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ABSTRACT

Forced Rayleigh Scattering (FRS) is a powerful technique for investigating heat and mass transfers in colloids. In the present work, we determine the Soret coefficient S_T and the thermal diffusion coefficient D_T of magnetic colloids (ferrofluids). It has been theoretically predicted that the thermal diffusion coefficient D_T of colloids depends both on the particle/solvent interfacial interaction and on the interactions between the colloidal particles. In order to understand the microscopic behavior of the Soret effect in these ionic magnetic colloids, experiments are performed on aqueous samples of various volume fractions Φ and ionic strengths. The dominant effect on the Soret coefficient comes here from the particle/solvent interaction and determines its sign. Interparticle interactions have an influence on S_T in the moderate concentration range where virial like expansions are possible. In this range ($\Phi \leq 0.10$) and within the experimental error bar, the thermal diffusion does not depend on the ionic strength of the dispersion and the Φ-dependence of the friction coefficient is comparable to that of hard spheres. At larger concentrations, the thermal diffusion drastically decreases as the colloid approaches its dynamical glass transition.

KEYWORD: Ferrofluids, Forced Rayleigh Scattering, thermal diffusion, Soret effect, friction, dynamical arrest.

1. INTRODUCTION

While advances in thermodiffusion have focused primarily on polymer solutions, studies on colloids are fairly recent developments. The effect of the modification of the interactions between the colloidal particles on the Soret coefficient has however been modeled [1,2,3,4]. In micellar solutions, Piazza *et al.* [5] have observed that electrostatic interactions play a crucial role in thermal diffusion. The aim of the present work is then to provide new experimental evidences of the influence of the interparticle interactions on thermal diffusion in ionic ferrofluids up to dense systems inside which slow dynamics is observed [6,7]. For that purpose, the Forced Rayleigh Scattering (FRS) technique, already fruitful for magnetic colloids [8,9,10], is used to measure the translational diffusion and the Soret coefficients.

We report experimental measurements of Soret and thermal diffusion coefficients for well-controlled ionic magnetic colloids as a function of the particle concentration and the ionic strength.

2. EXPERIMENTAL DETAILS AND METHOD

2.1 Ferrofluids

Ferrofluids are colloidal dispersions of magnetic nanoparticles dispersed in a carrier liquid. The nanoparticles are synthesized according to Massart's method [11]. At neutral pH, a negative superficial charge (-0.2 C.m^{-2}) is ensured by the adsorption of citrate ions and compensated by free sodium ions. The magnetic particles are roughly spherical with a log-normal distribution of magnetic diameters (mean diameter $d_0 = \exp <\ln d> = 9.8$ nm and a distribution width of $\sigma = 0.25$ [12]). The corresponding structural charge per particle is $400\,e$. The colloidal phase diagram of these dispersions is discussed in Ref. [12] and has been more generally and comprehensively described in Ref [13]. The interparticle repulsions can be finely tuned by the ionic strength of the dispersion, locating precisely the suspension in the phase diagram. Experiments are performed with three ferrofluid series of free citrate concentration [cit]$_{free}$: 0.03 mol/L, 0.08 mol/L and 0.10 mol/L. The citrate molecules, coating the particles, not only induce a steric repulsion but, since they are charged, yield an electrostatic repulsion attested by an electrokinetic potential of the order of $\zeta = -30$mV. The volume fraction, defined here as the volume fraction of magnetic material, is ranging from 0.01 to 0.23 always below Φ^*, the volume fraction above which the system presents a broad distribution of relaxation times and an aging behavior as evidenced by magneto-optical measurements [6] and X-ray Photon Correlation Spectroscopy [7].

2.2 Theoretical background

According to the usual transport phenomena theory, Φ the nanoparticle volume-fraction, J_m the volume-fraction flow density and T the temperature in the sample obey the following equation:

$$\mathbf{J}_m = -D_m \left(\nabla \Phi + \Phi (1-\Phi) S_T \nabla T \right), \tag{1}$$

where the coefficients D_m and S_T are the collective mass diffusion and the Soret coefficients, respectively. Following Ref. [5,14,15], the Soret coefficient S_T is proportional to the osmotic compressibility $\chi_T(\Phi)$ of the dispersion and writes:

$$S_T = S_{T0} \chi_T(\Phi), \tag{2}$$

where S_{T0} is the value of S_T at infinite dilution. The collective mass diffusion coefficient D_m writes:

$$D_m = \frac{k_B T}{f(\Phi) \chi_T(\Phi)}, \tag{3}$$

where $f(\Phi)$ is the viscous friction coefficient and $k_B T$ is the thermal energy. The thermal diffusion coefficient writes then:

$$D_T = S_T D_m = \frac{k_B T S_{T0}}{f(\Phi)}. \tag{4}$$

3. RESULTS AND DISCUSSION

Our Forced Rayleigh Scattering (FRS) experimental set-up and the two timescale model used for the Soret coefficient determination are described in detail in our previous work [10]. For the present ferrofluids, it is possible to discern three regimes of volume fraction: i) the moderately concentrated regime where it is possible to express thermodynamic quantities in terms of virial-like expansions [16], ii) the concentrated dispersions for which these expansions are no more valid and where effects related to the approach to the glass transition begins to be felt ($\Phi < \Phi^*$) [6], iii) the highly concentrated regime

($\Phi > \Phi^*$), for which no measure have been feasible, and where slow dynamics and aging have been evidenced [6,7] .

3.1 Moderately concentrated regime

For $\Phi \leq 0.10$, the osmotic pressure can be expanded in terms of virial coefficients [17]. In this range and at the first order in Φ, the isothermal compressibility χ_T of the dispersion can be written as:

$$\chi_T = k_B T \left(\frac{\partial(\Pi V)}{\partial \Phi} \right)^{-1} = \frac{1}{1 + K_T \Phi}, \qquad (5)$$

V being the volume of a nanoparticle and K_T a coefficient proportional to the second virial coefficient. K_T is thus related in sign and amplitude to the balance of interactions between particles. In a similar way, the friction coefficient can be expanded as:

$$f(\Phi) = f_0(1 + K_F \Phi), \qquad (6)$$

where f_0 is the viscous friction coefficient at infinite dilution and K_F is a coefficient associated to the Φ-dependence of the friction. Virial-like expansions of the Soret coefficient and of the thermal diffusion coefficient then writes in the moderated concentration limit:

$$\frac{1}{S_T} = \frac{1}{S_{T0}}(1 + K_T \Phi), \qquad (7)$$

and

$$\frac{1}{D_T} = \frac{1}{D_{T0}}(1 + K_F \Phi), \qquad (8)$$

where D_{T0} is the thermal diffusion coefficient at infinite dilution ($D_{T0} = k_B T\, S_{T0}\, / f_0$). Figure 1a shows $1/S_T$ as a function of the volume fraction in the range $\Phi < 0.10$ at three [cit]$_{free}$ values ([cit]$_{free}$ = 0.03, 0.08 and 0.1 mol/L) and illustrates equation (7). Table 1 collects the determinations of K_T and S_{T0} associated to this expansion.

The values of K_T are in fair agreement with those obtained by SANS determinations of the compressibility χ_T [18]. They are indeed all positive, meaning that the balance of interparticle interactions is here repulsive, the samples lie in the "fluid domain" of the phase diagram [6,12]. K_T indeed decreases with [cit]$_{free}$, the screening of the electrostatic interaction progressively reducing the second virial coefficient.

However ferrofluids do not exhibit the same behavior as micellar solutions where strong variations of both S_{T0} and K_T with the ionic strength have been observed by Piazza *et al.* [5], even changing the sign of S_T (see fig. 2 in [14]). As for acidic aqueous ionic samples [10], the Soret coefficient of the citrated-decorated samples is always negative (see figure 1a). The sign of the Soret coefficient in ferrofluids strongly depends on the nature of the carrier liquid and of the stabilization [10]. The origin of the Soret effect in these materials lies in the immediate surrounding of the nanoparticles, the particle/solvent interactions playing indeed a major role. Here, the value of the Soret coefficient at infinite dilution S_{T0} is almost independent on [cit]$_{free}$. (see table 1).

Figure 1b illustrates the expansion (8) showing the variations, as a function of Φ, of the inverse thermal-diffusion-coefficient $1/D_T$. All the dispersions at the various [cit]$_{free}$ values are reported for $\Phi \leq 0.10$. Within the experimental error bar, no dependence on [cit]$_{free}$ is detected for $1/D_T$ and the Φ-dependence is well adjusted with the "hard sphere" friction coefficient (K_F = 6.55 [19] as in Ref. [16]). The thermal diffusion coefficient at infinite dilution D_{T0} is here extrapolated to $2.3\ 10^{-12}$ m^{2}K^{-1}s^{-1}. The agreement between the experiment and the "hard sphere" model is indeed rather good for $\Phi \leq 0.10$.

3.2 Concentrated regime

In figures 2a and 2b, are presented, in log-log representations, the Φ-dependences of the compressibility, the Soret and the thermal diffusion coefficients in the whole range of volume fractions for the various samples studied here. Note that the concentrated regime ($\Phi \geq 10\%$) is here only explored with samples at [cit]$_{free}$ = 0.03 and 0.08 mol/L.

In figure 2a, are compared, as functions of Φ, the variations of the compressibility χ_T determined by SANS (full symbols) and of the ratio S_T / S_{T0} (open symbols). As the volume fraction increases, both quantities decrease similarly, down to a value of the order of a few percents. Figure 2b shows the

variations of the thermal diffusion coefficient $D_T = D_m S_T$ (in absolute value). At high volume fractions, this coefficient decreases drastically.

These observations have to be associated to the dynamical arrest of the dispersions, occurring at the approach of the volume fraction Φ^* pointed by an arrow on figures 2a and 2b. Φ^* is the volume fraction above which the system becomes a "glass-forming fluid" and exhibits slow dynamics that can be evidenced by magneto-optical birefringence for instance [6]; here $\Phi^* \approx 25\%$ for $[cit]_{free} = 0.03$ and 0.08 mol/L. Near Φ^*, since the compressibility χ_T decreases, the Soret coefficient decreases correspondingly according to equation (2). Likewise, the viscous friction coefficient diverges, hence the thermal diffusion coefficient decreases drastically following equation (4). As a result, FRS measurements are not possible beyond Φ^*.

A similar behavior has been observed in [20,21] with polymeric solutions in good solvent at high polymeric concentration, approaching the glass transition of the system. However in [20], this slowing down was associated to a similar decrease of D_m. In the present case, the observations are closer to the ones of Ref. [21] because of the rather strong interparticle repulsion ($K_T \geq 15$). In equation (3), the decrease of $\chi_T(\Phi)$ partially compensates the divergence of $f(\Phi)$.

At large concentration, and for $[cit]_{free} = 0.03$ and 0.08 mol/L, the Φ-dependence of D_T, and thus of $f(\Phi)$, can be adjusted by the following power law :

$$|D_T| = \frac{k_B T |S_{T0}|}{f(\Phi)} = |D_{T0}| \cdot \left(\frac{\Phi^* - \Phi}{\Phi^*}\right)^\alpha \qquad (9)$$

with $\alpha = 1.17$ and $D_{T0} = 2.3 \pm 0.2 \ 10^{-12} \ m^2 K^{-1} s^{-1}$. Let us note however that further experimental investigations are necessary to probe in details this divergence. Indeed the power law (9) may depend on the timescale of the experiment, the samples are likely to age in the vicinity of Φ^*. Moreover the volume fraction Φ^* is $[cit]_{free}$–dependent: Φ^* is divided by 2 if $[cit]_{free}$ is decreased by a factor of 10 [6].

4. CONCLUSION

By studying various ionic ferrofluid samples with several volume fractions and ionic strengths, we have tried in this paper to shed some light on the contribution of the interparticle interactions to the Soret coefficient and to the thermal diffusion .

The Soret coefficient S_T in these citrate-decorated samples is always negative whatever the ionic strength of the dispersion (related here to $[cit]_{free}$, the concentration of the free citrate ions). In contrast to micellar solutions, the Soret and the thermal diffusion coefficients at infinite dilution, respectively S_{T0} and D_{T0}, are not strongly dependent on the ionic strength.

At intermediate concentrations ($0 \leq \Phi \leq 0.10$), the Soret coefficient is found to vary in the same way as the compressibility of the system with a positive second virial coefficient, as expected in these repulsive dispersions. This second virial coefficient decreases as $[cit]_{free}$ increases, the repulsion being progressively screened. The thermal diffusion coefficient, inversely proportional to the friction coefficient, exhibits a behavior similar to that of a hard sphere system.

At larger volume fractions, the Soret coefficient collapses because the compressibility of the system becomes very small. The thermal diffusion coefficient also decreases dramatically because the friction coefficient diverges close to Φ^*, the volume fraction above which the system becomes a "glass-forming fluid" [6,7].

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FIGURES AND TABLE CAPTIONS:

Figure 1: $\Phi-$dependence for $\Phi < 0.1$ of the inverse Soret coefficient $1/S_T$ and of the inverse thermal diffusion coefficient $1/D_T$ at three $[cit]_{free}$ values: $[cit]_{free}$ = 0.03 mol/L (Δ), 0.08 mol/L ($\blacksquare$) and 0.1 mol/L (o). *Figure 1a*: $1/S_T$ (main graph) and S_T (inset). Lines stand for linear fits according to Eq. (7). The fits parameters are reported in Table 1. *Figure 1b:* $1/D_T$ (main graph) and D_T (inset). The full line is an extrapolation of the Hard sphere model (K_F = 6.55) with D_{T0}=2.3 10^{-12} $m^2K^{-1}s^{-1}$.

Figure 2a: Φ-dependence for $[cit]_{free}$ = 0.03 mol/L (o), 0.08 mol/L ($\Diamond$) and 0.1 mol/L ($\square$) of the compressibility χ_T (full symbols) and of S_T / S_{T0} (open symbols), the Soret coefficient normalized to its value at $\Phi = 0$. The dashed line is a guide for the eye.

Figure 2b: Φ-dependence of the absolute value of the thermal diffusion coefficient at $[cit]_{free}$ = 0.03 mol/L (o), 0.08 mol/L ($\Diamond$) and 0.1 mol/L ($\square$). The full line is a fit of the data according to Eq.(9). The arrows mark the volume fractions Φ^* above which the system presents, for $[cit]_{free} \approx 0.03 - 0.08$ mol/L, slow magneto-optical relaxations.

Table 1: Interaction parameters K_T as determined at low Φ by SANS [20] and FRS at various $[cit]_{free}$; S_{T0} is the extrapolated value of S_T at infinite dilution.
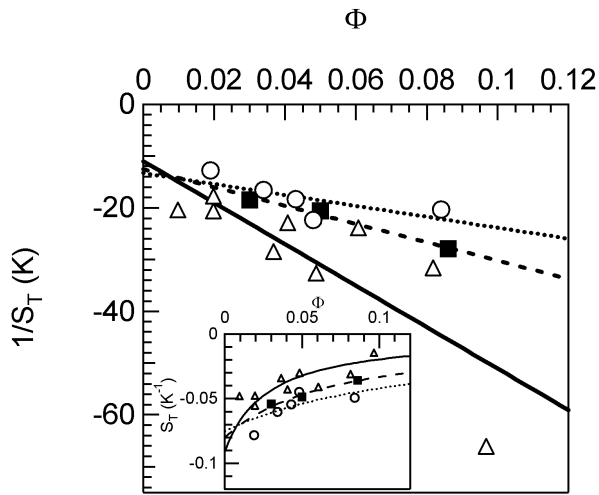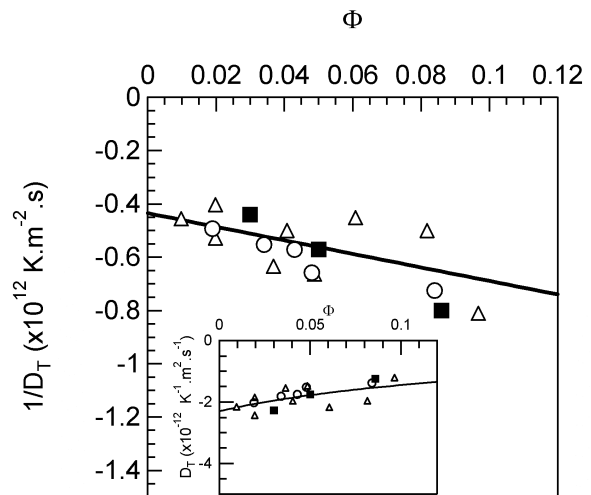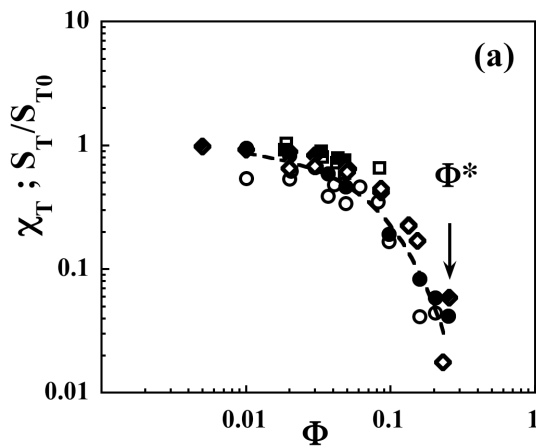
Figure 1a

Φ

Figure 1b

Φ

Figure 2a

Figure 2b
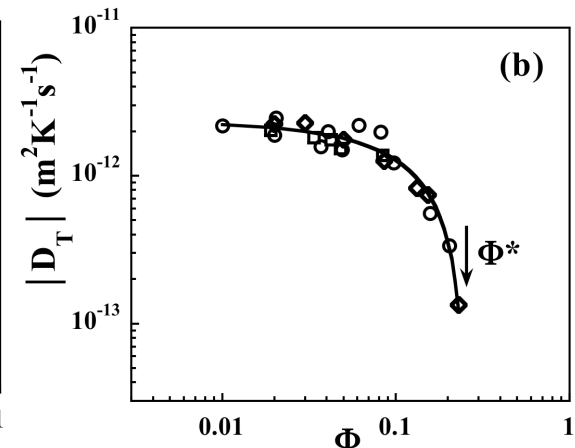
Table 1

[cit]$_{free}$ (mol/L)	K_T (SANS) $\chi_{T^{-1}} = 1 + K_T\Phi$	K_T (FRS) $S_T = S_{T0} / (1 + K_T\Phi)$	S_{T0} (K^{-1})
0.03	30±3	37±7	-(9±1) 10^{-2}
0.08	16±2	14±5	-(8±1) 10^{-2}
0.1	7±2	8±6	-(7.5±1) 10^{-2}