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Original article

Effect of laser radiation on magnetite nanoparticles in deposited ferrofluid

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ABSTRACT The processes in a system of nanoparticles of a concentrated colloidal solution of magnetite induced by laser light with a wavelength of 650 μm have been studied. It was found that radiation focused on a drying drop of this substance, under certain conditions, leads to the formation of large accumulations of particles, in some cases strongly protruding above the surface of the sediment or, on the contrary, to their displacement from the illuminated area. A qualitative discussion of possible mechanisms of the observed phenomena is carried out.

KEYWORDS laser beam, optical force, magnetic fluid, ferrofluid.

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1. Introduction

The study of magnetic liquids or ferrofluids (FFs) has recently become particularly relevant due to their possible application in biomedicine [1, 2], as well as because of their unique optical properties that are promising for creating various photonics devices [3]. It has been proposed, for example, to use such materials in sensors [4–6], modulators [7], Bragg gratings [8] and many other optoelectronic instruments [9]. In all cases, an important fact was the sensitivity of these substances to the magnetic field, which leads to the formation of aggregates of nanoparticles composing ferrofluid [10, 11], and, as a consequence, a change in its characteristics. The latter, however, can also occur under the influence of light itself. It is known, for instance, that it can induce the clusters [12].

In general, as has been shown in many works, the effect of light on FF turns out to be different depending on the conditions, since the optical forces acting on particles can be attractive or repulsive [13–19]. It was found that in solid polymer composites, even at relatively low radiation power densities, nanoparticles are electrically polarized [20]; it is natural to extend this effect to liquids as well. Herewith, it should be borne in mind that polarized particles can both be drawn into the light beam and pushed out of it [13, 16]. The results of the always present heating are similar, determined by the sign of the thermal diffusion coefficient [17]. The competition of polarization and thermal phenomena creates a complex and not always unambiguous picture of the light effect on FF.

Undoubtedly, the information about the specificity of the processes in illuminated colloids is important for analyzing the operation of any optical device where such a substance is used. Since it is not complete enough at the moment, further studies of the behavior of nanoparticles in the light field are required. In this work, we investigated the structures formed by magnetic nanoparticles when they are deposited on a substrate in a laser beam focused on a drying drop of highly concentrated FF.

2. Samples and experiment

Ferrofluids are colloidal solutions of magnetically ordered compounds suspended in an appropriate carrier. As a solid phase ferrites are often used, although there are many other options. Liquid media are diverse, with water (this is essential for biological applications) and hydrocarbons (e.g. kerosene) being very common. The properties of these materials depend on the method of their stabilization, that is, on how the particles are prevented from sticking together. This is usually done by applying the surfactant onto the surface of nanoparticles; sometimes the structure of such a layer can be quite complex. In aqueous solutions, for this purpose, a coating by electric charge is widely created (ion stabilization). In some cases, additional stabilizing admixtures are added to the carrier composition (more details on the principles of obtaining and using of FFs can be found, for example, in the review [21]).

In this work, we used aqueous and kerosene-based solutions of magnetite Fe_3O_4, both commercial and self-synthesized, with different types of stabilization. Basic information about the samples is given in the Table 1 (the compositions of the stabilizer and additives for samples No. 1 and No. 2 were not specified by the manufacturer in more detail than indicated). The approaches used in the synthesis of materials are described in [22]. In all cases, magnetite nanoparticles had a characteristic size of about 10 nm. Solution No. 3 was prepared from the centrifuged sediment of the ion-stabilized fluid by diluting it in water. Solution No. 4 was obtained by dilution in kerosene of a paste-like precursor, obtained during the reaction of an ammonia water precipitation of solution of $FeCl_3$ and $FeSO_4$ with subsequent condensation with oleic acid (the same sample was used in [23]). In this case, a small uncontrollable amount of the latter substance passes into the liquid phase.

TABLE 1. The main characteristics of the samples used

No	Liquid carrier	Coating	Additives, vol. %	Initial concentration of solid phase, vol. %	Origin
1	Water	Organic stabilizer	Organic oil, 18	27	Commercial
2	Kerosene	Polymer stabilizer	Organic oil, 22	18	
3	Water	Ionic	–	20	Self-synthesized
4	Kerosene	Monomolecular (nominally) layer of oleic acid	Impurity of oleic acid, < 5 %	20	

To obtain different concentrations n, the samples were diluted with the appropriate carrier liquid from the initial concentration indicated in Table 1 to 5 vol. % (further, the volume percentages of the solid phase content are given everywhere). The solutions were treated in an ultrasonic bath for one hour.

The experiments were performed as follows. The liquid was applied in several drops onto a glass plate and distributed over it so that the resulting layer had a thickness of about 1 mm. Then, using a mirror, a laser beam was directed at the liquid, focused in such a way that the focus was inside it. A semiconductor CW laser with a wavelength of 650 μm and a power of 40 mW was used. The estimated power density in the focal spot was approximately 10 kW/cm^2. After drying for several hours at continuous radiation exposure, the trace of light was formed on the surface of the sediment. Its appearance depended on the sample, and this was the subject of the investigation.

The traces were studied by microscopes. One of them (Micro 200T-01), having a short focal length, made it possible to obtain images of a sample illuminated from above or below, and also, by adjusting the depth of field, to estimate the height of the object's protrusion above the surface h (since this method gives one only qualitative results, in the graphs below errors are not indicated). The other (Altami SM0745-T) had a larger focal length, which made it possible to rotate the sample at an angle convenient for recording its lateral image.

The shape of the object formed near the focus was influenced by the composition of nanoparticle coating, additives, and the concentration of the deposited material. In certain cases significant accumulations of matter could be observed on the surface of the sediment, but even at low n, the trace of the laser radiation was visible. The criterion for its linear size was taken to be $D = 2\sqrt{S/\pi}$, where S is its area (it should be noted that, despite the fact that the shape of the laser trace was not ideal, it was almost always close to a circle).

3. Results and discussion

The micrographs shown in Fig. 1 illustrate the effect of light on aqueous solutions obtained by dilution of composition No. 1 (see Table 1). In these cases, a pronounced effect of nanoparticles being drawn into the laser beam is observed. The images are obtained with a short-focus microscope as the top views. On Figs. 1a,c,d, the surface of the sediment is illuminated from above, in Fig. 1b, the illumination is made from below to emphasize the boundary of the spot. It can be seen that a dense (opaque) clot appears near the area of focused radiation, the size of which correlates with the concentration of the colloid. In Fig. 1b, there is certain heterogeneity of the sediment outside the light-induced trace, but it is obvious that on average, it is much thinner than in the trace.

Lateral images obtained for the same samples using a long-focus microscope show that at large n, light-induced aggregates can noticeably protrude above the surface. As an example, Fig. 2 demonstrates the type of laser trace for the sample with n = 20 % at two viewing angles. In Fig. 2a, the cone-shaped formation, elongated in the direction of the laser beam, is clearly visible. Its height h was estimated as 230 μm. It should be noted that this value, as well as the dimension of the "base" of this structure, is significantly smaller than the average diameter D, measured by Fig. 1b. However, it should be borne in mind that the darkened area that practically does not rise above the surface is several times larger than the protruding object – this is somewhat better detected by another rotation of the sample (Fig. 2b).

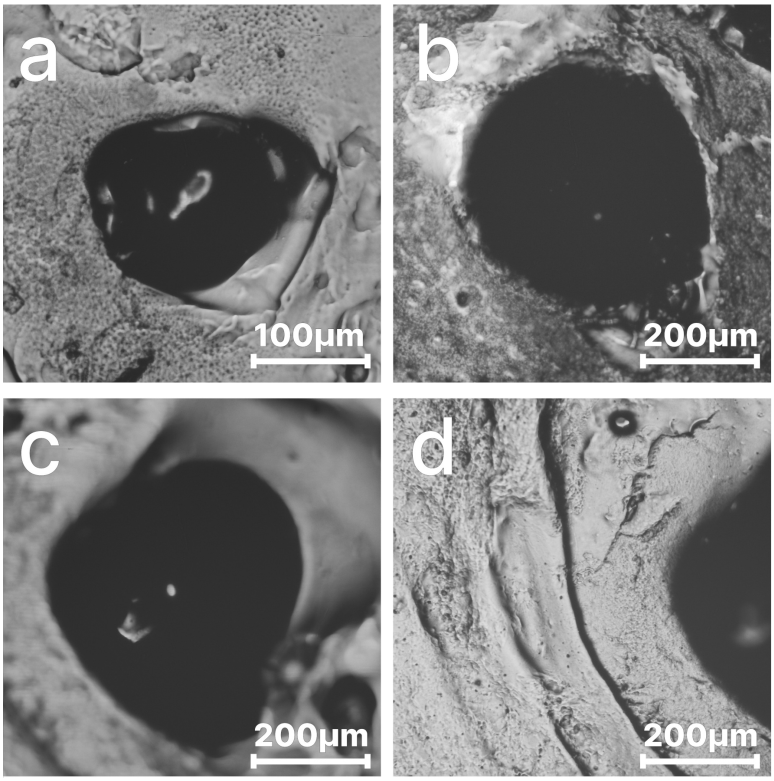

FIG. 1. Structures formed on the surface of the sediment of aqueous ferrofluids obtained from solution No. 1 (top view). a – $n = 12$ %; b – $n = 20$ % (bottom illumination); c – $n = 27$ %; d – edge of the laser trace in FF with $n = 27$ %

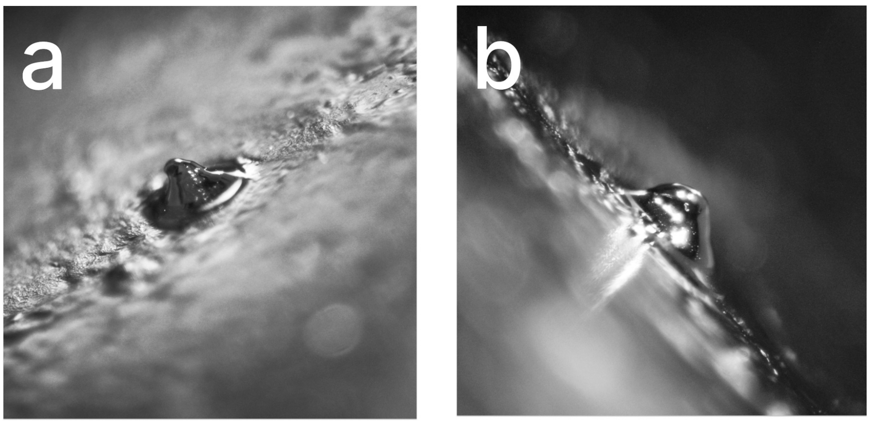

FIG. 2. Trace formed by laser radiation in precipitated aqueous solution of FF with $n = 20$ % (lateral view). Figures a and b refer to different orientations of the sample

The action of light on kerosene-based materials with another type of stabilization (initial solution No. 2, Table 1) turns out to be opposite. As can be seen from Fig. 3, in this case, the laser radiation leads to an outward movement of nanoparticles from irradiated area. Herewith, a ring-shaped object appears with a solid phase substance completely displaced from the central region. The opening has approximately the same size as the size of the dark spot for aqueous material with the same n (Fig. 3a, micrograph obtained with illumination from below). Such phenomena were observed at concentrations from 18 to 10 %.

Aqueous samples based on solution No. 3 displayed the effect of particles being drawn into the beam, but the appearance of a strongly protruding object was not registered. It should be noted that these substances are the "cleanest" of the used ones, i.e. its nominally do not contain any organic additives, unlike for other substances, where a certain "gluing effect" was manifested during precipitation that promotes the formation of a relatively smooth surface. In contrast, the

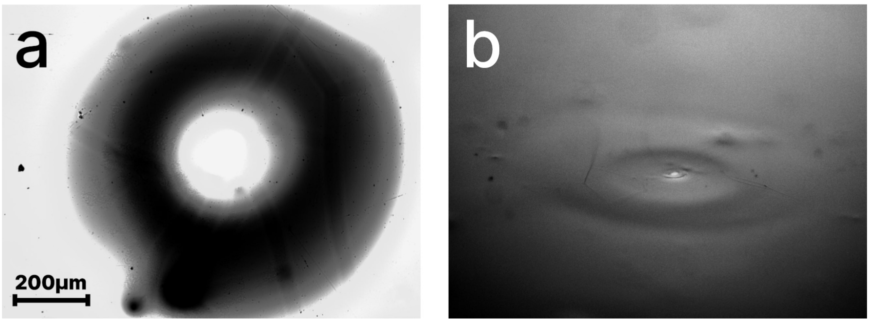

FIG. 3. Trace formed by laser radiation in a precipitated solution of FF based on kerosene (No. 2) with $n = 10$ %. a – top view, bottom illumination; b – lateral view

precipitates of solutions No. 3 were strongly cracked, which made it difficult to measure the aggregate height h, although the size of the spot D was easily determined.

The dependences of the geometric characteristics of laser traces on the concentration are shown in Fig. 4. Their increase with the growth of n can be remarked as a trend (though for large n this is apparently violated). Let's add that at $n < 5$ %, the traces usually were also observed, but less pronounced and not protruding above the surface.

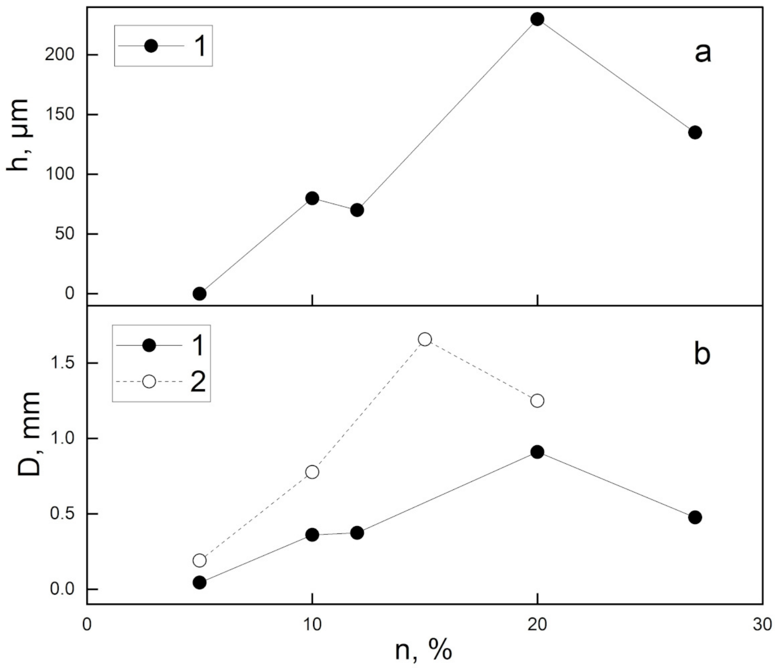

FIG. 4. Dependence of the geometric characteristics of the aggregates formed in aqueous solutions on the solid phase content, 1 – samples with organic stabilization (dilution from the initial substance No. 1); 2 – samples with ionic stabilization (dilution from initial substance No. 3). a – the height of the unit protrusion above the sediment surface; b – the size of the spot in the sediment plane. (The lines on the graph are drawn for ease of perception)

To some extent, solutions based on kerosene colloid No. 4 are of a special case. As it is seen from Fig. 5, which shows micrographs related to samples with $n = 10$ % (Fig. 5a) and $n = 20$ % (Fig. 5b), a height occurs in the area of irradiation, but near it one observes the formation of a deepening – the image resembles a crater. Also it should be noted that at a fairly large distance from the center of this object, a certain wave-like structure can be noticed (a similar sometimes was observed for other samples, see the edge of the laser-induced spot in Fig. 1d).

The results presented above cannot be strictly analyzed at this time; however, it is obvious that qualitatively one can come to some general ideas concerning to the behavior of nanoparticles in a laser beam. The most significant thing is the fundamentally different nature of the optical force acting on nanoparticles of the same composition (i.e., the material of the magnetic core) but with different solvents – from pronounced retraction into the light field to equally well-observed expulsion from it (Figs. 1 and 3). Of course, this is in agreement with the works mentioned above, since (even under

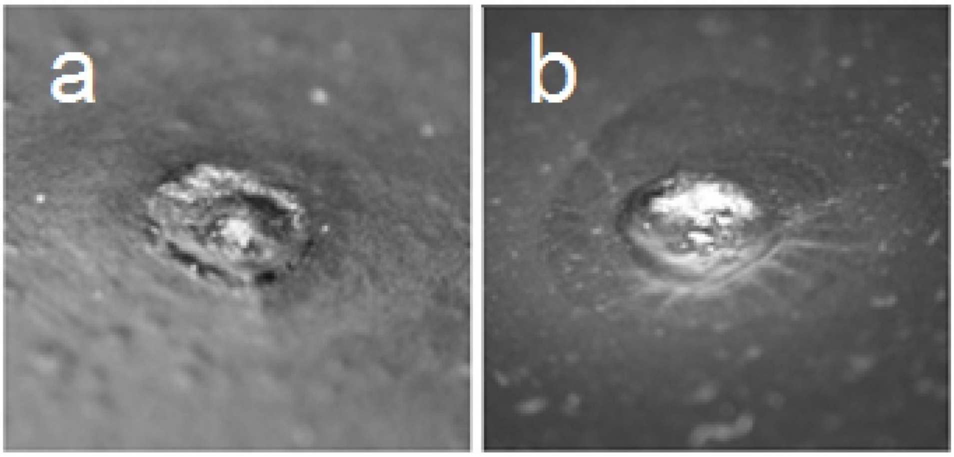

FIG. 5. Lateral view of the laser trace in precipitated FF based on paste and kerosene. a – $n = 10$ %; b – $n = 20$ %

the assumption that the laser radiation creates the same polarizations in particles) optical-induced movement can occur in different ways owing to the fact that it is determined by many mechanisms.

Polarization effects, which by themselves can lead to the appearance of forces of different signs [12, 13], are complemented by thermodiffusion, which depends on the sign of the Soret coefficient [17, 24]. (It should be noted that there may also be a time dependence here [17, 18], however, we believe that in our case, we are dealing with a steady-state process, since the time of the experiment significantly exceeds the characteristic times of the evolution of optical responses mentioned in literature). An important fact should be pointed out that there are two cases with opposite results for polar and nonpolar solvents (Figs. 1 and 3). Apparently, the optical polarization of the medium should indeed be taken into account, but attention should also be paid to the fact that samples from solutions No. 3 and 4, being made on the basis of water and kerosene, give one similar results (results shown in Fig. 5 may not be interpreted quite unambiguously, but nevertheless, here, in the center of the laser trace, an accumulation of substance is clearly visible). A significant role for the optical radiation action on FFs must be played by the thermal parameters of solvents responsible for the appearance of temperature gradients. They differ not only for different carrier liquids (the thermal conductivity of water is several times higher than that of kerosene), but perhaps also for the same liquids with different additives (see Table 1).

Finally, it should be taken into consideration that in all the materials studied, the coatings of nanoparticles are different. The interaction of the surfactant with the adjacent layers of material leads to the formation of the layer of nonmagnetic substance. If its thickness is one or two lattice constants, the volume of the shell turns out to be approximately 50 % of the total volume of the particle. Since the electromagnetic field of a light wave can cause polarization in such a substance too, it should be assumed that with the same magnetic cores, the total polarizations of nanoparticles of FFs with different types of stabilization differ.

To summarize, we can say that the interaction of the laser beam with polarization induced in the materials of the core and shell of the particle, the type and thermal characteristics of the liquid medium, as well as the direction of thermal diffusion produce a combination of factors leading to the appearance of optical force acting on the particle. Depending on their sign and magnitude, this force can be directed inward or outward in relation to the beam, thus forming condensations or rarefactions of nanoparticles in the FF thickness, which, when deposited, create structures observed in our experiments.

4. Conclusion

In this work, the phenomena associated with the laser beam action on nanoparticles of various ferrofluids lead to the formation of distinct patterns on the surface of their sediment were discovered. It has been established that the optically induced force responsible for their appearance depends on the properties of the liquid, creating an areas with a substance suppressed from it, or, oppositely, with its accumulation, sometimes in the form of large objects strongly protruding in the direction of the beam.

This information may be useful in further studying the behavior of ferrofluid nanoparticles in a light wave.

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