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Observation of the processes of formation and growth of aggregates in a magnetic fluid by laser correlation spectroscopy

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The laser correlation spectroscopy technique is applied to the study of magnetic fluids placed in a magnetic field. Colloidal solutions of magnetite in kerosene and water are used as samples. It is shown that switching on the field leads to the rapid appearance of large aggregates of nanoparticles of the dispersed solid phase, which continue to grow after that, and in a field of the order of hundreds of oersteds the average size of the aggregates increases three to five times with a characteristic time estimated in minutes.

Keywords: magnetic fluid, aggregate, laser correlation spectroscopy.

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Magnetic fluids (MFs) are colloidal solutions with their solid phase being a magnetically ordered substance, which lends certain unique qualities to them [1,2]. These materials have been discovered several decades ago and are still being studied extensively. For example, they are currently planned to be used in various photonic devices [3–6]. The examination of application potential of MFs in biology and medicine is also a promising trend [7–9].

The formation of structures in MFs under the influence of a magnetic field is the main factor that governs the properties of these substances and the features of their application in the above-mentioned fields and various other areas. It is known that a magnetic field induces the emergence of aggregates in MFs in the form of extended formations oriented along it. Their dimensions depend on field strength H, the characteristics of the medium, the type of solid phase material, and other factors [10]. Being aggregates of many nanoparticles, they grow to a significant size (a thickness on the order of tens of micrometers and, as a rule, a much greater length [11]). The emergence and evolution of such aggregates is one of the topical issues in the physics of dispersed systems, which is of particular significance for biomedical applications [12].

Laser correlation spectroscopy (LCS), which is based on the analysis of scattered radiation, provides data on the size and behavior of microparticles in solutions [13] and has been applied numerous times to MFs. However, reports from experiments carried out with the application of H, which is essentially the main cause of agglomeration, are extremely rare. This is largely attributable to the fact that standard LCS devices do not allow for the application of a magnetic field. However, the authors of [14] have managed to perform such measurements, but the obtained data covered only the region of weak fields and are, in general, preliminary in nature. The need for a more detailed investigation of the structures induced in various MFs by sufficiently strong fields and the dynamics of their formation is evident, which is why this was made the goal of the present study. To achieve it, the LCS method was supplemented with the possibility of application of a field varying within several hundred oersteds to a sample.

The samples were aqueous and kerosene solutions of magnetite Fe_3O_4 with organic and polymer stabilization purchased at „Mir Magnitov“ and produced by OOO ”NPP” AM-Kub (i. e., commercial MFs). The approximate size of individual colloidal particles was 10 nm. These fluids were diluted from initial solid phase concentrations ϕ of several tens of percent to concentrations $\phi = 0.0023-0.027\,\%$, which were highly transparent but still provided a sufficiently strong scattered radiation signal.

The procedure of LCS experiments is illustrated in Fig. 1. The block diagram of the setup is shown in Fig. 1, *a*. A laser beam (He–Ne, $\lambda = 633$ nm) was focused on the sample positioned in a cell. Radiation scattered by the MF at an angle of 90° was fed into optical fiber, propagated along it, and was detected by a photomultiplier (Hamamatsu H10723-20). The focal length of the lens was 5 cm, and the distance from the focal point to the end of the receiving fiber was 7 cm. The core diameter of the latter was 50 μm, and its axis was perpendicular to the laser beam and to the input and scattered radiation polarization. With this geometry, the signal intensity was fairly high. The signal was then processed in an electronic circuit consisting of an analog-to-digital converter and a computer. Comparing the intensities of scattered light and radiation transmitted through the fluid, we found that scattering could be considered single. The algorithm of processing (its time was approximately equal to 5 min per measurement) was based on correlation analysis

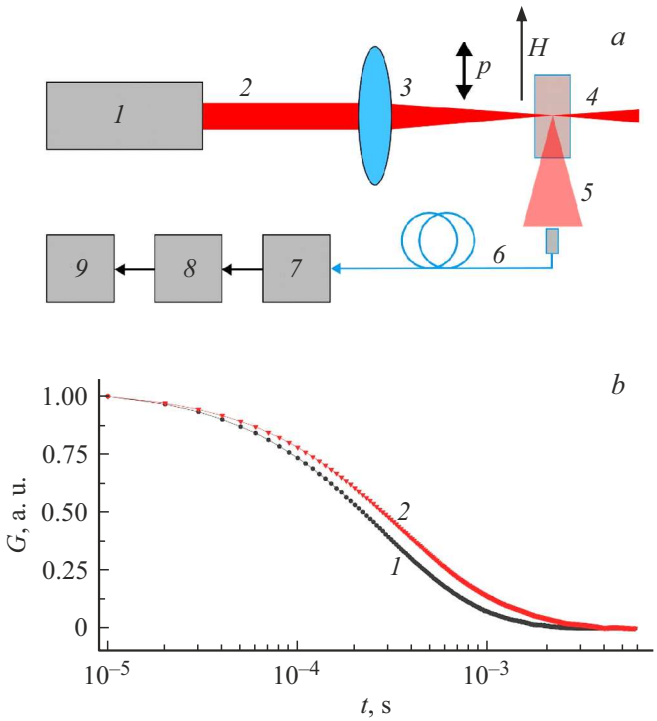

Figure 1. On the LCS experiment procedure. *a* — Block diagram of the setup. *1* — Laser, *2* — laser beam, *3* — lens, *4* — sample cell, *5* — scattered radiation, *6* — optical fiber, *7* — photodetector, *8* — analog-to-digital converter, and *9* — computer. Radiation polarization p and magnetic field orientation H are indicated. *b* — Examples of normalized autocorrelation functions G for an aqueous solution ($\phi = 0.027$ vol.%) at $H = 0$ (*1*) and 400 Oe (*2*).

of fluctuating scattered radiation. The distribution of size of scattering objects d was extracted from the autocorrelation functions of this signal (see the examples in Fig. 1, *b*) and is presented below in the form of dependences of relative intensity I of scattered radiation on d. Certain details pertinent to this analysis may be found in [15], where the same setup and methodology were used.

The magnetic field was produced by an electromagnet with a ferrite core with an approximate relative permeability of 2000, which provided a magnetic field strength up to 400 Oe at supply currents up to several amperes. It could be oriented both along the laser beam and perpendicular to it. However, since the effects associated with H were found to be virtually undetectable in the first case, all measurements were performed in an orthogonal field, which was aligned with the plane of polarization of incident radiation (Fig. 1).

Kerosene- and water-based samples behaved in qualitatively similar ways: application of the field induced the formation of aggregates significantly larger than those already present at $H = 0$. This was manifested as a significant broadening of the $I(d)$ distribution that evolved with H. Representative results illustrating each of these cases are reported below.

The typical temporal variation of the distribution function in the aqueous solution is shown in Fig. 2. In the experiment, it was recorded before the application of the field and at certain time intervals t after it. It is evident that $I(d)$ shifts fairly rapidly toward larger d when H is applied. Given the complex varying structure of this function, it is almost impossible to trace the motion of individual peaks; therefore, the median of the distribution (the d value separating equal areas below the $I(d)$ curve) was used to characterize it. Inset I in Fig. 2 illustrates the growth of median d_{mw} of the aqueous MF with time after the application of field $H = 400$ Oe. The field dependence of this parameter is shown below (Inset II in the same figure). Here and elsewhere, the moment of measurement is assumed to correspond to the middle of the interval within which the signal is accumulated and processed (i. e., $t = 2.5$ min after switching on H).

The field dependence of d is illustrated using the example of experiments with the kerosene-based sample (Fig. 3). In this case, the $I(d)$ function was first determined in zero field and then in a field intensifying with each new measurement (with the measurement starting immediately after switching the field on). Inset I in Fig. 3 shows the growth of median d_{mk} of the specified MF as a function of H, and Inset II shows the time dependence of this parameter.

In zero field, the $I(d)$ function has a fairly complex shape in both studied substances. Multiple peaks are indicative of the presence of certain formations in the initial solutions (curves *1* in Figs. 2 and 3); i. e., they contain both individual particles with a hydrodynamic diameter on the order of tens of nanometers and relatively large scattering centers (note that the initial size distribution in aqueous MFs is significantly wider than in kerosene ones).

The application of H leads almost immediately to the rearrangement of $I(d)$ due to the emergence and growth of large agglomerates (curves *2* and *3* in Fig. 3). The shifted peaks cannot be identified with any centers of the initial solutions, since, in addition to the fact that the pattern becomes qualitatively different at $H \neq 0$, it evolves with a change in positions of the maxima (curve *3* for the aqueous MF in Fig. 2 makes this particularly evident). Thus, it can be argued that aggregates in a magnetic field do not simply grow due to the addition of single and weakly agglomerated colloidal nanoparticles, but form a new complex system of objects with increased average sizes. To a somewhat lesser extent, this applies also to kerosene-based samples: a fairly rapid emergence of a strongly broadened, yet single peak was observed in experiments with them at $H = 400$ Oe. This is illustrated by curve *3* in Fig. 3, where the presence of a very small number of particles unaffected by the field (presumably non-magnetic) is also discernible. In general, the properties of aqueous and kerosene-based MFs are similar, although the average sizes of aggregates in the aqueous solution are several times greater (see the plots for the corresponding medians in the insets to Figs. 2 and 3).

Since the formation of structures from particles is associated with their motion in the carrier fluid, it should be

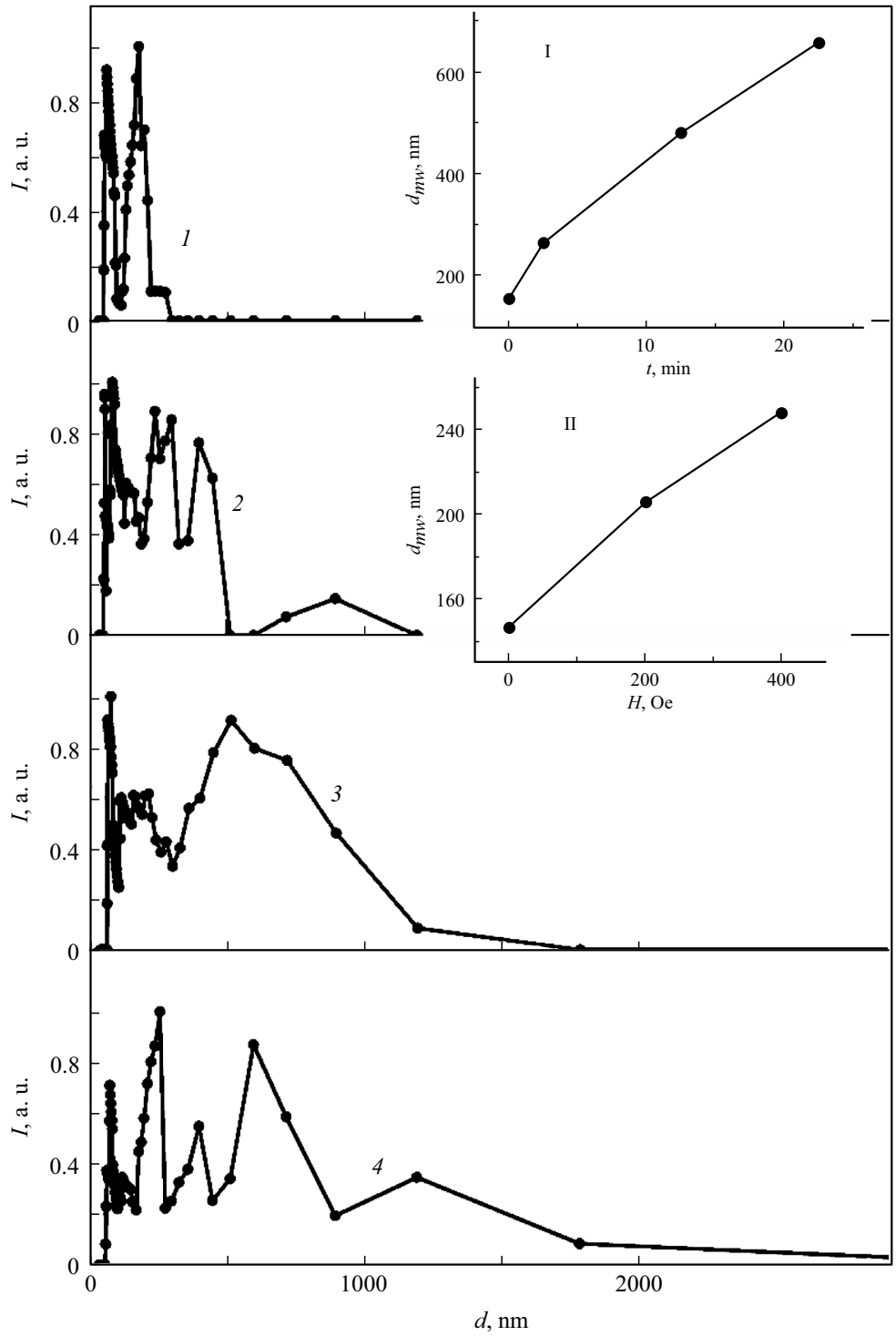

Figure 2. Variation of the size distribution of scattering centers in the water-based MF ($\phi = 0.027$ vol.%) at $H = 0$ and 400 Oe with time. *1* — $t = 0$ ($H = 0$), *2* — $t = 2.5$ min ($H = 400$ Oe), *3* — $t = 12.5$ min ($H = 400$ Oe), and *4* — $t = 22.5$ min ($H = 400$ Oe). Insets: I — time dependence of the median value at $H = 400$ Oe ($H = 0$ for the origin point); II — dependence of the median value on the magnetic field strength at $t = 2.5$ min.

largely governed by the properties of the latter (above all else, its viscosity). Indeed, the rates of processes turned out to be different in solutions that differed greatly in this parameter: the characteristic process time for aqueous and kerosene samples was estimated at 4–5 and 1.0–1.5 min, respectively (see Inset I in Fig. 2 and Inset II in Fig. 3). This result is quite consistent with the existing concepts of agglomeration in MFs.

The efficiency of laser correlation spectroscopy in studying aggregation in magnetic colloids under the influence

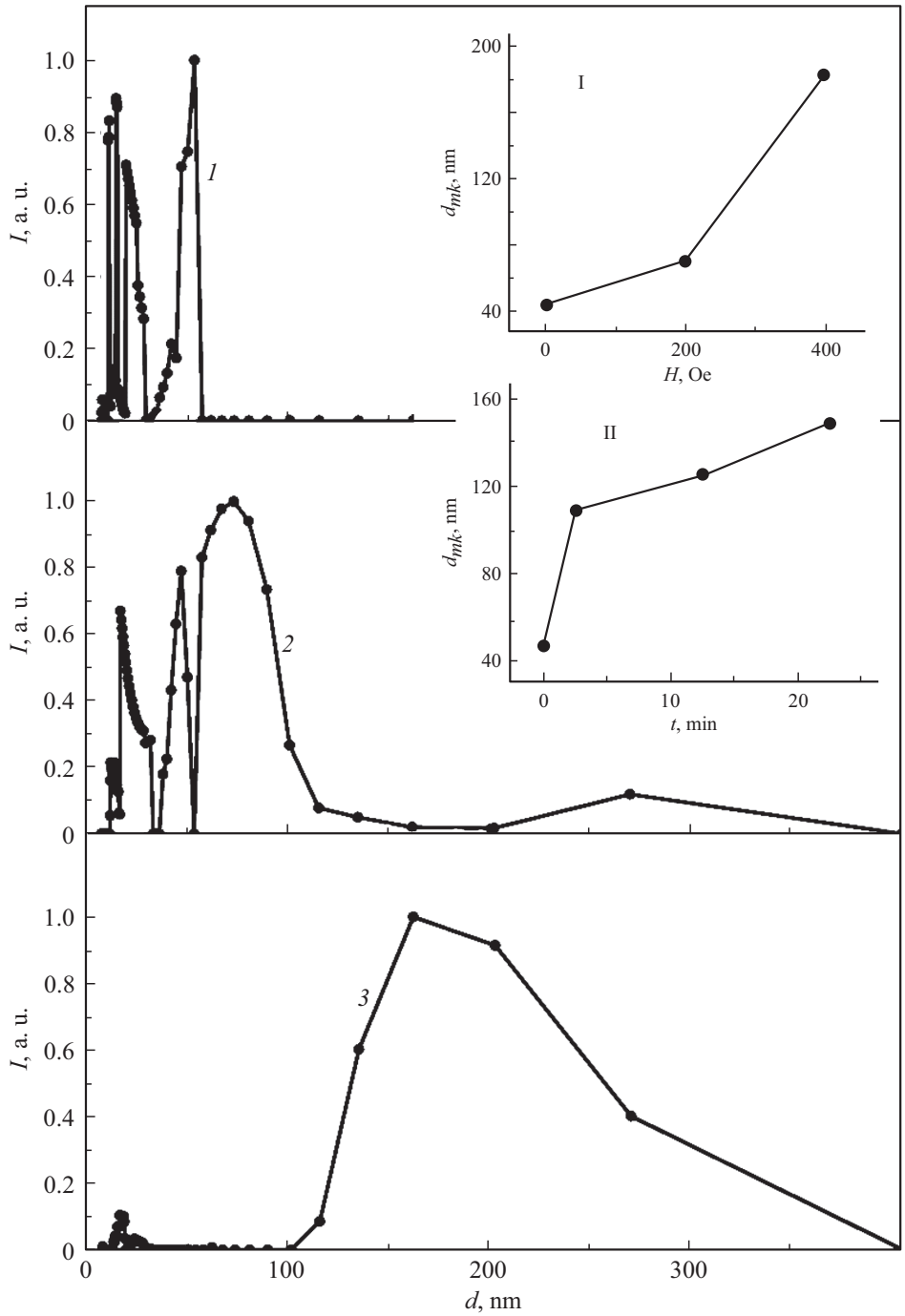

Figure 3. Variation of the size distribution of scattering centers in the kerosene-based MF ($\phi = 0.0023$ vol.%) with magnetic field strength. *1* — $H = 0$, *2* — $H = 200$ Oe ($t = 2.5$ min), and *3* — $H = 400$ Oe ($t = 2.5$ min). Insets: I — field dependence of the median value; II — time dependence of the median value at $H = 400$ Oe ($H = 0$ for the origin point).

of a magnetic field was demonstrated. The parameters characterizing aggregation were estimated using this method in experiments with samples with different carrier fluids. It was demonstrated that the patterns of formation of large aggregates in the examined cases are similar.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] O. Oehlsen, S.I. Cervantes-Ramírez, P. Cervantes-Avilés, I.A. Medina-Velo, ACS Omega, **7** (4), 3134 (2022). DOI: 10.1021/acsomega.1c05631
[2] P. Ryapolov, A. Vasilyeva, D. Kalyuzhnaya, A. Churaev, E. Sokolov, E. Shel'deshova, Nanomaterials, **14** (2), 222 (2024). DOI: 10.3390/nano14020222
[3] M. Taghizadeh, F. Bozorgzadeh, M. Ghorbani, Sci. Rep., **11** (1), 14325 (2021). DOI: 10.1038/s41598-021-93568-z

[4] S. Han, S. Pu, Z. Hao, C. Zhang, W. Liu, S. Duan, J. Fu, M. Wu, P. Mi, X. Zeng, M. Lahoubi, Opt. Lett., **48** (17), 4504 (2023). DOI: 10.1364/OL.499780
[5] V. Dave, R.V. Mehta, Optik, **311**, 171925 (2024). DOI: 10.1016/j.ijleo.2024.171925
[6] N.V. Kamanina, A.S. Toikka, Ya.V. Barnash, D.N. Redka, S.V. Lihkomanova, Yu.A. Zybtsova, P.V. Kyzhakov, Z.M. Jovanovi, S. Jovanović, Liq. Cryst. Their Appl., **22** (4), 83 (2022). DOI: 10.18083/LCAppl.2022.4.83
[7] M. Monteserín, S. Larumbe, A.V. Martínez, S. Burgui, L. Francisco Martín, J. Nanosci. Nanotechnol., **21** (5), 2705 (2021). DOI: 10.1166/JNN.2021.19062
[8] V. Socoliuc, M.V. Avdeev, V. Kuncser, R. Turcu, E. Tombácz, L. Vékás, Nanoscale, **14** (13), 4786 (2022). DOI: 10.1039/d1nr05841j
[9] A.E. Minuti, G. Stoian, D.D. Herea, E. Radu, N. Lupu, H. Chiriac, Nanomaterials, **12** (9), 1488 (2022). DOI: 10.3390/nano12091488
[10] S. Chikazumi, S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima, M. Setogawa, Y. Kurihara, J. Magn. Magn. Mater., **65**, 245 (1987). DOI: 10.1016/0304-8853(87)90043-6
[11] I.V. Pleshakov, A.A. Alekseev, E.E. Bibik, V.I. Dudkin, T.Yu. Kudryashova, E.K. Karseeva, T.A. Kostitsyna, E.A. Medvedeva, Nanosyst.: Phys. Chem. Math., **14** (5), 544 (2023). DOI: 10.17586/2220-8054-2023-14-5-544-548
[12] V.I. Petrenko, M.V. Avdeev, L. Bulavin, L. Vekas, L. Rosta, V.M. Garamus, R. Willumeit, V.L. Aksenov, J. Phys.: Conf. Ser., **345** (1), 012028 (2012). DOI: 10.1088/1742-6596/345/1/012028
[13] J. Stetefeld, S.A. McKenna, T.R. Patel, Biophys. Rev., **8** (4), 409 (2016). DOI: 10.1007/s12551-016-0218-6
[14] E.K. Nepomnyashchaya, A.V. Prokofiev, E.N. Velichko, I.V. Pleshakov, Yu.I. Kuzmin, J. Magn. Magn. Mater., **431**, 24 (2017). DOI: 10.1016/j.jmmm.2016.10.002
[15] E.K. Nepomniashchaia, E.T. Aksenov, T.A. Bogomaz, E.N. Velichko, J. Opt. Technol., **82** (3), 162 (2015). DOI: 10.1364/JOT.82.000162

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