Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Resolving particle size modality in bi-modal iron oxide nanoparticle suspensions

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ARTICLE INFO

Article history: Received 30 June 2014 Accepted 16 August 2014 Available online 26 August 2014

Keywords: Iron oxide nanoparticle Bi-modal size distribution characterization Complex ac-susceptibility Small angle X-ray scattering Modeling

ABSTRACT

Particle size modality in bi-modal iron oxide suspensions was resolved by exploiting complex acsusceptibility (ACS), small angle X-ray scattering (SAXS) and photon cross-correlation spectroscopy. To explain dynamic magnetic response of bi-modal suspensions, the Debye model was expanded to a linear superposition form allowing for the contribution of both particle fractions. This modified and adopted model is able to resolve the bi-modal particle size distributions. The SAXS curves of mono- and bi-modal suspensions were fitted well using a Monte Carlo simulation scheme, allowing the detection of bi-modal particle size distributions with high precision.

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1. Introduction

Magnetic nanoparticles (MNPs) gain a lot of scientific and technological attention in the last two decades owing to their applicability in various biomedical applications [1,2]. It is well known that particle size distribution (PSD) plays a crucial role in classifying and targeting appropriate applications for MNP suspensions [3]. The static and dynamic magnetic responses of MNPs – the most application relevant properties – depend significantly on the PSD [4,5]. Seemingly, there is a great need to define these particle parameters precisely. Additionally, for researchers in the field of magnetic nanomaterials, it is important to understand how PSD results acquired from different measurement techniques can be interrelated.

Up to now, a few studies have been dedicated to the topic of analyzing multi-modal nanoparticle suspensions [6–8]. And yet, there has been little effort to define a set of complementary analysis techniques, being capable of resolving the PSD in bimodal suspensions. In a prime study, Thünemann et al. combined an A4F fractionation instrument with small angle X-ray scattering to simultaneously fractionize and analyze the PSD of Resovist nanoparticles different fractions [6]. Jamting et al. investigated bimodal dispersions of latex spheres using dynamic light scattering. Having applied an alternative model defining the auto-correlation function as a weighted distribution of decay rates, they succeeded in resolving the PSD of a mixture of 80 and 100 nm particles [7]. Indeed, analysis of bi-modal nanoparticle suspensions is still a

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http://dx.doi.org/10.1016/j.jmmm.2014.08.050 0304-8853/© 2014 Elsevier B.V. All rights reserved. great challenge, particularly when the difference between fractions' PSD is minor. Moreover, studying complex magnetic ferrofluids more deeply to elucidate the challenges one has to tackle for interpreting and reconstructing experimental results is a necessity for further progress in magnetic nanoparticle-based applications.

In this study, we aim at resolving the PSD of spherical iron oxide nanoparticle suspensions with a well distinct bi-modal size distribution. The samples were tailored via mixing almost fully Néel- and Brownian-relaxation-dominated iron oxide nanoparticles at different volume fractions. A combination of complex acsusceptibility (ACS), small angle X-ray scattering (SAXS) and photon cross-correlation spectroscopy (PCCS) was utilized to thoroughly analyze the sample PSD using techniques based on different physical principles. The ACS curves were simulated using the Debye model modified and adopted to bi-modal samples. The SAXS curves were reconstructed by applying a Monte Carlo simulation scheme. The PSD results obtained from the applied methods are discussed and correlated.

2. Materials and methods

2.1. Design of experiments

The oleic acid capped spherical iron oxide nanoparticles with a mean core diameter of 12 nm, f_1 , and 25 nm, f_2 , were synthesized using a thermal decomposition procedure published in [5]. The particle mean core diameter was estimated from magnetorelaxometry (MRX) and TEM investigations [9]. The f_1 nanoparticles almost entirely relax via the Néel mechanism whereas the f_2 ones







 Table 1

 Mixing ratios of bi-modal suspensions used in this study. Numbers are volume percent.

Fraction	Notation							
	S1	S2	S3	S4	S5	S6		
$f_1 (12 \text{ nm})$ $f_2 (25 \text{ nm})$	100 0	80 20	60 40	40 60	20 80	0 100		

are majorly thermally blocked and relax via the Brownian mechanism. The mixing ratios of the bi-modal samples measured in the current study are summarized in Table 1.

2.2. Analytical methods

Three different analytical methods have been used to characterize the samples and also examine to what extent these techniques are capable of resolving a bi-modal PSD. Photon cross-correlation spectroscopy (PCCS) was performed on non-aqueous particle dilutions with a NanoPhox device (Sympatec, Germany) operating in a cross-correlation mode collecting 90° back-scattered signals. The complex ac-susceptibility (ACS) measurements were carried out using a setup operating from 1 kHz to 1 MHz at a magnetic field amplitude of 95 μ T. The small angle X-ray scattering (SAXS) analysis was performed utilizing a SAXSess instrument (Anton Paar, Austria) operating at a slit collimation mode using a Cu-K α X-ray source. The SAXS measurements were carried out on particle suspensions in tetrahydrofuran (THF) at a particle concentration of 1–2 mg/ml. The measured intensity was corrected by subtracting the intensity of a capillary filled with pure THF. After background correction the scattering data was de-convoluted (slit-length de-smearing). All data processing was performed with the SAXSquant 3.5 software (Anton Paar, Austria).

3. Theory

3.1. Debye model

The response of magnetic nanoparticles to an alternating magnetic field can be described using the Debye model in a complex form given by [10]

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \quad \text{with} \quad \chi'(\omega) = \frac{\chi_0}{1 + (\omega\tau_{\text{eff}})^2}$$

and $\chi''(\omega) = \frac{\chi_0 \omega \tau_{\text{eff}}}{1 + (\omega \tau_{\text{eff}})^2},$ (1)

in which χ' and χ'' are the real and the imaginary part of acsusceptibility. Taking particle core $f(d_c)$ and hydrodynamic $f(d_h)$ size distributions into account, the imaginary part can be written in a double integration form [11]

$$\frac{\chi''(\omega)}{\chi_0^*} = \int_0^\infty f(d_h) \int_0^\infty \frac{d_c^0 \cdot f(d_c) \cdot \omega \tau_{eff}}{1 + (\omega \tau_{eff})^2} dd_c dd_h$$

with $\tau_{eff} = \frac{\tau_B \tau_N}{\tau_B + \tau_N}$ and $\chi_0^* = \frac{\mu_0 n M_s^2}{3k_B T} \left(\frac{\pi}{6}\right)^2$, (2)

with d_c and d_h particle core and hydrodynamic size, $\tau_B = \pi \eta d_h^3/2k_B T$ and $\tau_N = \tau_0 \exp(K\pi d_c^3/6k_B T)$ Brownian and Néel time constant, M_s saturation magnetization, K effective anisotropy constant, η solvent viscosity, n particle number density and k_B Boltzmann constant. The PSD can be described with a log-normal distribution function given by

$$f(d_i, \mu_i, \sigma_i) = \frac{1}{\sqrt{2\pi}\sigma_i d_i} \exp\left[-\frac{(\ln d_i - \ln \mu_i)^2}{2\sigma_i^2}\right],\tag{3}$$

in which μ_i and σ_i are geometric mean and standard deviation, respectively, and d_i is the particle core or/and hydrodynamic diameter.

In the case of magnetic suspensions with a bi-modal PSD, the Debye model can be given as a linear superposition of two Debye terms, each one counting for a single particle fraction. The formula can be written as

$$\frac{\chi''(\omega)_{bi-mod}}{\chi_0^*} = \left(\frac{k}{m_1}\right) \cdot \chi''(\omega)_{f_1} + \left(\frac{1-k}{m_2}\right) \cdot \chi''(\omega)_{f_2}$$
with $k = n_1 \frac{m_1}{n_1 m_1 + n_2 m_2}$ and $m_i = \int_0^\infty d_c^6 \cdot f_i(d_c) dd_c.$ (4)

k is the number-weighted fraction of Néel-relaxation-dominated nanoparticles introduced by Yoshida et al. in [12].

3.2. Small angle X-ray scattering

Small angle X-ray scattering is a sensitive technique for measuring average particle size and shape. The particles with a size in the range of 1-100 nm scatter the incident X-ray radiation due to the electron density difference between particles and solvent [13]. The scattering pattern is a function of *q*, named as scattering vector length and expressed by

$$q = \frac{4\pi}{\lambda} \cdot \sin\left(\theta\right). \tag{5}$$

The scattering intensity function of an *i* indexed fraction of spherical particles with a size distribution, $f_i(R)$, can be written as

$$I_i(q) = k \frac{\phi_i}{\langle V_i \rangle} (\rho - \rho_s)^2 \int_0^\infty f_i(R) R^6 [F(qR)]^2 dR,$$
(6)

with *k* an instrumental constant, ϕ_i particle volume fraction and $(\rho - \rho_s)^2$ particle and solvent electron density difference. The particle average volume and the scattering amplitude of a sphere is $\langle V_i \rangle = 4/3\pi \langle R_i \rangle^3$ and $F(qR) = (qR)^{-3} [\sin (qR) - qR \cos (qR)]$, respectively [6,13].

4. Results and discussion

The intensity auto-correlation functions $g^{(2)}(\tau)$ are plotted in Fig. 1(a). It can be seen that the $g^{(2)}(\tau)$ function shifts slightly to larger correlation times in S2 sample compared to S1. Interestingly, by having 40 vol% f_2 in the mixture, the $g^{(2)}(\tau)$ function decay trend resembles the S6 one and remains the same regardless of having more f_2 portion in bi-modal samples. The dependence of light scattering to the sixth power of particle hydrodynamic radius based on the Rayleigh scattering theory accounts for the observed behavior [14]. The rise in the correlation function amplitude after adding f_2 fraction can be explained by the fact that larger particles scatter more intensively. The particle number-weighted hydrodynamic size histograms, plotted in Fig. 1(b), were obtained from the fit to the correlation functions using a non-negative least square (NNLS) algorithm implemented in the PCCS instrument proprietary software. The results are summarized in Table 2. It was not possible to observe a bi-modal size distribution for mixed samples even by employing NNLS fit algorithm. The only visible feature is a non-linear growth of the particle mean diameter towards the size of f_2 fraction. This again implies the dominance of larger particles in PCCS measurements.



Fig. 1. (a) Intensity auto-correlation function versus correlation time and (b) numberweighted hydrodynamic size histogram of all the samples (refer to Table 1).

Table 2

Comparison of mean hydrodynamic and core diameters obtained from different analysis methods. Sizes are given in nanometer.

Notation	$d_{hDLS}^{f_1+f_2}$	$d_h^{f_1}/d_{hACS}^{f_2}$	$d_c^{f_1}/d_c^{f_2}_{SAXS}$
S1	15.7	15/-	13/-
S2	22.6	14/32	13/26
S3	24.3	15/32	13/26
S4	28.1	16/29	14/26
S5	28	13.5/31	15/26
S6	28	-/32	-/25

The normalized real and imaginary parts of ACS measurements are plotted in Fig. 2(a) and (b). By looking at the real part curves, it is clearly seen that the drop of χ' signal amplitude over frequency increases stepwise as the volume fraction of f_2 enlarges. The fall in the signal is the characteristic feature of particles in which the magnetic moments have difficulties in following the alternating magnetic field at higher frequencies. In Fig. 2(b), the typical imaginary peaks appearing at the frequency where $\omega \tau = 1$ are seen. To extract the PSD from ACS measurements, Eq. (4) was fitted to imaginary ACS curves using Levenberg-Marquardt nonlinear least square fit routine. The reconstructed curves are displayed as solid lines in the same graph. The obtained PSD, anisotropy constant K and number-weighted fraction of Néel relaxing particles k are summarized in Table 3. The particle core size distribution kept constant in the simulations as obtained from MRX and TEM measurements in order to boost fit quality.

The hydrodynamic PSD results obtained for each fraction are consistent. Remarkably, the anisotropy constant *K* value of f_1 particles is a factor of two larger than the one calculated for f_2 ones. From our earlier investigation on these particles, we know that the larger



Fig. 2. Normalized real (a) and imaginary (b) parts of ac-susceptibility measured on 150 μ l particle suspensions at room temperature. The solid lines in (b) are the best fit obtained using Eq. (4).

Table 3

Results obtained from modeling of the ac-susceptibility curves using the standard and expanded Debye models given in Eqs. (2) and (4).

Notation	S1	S2	S3	S4	S5	S6
$d_h^{f_1}(nm)$	15	14	15	16	13.5	_
$\sigma_{h}^{f_{1}}$	0.05	0.02	0.05	n.d. ^a	0.01	-
$d_c^{f_1}(nm)$	12 ^b	12	12	12	12	_
$\sigma_c^{f_1}$	0.16	0.15	0.14	0.14	0.16	-
$K^{f_1}(J/m^3)$	8800	9700	9000	10,300	9000	-
$d_h^{f_2}(nm)$	-	32	32	29	31	32
$\sigma_{h}^{f_{2}}$	-	n.d.	0.02	0.2	n.d.	0.01
$d_c^{f_2}(nm)$	-	25 ^b	25	25	25	25
$\sigma_c^{f_2}$	-	0.03	0.13	0.33	0.08	0.15
$K^{f_2}(J/m^3)$	_	4700	4000	4300	4700	3800
k_{cal}^{c} (%)	97	89	71	56	42	16
k_{est}^{d} (%)	95	85	71	55	41	21

^a Not defined.

^b Mean core diameters as determined from MRX and TEM were kept fixed.

^c Number-weighted fraction of Néel relaxing particles obtained from the fit to ACS curves with Eq. (4).

^d Estimated experimentally via dividing the ACS real part χ' signal amplitude at MHz to the one at kHz regime.

particles consist of a mixture of FeO and Fe_3O_4 phase exhibiting a much lower blocking temperature, proportional to the relaxation energy barrier, than expected [5]. This furthermore indicates that the simulated *K* values are physically reasonable.



Fig. 3. (a) Experimental (markers) and reconstructed (solid lines) SAXS curves of mono- and bi-modal samples and (b) resultant volume-weighted particle core size distributions.

The measured SAXS curves of the samples S1 to S6 are characteristic for non-interacting particles as can be seen in Fig. 3(a). We applied a Monte-Carlo evaluation procedure as recently published by Pauw et al. [15] for the determination of particle size distributions. This procedure has the advantage that it needs no a priori assumptions of the type of size distribution, making it ideal for analyzing multi-modal distributions. The results of the reconstructed SAXS curves and the corresponding volume weighted size distributions are given in Fig. 3(a) and b, respectively. It can be seen that the experimental SAXS curves are well fitted. Clearly separated peaks of the size distributions are present with maxima at 13 nm (S1), 13 and 26 nm (S2), 13 and 26 nm (S3), 14 and 26 nm (S4), 15 and 26 nm (S5) and 25 nm (S6). The uncertainties of these values are about 1 nm. A summary is given in Table 2. These results show that SAXS allows the detection of bi-modal iron oxide nanoparticle suspensions with high precision. Measurement times of 10 min per sample were sufficient by employing a commercially available SAXS instrument. Here, no highly intense and brilliant synchrotron X-ray source was needed since the contrast of the MNPs in suspension is high.

In summary, we have shown that PCCS cannot resolve a bimodal size distribution particularly if the fractions' mean diameters have the same order of magnitude and thus its results can be potentially misleading. It turned out that ACS analysis is a powerful tool for analyzing bi-modal samples containing fractions of fully Néel- and Brownian-relaxation-dominated particles. This study suggests that SAXS is a reliable technique for studying complex multi-modal nanoparticle suspensions if an *a priori* knowledge of particle shape is available.

5. Conclusions

In this study, we have attempted to resolve particle size distribution in bi-modal spherical iron oxide nanoparticle suspensions using complex ac-susceptibility, small angle X-ray scattering and photon cross-correlation spectroscopy. Having expanded the Debye model to a linear superposition form, we were able to simulate the dynamic magnetic response of the bi-modal samples and eventually obtain bi-modal size distributions. This numerical approach is more reliable when one particle fraction relaxes via Néel and the other via Brownian mechanism. Having fitted the SAXS curves applying a Monte Carlo simulation method, we succeeded in distinguishing both particle size modes in bi-modal nanoparticle suspensions accurately.

Acknowledgments

The authors would like to thank EU funding via the European Commission Framework Programme 7 under NANOMAG Project (NMP-LA-2013-604448). We thank Brian R. Pauw and Ingo Breler for providing the Monte Carlo SAXS data interpretation program.

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