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# Forced Rayleigh scattering experiments in concentrated magnetic fluids: effect of interparticle interactions on the diffusion coefficient

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**Abstract**

The structure and dynamics of concentrated aqueous magnetic fluids with tunable interparticle interaction are investigated by small angle neutron scattering and forced Rayleigh scattering. The structure factor and the collective diffusion coefficient are determined. An effect of the interparticle interaction on the diffusion coefficient is observed and related to thermodynamic data with a good agreement.

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## 1. Introduction

In the framework of a general study on concentrated magnetic colloids with well-defined isotropic repulsion and anisotropic dipolar interactions, we present here translational diffusion measurements. While the static structural properties of such concentrated dispersions, with and without an applied magnetic field, have been explored in detail in [1,2], their dynamical properties are less investigated.

The magnetic fluids studied here are constituted of maghemite nanoparticles $\gamma$-$Fe_2O_3$ coated with citrate molecules that ensure them a negative superficial charge. They are dispersed in water at pH 7 with a volume fraction $\Phi$ ranging from 1% up to 25%. The particle diameters $d$ follow a lognormal distribution characterized here by $d_0 = (\langle \ln d \rangle) = 9.8\,\mathrm{nm}$ and $\sigma = 0.25$. The dipolar parameter $\gamma/\Phi = \mu_0 m_s^2 V/kT$ that quantifies the dipolar interactions between two particles compared to thermal energy, is 32 for this ferrofluid. In these systems, for a fixed $\gamma/\Phi$ ratio, the interparticle interactions can be tuned by changing the osmotic pressure $\Pi$ of the suspensions. The latter is controlled by the ionic strength of the solution. Therefore, a phase diagram $\Pi$–$\Phi$ [1] determines the structure and the properties of the dispersions.

*For high pressures*, following a line at constant ionic strength, the dispersion is fluid, up to a limiting volume fraction above which the sample becomes solid. The structure factors $S(q)$ plotted on Fig. 1 are obtained by small angle neutron scattering experiments (SANS) [1]. They are the counterparts of the radial distribution

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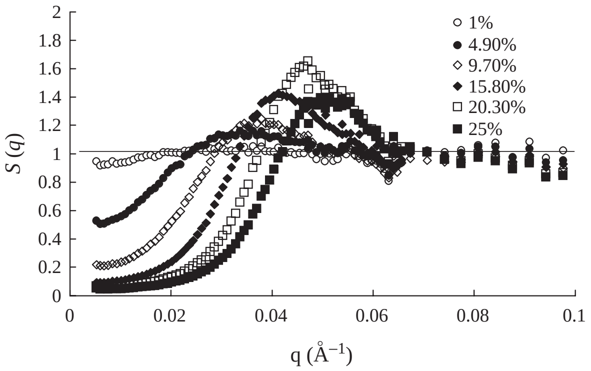

Fig. 1. Structure factors $S$ versus the scattering vector $q$ for [citrate] $= 0.03\,\mathrm{mol\,L^{-1}}$ and increasing volume fractions (SANS experiments, ILL, Grenoble, France).

functions in the reciprocal space. The value of $S$ at $q = 0$ is related to the compressibility of the suspension and the maximum gives the most probable distance $\delta_{\mathrm{mp}}$ between particles ($q_{\max} = 2\pi/\delta_{\mathrm{mp}}$). In this study, the compressibility is low and $\delta_{\mathrm{mp}} \sim \Phi^{-1/3}$, which means that the interparticle interaction is strongly repulsive. All the samples are fluids apart from the most concentrated one ($\Phi = 25\%$) which is a solid. Yet, due to the remaining polydispersity, the solid is a glass, not a crystal, i.e. it presents an amorphous structure. While increasing $\Phi$ in the fluid phase, a drastic evolution of the rotational diffusion time $\tau_{\mathrm{rot}}$ can be measured by magneto-optical birefringence relaxation: this time is increased by 9 orders of magnitude while increasing the volume fraction toward the solid phase [3]! This behavior is also characteristic of a glass transition.

*For low pressures*, following a line at constant ionic strength and increasing the volume fraction from low values, the dispersion—at first similar to a gas of nanoparticles—undergoes a liquid-gas transition (associated to a critical point). At higher $\Phi$, the dispersion is then similar to a liquid (monophasic) and becomes a solid above a given threshold of volume fraction. In this area, the interactions are globally attractive, and the solid is there an attractive glass [1].

In the present paper, forced Rayleigh scattering is used to measure the collective translational diffusion coefficient $D_{\mathrm{tr}}$ of the nanoparticles along lines at constant ionic strength in the fluid area, i.e. for high osmotic pressures and globally repulsive interactions.

## 2. Experimental details

The principle of the Rayleigh scattering is the following. Spatial modulations of concentration are induced by thermodiffusion (Ludwig–Soret effect) inside the colloid thanks to the standing interference fringes of two coherent laser beams at $\lambda = 532\,\mathrm{nm}$. Indeed, a temperature grating arises due to the strong optical absorbance of the sample [4–7]. A He–Ne laser probe beam is diffracted by the spatial modulations of the optical index in the sample. The diffusion coefficient $D_{\mathrm{tr}}$ is deduced from the relaxation of the first-order intensity of the diffraction pattern when the two pump beams are switched off. In the citrated ferrofluids considered here, the Soret coefficient is negative, i.e. the nanoparticles move toward hot regions [5–7]. This technique is specific to ferrofluids: due to their strong Soret coefficient, it is possible to measure $D_{\mathrm{tr}}$ in concentrated samples, which is not possible, due to light absorption, with standard dynamic light scattering for example. In the present study, the sample is put in a $10\,\mu\mathrm{m}$ thick quartz cell. Neutron spin echo measurements can also be used, however it is a much more complicated and heavy experiment which probes more local scales [8].

Forced Rayleigh scattering allows measuring the relaxation time $\tau_{\mathrm{tr}}$ of the concentration modulations for several scattering vectors $q$. The relaxation of the thermal modulations has also been measured [5–7] and is $10^3$ faster. Consequently, the two phenomena can be decorrelated. Practically $q$ is calculated from the spatial interfringe of the interference pattern. The quantity $1/\tau_{\mathrm{tr}}$ is found to be proportional to $q^2$, which means that the motion is diffusive. The slope associated to this linear variation gives the diffusion coefficient $D_{\mathrm{tr}}$.

## 3. Results and discussion

To examine the effect of interparticle interaction on the collective diffusion coefficient, the interaction is tuned by adjusting the ionic strength and the volume fraction $\Phi$ of the nanoparticles.

At low ionic strength ([citrate] $= 0.003\,\mathrm{mol\,L^{-1}}$—strongly repulsive interparticle potential $U$) no spatial modulation of concentration is detected, in good agreement with recent theoretical works [9,10]. Indeed,