

ON ESTIMATION OF A CHARACTERISTIC SIZE OF AGGREGATES IN SUSPENSION OF NANODISPERSED MAGNETICS FROM THE DECAY CURVES OF TRANSMITTED LIGHT INTENSITY WHEN REMOVING THE APPLIED MAGNETIC FIELD

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INTRODUCTION: Suspensions of magnetic particles are always aggregated [1, 2] and become optically anisotropic when subjected to a magnetic field; in particular, an increase (or sometimes decrease) in light transmission parallel to the applied magnetic field is observed. The large magnetically-induced optical anisotropies can be explained by the orientation or aggregation into the strings of large aggregates that are already present in the absence of the magnetic field [1]. Microscopically-visible strings of the order of 1 μ m have been reported [3]. The strings can be several particles (chains) thick [1]. Estimation of the characteristic size of aggregates (effective magnetic moment of aggregates or strings) in suspension is rather important for magnetic carriers for scientific and clinical applications. The aim of the work is to estimate the characteristic size of aggregates in suspensions of nanodisperse magnetite and iron from decay curves of transmitted light intensity when removing the applied magnetic field.

METHODS: Experiments were done with suspensions of magnetite and stabilized metal iron in physiological solution (0.05 g/l, average particles core size of 25 nm and 80 nm, respectively). Electron micrographs are given in Fig. 1.

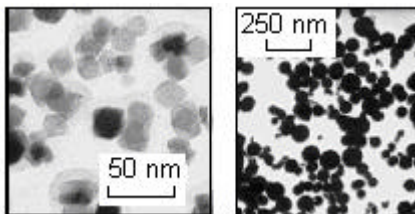


Fig. 1: Electron micrographs of nanodispersed magnetite (left) and iron (right) samples.

Preparation and characterization of the materials were published elsewhere [4]. Magnetic field $H=20$ Oe was applied along the optical axis of the red light 2 minutes after sonication of suspensions and

removed after approaching the steady state. Light transmission decay curves (represented in Fig. 2, curve a) were registered and analyzed.

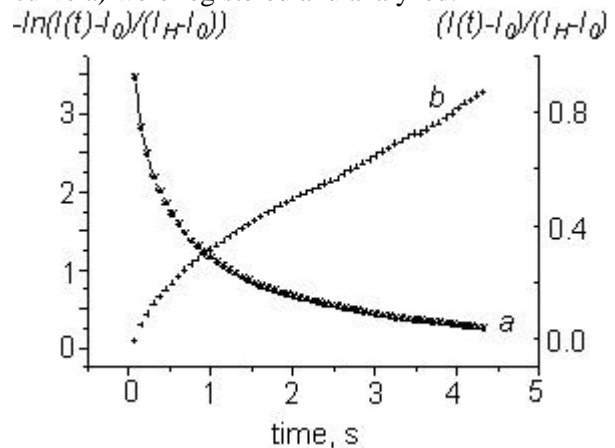


Fig. 2: Relative alteration of transmitted light intensity (a) and the same value in logarithmic coordinates (b) as a function of time after removal of the external magnetic field $H=20$ Oe for a suspension of nanodispersed iron with mean particles size of about 80 nm, $T=300$ K. I_H and I_0 are transmitted light intensities in the magnetic field H applied along the optical axis and at $H=0$, respectively.

RESULTS AND DISCUSSION: We are treating the medium as a diluted suspension of magnetic particle aggregates in Newtonian fluid. Aggregates of magnetic particles are considered as rigid bars with zero buoyancy. We assume that they are sufficiently large to interact with dispersion medium as hydrodynamic bodies, that they are sufficiently small for their orientation to be determined, and that by rotational Brownian movement they possess a temporary magnetic moment p and are oriented in an applied magnetic field H . To derive the equations, which determine the orientation of suspended aggregates, we have made use of the structural approach common for rheology of similar systems with no regard for hydrodynamic and magnetic interaction between strings.

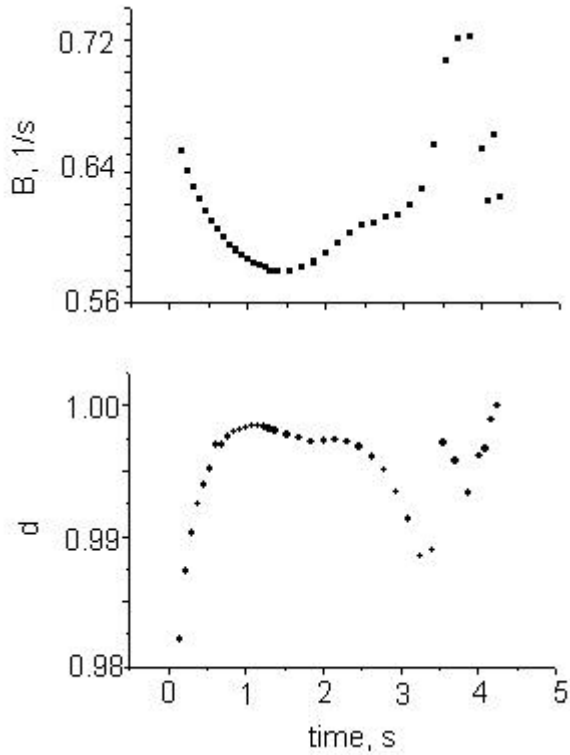


Fig. 3. The slope (B) of the line b from Fig. 2 and the coefficient of determination (d) as a function of the starting time point for regression analysis.

Taking into account hydrodynamic forces, rotational Brownian movement and moment of forces of the external magnetic field, rotational movement of aggregates is defined by the following equation

$$\dot{n}_i = D_r \mathbf{a} (h_i - h_i n_i n_i) - D_r \frac{\int \ln F}{\int n_i}. \quad (1)$$

Here $\mathbf{a} = pH / kT$, where p is the aggregate magnetic moment, H is the magnetic field, k is the Boltzmann constant, T is the temperature, n_i is the unit vector directed along the symmetry axis of a suspended aggregate, h_i is the unit vector directed along the external magnetic field, F is the distribution function of angular positions of aggregate symmetry axes of aggregates, $D_r = kT / f_p$ is the rotational Brownian diffusion coefficient of aggregates, f_p is the rotational friction coefficient of aggregates with respect to an axis perpendicular to the main axis of an aggregate, \dot{n}_i is the local time derivative of n_i .

The distribution function F in the phase space of n_i coordinates satisfies the equation:

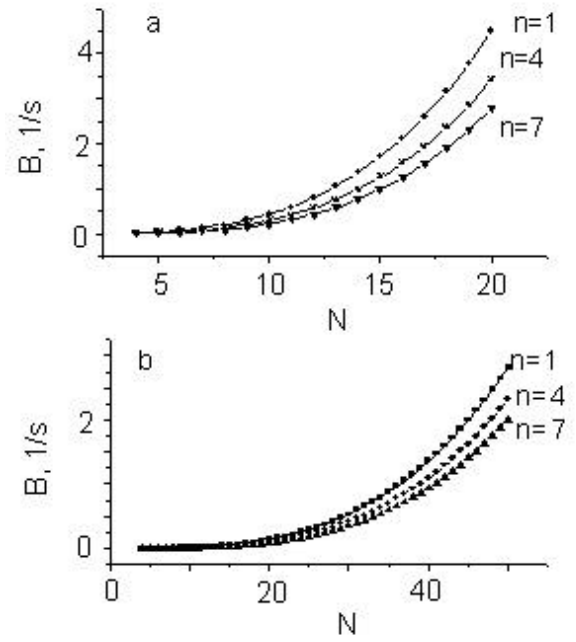


Fig. 4. Calculated from Eq. (6), the maximum rotation relaxation time of magnetic particle aggregates ($t_1=1/B$) after removing of the external magnetic field as a function of average number of particles in a chain N depending upon the number of chains (n) in a "string" for particles with mean outer diameters of 80 nm (a) and 25 nm (b), in water medium, $T=300$ K; q was taken to be N , $N/2$ and $N/3$ for $n=1$, $n=4$ and $n=7$, respectively.

$$\frac{\int F}{\int t} + \frac{\int (F \dot{n}_i)}{\int t} = 0, \quad (2)$$

where t is the time.

For coinciding directions of the steady magnetic field and the light beam realized in the experiment, equation (2) with account for (1) can be represented as follows:

$$\frac{\int F}{\int t} = \frac{D_r}{\sin q} \frac{\int (\sin q \frac{\int F}{\int q} + \mathbf{a} \sin^2 q F)}{\int q}, \quad (3)$$

where q is the angle between the external magnetic field and n_i vector. In the external magnetic field the orientation of aggregates is characterized by the stationary distribution function

$$F(\mathbf{q}) = \frac{1}{4\pi} \frac{\mathbf{a}}{sh \mathbf{a}} e^{\mathbf{a} \cos q}$$

Table 1.

Sample	t_s, s	$B = \frac{1}{t_1}, 1/s$	d	N(n=1)	N(n=4)	N(n=7)
M3	1.0	0.5545	0.987	44	46	49
S7	1.38	0.579	0.998	15	17	18

as the solution of Eq. (3) at $\frac{F}{q} = 0$. Upon removing the field, a reorientation of aggregates occurs, and at $\mathbf{a} \ll 1$, the distribution function F is defined by $\frac{F}{q} \neq 0$ as

$$F(\mathbf{q}, t) = \frac{1}{4p} [1 + \mathbf{a} \cos qe^{-\frac{t}{t_1}}] \quad (4)$$

where

$$t_1 = \frac{1}{2D_r} \quad (5)$$

is the characteristic decay time of the orientation of aggregates.

When \mathbf{a} is large, higher terms of the expansion of F in \mathbf{a} containing an infinite series of relaxation times

$t_i = \frac{1}{i(i+1)D_r}$, $i \geq 1$, should be taken into account.

As $t_1 > t_i$ ($i \geq 2$), formula (4) holds true at t and \mathbf{a} sufficiently large. The existence of a long linear region at large t on experimental curves plotted in logarithmic coordinates (Fig. 2, curve b) supports this treatment and enables one to estimate the maximum relaxation time t_1 , and hence, geometric parameters of an aggregate, taking into account the well-known expression for the rotational diffusion coefficient of rigid bars:

$$D_r = kT \frac{3 \ln(2q) - 0.8}{\pi h L^3}, \quad (6)$$

where h is the dynamic coefficient of liquid viscosity, L is aggregate length and q is the aggregate length/diameter ratio.

To choose a linear region of the curve (Fig.2, curve b) for the calculation of t_1 , the dependence of the coefficient of determination d and the slope $B = \frac{1}{t_1}$ on the starting time point t_s within the

linear regression model, were analyzed. Here,

$d = 1 - \frac{S_r^2}{S^2}$, where S_r^2 is the sum of squared differences between the y -values estimated for points and their actual values, and S^2 is the total sum of squares (the sum of squared differences between the actual y -values and the average of the y -values). We note that t_s was chosen at the maximum of the determination coefficient (Fig. 3).

Table 1 shows obtained values of t_s , t_1 , d and the corresponding aggregate lengths for various numbers of chains in a string (Fig. 4) for two examined samples of magnetic nanoparticles. Aggregates were estimated to be 44, 46 and 49 particles in length (1.1, 1.15 and 1.33 μ m) for magnetite and 15, 17 and 18 particles in length (1.1, 1.15 and 1.33 μ m) for iron, assuming strings of 1, 4 and 7 chains, respectively.

CONCLUSIONS: The physical model and equations derived for the distribution function of angular positions of the symmetry axes of aggregates enable one to estimate the rotational Brownian diffusion coefficient and, hence, the characteristic size of aggregates in suspensions of magnetic nanoparticles from decay curves of the transmitted light intensity when removing the applied magnetic field.

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