A comparative study of the determination of ferrofluid particle size by means of rotational Brownian motion and translational Brownian motion

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Received 21 November 2000

Two methods, the Toroidal Technique and the Forced Rayleigh Scattering (FRS) method, were used in the determination of the size of magnetic particles and their aggregates in magnetic fluids. The toroidal technique was used in the determination of the complex, frequency dependent magnetic susceptibility, $\chi(\omega)=\chi^{'}(\omega) - \mathrm{i}\chi^{''}(\omega)$ of magnetic fluids consisting of two colloidal suspensions of cobalt ferrite in hexadecene and a colloidal suspension of magnetite in isopar m with corresponding saturation magnetisation of 45.5 mT, 20 mT and 90 mT, respectively. Plots of the susceptibility components against frequency f over the range 10 Hz to 1 MHz, are shown to have approximate Debye-type profiles with the presence of relaxation components being indicated by the frequency, $f_{\max}$, of the maximum of the loss-peak in the $\chi^{''}(\omega)$ profiles. The FRS method (the interference of two intense laser beams in the thin film of magnetic fluid) was used to create the periodical structure of needle like clusters of magnetic particles. This creation is caused by a thermodiffusion effect known as the Soret effect. The obtained structures are indicative of as a self diffraction effect of the used primary laser beams. The relaxation phenomena arising from the switching off of the laser interference field is discussed in terms of a spectrum of relaxation times. This spectrum is proportional to the hydrodynamic particle size distribution. Corresponding calculations of particle hydrodynamic radius obtained by both mentioned methods indicate the presence of aggregates of magnetic particles.

PACS: 75.50.M, 05.40, 42.65.D, 35.20.M
Key words: magnetic fluids, particle size distribution, Brownian motion

1 Introduction

Magnetic fluids consist of colloidal suspensions of nanoparticles of ferromagnetic or ferrimagnetic materials dispersed in a carrier liquid and stabilised electrostatically or by a suitable organic surfactant. In the latter case the surfactant coating of the particles creates an entropic repulsion between particles [1,2] such that thermal agitation alone is sufficient to maintain them in a stable dispersion. The particles are single-domain and are considered to be in a state of uniform magnetisation with magnetic moment, $m = M_{\mathrm{s}}V$, where M_{s} is the saturation magnetisation of the material and V is the volume of the particle. The preferred orientation of the magnetic moment is along an axis, or axes of easy magnetisation and this direction depends generally on a combination of shape and magneto-crystalline anisotropy denoted by the symbol K. Also when in suspension their magnetic properties can be described by the Langevin function ($L(\xi)$, where $\xi = mV/k_{\mathrm{B}}T$), suitably modified to take account of a distribution of particle sizes. The formation of aggregates [3–5] can arise due to the effects of short range van der Waals attraction or by the effects of magnetic dipolar interactions between particles [6]. Aggregation can arise due to incomplete coverage of the particles with surfactant during the preparation process or simply weak absorption in which an equilibrium exists between the absorbed surfactant and the surfactant free in solution. Since magnetic fluids have application in many areas it is of the utmost importance that the fluids are free from the presence of aggregation in order to maintain fluid stability. Here we report on the results of particle aggregate distribution obtained for three ferrofluid samples by means of toroidal technique [7] and FRS method [8].

2 Relaxation mechanisms

The magnetic moment of the particles may relax through either rotational Brownian motion of the particle within the carrier liquid, with relaxation time τ_{B} [9] or through the Néel mechanism with relaxation time τ_{N} [10]. The Brownian relaxation time τ_{B} is given by

$$\tau_{\mathrm{B}} = \frac{4\pi r^3 \eta}{k_{\mathrm{B}}T}\,, \tag{1}$$

where r is the hydrodynamic radius of the particle and η is the dynamic viscosity of the carrier liquid. In the case of the Néel relaxation mechanism, the magnetic moment may reverse direction within the particle by overcoming an energy barrier, which for uniaxial anisotropy, is given by KV, where K is the anisotropy constant of the particle. This reversal time may be described approximately in terms of Brown's expression [11] for high and low barrier heights, as,

$$\begin{aligned} \tau_{\mathrm{N}} &= \tau_0 \sigma^{-1/2} \exp(\sigma), && \sigma \geq 2, \\ \tau_{\mathrm{N}} &= \tau_0 \sigma, && \sigma \ll 1; \end{aligned} \tag{2}$$

τ_0 is a damping or extinction time having an often quoted approximate value of 10^{-9}s [12] and $\sigma = KV/kT$, where k is Boltzmann's constant and T is the temperature. A distribution of particle sizes implies the existence of a distribution of relaxation times, with both relaxation mechanisms contributing to the magnetisation. They do so with an effective relaxation time τ_{eff} [13,14], where

$$\tau_{\text{eff}} = \frac{\tau_{\text{N}}\tau_{\text{B}}}{(\tau_{\text{N}} + \tau_{\text{B}})}, \tag{3}$$

the mechanism with the shortest relaxation time being dominant. Thus if $\tau_{\text{N}} \gg \tau_{\text{B}}$ then from (3) $\tau_{\text{eff}} = \tau_{\text{B}}$ whilst if $\tau_{\text{N}} \ll \tau_{\text{B}}$, $\tau_{\text{eff}} = \tau_{\text{B}}$. A critical value for the particle volume occurs when $\tau_{\text{N}} = \tau_{\text{B}}$ [13,15].

3 Measurement of complex susceptibility (Method 1)

The frequency-dependent, complex, relative magnetic susceptibility, $\chi(\omega)$, may be written in terms of its real and imaginary components, where

$$\chi(\omega) = \chi^{'}(\omega) - \mathrm{i}\chi^{''}(\omega)\,. \tag{4}$$

The theory developed by Debye [16] to account for the anomalous dielectric dispersion in dipolar fluids may be used [17,18] to account for the analogous case of magnetic fluids. According to Debye´s theory the complex susceptibility, $\chi(\omega)$, has a frequency dependence given by the equation,

$$\chi(\omega) - \chi_\infty = \frac{\chi_0 - \chi_\infty}{1 + \mathrm{i}\omega\tau_0}, \tag{5}$$

where

$$\chi_0 = \frac{nm^2}{3kT\mu_0} \tag{6}$$

and

$$\tau_0 = \frac{1}{\omega_{\max}} = \frac{1}{2\pi f_{\max}}, \tag{7}$$

where $f_{\max}$ is the frequency at which $\chi^{''}(\omega)$ is a maximum, n is the particle number density and χ_0 and χ_∞ indicate susceptibility values at $\omega = 0$ and at very high frequencies. In general one can anticipate a single loss peak in the susceptibility profile, however circumstances can arise whereby the particle distribution appears as a two-fraction model and exhibits two loss peaks [19], as in the case of two of the samples reported on here. For a distribution of particle sizes a distribution of τ will exist so that $\chi(\omega)$ may also be expressed in terms of a distribution function, $F(\tau)$, giving

$$\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty)\int_0^\infty \frac{F(\tau)\mathrm{d}\tau}{(1 + \mathrm{i}\omega\tau)}\,. \tag{8}$$

4 The Forced Rayleigh Scattering (FRS) method (Method 2)

The concentration variations of particles due to the laser-beam induced thermal diffusion in liquid mixtures (known as Soret effect) were observed in number of works [20–22]. The theoretical aspects of the Soret effect in fluids containing nanoparticles were studied by Tabiryan and Luo [23]. The concentration optical grating of fine magnetic particles in magnetic fluids due to their interaction with laser beam was first experimentally proved by Bacri et al. [8] by means of the FRS experiment. The dynamics of the observed effect was discussed in terms of a single relaxation time (monodisperse particle size distribution and the co-operative diffusion coefficient of the magnetic particles). However the size distribution of magnetic particles in magnetic fluids is never monodisperse. It means that results should be discussed in terms of a spectrum of relaxation times due to the polydispersity of particle size.

For experiments we have used an optical cell 20μm thick filled by magnetic fluid. The interference field was created by two coherent laser beams ($\lambda = 530\,n$m) crossing the above mentioned optical cell. These beams were obtained by splitting a beam from Zeiss Argon laser ILA 120. The power used was 50 mW. When the two laser beams interfere for a few seconds an optical grating was easily observed by the presence of self diffraction effect of the primary laser beams. If one of the two pump laser beams is switched off the concentration optical grating smear out in a few seconds. The dynamics of this process was observed through the intensity measurement of the first order of the diffracted pattern of the self-diffraction effect. Experimentally, the relaxation curve of this first order diffracted signal should in principle be a single decay of the form,

$$\frac{I(t)}{I(0)} = \exp\left(-\frac{t}{\tau}\right), \tag{9}$$

where τ is relaxation time. If the laser interference field is removed, the ferrofluid particles thermally relax towards randome positions with relaxation time (according to the Perrin´s law [24], given by

$$\tau_{\mathrm{R}} = \frac{1}{6D}, \tag{10}$$

where D is the diffusion coefficient of Brownian rotation of a ferrofluid particle given by

$$D = \frac{k_{\mathrm{B}}T}{8\pi\eta R_{\mathrm{H}}^3}, \tag{11}$$

where R_{H} is the hydrodynamic radius of the ferrofluid particle and η is carrier fluid viscosity. Using equations (10) and (11) it is easy to obtain for thermal relaxation time the following equation

$$\tau_{\mathrm{R}} = \frac{4\pi R_H^3\eta}{3k_{\mathrm{B}}T}. \tag{12}$$

The comparison of the equations (1) and (12) yields relation between Brownian relaxation time and thermal relaxation time as

$$\tau_{\mathrm{R}} = \tfrac{1}{3}\tau_{\mathrm{B}}. \tag{13}$$

This consideration only applies in the case of monodispersed magnetic particles. Owing to the existence of particle size distribution $I(t)/I(0)$ is not a simple exponential function of time and thus, because of the polydispersity of particles, the time dependence of the intensity is given by formula:

$$\frac{I(t)}{I(0)} = \int_0^\infty \mathrm{e}^{-t/\tau_\mathrm{R}} F(\tau_\mathrm{R}) \mathrm{d}\tau_\mathrm{R} \,, \tag{14}$$

where $F(\tau_\mathrm{R})$ is a spectrum of relaxation times. The function, $F(\tau_\mathrm{R})$, is directly proportional to the hydrodynamic particle size distribution function using Eq. (12). For the calculation of the spectrum of relaxation times $F(\tau_\mathrm{R})$ the method used was based on the discrete fast Fourier transformation [25]. This method is well-known for the calculation of the activation energy spectrum for the deformation processes in amorphous metals [26].

5 Results and discussion

The measurement of frequency-dependent complex susceptibility and the FRS method were accomplished with three magnetic fluids, namely Fluids 1, 2 and 3, with corresponding saturation magnetisation of 45.5 mT, 20 mT and 90 mT, respectively. The measurement of complex susceptibility was carried out at room temperature by means of the toroidal technique and the HP 4192 A LF Impedance Analyser, over the frequency range 10 Hz to 1 MHz. The three fluids consisted of two suspensions of cobalt ferrite in hexadecene (Fluids 1 and 2) with a viscosity of 1.5×10^{-3}Nsm^{-2}, and of a suspension of magnetite in isopar m (Fluid 3), with a viscosity of 0.5×10^{-3}Nsm^{-2}. The corresponding median magnetic particle diameters were 11 nm; 9.2 nm and 10 nm respectively, as determined by electron microscopy. The normalised plots of $\chi^{'}(\omega)/\chi(0)$ and $\chi^{"}(\omega)/\chi(0)$ against f(Hz) for the three fluids are shown in Figs. 1a,b,c, respectively. $\chi(0)$ was taken as the value $\chi'(\omega)$ at 10 Hz with Fluids 1, 2 and 3 having corresponding values of 0.51, 0.27 and 1.01, respectively. From Fig. 1a it can be seen that the complex susceptibility curves for Fluid 1 have a Debye-type profile with the peak in the $\chi^{"}(\omega)$ component occurring at an approximate frequency of 1 kHz. From Eq. (1) a hydrodynamic radius of 32 nm is obtained. This value of hydrodynamic radius is greater than the value of magnetic radius plus surfactant thickness (say 2–4 nm), and is thus indicative of the existence of aggregation at a frequency of 1 kHz. In the case of the susceptibility components of Fluid 2, in Fig. 1b, the presence of two loss peaks are evident at frequencies of 40 Hz and 2 kHz. The corresponding hydrodynamic radii are 95 nm and 26 nm, respectively. Again these values of hydrodynamic radii are greater than the value of magnetic radii plus surfactant thickness and are thus indicative of the existence of two separate distributions of aggregates. In Fig. 3 a loss-peak occurs in the $\chi^{"}(\omega)$ component at $f_{\max 1} = 0.2$ MHz which corresponds to an average relaxation time of 0.8 μs. At this frequency we would anticipate a contribution from both Néel and Brownian relaxation mechanisms. Using Brown's equation for Néel relaxation (Eq. (2)) necessitates the insertion of a value for the

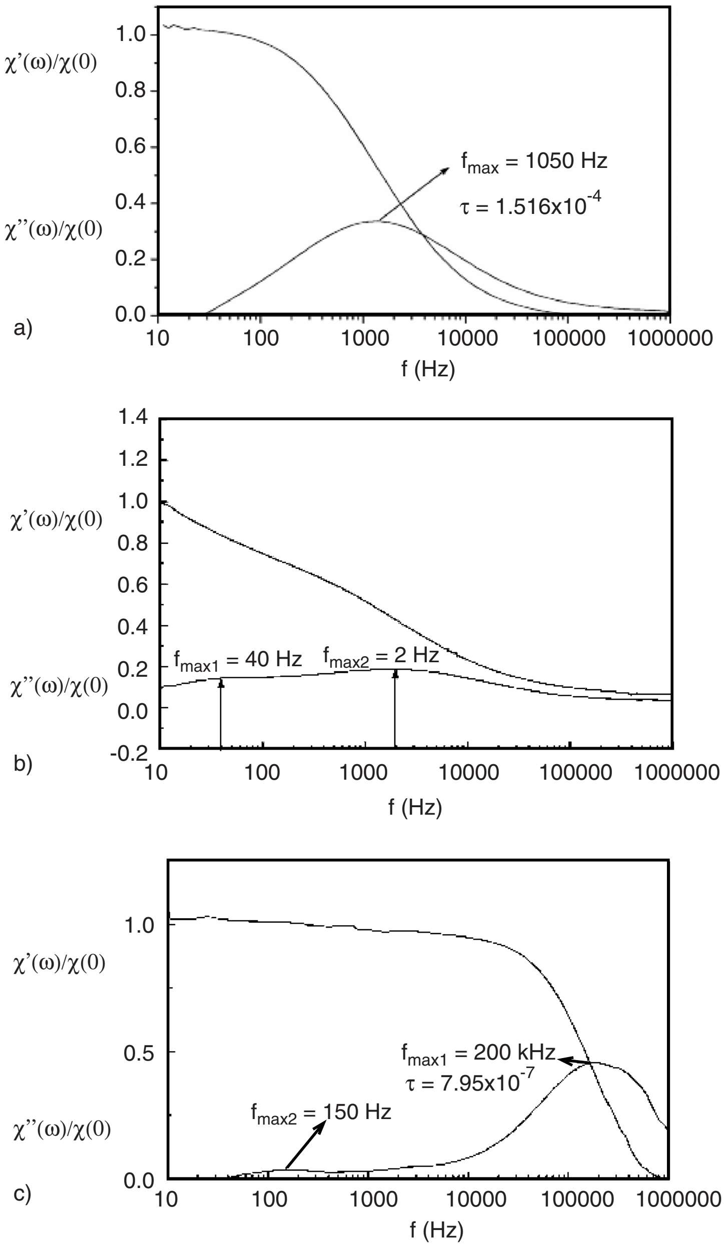

Fig. 1. Normalised plot of $\chi^{'}(\omega)$ and $\chi^{"}(\omega)$ against f in Hz, for Fluid 1 (a), 2 (b), and 3 (c).

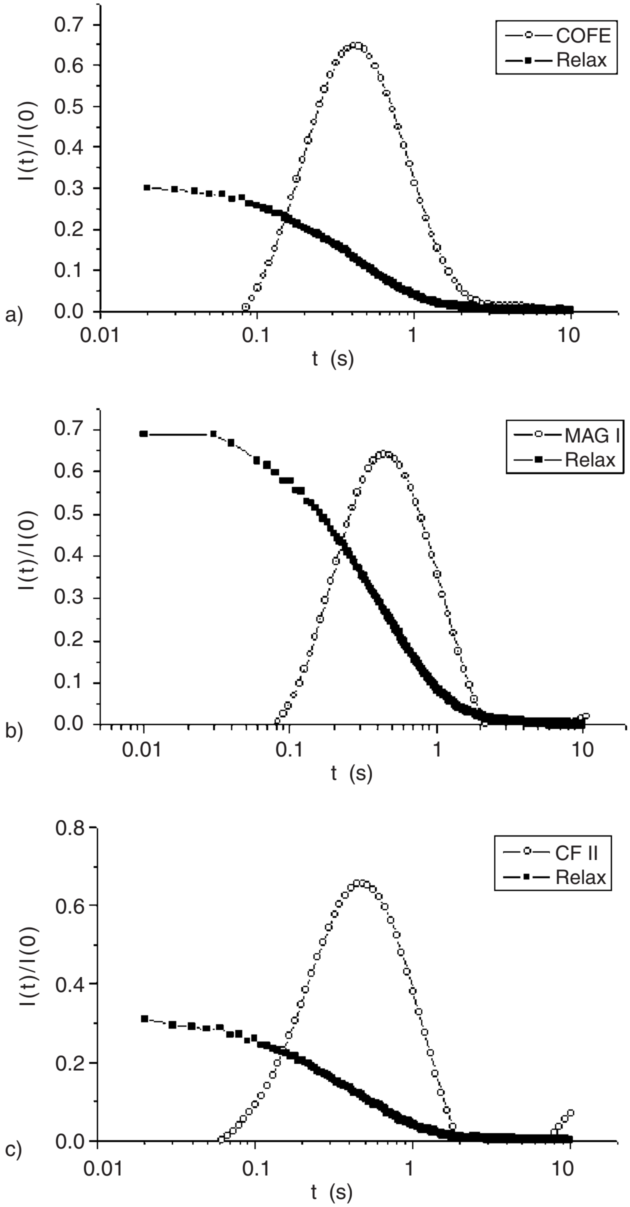

Fig. 2. The time dependence of relaxation signal of the relative intensity $I(t)/I(0)$ of the first order of diffracted pattern and the corresponding spectrum of relaxation times of Fluid 1 (a), 2 (b), and 3 (c).

anisotropy constant, K. The references [27,28] give values of K over the range $(1\text{–}5)\times10^4\,\mathrm{J/m^3}$. Using value of $K = 2\times10^4\,\mathrm{J/m^3}$ we obtain magnetic particle radius of $r = 7.2\,\mathrm{nm}$, whilst using the value of $K = 4\times10^4\,\mathrm{J/m^3}$ gives a magnetic particle radius $r = 5.7\,\mathrm{nm}$, which is a good approximation to the median particle radius value of 5 nm. However, using the equation (3) for Brownian relaxation and a value of $\eta = 0.5\times10^{-3}\mathrm{Nsm^{-2}}$, we obtain a hydrodynamic radius of 8 nm, which is a good approximation to the median particle radius plus surfactant. Thus for this sample the approximate condition of $\tau_\mathrm{N} = \tau_\mathrm{B}$ exists and is an indication of the condition of critical particle volume, thus neither relaxation mechanism is dominant as pointed out in references [14,19]. In the same figure there is also the indication of a small loss-peak at $f_{\max 2} = 150\,\mathrm{Hz}$. This corresponds to a hydrodynamic radius of 89 nm and is also indicative of the presence of aggregation.

The results of Method 2 are illustrated in Fig. 2; these plots represent time dependences of the relaxation signal of the relative intensity of the first order of diffracted patterns and the corresponding spectrum of relaxation times. From these figures it can be seen that there is only one peak in the profiles and from the corresponding times we computed sizes of magnetic particles or their aggregates. For Fluid 1 radius was 513 nm, whilst for Fluid 2 and 3 the radii were 533 nm and 750 nm. The comparison of the results obtained by both used methods are shown in Table 1.

Table 1. The comparison of radii of magnetic particles and their aggregates obtained by Method 1 and Method 2.

	Method 1		Method 2	
	r_1 (nm)	r_2 (nm)	r_1 (nm)	r_2 (nm)
Fluid 1	–	32	–	513
Fluid 2	26	95	–	533
Fluid 3	5.7–7.2/8	89	–	750

6 Conclusions

From the complex magnetic susceptibility measurements all the samples were found to have an approximate Debye type profile over the measured frequency range, with average particle radii indicative of the presence of aggregation. The aggregates had radii ranging from 26 nm to 95 nm, far greater than the corresponding mean particle radii which ranged between 4.5 nm and 5.5 nm, respectively, as determined by electron micrograph. These experimental results show that the investigated magnetic fluids have a natural tendency to form aggregates of magnetic particles. The presence of aggregation was also observed by the FRS method too. As can be seen from Table 1, the sizes of aggregates determined by FRS method are in an interval of (513–750) nm. They are approximately one order larger than the sizes of the aggregates obtained by Method 1. With Method 2, the decay of stripes of magnetic particles goes through a channel of big aggregates, which are unlike the aggregates usually found in magnetic fluids. These big aggregates are probably created by the used FRS technique and by the natural tendency to form aggregates of magnetic particles in magnetic fluids studied. Also the exact arrangement of the magnetic moments of magnetic particles in stripes and clusters is unknown, however it is possible that magnetic moments are parallel or they create closed loops that have no macroscopic magnetic moment. However, whilst the exact reason for the discrepancy between the results obtained with the two diffrent methods is as yet unknown, it may be that the origin of the difference may lie in the probing methods of both techniques. In the case of the Method 1 (unlike Method 2, where the probing technique may in fact give rise to aggregation), the probing field is of a low level so as not to induce aggregation, thereby enabling any existing aggregates in the sample over the measure frequency range to be identified. If indeed the aggregates identified by Method 2 did exist naturally in the samples then they would not be detected by Method 1 since aggregates of such sizes would have a loss-peak below 1 Hz, which is outside the measurement range of the toroid. It is hoped that a detailed investigation of the influence of an external magnetic field and volume concentration of magnetic particles on the observed responses may lead to the clearer understanding of the processes involved.

Acknowledgement is due to B.K.P.Scaife for useful discussions and also the Irish Higher Education Authority and the Slovak Academy of Sciences (within the framework of Project No.7020) and NATO (within the framework of Project No. LST. CLG.977500), for partial funding of this work.

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