Forced Rayleigh Experiment in a Magnetic Fluid

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A spatial modulation of colloidal concentration of nanoscopic magnetic particles is written in a ferrofluid solution inside the fringes of a forced Rayleigh scattering device. The relaxation time of this transient grating is inversely proportional to the square of the characteristic wave vector and thus to the cooperative diffusion coefficient of particles. If an external magnetic field is applied in the plane of the fringes and perpendicularly to these ones, the experimental diffusion coefficient increases, due to local magnetic field gradients in the spatially inhomogeneous magnetic medium.

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Forced Rayleigh scattering (FRS) is a powerful technique to study heat and mass transfers in liquids [1]. In pioneering FRS experiments [2–4], a holographic grating of spacing Λ is created by a pair of crossed interfering laser beams in the studied medium, either a solid or a liquid. A thermal phase grating is thus generated in the absorbing medium and the thermal diffusivity is determined through the characteristic time τ_θ of relaxation of the transient modulation: typically with an interfringe $\Lambda = 10\ \mu\text{m}$, τ_θ is $\approx 1\ \mu\text{s}$ for ruby and $\approx 100\ \mu\text{s}$ for glycerine or methanol [4]. On one hand, with a similar technique, a massic diffusion can be measured in a polymeric solution [5,6] or in a colloidal solution [7] labeling some macromolecules or some colloidal particles with a photochromic probe and writing a spatial modulation of concentration of photoexcited entities in the solution. On the other hand, it is possible via optical forces to induce spatial periodic patterns [8] inside suspensions of μm-sized latexes or via osmotic pressure effects to induce phase separation and μm-droplet nucleation in microemulsions [9].

Synthesis and study of complex magnetic media, based on nanoscale magnetic particles, is an up to date [10–15] and promising field of research which has expanded recently because of its numerous technological applications [16]. In the present work, we are dealing with a magnetic liquid (ML) [17] which is a colloidal suspension of nm-sized magnetic particles in a liquid carrier. If the conditions of colloidal stability of ML have been extensively studied [18–20], massic diffusion coefficients of particles have been seldom measured [21] and only by quasielastic light scattering (QLS) in the very dilute regime. Here, we show that, thanks to a FRS technique, we are able to measure this diffusion coefficient in a ML of volume fraction 10% and to study the effect of the specific external parameter of ML: an applied magnetic field.

We observe that our FRS writing grating induces inside the ML a spatial modulation of concentration without a tracer. The writing process which is complex, mixing both electrostrictive and thermophoretic effects, is not studied here in detail and will be contained in a forthcoming paper. This work deals with the relaxation of the concentration grating. We verify experimentally that it is a pure diffusive process related to a mass transfer of particles inside a monophasic colloid. In this experiment, for the first time with a FRS technique, we measure a cooperative mass diffusion coefficient in a colloid: by opposition to the self-diffusion coefficient obtained with solutions of a few photochromic labeled macromolecules [5], very similar to what is measured with a standard quasielastic light scattering experiment [21], but in a much higher range of colloidal concentrations. Our colloid is a magnetic one: We show experimentally that, if an external magnetic field is applied perpendicularly to the fringes of the grating (and in the grating plane), the measured diffusion coefficient is an increasing function of the field. This effect is explained in terms of local magnetic field gradients, in this spatially modulated magnetic material.

The experiment is performed with an acidic ionic ferrofluid ($p\text{H} = 2$), chemically synthesized through Massart's method [22]. It is an aqueous colloidal solution of maghemite (γ-Fe_2O_3) particles, each bearing a negative superficial density of charges, roughly equal to $0.2\ \text{C/m}^2$ [23] which allows an electrostatic stabilization of the solution. The volume fraction of particles is $\Phi = 10\%$ as measured by chemical titration of iron, the magnetic volume fraction being slightly smaller $\cong 9\%$. Measurements of magnetic susceptibility and magnetic birefringence relaxation on a dilute sample lead for the magnetic particles to a magnetic radius [24] $R_M = 6$ nm (using bulk magnetization $m_s = 4 \times 10^5$ A/m) and to an hydrodynamic radius [25] $R_H = 15$ nm, larger than R_M. The colloidal stability [18] is checked through two kinds of experiments: small angle x-ray scattering (SAXS) [26] in zero magnetic field (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay) and optical diffraction [27] under magnetic fields up to 160 kA/m. SAXS spectra obtained in zero field are very similar to those of Ref. [28] obtained by small angle neutron scattering on comparable samples. An order of magnitude of thermodynamic interparticle interactions can thus be derived (in zero field, at room temperature and up to $\Phi = 8\%$): $\partial[\Phi(\partial\mu(H = 0)/\partial\Phi)]/\partial\Phi \cong 20kT$ [$\mu(H = 0)$ is the chemical potential of the solution in zero field, k is the Boltzmann constant, and T is the temperature]. In zero magnetic field, a local increase of temperature or of volume fraction of magnetic particles, at constant concentration of counterions (here NH_3^-), is unable [18,23] to induce a phase separation in the colloid.

The sample is put in an optical cell, 10 μm thick, between the pole pieces of an electromagnet which provides us with a uniform magnetic field, lying in the plane of the cell, ranging from 0 to 160 kA/m. To create a transient grating in the ferrofluid sample we use a high peak power (0.2 MW), pulsed and frequency doubled Nd:YAG laser ($\lambda_g = 0.53$ μm). The beam is split in two parts of equal intensities. These two pump beams intersect in the ferrofluid with a definite angle θ building up a spatially periodic intensity distribution in the sample $I(x) = 2I_0(1 + \cos qx)$, with $q = 2\pi/\Lambda$ and $\Lambda = \lambda_g/2\sin(\theta/2)$; Λ is the interfringe distance in the x direction. Maximum average power is limited (<0.2 W) to prevent the sample from being destroyed. A grating is induced and its dynamics is probed through the first order of the diffracted pattern of a continuous HeNe laser beam of lower intensity ($\lambda_r = 0.63$ μm, 3 mW).

When the two green power-laser beams interfere for a few seconds, a grating can be easily observed in the colloidal solution with a red light working microscope: a typical picture is given in Fig. 1(a). Nothing else but a modulation of colloidal particle concentration could give rise to such an absorption grating picture. However, the presence of a superimposed index grating is not excluded by this direct visual observation and it would enhance the diffracted signal. If one of the two green beams is switched off, the fringes smear out in a few seconds: Typical variations of the first order diffraction from the probing red laser are presented in Fig. 1(b) as a function of time. Experimentally, the relaxation of this first order diffracted signal is a single exponential decay. In Fig. 2(a), the inverse of its characteristic time τ_D^{-1} is plotted as a function of q^2, the square of the characteristic wave vector, for various magnetic field strengths H (H being perpendicular to the fringes). Within the experimental error bars, τ_D^{-1} is directly proportional to q^2 for any value of H. This direct proportionality probes here the total lack of recombination processes [29,30] and allows us to define an experimental diffusion coefficient: $D^{\exp} = (2\tau_D q^2)^{-1}$, the detection being homodyne with an incoherent background intensity less than 1% of the coherent signal [6]. $D^{\exp}$ accuracy ranges from 2% for $H = 0$ to 5% for $H = 120$ kA/m. τ_D is of the order of a few seconds which is much larger than the thermic characteristic times of the problem: the thermal relaxation nanoparticle/solvent $\approx$1 ps and thermal relaxation of a 30 μm grating $\approx$1 ms.

All these points [absorption grating of Fig. 1(a), single exponential relaxation process with $\tau_D^{-1} \propto q^2$, and order of magnitude of the relaxation time] settle the fact that, in this forced Rayleigh experiment, a concentration grating of colloidal particles is induced and that, by measuring the characteristic relaxation time of this pattern, we can determine an effective massic diffusion coefficient of the nanoscopic particles. To our knowledge this is the first time that this effect has been reported in a colloid.

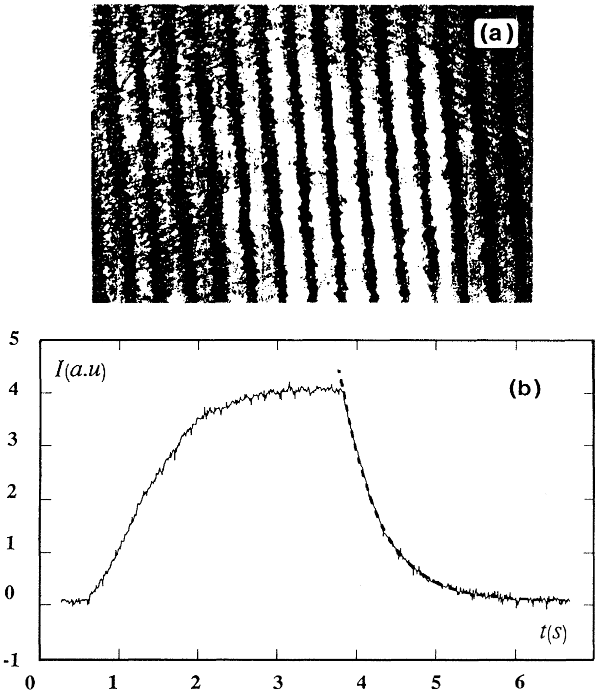

FIG. 1. (a) Direct picture of the concentration pattern with $\Lambda = 36$ μm. (b) Time dependence of the diffracted signal if the writing grating is applied during $\approx$4 s. The dotted line is the single exponential best fit of the intensity relaxation with $\tau_D = 0.6$ s [(a) and (b) both correspond to $q^2 = 3 \times 10^{10}$ m^{-2}].

In zero magnetic field we measure $D_0^{\exp} = 2.7 \times 10^{-11}$ m^{2}s^{-1}. This value is independent of the polarization direction of the probing laser and has to be compared to the Stokes-Einstein diffusion coefficient: $D_0 = kT/f_0 = kT/6\pi\eta_0 R_H = 1.4 \times 10^{-11}$ m^{2}s^{-1}, f_0 being the friction coefficient $f(\Phi)$ at volume fraction $\Phi = 0$, η_0 the carrier viscosity (here water), and R_H the hydrodynamic radius taken equal to the experimental value obtained from birefringence relaxation measurements. The discrepancy between D_0 and $D_0^{\exp}$ can be ascribed to an effect of interparticle interactions inside the colloid. For a finite volume fraction Φ of colloidal particles and in the linear regime the generalized Stokes formula is

$$\begin{aligned} D_0(\Phi) &= \Phi(\partial\mu(H = 0)/\partial\Phi)/f(\Phi) \\ &\cong D_0[1 + (\kappa_T - \kappa_f)\Phi], \end{aligned} \tag{1}$$

coefficients κ_T and κ_f accounting, respectively, for thermodynamic and hydrodynamic interactions in the framework of a hard sphere liquid [31] $\kappa_f = 6.55$. Assuming that this linear description is still valid at a 10% volume

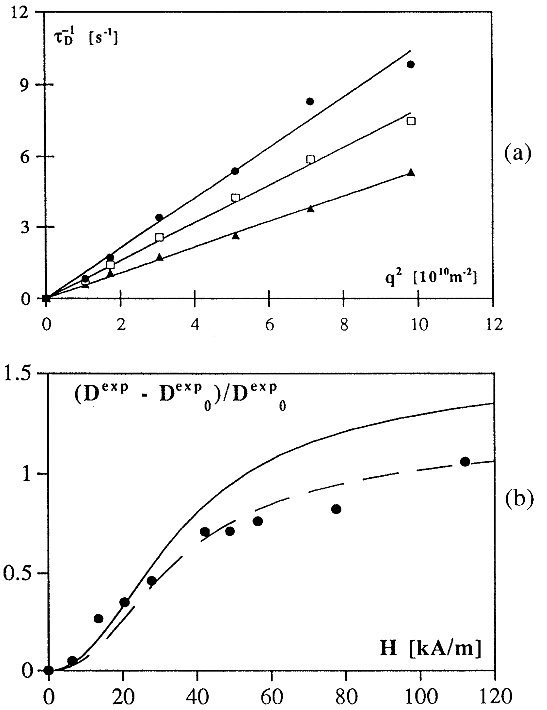

FIG. 2. (a) Plots of τ_D^{-1} as a function of q^2 for various applied fields H: D^{exp} is the slope of the linear best fit (▲: $H = 0$ kA/m, $D^{\mathrm{exp}} = 2.7 \times 10^{-11}$ m^{2}s^{-1}; □: $H = 28$ kA/m, $D^{\mathrm{exp}} = 4 \times 10^{-11}$ m^{2}s^{-1}; ●: $H = 112$ kA/m, $D^{\mathrm{exp}} = 5.4 \times 10^{-11}$ m^{2}s^{-1}). (b) Reduced variations of D^{exp} (black dots) as a function of applied field H compared to theoretical expressions (4) (full line) and (5) (dotted line).

fraction $D_0(\Phi) = D_0^{\mathrm{exp}}$ implies $\kappa_T \approx 16$ very close to 20, the experimental order of magnitude from Ref. [28].

If an external magnetic field is applied, the relaxation time decreases [Fig. 2(a)], leading to an increase of the experimental massic diffusion coefficient. In Fig. 2(b) the variation of the ratio $[D^{\mathrm{exp}}(H) - D_0^{\mathrm{exp}}]/D_0^{\mathrm{exp}}$ is plotted versus H. In this magnetically stable colloid, the expected effect of magnetic interparticle interactions under field would be, in a mean-field description, a decrease of $D^{\mathrm{exp}}(H)$ because this interaction is attractive. The observed $D^{\mathrm{exp}}(H)$ increase effects the particles, via dipolar interactions [32], of magnetic field gradients arising in this field geometry from the concentration grating of magnetic particles. We propose later a theoretical model accounting for the magnetic field dependence of D^{exp}. Figure 2(b) presents a comparison between our experimental data and this model.

Decoupling, because of their largely different time scales, thermic and massic diffusion fluxes, the evolution of particle volume fraction is described in one dimension, by $\partial\Phi/\partial t = -\partial j_x/\partial x$. The diffusion flux j_x is, according to nonequilibrium thermodynamics, equal to $j_x = -\Phi(\partial\mu/\partial x)/f(\Phi)$. These two equations allow a determination of the diffusion coefficient in the presence of field. In our experiment we use a magnetic field perpendicular to the fringes, the chemical potential μ depends on both particle concentration and external field strength. It can be written $\mu = \mu(H = 0) + \mu_H$ [33].

In a first step we neglect local field effects ($\partial\mu_H/\partial\Phi \cong 0$), and we approximate the magnetization of the colloid by the Langevin formula $M = \Phi m_s L(\xi)$, where $L(\xi) = \mathrm{cotanh}(\xi) - \xi^{-1}$ and $\xi = \mu_0 m_s VH/kT$, μ_0 being vacuum permeability and m_s particle magnetization. Using the Maxwell relation $(\partial\mu/\partial H)_\Phi = -\mu_0 V(\partial M/\partial\Phi)_H$, the particle diffusion flux may be written

$$\begin{aligned} j_x = &- [\Phi/f(\Phi)][\partial\mu(H = 0)/\partial\Phi]\partial\Phi/\partial x \\ &+ [\Phi/f(\Phi)]\mu_0 m_s VL(\xi)\partial H/\partial x \,. \end{aligned} \qquad (2)$$

The particle concentration evolution is then given by

$$\begin{aligned} \partial\Phi/\partial t = &- (\partial[D_0(\Phi)\partial\Phi/\partial x])/\partial x \\ &- \partial[\Phi\mu_0 m_s VL(\xi)(\partial H/\partial x)/f(\Phi)]/\partial x \,, \end{aligned} \qquad (3)$$

where $D_0(\Phi)$ is the Stokes diffusion coefficient of Eq. (1). The magnetic field strength H is determined from the Maxwell equation in the magnetostatic approximation $\partial[H + m_s\Phi L(\xi)]/\partial x = 0$, leading to $\partial H/\partial x$ as a function of $\partial\Phi/\partial x$. Performing an expansion of Eq. (3) in the limit of small variations of volume fractions, with respect to the equilibrium one Φ, we obtain a diffusion coefficient $D_\parallel$ of the particles along the field lines larger than the thermal one and equal to

$$D_\parallel = D_0(\Phi) + \gamma[kT/f(\Phi)]L^2(\xi)/[1 + \gamma L'(\xi)], \qquad (4)$$

$L'(\xi)$ being the first derivative of $L(\xi)$ and γ the reduced parameter of magnetic dipolar interaction, $\gamma = \mu_0 m_s^2 V\Phi/kT \cong 4.1$, using the magnetic volume of particles $V = 4\pi R_M^3/3$ as deduced from initial susceptibility measurements and taking $\Phi = 9\%$ equal to the magnetic volume fraction, smaller than the colloidal volume fraction and deduced from saturation magnetization measurements. In this approximation, $D_\parallel$ appears as an increasing function of ξ, thus of H and formula (4) expresses the main effect of an external field perpendicular to the magnetic fringes: It adds a driving force parallel to the gradient of effective magnetic field. Reduced field variations of $D_\parallel$, as deduced from expression (4), are plotted in Fig. 2(b), with $kT/f(\Phi)$ equal to its experimental value $D_0(\Phi)/(1 + \kappa_T\Phi) \cong D_0^{\mathrm{exp}}/2.6$.

In fact, with such a large magnetic volume fraction, the previous magnetic approximation is too rough, local field effects are now taken in account together with an effective field description of the magnetization of the colloid [33], $M = \Phi m_s L(\xi_e)$ with $\xi_e = \xi + \lambda\gamma L(\xi_e)$ and λ the local mean-field factor ($\lambda = 0$ in the noninteracting limit, $\lambda = \frac{1}{3}$ in the classical Lorentz description [34]). The magnetic part of the chemical potential is then $\mu_H = -kT\ln(\sinh\xi_e/\xi_e)$ and expression (4) transforms in [35]

$$\begin{aligned} D_\parallel = &\ D_0(\Phi) + \gamma[kT/f(\Phi)] \\ &\times \{L^2(\xi_e)/[1 + \gamma(1 - 2\lambda)L'(\xi_e)] \\ &- \lambda L^2(\xi_e)/[1 - \lambda\gamma L'(\xi_e)]\}\,. \end{aligned} \qquad (5)$$

In this mean-field description, the net supplementary effect of magnetic interactions is a decrease of $D_{\|}$ with respect to expression (4); this small additional decrease is the only existing effect on D_{exp} if the field is parallel to the fringes [35]. The field dependence of theoretical expression (5) is compared to experiments in Fig. 2(b) using an adjusted value of $\lambda = 0.22$ which could be related to the shape of the magnetic particles.

In conclusion, in the present forced Rayleigh scattering experiment, performed with a magnetic colloid, a mass transfer of particles is observed leading to the periodic spatial modulation of an absorbing grating. The characteristic relaxation time of this pattern is directly related to the cooperative diffusion coefficient of particles, similar to the quantity measured in a quasielastic light scattering experiment. The applied magnetic field modifies the characteristic times, as the mass transfer is sensitive here to the local magnetic field gradients. QLS and FRS lead to complementary results. To study magnetic colloids, the first technique is useful in the dilute regime but is easily hindered by absorbtion and multiple scattering at large concentrations. On the contrary, FRS requires a good contrast of the fringes, concentrated ferrofluids: at least $\Phi = 5\%$ with the present experimental setup. In the future, besides our next goal which is a clear reading of the complex writing process, such a FRS technique will be useful to study interparticle interactions: inside ionic ferrofluids as a function of ionic strength near the phase separation onset and inside any kind of ferrofluid as a function of applied magnetic field in various geometries with respect to the fringes. Moreover, recent numerical works [19,20] on these dipolar (ferro)fluids open new questions about the existence (under specific colloidal conditions: reducing interparticle repulsion [19]) of some dynamic internal structures such as living magnetic polymers, linear or ring shaped. This subject calls for further investigations of dynamic properties of such concentrated magnetic colloids: the present FRS technique could be an efficient tool to this end.

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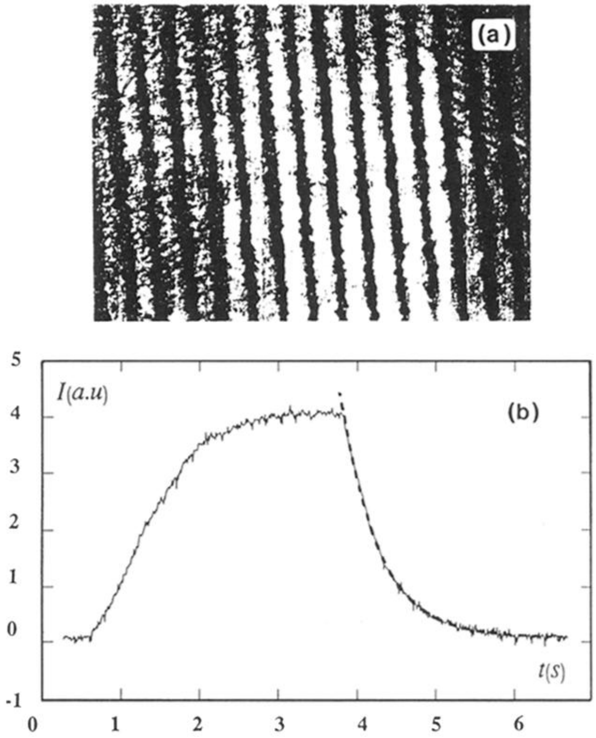

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