



## Research articles

## Concentration-dependent zero-field magnetic dynamic response of polydisperse ferrofluids

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## ABSTRACT

In this contribution, we discuss the experimental results obtained for seven ferrofluid samples with the same particle size distribution that differ only in concentration of magnetic material. The dynamic response to a weak linearly-polarised probing AC field is measured for each sample at five different temperatures. We investigate Cole-Cole diagrams and phase shifts in order to describe the impact of ferroparticle concentration on the initial magnetic susceptibility. Our findings show that the main contribution comes from the increasing effective viscosity of the ferrofluid that results in the growth of the Brownian relaxation time. This mechanism is very important for the systems containing even a small portion of large magnetic colloids. The influence of dipolar correlations was separately analysed using computer simulations.

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## 1. Introduction

Nowadays, magnetic nanocolloids are widely used in medical, technological and even art-related applications. For the suspensions of magnetic particles in liquid magnetopassive carriers (known as ferrofluids), the most important feature is the ability to actively react to the applied magnetic field, preserving the fluidity. Thus, any practical or scientific application of a ferrofluid relies on its magnetic properties, both static and dynamic. For the latter, magnetic AC susceptometry was shown to be an adequate technique for its analysis [1–6].

In this paper we focus on the influence of particle concentration on the zero-field magnetic dynamic response of magnetic nanocolloids. Assuming that the temperature is fixed in the experiment, one can name at least three different interrelated mechanisms, through which the ferroparticle concentration manifests itself. The first one, is simply the amplitude of the response, reflected also in the simplest Debye approach [7]. In the ideal gas approximation of the latter model, the real ( $\chi'_D$ ) and imaginary ( $\chi''_D$ ) parts of the dynamic initial susceptibility  $\chi_D = \chi'_D - i\chi''_D$  are given by the following expressions:

$$\chi'_D(f) = \frac{\mu_0 n}{3k_B T} \int_0^\infty \frac{1}{1 + [2\pi f \tau(x)]^2} m^2(x) p(x) dx, \quad (1)$$

$$\chi''_D(f) = \frac{\mu_0 n}{3k_B T} \int_0^\infty \frac{2\pi f \tau(x)}{1 + [2\pi f \tau(x)]^2} m^2(x) p(x) dx. \quad (2)$$

here,  $\mu_0$  stands for the vacuum magnetic permeability;  $k_B T$  is the thermal energy;  $m(x)$  and  $\tau(x)$  are the magnetic moment and the characteristic relaxation time of the randomly chosen ferroparticle having the diameter  $x$  of the magnetic core;  $f$  has a meaning of the probing AC field frequency. These expressions linearly depend on the number density  $n$ . However, entering the equations as a prefactor, the impact of  $n$  is usually significantly blurred by the intrinsic polydispersity of magnetic nanocolloids here described through the size-distribution  $p(x)$ . Moreover, the amplitude of the response cancels out in the Debye formalism when applying to the experimental measurements of the phase shift  $\Delta\phi = \arctan(\chi''/\chi')$ .

The second mechanism stems from the fact that ferrofluids never behave as an ideal superparamagnetic gas. The particles interact via magnetic dipole–dipole interaction, and the interparticle correlations are known to slow down the dynamic response [8–12]. The growth of the magnetic material concentration inevitably leads to the increase of these correlations as confirmed by Brownian Dynamics simulations [13]. Recently, we made the first attempt to analytically describe the contribution of dipolar interactions in the

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dynamic spectra of polydisperse magnetic nanocolloids, using perturbation theory [11]:

$$\chi'(f) = \chi'_b(f) + \frac{1}{3} \left\{ [\chi''_b(f)]^2 - [\chi'_b(f)]^2 \right\}, \quad (3)$$

$$\chi''(f) = \chi''_b(f) \left[ 1 + \frac{2}{3} \chi'_b(f) \right], \quad (4)$$

where both the real ( $\chi'$ ) and imaginary ( $\chi''$ ) parts of the susceptibility are expressed in terms of Debye susceptibilities (1) and (2). Importantly, the expressions (3) and (4) have the quadratic precision in ferroparticle concentration  $n$ .

The third mechanism is especially pronounced for the systems with a significant part of large particles, exhibiting Brownian relaxation. The latter is determined by the effective viscosity  $\eta$  of the media in which the relaxation takes place. The changes in the effective viscosity take place due to the perturbation in hydrodynamic fields caused by the colloids dispersed: once the concentration gets high enough for hydrodynamic fields of individual colloids to interact, instead of the single-particle relaxation, one observes collective effects. The growth of  $\eta$  with  $n$  leads to the overall slow-down of the dynamic response as shown, for example, in Refs. [14,15].

As mentioned above, all the three mechanisms are highly interconnected. To analyse their roles separately at various temperatures is an experimental challenge, related, in the first place, to the polydispersity of regular magnetic nanocolloids. Previously, we proposed to avoid the uncertainties caused by the polydispersity by using an accurate dilution procedure [16]. Here, we analyse the experimental results obtained for a standard magnetite-in-kerosene ferrofluid, with nanoparticles in it being stabilised by oleic acid. The polydispersity of our system can be described by the maximum of 9.3 nm and the standard relative width of 0.29. The fraction of particles with  $x \geq 18$  nm is approximately 1 per cent, *i.e.* there are not many particles with Brownian relaxation in our samples. Of course, 18 nm is just an approximate border between Brownian and Néel relaxation for magnetite particles, and this value can change depending on temperature. The basic sample was diluted in order to obtain seven samples S1–S7 with the same granulometric composition and different only in  $n$  (for experimental details, see, Ref. [12]). At room temperature, the values of the static saturation magnetisation measured in kA/m are: 22.6 (S1); 30.9 (S2); 43.2 (S3); 59.9 (S4); 75.9 (S5); 82.2 (S6); 88.7 (S7). Corresponding values for the volume fraction of magnetic material are 0.047 (S1), 0.065 (S2), 0.09 (S3), 0.125 (S4), 0.159 (S5), 0.172 (S6) and 0.186 (S7). Dynamic susceptibility was measured using thermostated mutual induction bridge [17] in the frequency range 100 Hz–100 kHz. In the experiment, the phase shift was measured at five different temperatures  $T_1 = 232$  K;  $T_2 = 252$  K;  $T_3 = 273$  K;  $T_4 = 300$  K and  $T_5 = 337$  K. Below we provide a detailed analysis of phase shifts and Cole-Cole diagrams. We employ computer simulations to understand the contribution of dipolar correlations to the phase shift.

## 2. Results and discussions

In Fig. 1 we plot Cole-Cole diagrams for experimental samples S1–S7. For high temperature (a) and (b) all the samples are exhibiting qualitatively similar behaviour. The shift here is mainly caused by the growing nanocolloids' concentration and is realised through the first mechanism described above. Importantly, similar behaviour of Cole-Cole diagrams in this  $T$ -range once again confirms the preservation of the granulometric composition on dilution. The kinking behaviour can be seen at any temperature, at  $T = 273$  K, the signs of folding become totally evident and are

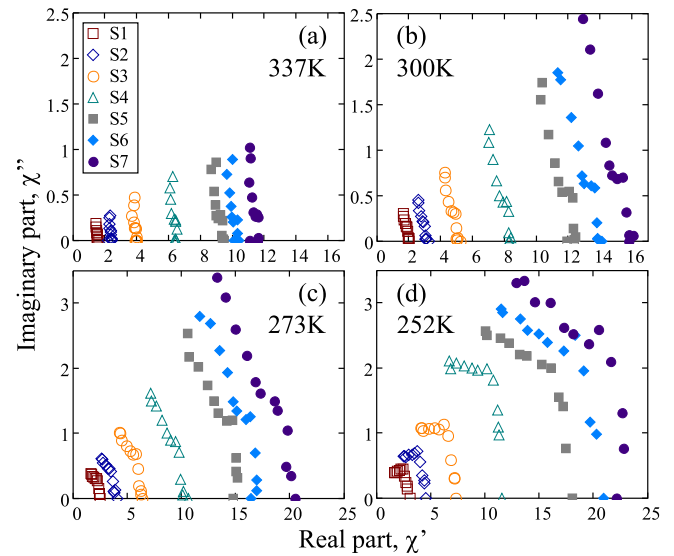


Fig. 1. Cole-Cole diagram for experimental samples S1–S7 for the high and intermediate values of  $T$ , provided in the figures. The legend is the same for (a)–(d).

especially pronounced for the most diluted samples S1 and S2. On further cooling (d), samples S1–S4 are showing a clear tendency to fold, whereas it is much less pronounced for samples S5–S7. The fact, that these differences occur at the fixed temperature, indicates the concentration-dependent evolution of the relaxation spectrum: the characteristic time of the Néel relaxation could be considered basically unchanged at fixed  $T$ , thus, what changes is the typical time for the rotational (Brownian) relaxation that depends on ferrofluid viscosity, and significantly increases with  $n$ . Indeed, the results of viscosity measurements for samples S1, S2 and S3 are provided in Table 1 and show the tripling of its value even though the concentration of S1 is almost half that of S3.

The folding behaviour is fully observed in Fig. 2 for the lowest temperature. Slight deviations in the folding behaviour for samples S6 and S7 again confirm the dependence of the relaxation spectra on ferroparticle concentration. It is worth mentioning that the linear scaling found for the high-frequency region of the Cole-Cole diagram is evidence of a similar decay for real and imaginary parts of the dynamic susceptibility with  $f$ . This scaling becomes evident especially in the log–log representation used in Fig. 2. This scaling, and not the one that could be obtained from Debye approximations Eqs. (1) and (2), underlines again the deviations of our samples from ideal superparamagnetic gas.

The impact of growing viscosity can be seen even more clearly in Fig. 3, where we plot the experimental data for the phase shift  $\Delta\phi$  as a function of frequency  $f$  in log scale. Here, we only show the results for samples S1, S3, S5 and S7 as the results for S2 are very close to those for S1; S4 looks similar to S5; and, finally S6 is basically indistinguishable from S7. At  $T = 337$  K (a) and 300 K (b) the curves can be divided into two groups. The value of  $\Delta\phi$  for low concentrated samples grows monotonically with  $f$ , whereas high concentrated ferrofluids exhibit a clear plateau for the intermediate frequencies ( $f \sim 10^3$  Hz). Similar plateaux can be observed for S5 and S7 at zero degrees Celsius (c). At the lowest temperature (d), the behaviour of  $\Delta\phi$  changes also for low-concentration samples, and the curves develop a characteristic flat part, but shifted towards higher  $f$ , as compared to the high-concentration samples.

The inflection point of  $\Delta\phi$  for S7 is situated lower than those for other samples. The overall trend observed in Fig. 3(a)–(d), namely the shift of the plateaux down and to the left with growing  $n$  can be attributed mainly to an increase of the effective viscosity, as the

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