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Bimodal distribution of the magnetic dipole moment in nanoparticles with a monomodal distribution of the physical size

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ABSTRACT

High-frequency applications of magnetic nanoparticles, such as therapeutic hyperthermia and magnetic particle imaging, are sensitive to nanoparticle size and dipole moment. Usually, it is assumed that magnetic nanoparticles with a log-normal distribution of the physical size also have a log-normal distribution of the magnetic dipole moment. Here, we test this assumption for different types of superparamagnetic iron oxide nanoparticles in the 5–20 nm range, by multimodal fitting of magnetization curves using the MINORIM inversion method. The particles are studied while in dilute colloidal dispersion in a liquid, thereby preventing hysteresis and diminishing the effects of magnetic anisotropy on the interpretation of the magnetization curves. For two different types of well crystallized particles, the magnetic distribution is indeed log-normal, as expected from the physical size distribution. However, two other types of particles, with twinning defects or inhomogeneous oxide phases, are found to have a bimodal magnetic distribution. Our qualitative explanation is that relatively low fields are sufficient to begin aligning the particles in the liquid on the basis of their net dipole moment, whereas higher fields are required to align the smaller domains or less magnetic phases inside the particles.

1. Introduction

High-frequency biomedical applications of magnetic nanoparticles depend on how rapidly the orientations of nanoparticle dipoles can be switched in an alternating magnetic field [1–5]. For therapeutic hyperthermia and magnetic particle imaging, the frequency range is typically 0.1–1 MHz, and the particles are often immobilized, so that dipolar re-orientation must occur inside the particles. As a result, even if the physical size of the particles is well controlled, it is their internal magnetic structure that is the most important. One of the ways to study the magnetic dipole moment of nanoparticles is by measuring the magnetization curve while the nanoparticles are in a dilute colloidal dispersion in a liquid. Thanks to the orientational freedom of the nanocrystals themselves in the liquid, the field-dependent magnetization can be described by the Langevin equation: $M(\alpha)=\coth(\alpha)-1/\alpha$, with $\alpha=\mu_0 mH/(k_B T)$, $\mu_0=4\pi\times10^{-7}\,\mathrm{TA}^{-1}\,\mathrm{m}$, m is the dipole moment, H is the external field in A/m, and $k_B T$ is the thermal energy. This assumes that the colloidal dispersion is sufficiently dilute for the particles to respond individually and that the equilibrium curve is without hysteresis. The situation would be different if the particles were immobilized. Then the orientations of the easy axes are fixed, and different behaviors are obtained depending on the magnetic anisotropy of the particles and on the orientations of the easy axes, for instance random or aligned with the external field [1]. This is crucial for said high-frequency applications, but here we focus on the magnetic characterization of dilute colloidal dispersions, where magnetic anisotropy is less of an issue.

In the absence of more information, it is usually assumed that the distribution of magnetic dipole moments in a sample with nanoparticles consists of a single log-normal distribution: $P(m)=[(2\pi)^{1/2}m\sigma]^{-1}\exp[-(\ln m-\ln m^*)^2/(2\sigma^2)]$, where σ and m^* describe the width and the center of the distribution, respectively. Such a distribution shape is a plausible assumption, but it has not always been confirmed in systems whose magnetic distribution was studied in more detail. A notable case is that of Resovist, the iron oxide particles suitable for biomedical imaging, particles whose magnetic distribution was found to be bimodal [6,7]. Moreover, we found that iron oxide nanoparticles with a low polydispersity of the physical size can nevertheless have a very high magnetic polydispersity [8]. There are several reports of similar iron oxide nanoparticles, size monodisperse, larger than 12 nm, prepared by thermal decomposition of precursors like iron oleate, which were found to have a complicated crystalline and magnetic internal structure [9–12]. Typically, a well crystallized

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magnetic core is surrounded by more defective, more highly oxidized phase, resulting in a lower than expected saturation magnetization. How well magnetic nanoparticles are crystallized and how well defined are their magnetic properties depend on the chemical synthesis procedure, as we discussed before [8]. Here, we focus on the question how to determine whether size-monodal particles are magnetically monomodal or not.

In order to extract magnetic dipole moment distributions from the magnetization curves of dilute ferrofluids, we recently implemented the non-regularized inversion method MINORIM [13]. We made our program available for different platforms via the web [14]. Our numerical approach is inspired from the model-independent analysis of colloidal size distributions from light scattering, as explained in greater detail in Ref. [13]. First, diamagnetic and possibly other linear contributions to the magnetization curve are removed by fitting the high-field part of the curve, which depends only on the average dipole moment, not its precise distribution [15]. The high-field regime starts at a user-selected value H^*. Second, the corrected curve is fitted in terms of N discrete values of the effective magnetic dipole moment m, ranging geometrically from a low to a high cutoff value. The smoothness of the calculated distribution is controlled via a number S of subsets, whose effect is to bring down the maximum number of subpopulations that can be resolved. The low cutoff value of m is given by $3k_BT/(\mu_0 H^*)$, and the high cutoff value is on the order of $k_BT/(\mu_0 \Delta H)$, with ΔH the experimental step size in the applied magnetic field near $H=0$.

In previous tests of our fitting approach, we were able to detect simultaneously the presence of nanoparticles of different sizes and to confirm the known ratio of their quantities [13]. Here, we use our inversion method to re-examine the magnetic polydispersity of different types of magnetic nanoparticles in the 5–20 nm range, particles that we earlier analyzed in terms of a single log-normal distribution of the magnetic dipole moment [8].

2. Methods

The chemical preparation and characterization of the studied magnetic nanoparticles were reported before in detail [8]. In summary, all the particles were iron oxide, capped with oleic acid, and ultimately transferred to the apolar liquid decalin. The "precipitates" were prepared by aqueous precipitation of iron salts [16]. The "spheres" were obtained by thermal decomposition of iron oleate in trioctylamine [17]. The "facets" and the "twins" were made by stepwise epitaxial growth from iron acetylacetonate precursor in diphenyl ether [18].

Transmission electron microscopy (TEM) was performed with a Tecnai 12 microscope operating at 120 kV. X-ray powder diffraction (XRD) was done with a Bruker ACS D8 Advance diffractometer. Magnetization curves were measured with a Princeton Micromag 2900 alternating gradient magnetometer (AGM) [19]. Except when indicated otherwise, the samples were dilute colloidal dispersions in decalin (volume fraction $< 1\%$). Magnetic dipole moment distributions were obtained from the magnetization curves by fitting using the inversion method MINORIM [13,14].

3. Results and discussion

Four types of iron oxide nanoparticles will each be examined in the same way. The fitted dipole moments will be presented as an effective magnetic diameter d_{eff}, calculated on the basis of a volume magnetization of 480 kA/m for pure magnetite. The magnetic distributions are magnetization-weighted, for comparison with volume-weighted data obtained by TEM and XRD. For each system, we first examine the effect of the high-field cutoff H^* and of the fitting parameters N and S, before giving a physical discussion of the results.

Iron oxide nanoparticles prepared by aqueous precipitation are analyzed in Fig. 1: the "precipitates". Here and with the other examined types of particles, the calculated distributions no longer depend on H^* beyond the effective size that corresponds to the

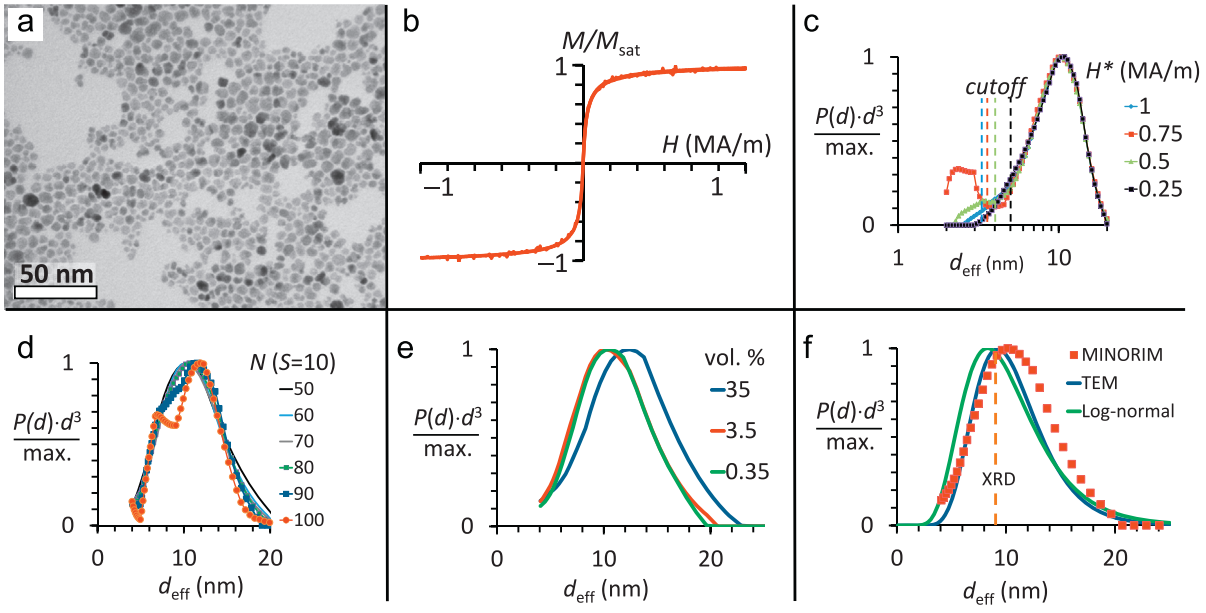

Fig. 1. Iron oxide nanoparticles prepared by wet precipitation: the "precipitates" [8]. (a) TEM micrograph, (b) magnetization curve of a liquid dispersion, and (c)–(f) analyses in terms of an effective magnetic diameter using the MINORIM inversion method [13,14]: (c) effect of the high field cutoff H^*, (d) effect of the bin sampling parameter N for $S=10$ ($H^*=0.5$ MA/m), (e) magnetic distributions obtained at three volume fractions (including 2 nm oleic acid shell; the iron oxide volume fractions are lower by a factor of 4), and (f) comparison with TEM, XRD, and a monomodal log-normal magnetic distribution [8]. The volume fraction in (b)–(d) is 3.5%, and (e) and (f) are calculated with $H^*=0.5$ MA/m, $N=60$, and $S=10$.