SEARCH FOR OPTIMAL WAY TO PRECISELY EVALUATE MAGNETIC RESPONSE OF IRON-OXIDE BASED NANOMATERIALS – A NEW STATISTICIALLY–BASED APPROACH

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Abstract

The theory of nonlinear regression models along with the statistical theory of design of experiment have been employed to investigate the dependence of magnetization of \(\gamma-\text{Fe}_2\text{O}_3\) nanosystem on an external magnetic field. Two analytical functions, each having different physical background, have been chosen to fit the experimental data and a degree of suitability of a particular function for a correct description of the magnetic response of the studied \(\gamma-\text{Fe}_2\text{O}_3\) nanosystem has been then evaluated. Utilizing the approach of experiment design, an optimized measuring procedure of the hysteresis loop of the investigated \(\gamma-\text{Fe}_2\text{O}_3\) nanosystem has been further proposed in order to improve the accuracy of estimations of nanosystem hysteresis-loop parameters and to reduce the financial costs and time consumption of the experiment.

Keywords: Magnetization, Langevin function, simplified Brillouin function, nonlinear and linearized regression models, D-optimal design of experiment.

1. INTRODUCTION

Nanomaterials raise a significant attention due to physico-chemical properties that make them promising for diverse practical applications. These nanomaterials characteristics often evolve as one of space dimensions of a given material falls down below approximately 100 nm [1]. In other words, every physical or chemical phenomenon driving a particular material physico-chemical feature is characterized by a typical length (usually of order of units or tens of nanometers) below which it ceases to exist and/or is significantly suppressed not participating on the overall physico-chemical behavior of the material any longer. Below such material sizes, phenomena, typical of atomic world or “nanoworld”, thus become dominant and often compete among themselves to finally establish a physico-chemical properties, exhibited by a nanomaterial, that are strongly size dependent. It is well known that nanomaterial characteristics are governed by finite-size and surface effects. While finite-size effects (or sometimes named as quantum effects) happen to be a consequence of a material size restriction causing electrons to be caught on energy levels inside quantum wells intensifying their significance with a fall in a nanomaterial size, surface effects arise from enhanced surface-to-volume ratio when bigger portion of nanomaterial atoms lie in its surface layers on lowering the nanomaterial size [1]. Surface atoms then suffer broken crystal symmetry and weaken bonds among their neighbors leading to disordered surface states having a parasitic effect on several physical properties of such a nanomaterial. On the other hand, enhanced surface-to-volume ratio is considered to be a fundamental aspect in nanomaterial reactivity and binding strategies. Thus, a compromise is always needed taking into account the nanomaterial requirements of an application for which a given nanomaterial is intended.

Nowadays, magnetic nanomaterials deserve much attention. Besides their technological utilizations including permanent magnets or recording information media, they have recently entered a realm of medicine where
they have become indispensable assistants in diagnostics and treatment processes. Among magnetic nanomaterials, iron oxides (mainly maghemite – $\gamma$-Fe$_2$O$_3$, and magnetite – Fe$_3$O$_4$) constitute the most important compounds owing to their unusual magnetic features such as superparamagnetism coupled with suitable biochemical characteristics (i.e., biocompatibility, biodegradability and non-toxicity) [2]. Utilizing classical magnetization measurements, the magnetic properties of nanomaterials are derived from the measured temperature dependence of magnetization and their magnetic responses under external magnetic fields. The latter magnetization dependence is better known as a hysteresis loop. Analyzing hysteresis loops acquired at various temperatures, one can draw a conclusion on important magnetic features exhibited by a nanomaterials including, for example, superparamagnetism at a given temperature and time window of the measurement technique, exchange bias phenomenon, degree of interparticle magnetic interactions, etc. Knowledge of these magnetic phenomena then finalizes a magnetic “picture” of a given nanomaterial on which basis one can decide whether it meets the magnetic requirements of the application or not. However, due to a complex mathematical function describing the magnetization vs. external magnetic field profile, the analysis of the hysteresis loop is sometimes simplified (often linearization of certain hysteresis loop regions) manifesting in inaccurate hysteresis parameters.

In this work, we present a new approach intended for analysis of acquired data from magnetization measurements of nanomaterials. This mathematical procedure employs statistical apparatus which serves as an evaluation mean for obtaining the values of the hysteresis loop parameters. The two analytical functions, i.e., Langevin (L-function) [3] and simplified Brillouin function – “Arrott” function (A-function) [4], describing the behavior of the material magnetization under an external magnetic field, are taken and analyzed within the framework of the theory of the regression models and methodology of the design of experiment. We particularly discuss the suitability of usage of the so-called D-optimal design criterion since it finally brings the most precise estimators of unknown values of the hysteresis-loop parameters. Within the experimental part, the proposed statistical approach is then tested with data originating from magnetization measurements carried out on the nanosystem composed of $\gamma$-Fe$_2$O$_3$ nanoparticles. As a result, we find out the values of the hysteresis-loop parameters and degree of suitability of a particular function for a correct description of the magnetic response of the studied nanosystem under an external magnetic field.

2. MATHEMATICAL BACKGROUND

The hysteresis loop measurement has been performed at 300 K and in 150 deterministic points $x_i$ selected from the interval from –70 000 to 70 000 Oe. The magnetization of $\gamma$-Fe$_2$O$_3$ nanosystem (synthesized according to [5]) has been recorded and three times under each value of the intensity of the external magnetic field and the three measurements in each point have been then averaged. Within mathematical approach, the L-function and A-function is given by

$$y_i = \psi_1 \coth (\psi_2 x_i) - \frac{\psi_1}{\psi_2 x_i} + \epsilon_i, \quad i = 1, \ldots, n,$$

and

$$y_i = \frac{\psi_1 \psi_2 x_i}{\sqrt{\psi_2^2 x_i^2 + 0.111}} + \epsilon_i, \quad i = 1, \ldots, n,$$

respectively, where $\psi_1$ and $\psi_2$ are unknown parameters representing certain physical parameters, $y_i$ denotes magnetization measured at a point $x_i$ representing the intensity of the external magnetic field and $\epsilon_i$ stands for the measurement error.
2.1 Nonlinear regression models

The theory of nonlinear regression models offers various approaches to fit the experimental data with given nonlinear curves. Within this work, we applied a procedure based on a linearization-ability of a given nonlinear function which secures that the parameter estimators found from a resulting linearized model are identically efficient as those acquired from the starting nonlinear model constructed on a basis of the known nonlinear function describing the given experiment [6]. In general, the nonlinear model is given by

$$y \square_n \left[ f(x, \psi) , \sigma^2 \mathbf{V} \right],$$

where \( y \) is the observation vector of the measurement, \( n \) represents the number of observations, \( \psi = (\psi_1, \psi_2) \) stands for the vector of indirectly measurable parameters, \( f(x, \psi) \) denotes the known nonlinear function and \( \sigma^2 \mathbf{V} \) represents the diagonal covariance matrix of \( y \) in the form of \( \text{Var}(y) = \sigma^2 \mathbf{V} = 0.002^2 \text{Diag}(1/3, \ldots, 1/3) \); here \( \sigma^2 \) is the error of the measuring device and \( \mathbf{V} \) stands for the known positively-definite matrix [6].

Based on the knowledge of the initial solution \( \psi(0) \) and utilizing the Taylor series expansion with the second- and higher-order terms excluded, the nonlinear model is transformed into a linearized counterpart. Then, the \( i \)-observation is described by

$$y_i \square_n \left[ f(x_i, \psi(0)) + F \delta \psi, \sigma^2 \mathbf{V} \right] = y_i - f(x_i, \psi(0)) \square_n \left[ F \delta \psi, \sigma^2 \mathbf{V} \right] \square Y, \quad i = 1, \ldots, n,$$

where \( \delta \psi = \psi - \psi(0) \) and \( F \) is the known design matrix acquired on the basis of the Taylor series expansion.

In particular, the \( i \)-th row of the design matrix for the L-function is given by

$$\left\{ \mathbf{F} \right\}_i = \left( \frac{\partial f(x_i, \psi)}{\partial \psi_1}, \frac{\partial f(x_i, \psi)}{\partial \psi_2} \right)_{\psi=\psi(0)} \begin{bmatrix} \coth(\psi_2 x_i) - \frac{1}{\psi_2 x_i} & -\frac{\psi_1 x_i}{\sinh^2(\psi_2 x_i)} + \frac{\psi_1}{\psi_2^2 x_i} \end{bmatrix},$$

and the \( i \)-th row of the design matrix constructed for the A-function is given by

$$\left\{ \mathbf{F} \right\}_i = \left( \frac{\partial f(x_i, \psi)}{\partial \psi_1}, \frac{\partial f(x_i, \psi)}{\partial \psi_2} \right)_{\psi=\psi(0)} \begin{bmatrix} \psi_2 x_i \sqrt{\psi_2^2 x_i^2 + 0.111}, & \psi_1 x_i \sqrt{\psi_1^2 x_i^2 + 0.111} - \frac{\psi_1}{\psi_2^2 x_i^2 + 0.111} \end{bmatrix},$$

where \( i = 1, \ldots, n \). Thus, we have constructed two almost identical linearized models of the indirect measurement of the vector parameter without constrains that differ only in the structure of the design matrix \( F \) due to different input functions (L-function and A-function). The results of these two models were then compared and were used to decide which function is better suited to fit the experimental data.

It is well-known that the best linear unbiased estimator \( \delta \psi \) can be obtained from \( \delta \hat{\psi} = (F' \mathbf{V}^{-1} F)^{-1} F' \mathbf{V}^{-1} Y \) when the value of the parameter \( \hat{\psi} \) is subsequently calculated from \( \hat{\psi} = \delta \hat{\psi} + \psi(0) \) [5]. The covariance matrix of this estimator can be then obtained from \( \text{Var}(\delta \hat{\psi}) = \sigma^2 (F' \mathbf{V}^{-1} F)^{-1} \).

If we construct the linearized model, we not only get the required estimations of the unknown physical parameters but we are also able to state the accuracies with which these estimations have been determined. In order to achieve an utmost optimization of the performed measurement, we have employed the theory of optimal design of experiment.

2.2 Optimal Design of Experiment

Before the experiment performance itself, it is necessary to determine the so-called goal parameters, i.e., the quantities of which values we want to obtain. If these parameters are not directly measurable (unknown physical parameters) we have to have a sufficient amount of other directly measurable quantities (the values
of the magnetization) which are bound by the known function (L-function and A-function) with these goal parameters. This is mathematically described within the two models constructed above. The design of experiment (DOE) then determines the measurement frequency of each directly measurable parameter in order to get an optimized result taking into account the selected criteria of optimization [7]. To do so we have to construct a function \( \delta \) given by \( \{e_1, \ldots, e_r\} \rightarrow \langle 0,1 \rangle \) and known as the experiment design function which represents a mapping from the set of directly measurable parameters. This function fulfills conditions such as \( \delta(i) = \delta(e_i) \geq 0, i = 1, \ldots, r \), and
\[
\sum_{i=1}^{r} \delta(i) = 1.
\]
where \( \delta(i) \) represents the relative number of replications of the \( i \)-component belonging to the vector of directly measurable parameters. The experiment design function is then used to construct the information matrix of experiment \( M(\delta) \) taking the form of
\[
M(\delta) = \sum_{i \in \text{Sp}(\delta)} \delta(i) \lambda_i f_i f_i',
\]
where \( f_i' = f'(e_i) \) denotes the \( i \)-th row of design matrix \( F \), \( \lambda_i \) is the \( i \)-th row of the diagonal matrix \( \Lambda \), constructed as an inverse matrix to the covariance matrix \( V \), and \( \text{Sp}(\delta) \) denotes the so-called support of experiment design, which is defined as \( \text{Sp}(\delta) = \{e_i: \delta(e_i) > 0\} \). Thus, the information matrix of experiment works only with points from the set of directly measurable parameters to which a nonzero value has been assigned by the experiment design function \( \delta \).

There are several types of commonly known criteria of optimization [7]. Since our aim is to estimate the values of the unknown parameters as accurately as possible, we have chosen a criterion of D-optimal design of experiment which results in a minimum volume of the confidence ellipsoid and, consequently, minimization of covariance matrix of the estimator of the unknown vector parameter \( \hat{\psi} \). The whole process runs in an iteration manner when we look for a such index \( i^* \), representing a point at which the sample magnetization is measured, for which the expression given by \( \{\lambda_i f_i' M^{-1}(\delta) f_i: i = 1, \ldots, r\} \) reaches its maximum value.

3. RESULTS AND DISCUSSIONS

The iteration process is used to find the statistically significant points among which the total number of 450 measurements \( N \) is the distributed following the ratio determined from resulting relative frequencies \( r_i \) calculated as \( r_i = \delta(i)N \).

Employing the D-optimal design of experiment (see Fig. 1), we have found two statistically significant points for the L-function (i.e., \(-70000\) and \(-20000\)) and two statistically significant points for the A-function (i.e., \(-70000\) and \(-18000\)). Since both functions are symmetric around the origin (even functions), the measurements have been also carried out in the two other points, i.e., \(20000\) and \(70000\) in the case of the L-function and \(18000\) and \(70000\) in the case of the A-function. Thus, for both functions, we have 4 points at which the sample magnetization has been measured with a determined relative frequency.

The results are then summarized in Table 1. As one can see, the above-mentioned linearized model for both functions has been firstly constructed both before implementation of DOE (initial observation vector \( y \) has been composed of 150 values when each value has been obtained as an average value of 3 measurements performed at each of 150 points \( x_i \)). We got estimations of the unknown vector parameters which have been then used for a construction of the D-optimal design of the experiment. Bearing in mind the results of the D-
optimal design, for both functions under investigation, we have constructed new models of indirect measurement of the vector parameter without constrains. These new models involve only points proposed by a procedure of the D-optimal design (new observation vector $y$ has been composed of only 4 values resulting from averaging of 112 or 113 measurements at 4 points $x_i$ selected by DOE).

![Fig. 1. D-optimal design of experiment for (a) L-function and (b) A-function.](image)

<table>
<thead>
<tr>
<th>Variable</th>
<th>L-function</th>
<th>A-function</th>
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<tbody>
<tr>
<td>$x_i$</td>
<td>$\delta^* (-70000) = \delta^* (-20000) = \delta^* (20000) = \delta^* (70000) = 0.25$</td>
<td>$\delta^* (-70000) = \delta^* (-18000) = \delta^* (18000) = \delta^* (70000) = 0.25$</td>
</tr>
<tr>
<td>$r(x_i)$</td>
<td>$r_{-70000} = r_{70000} = 112$, $r_{-20000} = r_{20000} = 113$</td>
<td>$r_{-70000} = r_{70000} = 112$, $r_{-18000} = r_{18000} = 113$</td>
</tr>
<tr>
<td>$\hat{\psi}$</td>
<td>$\hat{\psi} = \begin{pmatrix} 51.27519 \ 0.07940 \end{pmatrix} \times 10^{-3}$</td>
<td>$\hat{\psi} = \begin{pmatrix} 432.02105 \ 0.12137 \end{pmatrix} \times 10^{-4}$</td>
</tr>
<tr>
<td>Var($\hat{\psi}$)</td>
<td>$\text{Var}(\hat{\psi}) = \begin{pmatrix} 27.78794 &amp; -0.08877 \ -0.08877 &amp; 0.00034 \end{pmatrix} \times 10^{-8}$</td>
<td>$\text{Var}(\hat{\psi}) = \begin{pmatrix} 1295.068 &amp; -0.86053 \ -0.86053 &amp; 0.00077 \end{pmatrix} \times 10^{-10}$</td>
</tr>
<tr>
<td>$\hat{\psi}_\delta$</td>
<td>$\hat{\psi}_\delta = \begin{pmatrix} 50.97120 \ 0.08696 \end{pmatrix} \times 10^{-3}$</td>
<td>$\hat{\psi}_\delta = \begin{pmatrix} 464.92008 \ 0.10891 \end{pmatrix} \times 10^{-4}$</td>
</tr>
<tr>
<td>Var($\hat{\psi}_\delta$)</td>
<td>$\text{Var}(\hat{\psi}_\delta) = \begin{pmatrix} 17.00963 &amp; -0.05071 \ -0.05071 &amp; 0.00024 \end{pmatrix} \times 10^{-9}$</td>
<td>$\text{Var}(\hat{\psi}_\delta) = \begin{pmatrix} 1327.716 &amp; -0.61802 \ -0.61802 &amp; 0.00048 \end{pmatrix} \times 10^{-11}$</td>
</tr>
<tr>
<td>$S_e$</td>
<td>$S_e = 1.54641 \times 10^{-10}$</td>
<td>$S_e = 1.46906 \times 10^{-10}$</td>
</tr>
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</table>

Table 1. Summary of results of approximation of the L-function and A-function where $x_i$ are optimal points and their relative frequencies, $r(x_i)$ represents the number of performed measurements at points $x_i$, $\hat{\psi}$ denotes the estimator of the unknown vector parameter before DOE, Var($\hat{\psi}$) stands for the covariance matrix of the estimator $\hat{\psi}$ before DOE, $\hat{\psi}_\delta$ denotes the estimator of the unknown vector parameter after DOE, Var($\hat{\psi}_\delta$) stands for the covariance matrix of the estimator $\hat{\psi}_\delta$ after DOE and $S_e$ represents the residual sum of squares after DOE.

The resulting values of the estimators of the vector parameters were then introduced into the L-function and A-function to perform the approximation of the experimental data (see Fig. 2). Finally, we have calculated the value of the residual sum of squares $S_e$ for both functions. Since lower value of $S_e$ has been found for the A-function, this function seems better for description of magnetization behavior of $\gamma$-Fe$_2$O$_3$ nanosystem under
external magnetic field. Since the A-function is derived on quantum physics bases, one can conclude that the magnetic properties of the investigated $\gamma$-Fe$_2$O$_3$ nanosystem are most probably predominantly driven by finite-size effects.

Fig. 2. Approximation after DOE for (a) L-function and (b) A-function.

4. CONCLUSIONS

We have shown how the theory of nonlinear regression models in combination with DOE enables us to decide which function is better to use to fit the experimental data. Based on the physical background of the function describing the magnetic response of the nanosystem under an external magnetic field, one can identify effects driving the magnetic properties of the investigated nanoassembly as demonstrated in the presented case of $\gamma$-Fe$_2$O$_3$ nanosystem. In addition, it has been shown that the employment of DOE brings a significant improvement of accuracy of estimators of the vector parameter $\hat{\psi}$ on one hand and appreciable reduction of financial and time requirements of the experiment on the other hand. Thus, the proposed mathematical approach opens up a doorway on a way to precisely find the critical size parameter of the given nanosystem below which the finite-size (i.e., quantum) effects entirely govern the magnetic behavior of the assembly of nanoobjects.

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LITERATURE