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

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ABSTRACT

Particle size modality in bi-modal iron oxide suspensions was resolved by exploiting complex ac-susceptibility (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.

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 bi-modal 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 bi-modal 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 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 ac-susceptibility (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

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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 nm)	100	80	60	40	20	0
f_2 (25 nm)	0	20	40	60	80	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 μT. 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-Kα 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]

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

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

in which χ' and χ'' are the real and the imaginary part of ac-susceptibility. 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]

$$\frac{\chi''(\omega)}{\chi_0^*}=\int_0^\infty f(d_h)\int_0^\infty \frac{d_c^6\cdot f(d_c)\cdot\omega\tau_{eff}}{1+(\omega\tau_{eff})^2}dd_c dd_h$$

$$\text{with} \quad \tau_{eff}=\frac{\tau_B\tau_N}{\tau_B+\tau_N} \quad \text{and} \quad \chi_0^*=\frac{\mu_0 nM_s^2}{3k_BT}\left(\frac{\pi}{6}\right)^2, \tag{2}$$

with d_c and d_h particle core and hydrodynamic size, $\tau_B=\pi\eta d_h^3/2k_BT$ and $\tau_N=\tau_0\exp(K\pi d_c^3/6k_BT)$ 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

$$\frac{\chi''(\omega)_{bi-mod}}{\chi_0^*}=\left(\frac{k}{m_1}\right)\cdot\chi''(\omega)_{f_1}+\left(\frac{1-k}{m_2}\right)\cdot\chi''(\omega)_{f_2}$$

$$\text{with} \quad k=n_1\frac{m_1}{n_1m_1+n_2m_2} \quad \text{and} \quad m_i=\int_0^\infty d_c^6\cdot f_i(d_c)dd_c. \tag{4}$$

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

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

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

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

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.