CONDENSED MATTER

Anomalous Decay in Short Time Response of Ternary Mixtures with Ferrofluid

**I. M. Laczkowski · H. Mukai · P. R. G. Fernandes ·
R. S. Mendes · Luiz Roberto Evangelista**

Abstract We study the optical transmittance of ternary mixtures of water, glycerin and ferrofluids. These mixtures are subject to pulsed magnetic field and placed between crossed polarizers. After the magnetic field is switched off, the decay process is compared with q-exponential, stretched exponential, Mittag–Leffler, and one-sided Lévy stable functions. For short time, the experimental results are interpreted in terms of stretched exponentials. The parameters of this non-exponential relaxation are investigated as functions of temperature and the water, glycerin and ferrofluid concentrations.

Keywords Magnetic fluids · Ferrofluids ·
Magnetic liquids · Magneto-optical effects

1 Introduction

Ferrofluids are suspensions of small single domain ferromagnetic particles in a carrier liquid [1, 2]. These systems present induced magnetic birefringence under the action of magnetic field of various strengths and, for this reason, the optical transmittance of ferrofluids has attracted the interest of many groups [3–11]. These field-induced properties usually have special relaxation behavior that are particularly sensitive to the parameters characterizing the host medium. In this paper, we analyze the results of measuring the magnetic birefringence of different samples of ferromagnetic particles

in pure water and glycerin (a ternary mixture). The focus of our investigations is the characteristic relaxation times obtained from the transient behavior of the transmittance intensity. This ternary mixture was chosen for its biological and technological interest [12, 13]. A system formed by water and glycerin is useful to explore the contrasting character of these materials. Even if related mixtures have been investigated by other groups with several different approaches (see e.g. Refs. [11, 14–17]), we are reexamining their characteristic relaxation behavior and showing that it is richer than it is usually supposed to be. For this reason, it deserves a more embracing mathematical description considering generalized (non-exponential) distributions to account for the experimental behavior.

2 Experiment

The samples under study are composed of distilled water, bidistilled glycerin and mixtures of these two materials in different proportions. They were doped with ferrofluid material in three different concentrations: $0.1\,\mu$l/ml, $0.3\,\mu$l/ml, and $0.5\,\mu$l/ml. The water-based ferrofluid (EMG 607) used in our experiments were obtained from Ferrotec Corporation. The different mixtures were encapsulated between glass plates of dimensions $50.0\,\text{mm} \times 10.0\,\text{mm}$ (optical path) $\times\ 10.0\,\text{mm}$ and maintained in contact with a heat bath with a temperature control system whose precision is of $0.1°$C (circulating temperature bath). The lowest (highest) studied temperature is $5.8°$C ($66.7°$C). The experimental technique employed to induce order within the samples for the investigation of the magneto-optics relaxations consists in orienting the director field of each magnetic

I. M. Laczkowski · H. Mukai · P. R. G. Fernandes ·
R. S. Mendes · L. R. Evangelista (✉)
Departamento de Física, Universidade Estadual de Maringá,
Avenida Colombo 5790, 87020–900 Maringá, Paraná, Brazil
e-mail: lre@dfi.uem.br

grain inside the sample. The doped mixture is placed between crossed polarizers at 45° with respect to the magnetic field direction. The optical transmittance is measured using a standard technique with a He–Ne laser ($\lambda = 632.8$ nm, 10 mW) and a photodiode connected to an oscilloscope (Tektronix TDS 3012). The external pulsed magnetic field is applied perpendicularly to the laser beam direction. The magnetic field of about 500 G is a square wave with the frequency of 1.0 Hz controlled by a function generator (Stanford Research system DS335).

3 Non-exponential Relaxation

In this context, a typical normalized transmittance intensity is presented in Fig. 1a, in which we keep one of our ternary mixtures at a given temperature. Here this normalized transmittance intensity, $T(t)$, is the intensity of transmitted light across the sample as function of the time t, $I(t)$, divided by $I(0)$, i.e., $T(t) = I(t)/I(0)$. Note that the origin of time is chosen when the font of magnetic field is switched off. A first trial to analyze how the normalized transmittance decays is to compare it with a usual relaxation, $T(t) = \exp(-t/\tau)$, where τ is the characteristic time of the process. Our motivation for this first attempt is evident: the exponential decay is a very simple function that has proved appropriate in countless treatments, ranging from phenomenological approaches to more formal ones. In this case, $T(t)$

obeys the differential equation

$$\frac{dT}{dt} = -\alpha\, T \qquad (T(0) = 1)\,, \qquad (1)$$

with $\alpha = 1/\tau$.

As we can directly see from Fig. 1b, the monolog plot of our data deviates substantially from a straight line indicating an unusual (i. e., non-exponential or anomalous) relaxation process. We must therefore search for an alternative description for our data. Generalizations of the exponential behavior may be considered in order to encompass important aspects of the anomalous behavior. Particulary useful are those generalizations that resemble an exponential and depend on control parameters. For instance, $T(t) = [1 + (1/n)(t/\tau)]^{-n}$ recovers $\exp(-t/\tau)$ in the limit $n \to \infty$. In addition, we have $T(t) \sim t^{-n}$ for $t \gg n\tau$. Note also that letting $\alpha = -T^{1/n}/\tau$ in (1) yields the above $T(t)$ as a solution. Furthermore, this alternative for the exponential is central in the generalized statistical mechanics of Tsallis and its applications [18–20]; it corresponds to the Boltzman factor in this scenario and is usually referred to as the q-exponential. This function has been employed in several contexts such as the pioneering studies of luminescence by Becquerel [21, 22], sensitivity to initial conditions in nonlinear maps [19, 23] and complex systems [19, 20]. In view of the log-log plot in Fig. 1c, we may at first glance be tempted to employ the same procedure in our study of relaxation. Closer comparison

Fig. 1 Normalized transmittance T as a function of time t (in s) of the ternary mixture water (66.7%), glycerin (33.3%) and ferrofluid (0.1 μl/ml) at the temperature 43.5°C in **a** linear, **b** monolog, **c** log-log, and **d** stretched plots. The *circles* represent the data, and the *continuous line* in **d** is the stretched exponential (2) with $\beta = 1.51$ and $\tau = 2.2$ ms
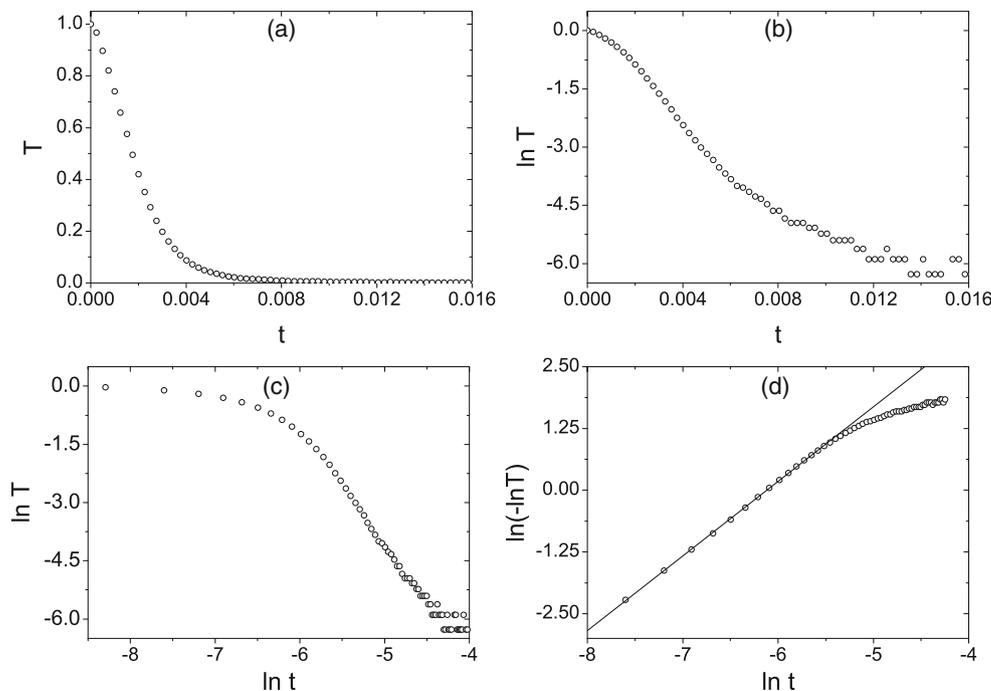
with the data nonetheless discards the *q*-exponential from the set of good candidates.

The stretched exponential

$$T(t) = e^{-(t/\tau)^{\beta}} \tag{2}$$

is another natural candidate to describe the anomalous relaxation of our ternary mixture. The exponential function is recovered in the limit $\beta \to 1$. Moreover, when compared with an exponential, the long-time behavior of the right-hand side of (2) is short (long) for $\beta > 1$ ($\beta < 1$). Strictly speaking, therefore, the relaxation is only stretched for $\beta < 1$. Nonetheless, following other authors, we take the liberty of referring to the function (2) as a stretched exponential even for $\beta > 1$. This generalization of exponential may be viewed as the solution of (1) for $\alpha = -\beta t^{\beta-1}/\tau^{\beta}$. What is more, just as well as the *q*-exponential, (2) can be obtained from a maximum entropy principle [24]. And its record of successful applications to relaxation phenomena is

comparable to that of the *q*-exponential. Examples are studies of the electrical polarization of glassy materials, a set including the seminal work of Kohlrausch [25–27], of hydrogenated amorphous silicon [28], and of economical systems [29]. Several applications to ferrofluids have also been reported [3, 4, 11]. To determine graphically whether the stretched exponential fits a given set of data well, a common practice is to plot $\ln\{-\ln[T(t)]\}$ as a function of $\ln t$ and check the linearity of the resulting curve. From (2), we expect a straight line, since $\ln(-\ln(T(t)) = A + B \ln t$, where $\tau = \exp(-A/B)$ and $\beta = B$. Figure 1d applies this procedure to our data and shows that a stretched exponential describes the short-time behavior very well.

If a fractional derivative $d^{\gamma}T/dt^{\gamma}$ ($0 < \gamma < 1$) is substituted for dT/dt in (1), a differential equation is obtained whose solution is a Mittag–Leffler function instead of the exponential [30, 31]. This non-exponential relaxation has been employed to discuss stress relaxation at constant strain [32], effects of thermal expan-
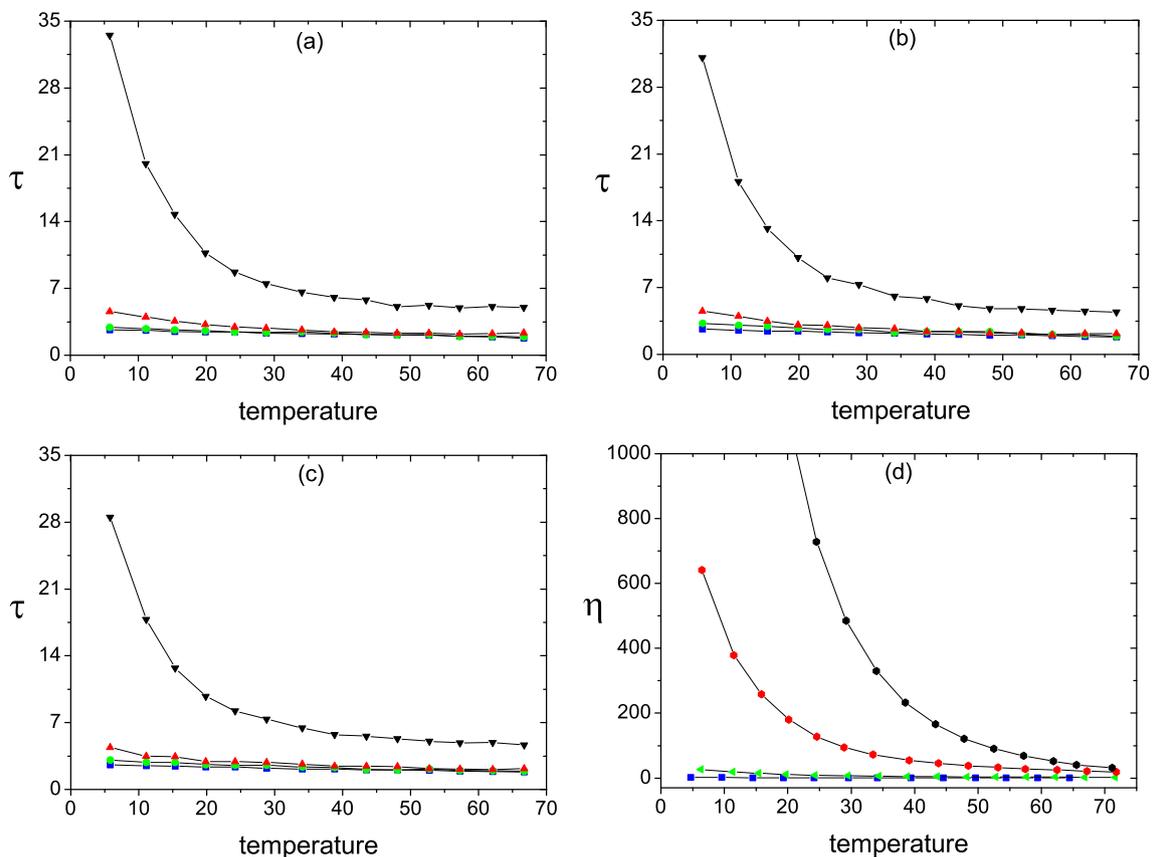
Fig. 2 (Color online) relaxation time τ (ms) as a function of temperature (°C) for three ferrofluid concentrations: **a** 0.1 μl/ml, **b** 0.3 μl/ml and **c** 0.5 μl/ml. **d** Glycerin viscosity (without ferrofluid) η (cP) versus temperature. The *down triangles*, *up triangles*, *circles*, and *squares* refer to mixtures with 0.0% (100.0%), 16.7% (83.3%), 40.0% (60.0%), and 100.0% (0.0%) water (glycerin), respectively
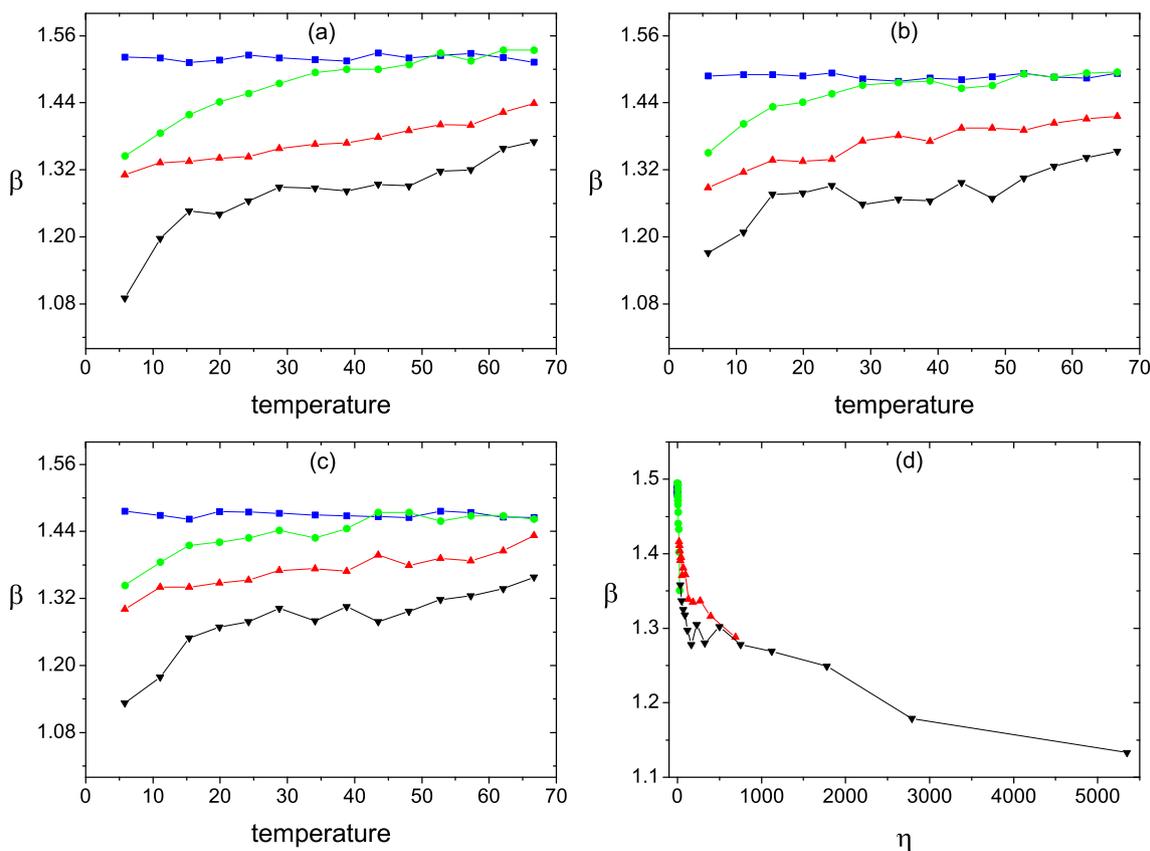
Fig. 3 (Color online) the exponent β in (2) as a function of temperature (°C) for three ferrofluid concentrations: **a** 0.1 μl/ml, **b** 0.3 μl/ml and **c** 0.5 μl/ml. **d** β as a function of temperature for ferrofluid concentration 0.3 μl/ml. The *down triangles*, *up trian-* *gles*, *circles* and *squares* represent mixtures with 0.0% (100.0%), 16.7% (83.3%), 40.0% (60.0%), and 100.0% (0.0%) water (glycerin), respectively

sion in granular systems [30], and relaxation dynamics of proteins [33], among other applications. Notice that this solution is positive for all $t \geq 0$ only if $\gamma \leq 1$. In this case, it has basically two regimes: a stretched exponential for short time and a power law for long times [31]. Under such conditions, the parameter β is smaller than the unity, in contrast to our data, which give $\beta > 1$ (see Fig. 1d). The fractional-derivative approach is therefore unsuitable to describe our data.

Variants of the Mittag–Leffler functions are the one-sided Lévy distributions $g_\alpha(t)$, which can be defined via the Laplace transform $\int_0^\infty e^{-st} g_\alpha(t)dt = e^{-s^\alpha}$, with $0 < \alpha < 1$ and $s > 0$. These functions have been applied in several contexts, such as condensed and soft matter physics [34, 35], geophysics [36], economics [37], and fractional kinetics [38]. Although explicit expressions for $g_\alpha(t)$ are only known for a few α's, certain properties of $g_\alpha(t)$ are well established (see Ref. [39] and references therein). For instance, its small-time behavior ($t \rightarrow 0^+$) is given by $g_\alpha(t) \propto t^{-\sigma} \exp(-At^{-\nu})$, where $\sigma = (2 - \alpha)/(2 - 2\alpha)$, $\nu = \alpha/(1 - \alpha)$ and $A =$

$(1 - \alpha)\alpha^{\alpha/(1-\alpha)}$. This behavior is sufficient to allow comparison with our data. For small t, not too close to $t = 0$, the agreement is good. On the other hand, we have $T(0) = 1$ and $g_\alpha(0^+) = 0$, which argues against modeling $T(t)$ with $g_\alpha(t)$.

Yet another generalization of the exponential stems from combining the stretched exponential with the q-exponential, as illustrated by the expression $T(t) = [1 + (1/n)(t/\tau)^\beta]^{-n}$. This relaxation function, the solution of (1) with $\alpha = -\beta t^{\beta-1}T^{1/n}/\tau^\beta$, has been employed, for instance, in investigations of anomalous diffusion [40] and turbulent flows [41]. Now, with three adjustable parameters at our disposal, more accurate fits become possible; yet, we are unable to match the entire curve.

Other approaches based on (1) may of course be used to discuss decay processes. For instance, the relaxation in ferrofluids has been investigated by means of the Bernoulli equation [42]. A myriad of generalizations of the exponential function results from convenient choices of α in (1). Even if we take advantage

of this mathematical freedom, however, it is likely that several adjustable parameters become necessary to fit the entire time dependence to our satisfaction.

To circumvent the difficulties associated with such artificial constructions we take a minimalist stance and restrict our analysis to a subset of our data. As illustrated by Fig. 1d, we have verified that stretched exponentials, with only two parameters, fit our data very well for short times t. Henceforth we will therefore consider only the short-time behavior of the transmittance in the ternary mixture.

4 Results

Fits of our data with the stretched exponential (2) yielded the relaxation time τ for several concentrations of water, glycerin and ferrofluid as a function of temperature. Figure 2a (Fig. 2b and c) refers to 0.1 μl/ml (0.3 μl/ml and 0.5 μl/ml) ferrofluid concentration and shows the decay of τ for growing temperature at fixed water (glycerin) percentage. The three figures show τ to be moderately sensitive to temperature changes in the absence of glycerin. Thus, for instance, for a ferrofluid concentration of 0.1 μl/ml, $\tau = 2.7$ ms at 5.8°C and $\tau = 1.8$ ms at 66.7°C. Figure 2d shows that the temperature dependence of the glycerin viscosity η follows the typical pattern, the viscosity decreasing rapidly as the temperature grows. These results are consistent with relaxation times that grow with the viscosity.

Consider now the stretched exponential parameter β. Initially, note that Fig. 3a–c show that β tends to 1.5 at high temperatures and is essentially constant for small glycerin density. This is consistent with Mertelj's et al's study of a ferrofluid with oleic-oil surfactant [11]. However, Fig. 3a–c also shows that β decreases with the ferrofluid concentration, at least in the absence of glycerin. Taking into account the typical concentrations of our ternary mixture (the ones in Fig. 3a–c), we are led to a general scenario: β tends to grow with temperature. From Figs. 2d and 3b, we can plot β as a function of the viscosity η. Typical curves are presented in Fig. 3d. The main trend shown in this figure is the decay of β with increasing η. The parameter β is very (not so) sensitive to changes in η for low (high) glycerin concentration.

Table 1 Values of τ at 66.7°C, τ_m, for several ternary mixtures of water, glycerin and ferrofluid

Ferrofluid\Water	0.0%	16.7%	40.0%	100.0%
0.1 μl/ml	1.8 ms	1.9 ms	2.1 ms	4.6 ms
0.3 μl/ml	1.9 ms	1.9 ms	2.2 ms	4.7 ms
0.5 μl/ml	1.9 ms	1.9 ms	2.2 ms	4.7 ms
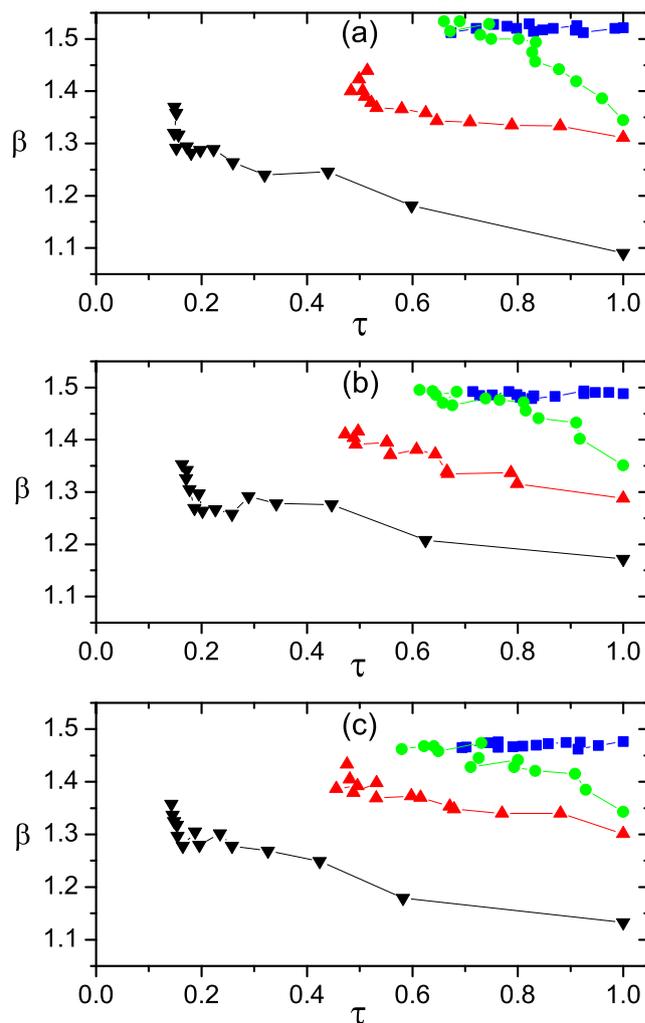
Fig. 4 (Color online) the exponent β in (2) as a function of the relaxation time τ scaled by the relaxation time τ_m, at 66.7°C, for three ferrofluid concentrations: **a** 0.1 μl/ml, **b** 0.3 μl/ml, and **c** 0.5 μl/ml. The *down triangles*, *up triangles*, *circles* and *squares* correspond to ternary mixtures with 0.0% (100.0%), 16.7% (83.3%), 40.0% (60.0%), and 100.0% (0.0%) water (glycerin), respectively

In an attempt to relate the parameters β and τ, we start out by eliminating the temperature from the data in Figs. 2 and 3. In the resulting Fig. 4a–c we show β as a function of τ/τ_m, where τ_m denotes τ at 66.7°C (see Table 1); this normalization is convenient since the range of τ is strongly dependent on the glycerin concentration. In consistency with our previous discussion, these plots show β to be essentially independent of τ in the absence of glycerin. More generally, β is a decreasing function of τ, and the maximum value of β decreases when the glycerin concentration. The decay of τ and the enhancement of β with temperature tend to make the stretched exponentials matching the experimental data short tailed.

5 Conclusions

In this work we investigated systematically the optical transmittance across ternary mixtures of water, glycerin and ferrofluid when the ferrofluid is aligned by a constant magnetic external field, which is suddenly switched off. We verified that, instead of exponential, the short-time decay of the relaxation is very well described by a stretched exponential. The long time behavior, by contrast, calls for additional investigation. Main tendencies are as follows: i) the relaxation time decreases with temperature; ii) the stretched-exponential parameter β stays relatively close to 1.5—very close for low glycerin concentrations—; iii) β decreases with viscosity; and iv) β is a decreasing function of the relaxation time. The good agreement should not be misconstrued for deep understanding of the mechanism leading to a stretched-exponential relaxation of mixtures such as the ones studied here. Regarded from a broader perspective, the incomplete understanding of non-exponential relaxation remains one of the many unresolved problems in physics [43]. The ferrofluid problem, in particular, may comprise several complex components—the aggregation of magnetic particles [10], to mention but one possibility—each of which would challenge thorough understanding of the system.

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