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THE APPLICATION OF PERTURBATIONAL STATISTICAL THEORIES TO THE INVESTIGATION OF THE STATIC MAGNETIZATION OF MAGNETIC FLUIDS

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Nonlinear dependence of the static magnetization on the sample concentration was experimentally found at concentrations above 1% for two ferrofluids with different degree of steric stabilization. The nonlinearity was found to be more pronounced in the case of the less stabilized ferrofluid. The processing with a ferrofluid magnetization model based on the method of perturbations of the pair distribution function was found to give an accurate qualitative description of the experimental data and fairly good quantitative values of the mean magnetic diameter of the particles by comparison with the value estimated from electron microscopy.

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1. Introduction

The magnetic fluids or ferrofluids are suspensions of magnetic nanoparticles dispersed in a carrier liquid [1]. In order to prevent agglomeration due to attractive van der Waals or magnetic dipole-dipole interactions a repulsive force between particles is created by means of steric hindrance or electrostatic repulsion. The ideal ferrofluid is a homogenous dispersion of isolated particles. In real ferrofluids, due to van der Waals or magnetic dipole-dipole interactions, the magnetic particles agglomerate spontaneously or under the action of external magnetic fields. The structural model of the magnetic fluid has important consequences on the validity of the theories concerned with the macroscopic magnetic, optic or rheological properties of the magnetic fluids.

Based on specific structural models, several models of the ferrofluid static magnetization have been developed and used in the interpretation of the experimental data. The Langevin equation [2] and its generalization to polydisperse magnetic particle suspensions developed by Chantrell et al. [3] neglect the magnetic dipole interactions between particles. Based on a statistical model of magnetic particle chain formation due to the magnetic dipole interactions, Zubarev et al. [4,5] developed an analytical model for the influence of linear chains on the static magnetization of ferrofluids. The effect of the magnetic dipole interactions between independent particles on the static magnetization of ferrofluids is accounted by Weiss mean effective field model [1] and by the perturbational statistical theory developed by Ivanov et al. [6,7].

With respect to the dependence of the magnetization on the ferrofluid particle concentration, the Langevin and Chantrell models predicts a linear increase with concentration while the Zubarev and Ivanov models predicts a cvasi-cuadratic increase with concentration.

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In a previous paper [8] we reported the experimental finding of quasi-cuadratic increase of the static magnetization of two ferrofluids with concentration and we analyzed the data with the early model of Zubarev [4] based on the hypothesis of rigid particle linear chains, analysis which resulted in values of the mean number of particles per chain of about 1.04. The later model of Zubarev [5] was based on the more realistic hypothesis of flexible particle linear chains, but when used to explain the same experimental findings it failed to fit the data, given the samples mean diameter particles determined from electron microscopy investigations. Therefore, we turned our attention to the possibility that it was not the particle agglomeration that explains the nonlinear dependence of the magnetization on the ferrofluid concentration, but rather the magnetic dipole-dipole interaction between the particles.

The aim of this paper is to present the analysis, based on a perturbational statistical theory of the ferrofluid static magnetization as developed by Ivanov et al. [6,7], of the nonlinear dependence on particle concentration of the static magnetization of two ferrofluids with different degrees of colloidal stabilization.

2. Samples description and experimental data

Two types of TR30 transformer oil based ferrofluids with magnetite particles produced by means of chemical coprecipitation method [11] were investigated: one with pure oleic acid (POA) and the other with technical grade oleic acid (TOA) surfactant. Unlike pure oleic acid, technical grade oleic acid contains several species of organic molecules with shorter cathens and less compatible with the carrier. Therefore, magnetic particles in the TOA ferrofluid will exhibit a greater tendency to agglomerate than those in the POA ferrofluid. The validity of this statement was confirmed by magneto-optical [12] and rheological experiments [13].

Several samples with different volume fractions of magnetite particles of each ferrofluid were prepared by dilution with transformer oil. In order to minimize the uncertainty of the diluted sample volume fractions, successive dilution was avoided as much as possible. The calculated dilution errors were low enough to leave out of question the possibility that the quadratic-like dependence of the magnetization on the concentration was due to propagating errors in the dilution process (for details see Ref. [8]).

Electron micrograph processing was carried out in order to evaluate the physical diameter distribution $f(D_p)$ of the magnetic particles, which was found to be a normal logarithmic type, with parameters values: $\sigma_p \cong 0.4$ and $D_{0p} \cong 8$ nm. The resulting mean physical diameter is 8.7 nm. Because of the existence of a nonmagnetic layer of about 0.85nm at the surface of magnetite nanoparticles [1], the particle magnetic diameter (D_m) and the sample magnetic volume fraction (Φ_m) are lower than their physical correspondents (D_p and Φ_p respectively). Thus the resulting mean magnetic diameter is 7 nm. Since no gravitational sedimentation of the highest concentration ferrofluids was observed and strong stirring was performed before dilution, it is reasonable to assume that all samples have fairly the same magnetic particle diameter distribution.

The static magnetization curves of POA and TOA ferrofluids were measured with a LakeShore 7300 vibrating sample magnetometer (VSM). The measurements were performed in two magnetic field intensity ranges: 0-700 kA/m and 0-10 kA/m at 300 K.

Using the domain magnetization of magnetite and the magnetization data measured in the range 0-700kA/m, the values of the magnetic volume fraction of the sample was calculated.

In Fig. 1 are plotted the magnetic volume fraction dependence of the POA and TOA ferrofluids static magnetization at two values of the field intensity: 5 and 10 kA/m. One observes that, except for the most diluted samples, the dependence is nonlinear at concentrations above 1% for both ferrofluids and the nonlinearity is more pronounced in the case of TOA ferrofluid. At field values above 50 kA/m the dependence was found to be linear for both ferrofluids.

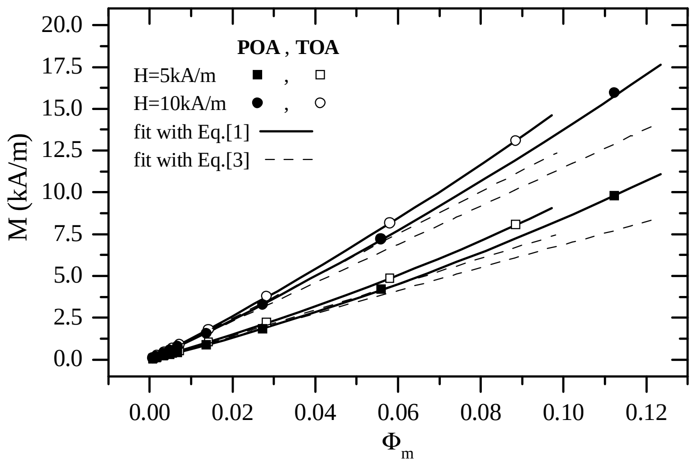

Fig. 1. Experimental and theoretical magnetic volume fraction dependence of magnetization for POA and TOA ferrofluids at two different values of external magnetic field intensity.

3. Theoretical basis

Because the interparticle magnetic dipole interactions are neglected, the Langevin and Chantrell theories of the ferrofluid static magnetization is suitable only to very diluted samples. In this sense, the Zubarev theory is also a Langevin type theory, in which the independent identical collection of nanoparticles is replaced by a set of systems in thermodynamical equilibrium, systems composed of identical n-particle chains. Usually, the ferrofluids used in practical applications have particle volume fractions ranging up to 10% or more when the average spacing between magnetic particles with average diameter of 8 nm can be as low as 16 nm or less. At this high value of particle packing neglecting the interparticle magnetic or dielectric dipole interactions leads to serious errors in theoretical predictions. Therefore, the aim of the perturbational statistical treatment of ferrofluids is to account for interparticle interactions in the modeling of ferrofluids macroscopic properties. A review of the perturbational statistical theories of ferrofluids is beyond the purpose of this paper. A detailed review can be found in Ref. [9]. Basically, the perturbational statistical theories consider either the interparticle magnetic dipole interactions as perturbations of the hard spheres interaction or the dipole-field interaction as a perturbation of the energy of the dipolar hard spheres.

Three of the most important perturbational statistical theories of ferrofluids are a) the *algebraic perturbation method* developed by Kalikmanov is a rigorous method of perturbations around dipolar hard spheres [10], b) the *thermodynamic perturbations method* developed by Yu. A. Buyevich and A. O. Ivanov is a standard hard-sphere perturbation theory [6] and c) the *method of perturbations of the pair distribution function* is a standard hard-sphere perturbation of the 2-particle correlation function developed by Ivanov and O. B. Kuznetzova [7], the later offering the advantage of possible future developments in the field of dielectric, optical and rheological properties modeling.

The main result of both the thermodynamic perturbations method and the method of perturbations of the pair distribution function (in the first order) is the expression of the ferrofluid static magnetization in arbitrary external magnetic field ($M_I(H)$) and accurate for particle volume fractions up to 15%.

For a ferrofluid with magnetic volume fraction Φ_m and identical particles with diameter D_m, the static magnetization $M_I(H)$ in the model of thermodynamic perturbations method is described by the following expression [6]:

$$M_I(H) = \Phi_m M_d L(\xi) \cdot \left[1 + \Phi_m \frac{\pi \mu_0 M_d D_m^3}{18kT} \left(\frac{1}{\xi^2} - \frac{1}{(\sinh \xi)^2} \right) \right] \quad (1)$$

where H is the external magnetic field intensity, M_d is the magnetite domain magnetization, L is the Langevin function and ξ is the Langevin function argument:

$$\xi = \xi\left(H, D_m\right) = \frac{\pi\mu_0 M_D D_m^3 H}{6kT}. \tag{2}$$

One can notice that Eq.1 predicts a quadratic dependence of the static magnetization on the ferrofluid concentration.

In the case of low concentration samples when the term quadratic in concentration can be neglected, Eq. 1 leads to the expression of Langevin magnetization $M_L(H)$:

$$M_L\left(H\right) = \Phi_m M_d L\left(\xi\right), \tag{3}$$

which leads to a linear dependence of magnetization on the ferrofluid concentration.

Both equations Eq. 1 and Eq. 3 can be generalized to a magnetic fluid with polydispersed particles by integration over the magnetic diameter distribution of the particle.

In the model of perturbation of the pair distribution function [7], the expression of the static magnetization is given by Eq. 1 with an additional term in the square brackets, with quadratic dependence on the magnetic volume fraction.

4. Results and discussions

The experimental data plotted in Fig. 1 was processed by means of nonlinear regression with the generalization of Eq. 1 and Eq. 3 to the case of a ferrofluid with polydispersed particles. The thick lines in Fig. 1 represent the theoretical curves given by Eq. 1 that fit the data. The dashed lines are the theoretical given by Eq. 3 that fit the data in the region of low concentrations. One can observe that the predictions with the Ivanov model fits the data accurately and, at high concentrations, deviates significantly from the Langevin model. The distribution of the particle magnetic diameters was assumed to have the same width as the distribution of the physical diameters ($\sigma_m = \sigma_p \cong 0.4$) and as the fitting parameter was considered the value of D_{0m}. The fit error for D_{0m} was less than 0.01nm and the nonlinear coefficient of determination was greater than 0.999.

In Table 1 are summarized the values of the mean magnetic diameter calculated with the use of the parameter D_{0m} as obtained from the fit with Eq. 1, for both ferrofluids at different values of the external magnetic field intensity.

Table 1. The values resulted from the data nonlinear regression for the mean magnetic diameter.

H (kA/m)	**POA** $\bar{D}_m$ **(nm)**	**TOA** $\bar{D}_m$ **(nm)**
1	6.1	6.4
2	6.1	6.5
3	6.2	6.5
4	6.2	6.5
5	6.2	6.6
6	6.3	6.6
7	6.3	6.6
8	6.3	6.6
9	6.3	6.6
10	6.4	6.6

One can observe that in the case of TOA ferrofluid the mean magnetic diameter values are greater than in the case of POA ferrofluid. Based on the findings from magneto-optical investigations [12], this could be explained by the formation of small spontaneous particle clusters due to poor stabilization in the TOA samples and thus leading to the increase in the mean magnetic diameter. In both cases the mean magnetic diameter is slightly increasing with field intensity which could be due to the formation of a small amount of magnetic induced particle chains.

In the case of POA ferrofluid the values of the mean diameter are less than the values estimated from the electron microscopy based on the value of the nonmagnetic layer thickness. This could be explained either by systematic errors in the electron micrograph processing or by the inadequacy of the nonmagnetic layer thickness value, which has been subject of debate in the literature.

Due to the relatively low values of the magnetic volume fractions, the same results for the mean magnetic diameter were obtained form the fit of the experimental data with the magnetization from the model of perturbations of the pair distribution function.

5. Conclusions

Nonlinear dependence of the static magnetization on the sample concentration was experimentally found at concentrations above 1% for two ferrofluids with different degree of steric stabilization. The nonlinearity was found to be more pronounced in the case of the less stabilized ferrofluid.

The magnetization models based on the methods of perturbations of the pair distribution function and of thermodynamic perturbations were found to give an accurate qualitative description of the experimental data and fairly good quantitative values of the mean magnetic diameter of the particles by comparison with the value estimated from electron microscopy. Therefore, one can conclude that the phenomenon of magnetic interparticle correlations plays an important role in the macroscopic properties of ferrofluids with particle volume fraction above 1%.

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