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Non-regularized inversion method from light scattering applied to ferrofluid magnetization curves for magnetic size distribution analysis

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ABSTRACT

A numerical inversion method known from the analysis of light scattering by colloidal dispersions is now applied to magnetization curves of ferrofluids. The distribution of magnetic particle sizes or dipole moments is determined without assuming that the distribution is unimodal or of a particular shape. The inversion method enforces positive number densities via a non-negative least squares procedure. It is tested successfully on experimental and simulated data for ferrofluid samples with known multimodal size distributions. The created computer program MINORIM is made available on the web.

1. Introduction

Magnetic nanoparticles have many applications that are the subject of current research. For example, in cancer therapy local hyperthermia can be generated by heating magnetic nanoparticles linked to cancer cells by applying an alternating magnetic field [1,2]. Another promising biomedical technique is magnetic particle imaging (MPI) [3], which also exploits the response of magnetic nanoparticles to alternating fields. Both of these biomedical applications ideally require magnetic particles that all have exactly the same (size dependent) magnetic resonance frequency [4,5], to obtain a maximum response at that frequency. For these and other applications, it is important to know how the magnetic properties are distributed across the entire population of nanoparticles. A widely adopted approach to determine the distribution of the dipole moments is by analysis of the magnetization of the sample as a function of external magnetic field strength.

The magnetization curves of ferrofluids are often fitted on the basis of an assumed shape of the distribution of the magnetic dipole moments, related more or less directly to the size distribution from transmission electron microscopy (TEM). Chantrell et al. [6] assumed a log-normal distribution, but other distributions such as a gamma function have been adopted as well [7,8]. The parameters of the log-normal distribution can either be derived from the low- and high-field limits of the magnetization curve [6,7] or from fitting the complete curve [9,10]. More specific models have also been proposed, like a core–shell model [11] to explain the discrepancy between magnetic diameter and physical diameter from TEM. For multimodal systems, the distribution can in principle be modeled with multiple peaks; one then faces the difficulty that an increasing number of fit parameters can make the results less reliable and physically less meaningful.

For dynamic light scattering as a colloidal characterization technique (DLS), there is a long tradition of obtaining particle size distributions without assuming the distribution shape but by applying discrete inversion methods [12]. Similar methods have also been used to derive magnetic particle size or dipole moment distributions from magnetization measurements [13–17]. An analysis technique that does not assume any shape of the particle distribution generally yields a better fit of the experimental magnetization curve.

Nowadays, many different inversion methods are available, such as genetic algorithms [13], maximum entropy [18], singular value decomposition (SVD) [19], simulated annealing [13], moment expansion [20], and non-negative least squares methods. The latter can be subdivided into a class of regularized methods, such as the CONTIN method [12,21,22], prominent in dynamic light scattering [12], and non-regularized methods [23]. The reconstruction of the magnetic size distribution by these techniques is not trivial and not necessarily robust. For example, the SVD method is highly sensitive to noise [6].

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For a good reconstruction based on the moments of the distribution, typically 10 moments are necessary to arrive at a reasonable approximation of the dipole moment distribution. Although these moments could be obtained via a fit of the magnetization curve with a Taylor expansion of the Langevin function, the number of terms required to describe a reasonable part of the data is large and therefore the reliability of the thus obtained moments is low. And although genetic algorithms can provide reliable distributions, these methods typically have a high computational cost.

In this paper, we apply a model-independent, non-regularized inversion method for the analysis of magnetization curves. It is adapted from a method designed by Strawbridge and Hallett [23] for the analysis of static light scattering measurements (SLS). This method does not assume unimodality nor other prior knowledge of the shape of the distribution of particle sizes or magnetic dipole moments. Using non-negative least squares procedures (NNLS), our method enforces positive number densities, unlike other methods that can give negative, unphysical results [15]. Our procedure is applicable to measurement data from alternating gradient magnetometry (AGM) as well as vibrating sample magnetometry (VSM).

In principle, our program is based on discrete sampling methods, originally developed by Pike et al. [24] as an exponential sampling technique, and later improved by Morrison et al. [25]. With the NNLS procedure based on Lawson and Hanson [26], a short execution time is obtained on the order of seconds or less using a state-of-the-art personal computer.

In the next section, the mathematical foundation of our model-independent method is presented. In the Results and Discussion section, the method is first demonstrated on real measurement data of ferrofluid samples with a known multimodal size distribution. This is followed by the analysis of simulated magnetization curves calculated for test distributions of the dipole moment. Gaussian noise is added to the simulated measurements to test the robustness of the inversion method.

2. Numerical methods

For a dilute dispersion of monodisperse non-interacting spherical magnetic nanoparticle dipoles, the total magnetic dipole moment M of the sample as a function of the applied magnetic field H is described by the Langevin function L, with

$$M(H) = M_{sat}L(H,\mu) = M_{sat}\left(\coth(\alpha) - \frac{1}{\alpha}\right)\alpha \quad = \left(\frac{\mu\mu_0 H}{k_B T}\right) \tag{1}$$

where M_{sat} is the magnetic moment of the sample under magnetic saturation conditions, μ is the magnetic dipole moment of a magnetic nanoparticle, μ_0 is the permeability of vacuum, k_B is the Boltzmann constant, and T is the absolute temperature. In case of a monodisperse ferrofluid with a number n of particles, M_{sat} corresponds to the magnetic moment $M_{sat} = n\mu$ when all magnetic dipoles are aligned in the limit of infinite applied field H. For a polydisperse or a multimodal colloidal dispersion, the sample magnetic moment is the sum of all contributing dipole moments, which for a continuous joint probability distribution function can be written as a distribution integral:

$$M(H) = \int_0^\infty \mu L(H,\mu)P(\mu)\,\mathrm{d}\mu \tag{2}$$

Here, the factor $P(\mu)\,\mathrm{d}\mu$ gives the number of particles with dipole moments between μ and $\mu+\mathrm{d}\mu$ and, similarly, $\mu P(\mu)\,\mathrm{d}\mu$ gives the contribution to the magnetic moment of the sample under saturation conditions.

In order to obtain the magnetic dipole moment distribution $P(\mu)$, we must solve Eq. (2) given the experimental magnetization curve $M_{\mathrm{exp}H}$ and using the Langevin function $L(H,\mu)$ from Eq. (1).

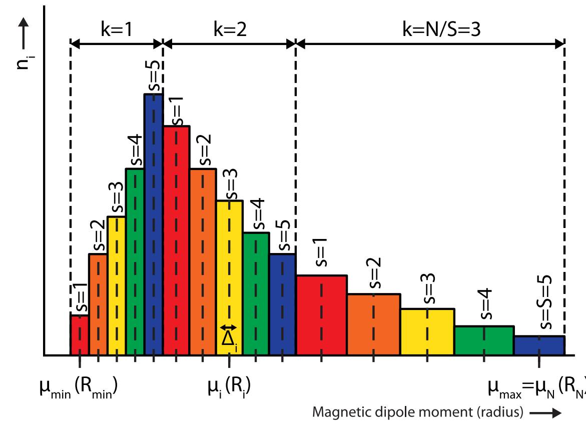

Fig. 1. Histogram showing an example of a dipole moment distribution with the dipole moments μ (or alternatively the particle radius R) binned in $N=15$ geometrically spaced bins, subdivided into $S=5$ subdomains. The meaning of the y-axis values depends on the definition of the probability factor $P(\mu)$ in the magnetization function (Eq. (2)).

This is in general an ill-conditioned problem; small experimental uncertainties such as noise can give rise to large, unphysical peaks in the distribution curve [12].

To address this problem, we rewrite Eq. (2) in a discrete form. The magnetic dipole moment domain is subdivided into a histogram of N intervals of which each bin spacing Δ_i has a center dipole moment μ_i and a bin content equal to the number amplitude n_i (see Fig. 1). The experimental magnetization curve consists of J points M_j each measured at a field strength H_j. The discrete form of Eq. (2) becomes

$$M_{exp}(H_j) = \sum_{i=1}^{N} \mu_i L(H_j,\mu_i)n_i \tag{3}$$

The basis vector $\mathbf{H}_j$ contains the experimental values of the magnetic field strength at which the measurements are made. The measurement output can be written as a column vector $\mathbf{M}_{exp}$ having the same length J. We describe the magnetic dipole moment distribution by a column vector $\mathbf{n}_{psd}$ of length N, with elements n_i in a basis μ_i. Eq. (3) can now be summarized using a $J\times N$ data transfer matrix $\overleftrightarrow{\mathbf{T}}$ that contains matrix elements T_{ji} equal to $\mu_i L(H_j,\mu_i)$ calculated using the Langevin function (see Eq. (1)):

$$\mathbf{M}_{exp} = \overleftrightarrow{\mathbf{T}}\cdot\mathbf{n}_{psd} \tag{4}$$

In the absence of experimental uncertainties, the number distribution $\mathbf{n}_{psd}$ can be solved from Eq. (4). Due to noise and other measurement uncertainties, statistical methods are needed to obtain the best magnetic dipole moment distribution n_i by minimizing the mean squares deviation ξ^2:

$$\xi^2 = \|[\mathbf{M}_{exp} - \overleftrightarrow{\mathbf{T}}\cdot\mathbf{n}_{psd}]\|^2 \tag{5}$$

The result of this inversion method is obtained without assuming prior knowledge of the form of the distribution (e.g., *log-normal* or *Gaussian*).

Regularization methods are often used in order to make the problem less ill-conditioned. In dynamic light scattering, the CONTIN method [12,21,22], based on the algorithm of Tikhonov [27,28], is a well-known example. A mathematical regularizing term is added to Eq. (5) to force a smooth outcome of the probability distribution n_i. The regularizer is the square norm of the first or a higher order derivative of the distribution function n_i itself, multiplied by a regularization strength parameter λ which determines the influence of this regularization term. The result is a