MEASUREMENTS OF ROTARY AND TRANSLATION DIFFUSION OF MAGNETITE NANOPARTICLES IN A HYDROCARBON BASED MAGNETIC FLUID

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Introduction. Magnetic fluids are artificial materials with a complex structure and a wide variety of compositions and methods of preparation. The structure of colloidal particles in magnetic fluids (size of the solvation sphere, level of aggregation, geometrical shape, etc.) is a highly important characteristic, which in many aspects determines their properties and longevity. However, since these particles are rather small – much smaller than the wavelength of visible light – their size may only be determined (without preparation of a liquid) by indirect methods. Studying the diffusion processes may be the way to investigate this structure.

One of the methods may be based on the rotation of the colloidal particles. Magnetic anisotropy allows controlling the orientation of these particles with an external field. That causes various optical, electromagnetic and mechanical phenomena connected with the orientation of the particles in the colloid [1]. Equilibrium orientation of the particles sets in within a certain period of time under the influence of thermal motion. This process may be interpreted as a rotary diffusion. Rotary diffusion may be displayed by rapidly changing the external magnetic field or turning it off. The process of equilibration for the orientation of the particles may be observed and relatively easy registered by, for example, the relaxation of optical anisotropy of the magnetic fluid [2]. The typical times for the relaxation process are from several to hundreds of microseconds and determined by the appropriate coefficient of rotary diffusion D_{R}, which depends on the viscosity of the carrier, size and shape of the colloidal particles [3]:

$$D_{\mathrm{R}} = \frac{kT}{6\eta V}\frac{1}{\delta}\,, \tag{1}$$

where k is the Boltzmann constant, T – temperature, η – viscosity of the carrier fluid, V is the volume of the particle, δ is a dimensionless function of the particle shape. Analysis of the relaxation curve enables to estimate the sizes of colloidal particles with certain assumptions about their shape.

Another method can be based on the translation diffusion. Translation diffusion is a spontaneous transition of substance in a particular volume occurring under the influence of thermal movement of the molecules. As known, the Fick's First Law describes the process of diffusion:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -D\frac{\mathrm{d}c}{\mathrm{d}x}\,S\,, \tag{2}$$

where Q is the amount of diffusing substance through the area S under the gradient of concentration. Theoretical dependence of the coefficient of translation diffusion D on the size of the diffusing particles is described by the Einstein's ratio [4]:

$$D = \frac{kT}{6\pi\eta r}\,, \tag{3}$$

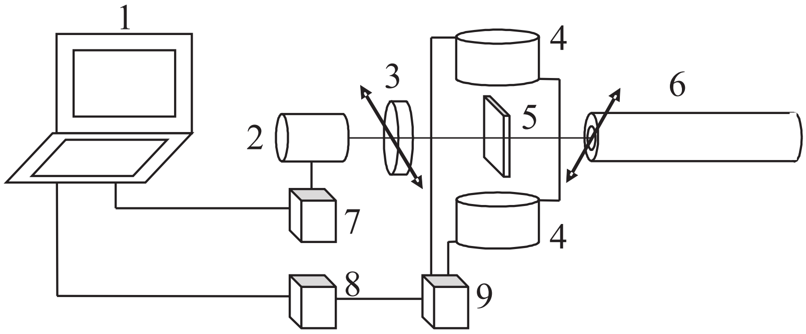

Fig. 1. The experimental setup to study rotary diffusion. 1 – PC, 2 – photo-detector, 3 – optical analyzer, 5 – experimental cell, 4 – pulse electromagnet, 6 – laser, 7 – digital oscilloscope PCS 500, 8 – pulse generator PCG 10/8016, 9 – powerful pulse amplifier.

where r is the radius of a particle. Thus, knowing the diffusion factor, viscosity and temperature, it is possible to define the size of the diffusing particles. This method is used at studying polymers [5].

1. Measurements of rotary diffusion of magnetic particles. The magnetic fluid used in experiments (sample TD5 prepared in the laboratory of Heat and Mass Transfer, Institute of Physics, University of Latvia) is a stabilized colloidal dispersion of magnetite Fe_3O_4 in tetradecane. Ferrite particles are nearly 10 nm in size. Oleic acid is used as a stabilizer. The rotational diffusion is measured according to the method of Ref. [2] with some modifications: the turnoff time for the magnetic field was reduced to less than 300 ns, a digital oscilloscope and a PC were used for measurements. The setup of the devices is shown in Fig. 1. Polarized light from laser 6 passes through a cell with a sample 5, which is under the influence of a pulse magnetic field of magnet 4. The plane of polarization of light is at an angle of 45° to the direction of the magnetic field. The light then hits an optical analyzer 3, whose plane of polarization is normal to the plane of polarization of laser light. The set functions in such manner so that no light hits a photo-detector 2 when the sample is isotropic. Main information was obtained by registrering the relaxation process of optical anisotropy after switching off the external magnetic field.

2. Direct measurement of the translation diffusion of colloidal particles in a magnetic fluid. The experiment on diffusion was carried out in a vertical flat 0.36 mm thick cell. At the initial stage of the experiment the cell was filled up to a certain level with the magnetic fluid of certain concentration. Then the carrier or a less concentrated fluid was added onto the surface of the magnetic liquid. A special lighter was used for the uniform background of the cell. The state of the diffusion border was registered after certain time intervals by a digital camera. The obtained snapshots were subjected to digital processing in order to define the distribution of concentration along the cell in various moments of time. In this connection the correspondence of concentration and darkness was obtained separately on the same set. The experimental setup for the study of translation diffusion is shown in Fig. 2.

3. Experimental results and treatment. Typical experimental data of single pulse measurement of rotary diffusion is shown in Fig. 3. Time dependence of two physical quantities was measured: the magnetic field on the sample and the intensity of passing light. The moment the magnetic field was switched off was taken as the zero point for the beginning of rotary diffusion from some oriented

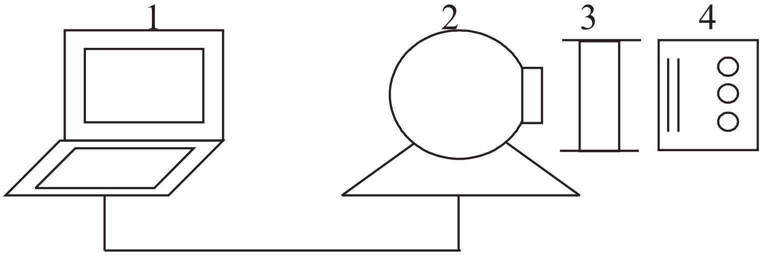

Fig. 2. The experimental setup to study translation diffusion. 1 – PC, 2 – TV camera JAI CV-S3200/3300, 3 – experimental cell, 4 – lighter SCHOTT KL1500 LCD.

state of magnetic particles to disordering state. From this point the intensity of light, in the simplest case, may be described by the expression [2]:

$$I(t) = I_0 \exp(-12 D_{\mathrm{R}} t) \tag{4}$$

The evaluation of the rotary diffusion coefficient D_{R} for the sample TD5 from this data gives a value of 26000 s^{-1} to 32000 s^{-1} at room temperature. According to (1), in the case of a spherical particle, this corresponds to a particle diameter of 26 nm to 28 nm ($T = 293\,\mathrm{K}$, $\eta = 2.32 \cdot 10^{-3}$ kg/(m · s)).

Experimental data for the translation diffusion consists of concentration fields in the experimental cell at fixed time points. To find the translation diffusion coefficient, the parametrical fit of the experimental concentration data was made using the theoretical solution of the one-dimensional diffusion problem [5]:

$$c^* = \operatorname{erf}\left(\frac{x}{2\sqrt{dt}}\right), \tag{5}$$

where $c^* = (2c - c_1 - c_2)/(c_1 - c_2)$, c_1 and c_2 are the concentrations in the experimental cell at the initial time point. The required diffusion coefficient D is a fitting parameter in this case.

Evaluation of the translation diffusion coefficient D for the sample TD5 from this data gives a value of $1.1 \cdot 10^{-11}$ m^2/s. In accordance with (3), this corresponds to the diameter of spherical particle of 17 nm.

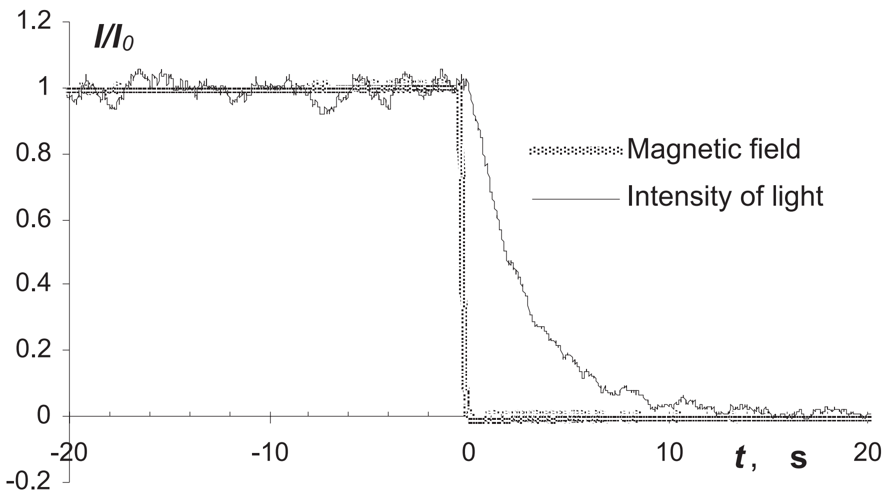

Fig. 3. Experimental data of pulse measurements.

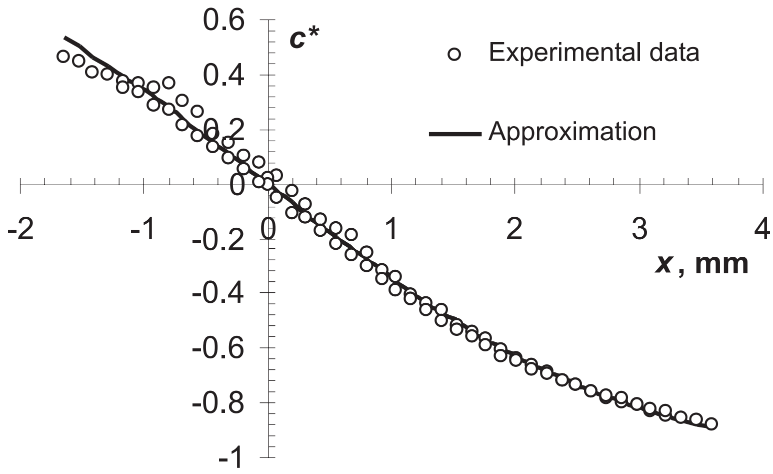

Fig. 4. The error function approximation of the concentration data in 64 hours after the beginning of diffusion.

4. Conclusion. Comparison of rotary and translation diffusion of magnetic particles in the given magnetic fluid shows some difference in effective particle diameters. This may be explained if the particles have a non-spherical shape. And, this difference may be eliminated using the form factor δ value of 3.8 to 4.8 in (1). For the long ellipsoid this corresponds to the radii ratio a/b of 4.35 to 5.1 [3].

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