The hydrodynamic size of magnetic carrier systems determined by means of Forced Rayleigh Scattering experiment

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Abstract. *A new method for the determination of size distribution of magnetic carrier systems and for the proof of successful immobilization of biomolecules to magnetic particles was developed. The method is based on Forced Rayleigh Scattering (FRS) experiment, in which a diffraction concentration grating is created in a thin sample of colloidal fluid due to the periodic spatial temperature modulation.*

Keywords: Forced Rayleigh Scattering, magnetic fluid, thermodiffusion, size distribution

1. Introduction

The physical and chemical properties of magnetic fluids are strongly influenced by the details of the size distribution of dispersed colloidal magnetic particles. To obtain the profile of the particles nanometer dimensions the magnetic measurements (VSM) and transmission electron microscopy (TEM) have been traditionally used, recently the atomic force microscopy (AFM) has been introduced. The aim of our work is to show, that the size distribution of magnetic particles can be obtained by means of the Forced Rayleigh Scattering (FRS) [1,2] experiment.

The idea of the FRS experiment is to investigate the diffraction of the light on a concentration grating, created in a sample of colloidal fluid due to the presence of the periodic spatial temperature modulation. The temperature modulation appears within a thin colloidal sample interacting with light, which is spatially modulated either after passing through a metallic grid, or as a result of the interference of two optical beams.

In colloidal fluid, the presence of temperature grating invokes the redistribution of colloidal particles. This leads to the creation of a concentration grating and thus to the space modulation of the absorption coefficient. Then the light passing through the sample diffracts on the created amplitude grating.

The redistribution of colloidal particles is the result of the thermodiffusion, a flow of colloidal particles invoked by the temperature gradient. This process is characterized by the Soret constant $S=D_T/D_{dif}$, where D_{dif} is the particle translation diffusion coefficient and D_T the thermal diffusion coefficient. The sign of the Soret constant represents the direction of the particle diffusion - positive if colloidal particles migrate against the temperature gradient, negative if the directions of the migration and the temperature gradient are identical.
In our work the thermodiffusion in colloidal fluids was studied and a method for the determination of the distribution of hydrodynamic diameters of magnetic particles in magnetic fluids, using the FRS experiment, was developed. By this method also the biological binding reactions were detected, which are recently investigated by SQUID, magnetorelaxometry and field-induced birefringence [3, 4].

2. Subject and Methods

Theory

Our theoretical analysis of the thermodiffusion process within the FRS experiment [5] was oriented on the finding of a connection between the relaxation of the concentration grating (after switching-off the periodical heating) and the relaxation of the intensity of a laser beam diffracted on this grating. We found out, that the amplitude of the periodic concentration space modulation decreases, after switching-off the periodically distributed heating, exponentially with the time constant

$$\tau = \frac{D^2}{D_{dif} \cdot 4\pi^2} = \frac{3\eta\, d_H D^2}{4\pi k_B T} \quad . \tag{1}$$

Here the Einstein-Stokes formula $D_{dif} = k_B T/3\pi\eta d_H$ was used, where η is the medium viscosity and d_H is the hydrodynamic diameter of moving particle; D is the space period of diffraction grating. Equation 1 holds for spherical or nearly spherical colloidal particles with uniform diameters. If the diameters can not be considered as the same for each particle, the concentration relaxation will not be monoexponencial. In magnetic fluids with real particle size distribution the relaxation phenomena are multiexponential and can be expressed as

$$I(t)/I(0) = \int \exp\left(-t/\tau_d\right) p\left(\tau_d\right) d\tau_d . \tag{2}$$

The diffracted beam intensity $I \sim n^2$, so its relaxation time $\tau_d = \tau/2$. The distribution of relaxation times $p(t_d)$ corresponds, regarding the theory of probability, to the particle size distribution:

$$p(\tau_d) = \frac{8\pi k_B T}{3\eta D^2} p(d_H) \tag{3}$$

In this sense the relaxation measurements of the diffraction intensity curves allow to determine the particle size distribution function.

Experiment

For the experimental observation of the self-diffraction in magnetic fluids the grid Forced Rayleigh Scattering (FRS) method was used: the warming light, provided by a high pressure mercury lamp, was spatially modulated after passing through the metallic grid (Fig. 1).
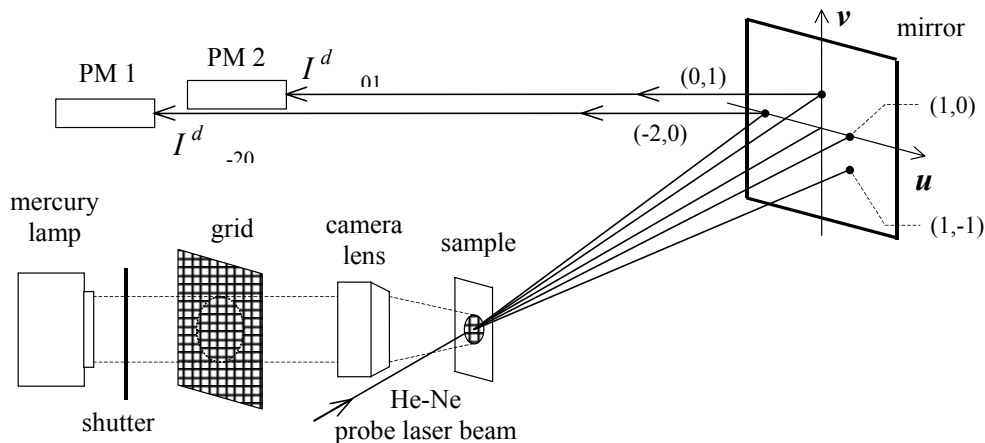

Fig.1. Grid forced Rayleigh scattering (FRS) experimental setup; built, placed and employed in Institute of Physics, University of Latvia, Salaspils, Latvia.

The created temperature and nanoparticle concentration profiles were experimentally detected and analyzed by diffracting a He-Ne probe laser beam on the grid image area in the sample.

The used magnetic fluids consisted of Fe_3O_4 nanoparticles, prepared by the precipitation of a mixture of ferric and ferrous salts. The obtained nanosized magnetic particles were dispersed in water and stabilized by sodium oleate. In these samples the immobilization of polysaccharide dextran was tested. A 20% (w/v) solution of dextran (Mr=60000) was added to the prepared magnetic fluid under continuous stirring, then the sample was centrifugated.

3. Results

The curves of the relaxation of diffracted beam intensity, observed after interrupting one of the interfering primary beams in water based magnetic fluid stabilized by sodium oleate, before and after the immobilization of dextran, are presented in Fig.2. The corresponding particle size distributions, obtained by the method for the calculation of the relaxation time spectrum from isothermal data using fast Fourier transformation [6], are presented in Fig.3.
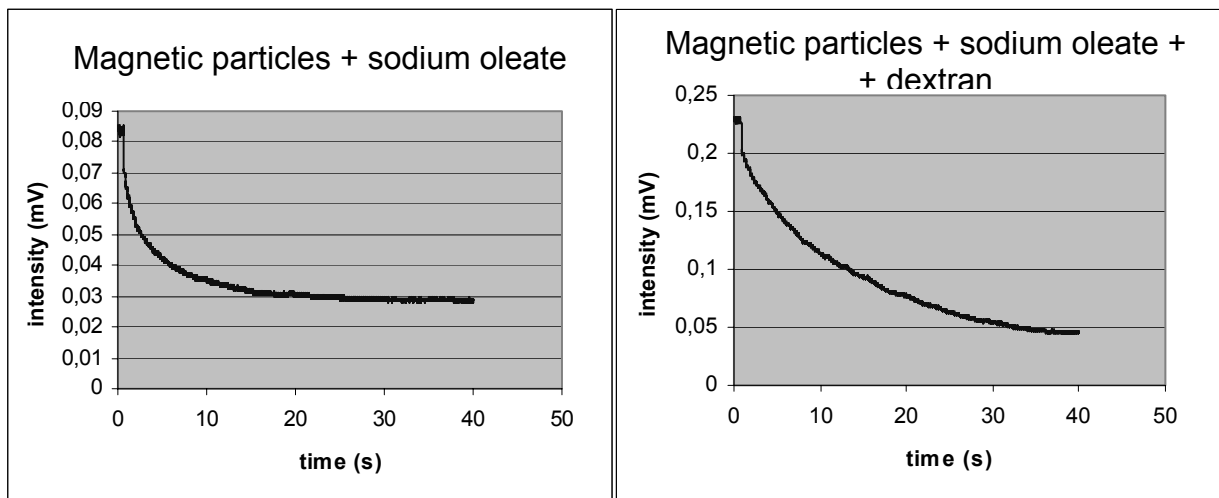

Fig.2. The time dependencies of the diffracted beam intensity for magnetic fluid stabiilized by sodium oleate, before and after the immobilization of dextran.
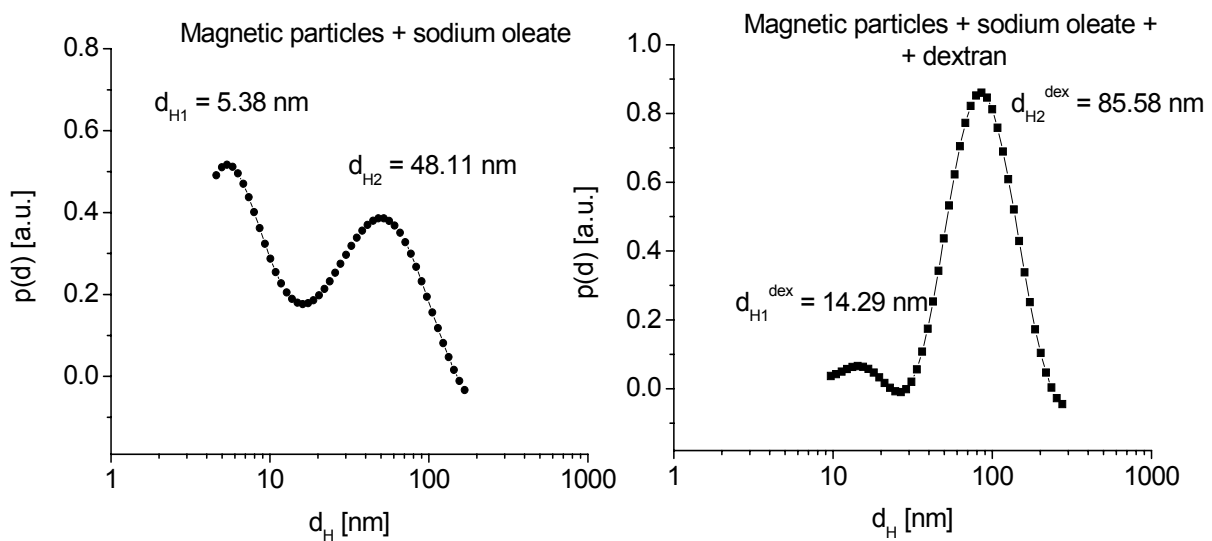

Fig.3. The distributions of the hydrodynamic diameters of magnetic particles in magnetic fluid stabilized by sodium oleate, before and after the immobilization of dextran.

It is obvious, that studied magnetic fluid is characterized by a bimodal distribution of the magnetic particles sizes. The hydrodynamic diameters corresponding to the maxima were d_{H1}=5.38 nm and d_{H2}=48.11 nm, before the dextran immobilization, and d_{H1}^{dex}=14.29 nm and d_{H2}^{dex}=85.58 nm, after the dextran immobilization, respectively. The increase of the hydrodynamic diameters of magnetic particles indicates the presence of bound dextran molecules.

4. Discussion and conclusions

The aim of this paper was to confirm, that using the Forced Rayleigh Scattering experiment the size distribution of magnetic particles in magnetic fluid can be determined and the successful binding of biological compounds to magnetic carriers can be verified. The results found for water-based magnetic fluids before and after the immobilization of dextran molecules to magnetic particles showed, that this technique can be exploited for the detection of the increased hydrodynamic diameter of magnetic particles after successful immobilization of biomolecules, for example. The comparison of found values of hydrodynamic diameters with those obtained by other methods (magnetization measurements, AFM, TEM) will be the subject of further investigation.

Acknowledgements

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