

On magnetic fluid synthesis and light scattering anisotropy parameter

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Nanostructured Fe₃O₄ particles were prepared by Fe^{II} and Fe^{III} acidic solutions co-precipitation at room temperature. The nanoparticles aggregation was prevented by using 25% tetramethylammonium hydroxide (N(CH₃)₄OH) solution as surfactant. The magnetic fluid density, viscosity and surface tension were measured using standard methods. The magnetic nanoparticles were characterized using a TESLA transmission electron microscope and the average size was 7.7 nm. Light scattering anisotropy was measured using an experimental setup consisting of a He-Ne laser, a cuvette, a sensitive detector, a data acquisition system and a computer. Light scattering intensity at angles between 0 and 9° was measured and the anisotropy parameter g was determined by the mean square method using a program that was written for this purpose. A possible magnetic nanoparticles sizing and concentration measurement procedure is suggested.

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1. Introduction

In the last decade, the design and synthesis of nanometer-scaled magnetic structures have been the subject of intense investigation. Magnetic fluids (also named ferrofluids) represent a well defined category of magnetically controllable nanomaterials with fluid properties. Magnetic fluids are dispersions of single-domain magnetic particles suspended in a carrier fluid [1]. Colloidal stability is assured by coating the particles with a shell of nonmagnetic molecular surfactants that prevent close approach of the nanomagnetic cores, thus considerably decreasing the particle aggregation via van der Waals or magnetic attraction forces. The magnetic colloidal particles usually have a small diameter (around 10 nm) that reduces the attractive particles interaction. Reaching and maintaining magnetic fluid stability is one of the main goals in manufacturing magnetic fluids because stable magnetic fluids have many industrial and biomedical applications [2].

The magnetic fluids appear to be a convenient system for studying disordered systems, because the particle size and concentration can be controlled by adjusting the parameters of the synthesis process [2].

Dynamic and static light scattering are important tools in investigating and characterizing the structural and dynamical properties of complex fluids, e.g. colloids [3].

If coherent light is incident on a medium with scattering centers a non-uniformly illuminated image is obtained, currently named speckled image, having a statistical distribution of the intensity over the interference field. The image changes in time as a consequence of the scattering centers (SC hereafter) complex movement of sedimentation and Brownian motion. This complex movement produces fluctuations of the image intensity in each location of the interference field, giving the aspect of "boiling speckles".

The speckled image can be observed either in free

space and is named objective speckle or on the image plane of a diffuse object illuminated by a coherent light source and it is named subjective speckle in [4]. The review paper [5] classifies the two types of speckled images as far field speckle and image speckle. In this work the objective speckle, respectively far field speckle is considered.

The scattering process modeling and characterization is not easy. The typical targets are biological cells that have characteristic dimensions several times higher than the incident light wavelength. For all of them the scattering phase functions, that describe the light scattering anisotropy, are strongly peaked in the forward direction. The light scattering anisotropy is conveniently characterized by the g parameter, which is currently defined as the mean cosine of the polar scattering angle θ , $g = \langle \cos(\theta) \rangle$. Consequently, for light scattering strongly peaked in the forward direction, the anisotropy parameter g is close to 1.

One of the targets frequently used to test the theoretical models is the Red Blood Cell (RBC) [6-10]. Numerous experiments reported results using collimated laser beams and detecting the far field [7, 10, 11]. Such typical light scattering procedure in assessing the light scattering properties of the nanoparticles that form the magnetic fluid was used in the work reported in this paper, as well.

Several empirical phase functions are currently used to fit the experimental data. The Henyey – Greenstein phase function as well as two parameters Gegenbauer kernel phase function are the most commonly used [7, 10, 12]. A new approach replaces the g parameter with an effective g which is a function of the optical depth of the suspension, like in [13,14].

In a previous paper [15] we reported on the preparation of ferrofluids containing superparamagnetic Fe₃O₄ nanoparticles by a chemical precipitation method.

In this study, we continue the study on the preparation, rheological characterization and light scattering anisotropy properties of a magnetic fluid containing superparamagnetic nanoparticles.

2. Experimental

Magnetic fluid synthesis. A convenient method that produces magnetic nanoparticles with narrow size distribution consists of chemical precipitation reactions, at room temperature. Nanostructured Fe_3O_4 particles were prepared by Fe^{II} and Fe^{III} acidic solutions co-precipitation, according to [16] modified by [17]. A 19.9g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ quantity was dissolved in 50 ml 2M solution of HCl and 54.1g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 200 ml 2M solution of HCl. 6.0 ml of ferrous chloride acidic solution and 24.0 ml of ferric chloride acidic solution were mixed in a beaker under vigorous and continuous magnetic stirring with 300 ml of 1M aqueous NH_3 solution, slowly added into the beaker by a pipette. The magnetite shortly appeared in the beaker as a black precipitate. Stirring was stopped and a strong magnet was used to settle the magnetite. The magnetite was washed several times with 1 liter of deionized water. Most of the liquid was decanted and disposed of, and the remaining solution was filtered to separate the supernatant. The aggregation of the magnetic particles was prevented by using 25% tetramethylammonium hydroxide ($\text{N}(\text{CH}_3)_4\text{OH}$) solution as surfactant. The magnetic particles, in amount of 2.16 g, were vigorously mechanically mixed with 6 ml tetramethylammonium hydroxide 25% solution.

Rheological investigation. Physical tests were performed to measure the rheological properties. The magnetic fluid density (picnometric method), viscosity (capillary method with an Ubbelohde viscosimeter) and surface tension (stalagmometric method) were measured using standard methods.

Magnetic nanoparticles size analysis. The magnetic particles were characterized by transmission electronic microscopy (TEM) using a TESLA device with a resolution of 1.0 nm (sample deposition of colloidal sheet after 104 times dilution).

Light scattering anisotropy. In this work the well known, one parameter Henyey Greenstein phase function (1) was used to fit the experimental data and to find the light scattering anisotropy parameter g of different samples:

$$f(\mu) = \frac{1}{2} \frac{1 - g^2}{(1 - 2g\mu + g^2)^{3/2}} \quad (1)$$

with $\mu = \cos(\theta)$ and θ the polar scattering angle.

A simple experimental setup was assembled. It consists of a He-Ne laser, a cuvette, a sensitive detector, a data acquisition system and a computer. First the detection system was calibrated in order to provide the functional dependence of the recorded voltage with the light intensity.

A schematic of the experimental setup is presented in Fig. 1.

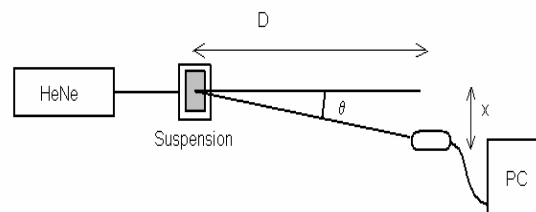


Fig. 1. The schematic of the experimental setup, view from above.

The cuvette-detector distance was $D=2.5$ m and x was modified gradually, changing the angle accordingly. The detector was a phototransistor.

The Henyey Greenstein phase function can not be measured directly. A detector has a finite transversal dimension d and can be seen from the active part of the cuvette as covering a certain solid angle, hence a polar angle interval $[\theta_1, \theta_2]$. Our detector had a $d=4$ mm which makes an angular opening of 0.0016 radians or 0.0917 degrees.

The light intensity that can be measured using a detector, which in our experiments was a phototransistor, is proportional with the integral of the phase function over the polar angle interval $[\theta_1, \theta_2]$, which is:

$$\int_{\mu_1}^{\mu_2} f(\mu) d\mu = F(\mu_1, \mu_2) = \frac{C(1-g^2)}{g} \left[\frac{1}{\sqrt{1+g^2-2g\mu_1}} - \frac{1}{\sqrt{1+g^2-2g\mu_2}} \right] \quad (2)$$

where $\mu_1 = \cos(\theta_1)$ and $\mu_2 = \cos(\theta_2)$ and C is a constant that must be determined simultaneously with the anisotropy parameter g . C depends of both SC concentration and type [20].

Light scattering intensity in the $[0.12^\circ, 2.5^\circ]$ polar angle interval was measured using the detector and a data acquisition system. Due to the “boiling speckle” aspect of the far interference field one measurement at one angle does not provide a realistic value. A 60 s time series recording for each angle was stored on the hard disk and processed later on. The average of the light intensity for each angle was used as the input for a program that fits F in (2) on the experimental data. The program written for this purpose minimizes χ^2 per point, defined as in (3) and writes the optimum values of the C and g parameters and the errors in finding the parameters, in respect to the fit.

$$\chi^2 = \frac{1}{n} \sum_{i=1}^n [F(\mu - \Delta\mu, \mu + \Delta\mu) - F_{\text{exp}}(\theta)]^2 \quad (3)$$

In (3) F is calculated with (2) for each data pair, $\Delta\mu$ is the half of the polar angle covered by the detector, as seen from the active area of the cuvette, and F_{exp} is the value of the scattered light intensity measured and averaged as described above.

3. Results and discussion

The magnetic fluid sample synthesized in our laboratory was dark brown, exhibited positive magnetic behavior in the presence of a permanent magnet, and kept their colloidal characteristics for up to 12 months. Low level of magnetic nanoparticles sedimentation in time was observed.

The results of the rheological measurements on magnetic fluid sample are presented in Table 1. The average values calculated on 10 measurements are presented. The volume fraction Φ of the magnetic particles in the magnetic fluid samples was determined from mass density measurements.

Table 1. The rheological measurements data and volume fraction.

Φ	Density (kg/m ³)	Surface tension (10 ⁻³ N/m)	Viscosity (10 ⁻³ kg/ms)
0.02	1059±2.14	80.94±0.79	2.02±0.02

A typical TEM image of tetramethylammonium hydroxide coated magnetic nanoparticles is show in Fig. 2. The TEM micrographs reveal that the size of coated magnetic nanoparticles ranges between 3 and 15 nm. The nanoparticles appear to have mostly spherical shape. TEM image size analysis was done on about 1000 particles of magnetic fluid sample.

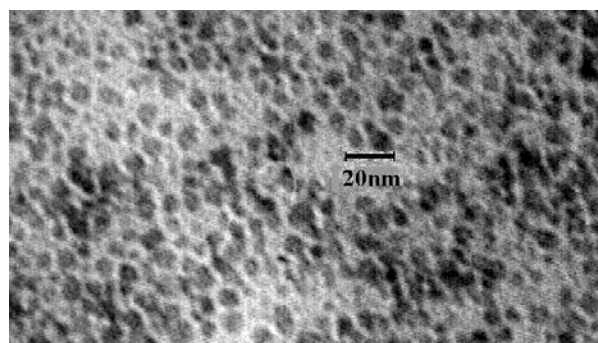


Fig. 2. TEM image of tetramethylammonium hydroxide coated magnetic fluid.

The diameter distribution histogram is presented in Fig. 3. The maximum of the histogram is located at about 7.7 nm.

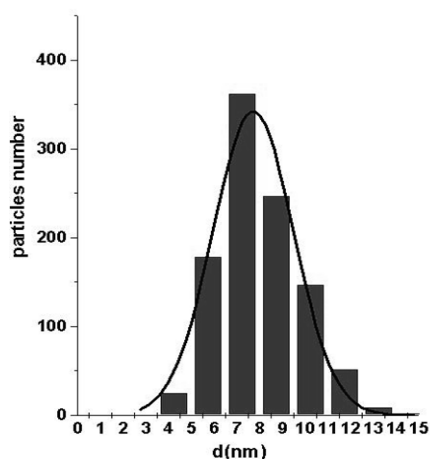


Fig. 3. The distribution histogram of magnetic particles coated with tetramethylammonium hydroxide.

For light scattering anisotropy study, magnetic fluid having a dilution of 0.001 volume ratio was used as a sample. Different samples were used as preliminary experiments. For each sample the light intensity was measured at different polar angles. The results of the fit, that is the values of the C and g, the anisotropy parameter together with the errors in determining them, in respect to the fit, are presented in Table 1, which also presents the results of the fit performed on different type of samples, having the same dilution.

Table 2. The results of the light scattering anisotropy measurement on magnetic fluid compared with the same parameter values for different biological samples having the same dilution.

No.	Sample	C, a.u.	ΔC , a.u.	g	Δg
1	Magnetic fluid in aqueous suspension	6.1	0.012245	0.99533	6.1e-005
2	Amidine in aqueous suspension	14.002	0.19192	0.99748	4.0e-006
3	Dilluted milk	28.9796	0.020408	0.99859	5.0e-006
4	Dilluted orange juice	22.7374	0.010101	0.99491	1.0e-005

Fig. 4. presents the plot of the experimental data and of the F function for the magnetic fluid and Fig. 5 for diluted amidine.

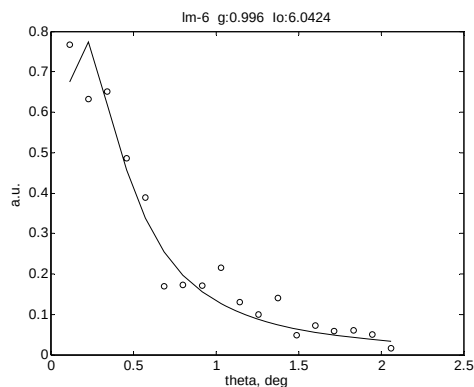


Fig. 4. The plot of the experimental data of scattered light intensity (circles) and of the F function for magnetic fluid.(solid line).

Examining Table 2 we notice that the values found for the g parameter are consistent with the anisotropy parameter reported in the literature [6-14] for biological cells, that is higher than 0.98. We consider this fact as a validation for our procedure, therefore we are confident that the value we measured for the g parameter is accurate. The C parameter describes the scattering properties of the medium and is connected with the individual scattering centers (hereafter SC) properties and with the SC concentration while the g parameter shows how close to the forward scattering is the average scattering angle. A value of 0 means perfectly isotropic scattering while a value of 1 means perfect forward scattering.

Our results, in Table 2 indicate that $g=0.99533\pm0.000061$. This means that the coated nanoparticles actually scatter light more anisotropic than biological particles, like amidine and fat particles in milk.

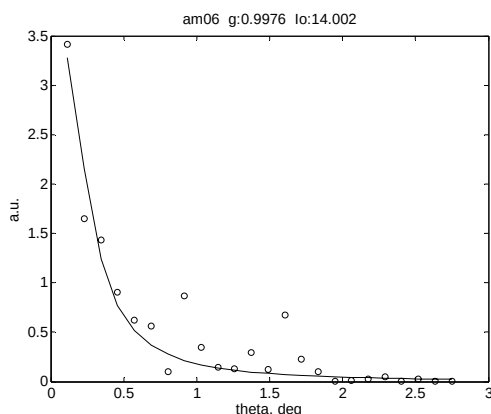


Fig. 5. The plot of the experimental data of scattered light intensity (circles) and of the F function (solid line) for sample diluted amidine.

If an experiment is performed on the same type of scattering centers, that is magnetic fluid manufactured using the same procedure, the C parameter will only

depend of the SC concentration in the small concentration range, as long as the optical depth, τ , defined in (4), is smaller than one [17-20]. If τ is smaller than 1 multiple scattering is improbable. In (4) H is the volume ratio of the SCs, d is the cuvette thickness, v is the individual average SC volume and σ is the scattering cross section of one SC.

$$\tau = H \frac{\sigma d}{v} \quad (4)$$

A calibration curve, concentration versus C value, can be plotted and used further on to assess the SC concentration in a sample that has an unknown concentration. This procedure to measure the magnetic fluid nanoparticles concentration in the extremely low values range (ppm), has not been, to our knowledge, described in other papers so far.

4. Conclusions

Stable magnetic colloid was prepared by using the tetramethylammonium hydroxide as surfactant substance in water dispersion. The synthesis parameters were adjusted in order to reach physical parameters in good agreement with the literature data.

We also performed a light scattering experiment to measure the magnetic fluid particles light scattering anisotropy. We found that the magnetic fluid particles actually scatter light more anisotropically than typical biological particles in suspension. The procedure we tested seems to be promising in measuring the nanoparticles concentration in the extremely low concentration range (ppm). As the scattering properties strongly depend on the particle size, the procedure, combined with the contrast analysis and with the speckle size analysis [12-13], will be developed toward particle sizing and identification. Work is in progress on this topic.

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