent with the value \( K_S \approx 1.2 \times 10^{-3} \) J/m\(^2\) adopted in Ref. 27 to describe the experimental hysteresis loops of solid samples containing the nanosize NiFe\(_2\)O\(_4\) particles.

On the subject of \( K_S \) values for NiFe\(_2\)O\(_4\), we remark also Ref. 28, where an example demonstrating the ability of the nickel-ferrite nanoparticles to considerably enhance their surface anisotropy in response to stresses is given. There, the NiFe\(_2\)O\(_4\) grains of the size about 8 nm in a silica matrix were studied. The strong surface magnetic anisotropy had been encountered and attributed to the stress accumulated at the particle-matrix interface. Recalling that the particles under

![Figure 5](image-url)
present study have a shell-core structure, where the shell is nonmagnetic and differs in content from the magnetized NiFe$_2$O$_4$ core, in our case, the interface stress contribution to the surface anisotropy might be suspected to add to $K_S$.

VI. CONCLUSIONS

With the aid of a self-consistent theoretical model, which takes into account the whole set of the degrees of freedom of single-domain grains suspended in a liquid, we examine the measurements of crossed-field dynamic birefringence in ferrofluids based on the nickel-ferrite nanoparticles. A major specific feature of these systems is that for them the dependence of the relaxation time $\tau$ on the amplitude of the bias field yields the slope $d \ln \tau / \ln H_C$ about $-1/4$. This intermediate value is considerably far from both limiting cases: zero (magnetically soft grains, e.g., maghemite) and minus one (magnetically hard nanoparticles, e.g., cobalt ferrite).

From our theoretical interpretation, it follows that the physical cause of the previously mentioned behavior of NiFe$_2$O$_4$ particles is that in the measurement field range, the amplitudes of the bias and internal anisotropy fields are comparable and none is dominating. To describe such a case, our theory has no alternatives. Applying it, we obtain the dependence, which fairly well describes the observed $\tau(H_C)$ behavior. Notably, we find that the power law $(H_C)^{-1/4}$, although being just an experimental trend, is able to resemble the actual behavior $\tau_{\text{exp}}(H_C)$ in some ranges of $H_C$ with acceptable accuracy.

The numerical estimation of the anisotropy parameter of NiFe$_2$O$_4$ particles yields the values, which by no means could be accounted for by the ferrite bulk anisotropy or by that due to the particle shape. The only reasonable explanation is to attribute this effect to the surface of the particles. The comparison of the values of $E_s/kT$ obtained here ($\approx 20$) with those from an independent estimation ($\approx 7$) indicates an agreement by the order of magnitude. As these numbers refer to the nanoparticles prepared by different methods, the discrepancy looks quite justifiable given the ability of NiFe$_2$O$_4$ grains to modify their surface anisotropy under external factors.

To our knowledge, the presented study is an example, where the particles of such an intermediate type of magnetic anisotropy are tested and characterized in simple dynamic experiments with ferrofluids. In this connection, we remark that the nickel-ferrite nanosystems are among the less studied ones and a considerable work on the subject is required.

Two of the authors (Y.L.R. and V.I.S.) acknowledge the partial financial support from the Russian Foundation for Basic Research (Projects 02-02-17221 and 04-02-96034) and from CRDF Award PE–009–0. This work was also supported by the Brazilian and French agencies through the contracts of international cooperation CAPES/COFECUB n°292/99 and CNPq/CNRS n°14286.