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# Structuralization of Magnetic Nanoparticles Induced by Laser Heating in Magnetic Fluids

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**Abstract** The structuralization of magnetic particles in magnetic fluids due to the thermodiffusion induced by laser light illumination was experimentally observed in two types of magnetic fluids: one based on a mineral oil with magnetite particles covered by a monolayer of oleic acid as a surfactant and the other a kerosene-based magnetic fluid sterically stabilized by a double layer consisting of oleic acid and dodecylbenzenesulphonic acid (DBS). Forced Rayleigh scattering (FRS) showed different behaviors of magnetic particle structuralization in the observed magnetic fluids. While for the case of mineral oil-based magnetic fluids, there was observed a positive thermodiffusion ($S > 0$), an indication of negative thermodiffusion ($S < 0$) was observed in magnetic fluids based on kerosene. This was also confirmed by the time-dependent decay of a grating of magnetic particles. Numerical simulation of aggregation for the case of negative thermodiffusion was confirmed by the observed aggregation after laser illumination in kerosene-based magnetic fluids and enabled an estimated value of the negative Soret constant in the magnetic fluid studied ($S \approx -10^{-2}\ \mathrm{K}^{-1}$).

**Keywords** Forced Rayleigh scattering · Magnetic fluid · Soret constant · Structuralization

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## 1 Introduction

The formation of magnetite nanoparticle structuralization in magnetic fluids may be observed as a consequence of concentration and thermal diffusion of nanoparticles. For example, temperature gradients can arise due to light absorption on the random concentration fluctuations of particles or on a well-defined geometrical structure such as a concentration diffraction grating. The light-induced heating of fluids can give rise to interesting phenomena, which depend upon the illumination character and type of illuminated fluid. In colloidal fluids, a temperature gradient invokes a flow of colloidal particles—thermodiffusion. This process is characterized by the Soret constant $S = D_T/D_{\text{dif}}$, where $D_{\text{dif}}$ is the particle translation diffusion coefficient and $D_T$ is a thermal diffusion coefficient. The method for determination of the Soret constant may be based on the forced Rayleigh scattering (FRS) experiment, in which a diffraction concentration grating is created in a thin sample of a colloidal fluid due to periodic spatial temperature modulation. From the time dependence of the grating decay, it is also possible to determine the sign of the thermodiffusion Soret constant $S$.

An interesting feature of thermodiffusion in magnetic fluids is that a positive ($S > 0$) or negative ($S < 0$) Soret effect can be observed, depending on the type of the studied fluid. If a magnetic fluid with a positive Soret constant is illuminated, a flow of colloidal particles against the temperature gradient direction occurs, i.e., the particles escape from the beam axis. In a magnetic fluid with a negative Soret constant, the directions of the concentration flow and the temperature gradient are identical, i.e., the local temperature increase attracts the absorbing particles into a warmer region. In such a magnetic fluid, an interesting phenomenon can be observed—the creation of a structure with "islands" of enhanced concentration, known as light-induced structuralization. Different techniques have been used to determine the Soret constant, particularly based on thermodiffusion columns [1] or on FRS [2]. The Z-scan technique [3], commonly employed to investigate the nonlinear properties of a medium, allowed us to make a classification of magnetic fluids based on the stabilization type, surfactant, carrier liquid, and the material of colloidal magnetic particles. The FRS method consists of the creation of a concentration optical grating in the magnetic fluid, due to its interaction with the interference field of two laser beams. The light passing through the sample diffracts on the created concentration grating; thus, the effect is also known as self-diffraction.

The goal of this work involved the study of thermodiffusion induced by laser illumination in two types of magnetic fluids (the first type was based on mineral oil and the second on kerosene) to look for a magnetic fluid with evidence of negative thermodiffusion.

## 2 Theory

A theoretical description of light-induced thermodiffusion in a magnetic fluid was based on an analysis of the created temperature distribution and its influence upon the distribution of colloidal magnetic particles. A thin sample ($xy$-plane) of the magnetic fluid was assumed to be illuminated with a harmonically changing intensity in the direction normal to the light propagation direction. The formulas for temperature and concentration modulations, which could be used to describe the phenomena observed in magnetic fluids at intense illumination, are found in [4]. At such intense illumination, large changes of the particle concentration are present, which influence the light absorption coefficient, and in this way, also the heating distribution. Thus, the formula for the amplitude of the temperature distribution, found in [4], had to include the space and time dependences of the colloidal particle concentration $n$ $(x, y, t)$;

$$T_0 = \frac{I_0 \alpha_0}{2(\lambda\Omega^2 + \lambda')} n(x, y, t), \tag{1}$$

where $I_0$ is the amplitude of the space dependence of the illumination, varying with the period $2\pi/\Omega$ in the $x$ -direction, $\alpha_0$ the absorption coefficient corresponding to the unit volume concentration, $\lambda$ the thermal conductivity coefficient of the studied fluid, and $\lambda'$ the heat outlet coefficient. Here, it should be mentioned that Eq. 1 is valid for both the periodic heating distribution caused by periodic illumination and the periodic heating due to the periodic distribution of the particle concentration. The formula describing the development of the possible periodic-in-space (harmonic) inhomogeneity of the magnetic particle concentration in a two-dimensional sample was found in the form,

$$\frac{\partial n}{\partial t} = D_{\text{dif}}(1 + SKnI_0)\left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2}\right). \tag{2}$$

In this equation, the substitution $K = 2\alpha_0(\lambda\Omega^2 + \lambda')$ was used. On the basis of any distribution of the particle, the concentration can be expressed by a Fourier integral (sum of harmonic dependences with different space frequencies $\Omega_m$); using Eq. 2, the development of any fluctuation could be predicted. The nonlinear Eq. 2 is useful for a qualitative description of the structuralization process connected with illumination of the magnetic liquid with a negative Soret constant $S$. If the Soret constant fulfills the inequality,

$$S < -\frac{1}{Kn_0 I_0} \tag{3}$$

(where $n_0$ means a mean concentration), then a randomly occurring concentration maximum will increase and a minimum will decrease. In other words, if a sample of a magnetic fluid with a negative Soret constant is illuminated, then, after the intensity of the light reaches the value,

$$I_0^{\text{c}} = \frac{1}{Kn_0\,|S|}, \tag{4}$$

for which the inequality, Eq. 3, is fulfilled, a structure with "islands" of enhanced concentration will arise. It is because instant fluctuations (which are always present) are amplified. A simulation of the development of such a structure (structuralization)

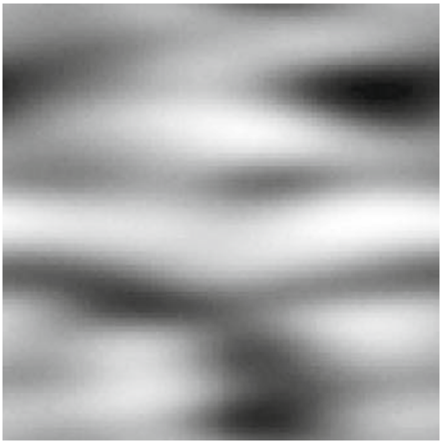

**Fig. 1** Illustration of numerical modeling of the developed structuralization in a magnetic fluid with $S < 0$ after illumination when the intensity reached the critical value $I_0^c$

in a magnetic fluid with a negative Soret constant was made by computer simulation of Eq. 2. Figure 1 illustrates the state of a thin magnetic fluid sample with a developed concentration structure after the light intensity reached the critical value $I_0^c$. It is well known that if only a stationary concentration gradient is present in the sample, the particle diffusion flux is oriented into the places with a lower concentration, and after some time, an equilibrium state is reached [5–7]. If also a temperature gradient is present, particles will diffuse from higher to lower temperatures when $S > 0$. In the case when $S < 0$, the thermodiffusion flux may cause that the particles diffuse into places at higher temperatures. In the sample, which is illuminated by an external homogeneous light field, structuralization will occur if stochastic inhomogeneities take place in the sample. This is due to increases in the temperature by the different absorption of light in such places.

Verification of the above-mentioned considerations has been performed by measurements on the samples of kerosene- and mineral oil-based magnetic fluids.

## 3 Measurements

The existence of a magnetic fluid with negative thermodiffusion is unique in the world. According to one existing theoretical article [8], negative thermodiffusion can occur in magnetic fluids stabilized with a double-layer surfactant but not with one layer. Structuralization of the magnetic particle concentration was experimentally observed in magnetic fluids based on mineral oil with magnetite particles (10 nm in diameter) covered by oleic acid as a monolayer surfactant and a kerosene-based magnetic fluid with the same magnetite particles and the same volume concentration ($\phi = 0.01$) sterically stabilized by a double layer consisting of oleic acid and dodecylbenzene-sulphonic acid (DBS) [9]. The magnetic fluid based on kerosene stabilized with a monolayer, i.e., oleic acid was studied, but the results of structuralization showed a positive thermodiffusion and were not very representative for comparison. A thin sample of a magnetic fluid (thickness of 100 μm) was illuminated by a laser beam

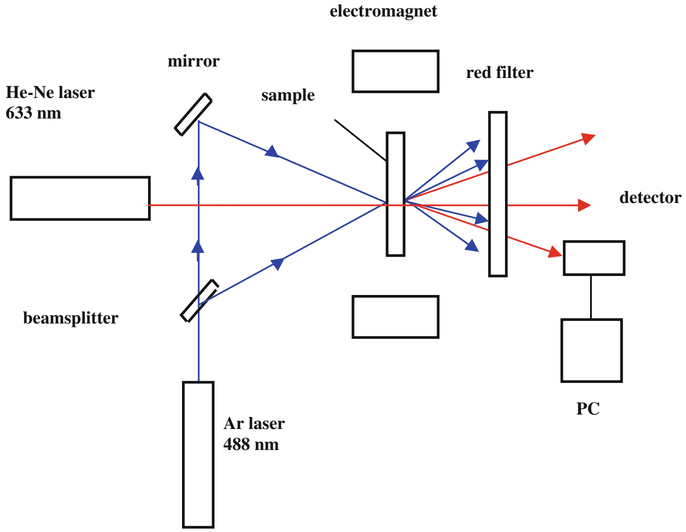


**Fig. 2** Experimental setup for forced Rayleigh scattering

with $\lambda = 488$ nm, generated by Zeiss Ar laser ILA 120 with a power ranging from 0 mW to 150 mW. The radiant power in the sample was amplified by a converging lens. The whole process, from the beginning of heating to the structure development, was photographed from the ground-glass screen and then digitized. An indication of a negative value of the Soret constant was also verified by the FRS experiment, for which the setup consisted of a Zeiss Ar laser, a beam splitter, a mechanical shutter, a thin sample of magnetic fluid (thickness 5 μm), and a photodetector connected to a PC (Fig. 2). The beam splitter gave two coherent beams providing an interference field in the sample. The generated space period of the interference field was in the range from 5 μm to 200 μm.

## 4 Results

In the case of the FRS experiment, a concentration grating was created in the interference field of two coherent laser beams. Figure 3 shows the picture from the ground-glass screen that illustrates the situation observed in the kerosene-based magnetic fluid. Here, the created concentration grating is shifted according to the interference one, as the particles are attracted to the hot regions (light stripes in the interference grating). For comparison, Fig. 4 shows the situation observed in the magnetic fluid with a positive Soret constant, where both gratings overlap.

It is convenient to study the kinetics of nanoparticles using the predetermined structure of the light field. Such a structure may be, for instance, a grating formed by use of two crossed coherent laser beams interfering in places of their intersection. The sample of a colloidal liquid in the form of a thin layer (thickness about 60 μm) was inserted into the interference field, and a periodic thermal field was thus formed. Due to the

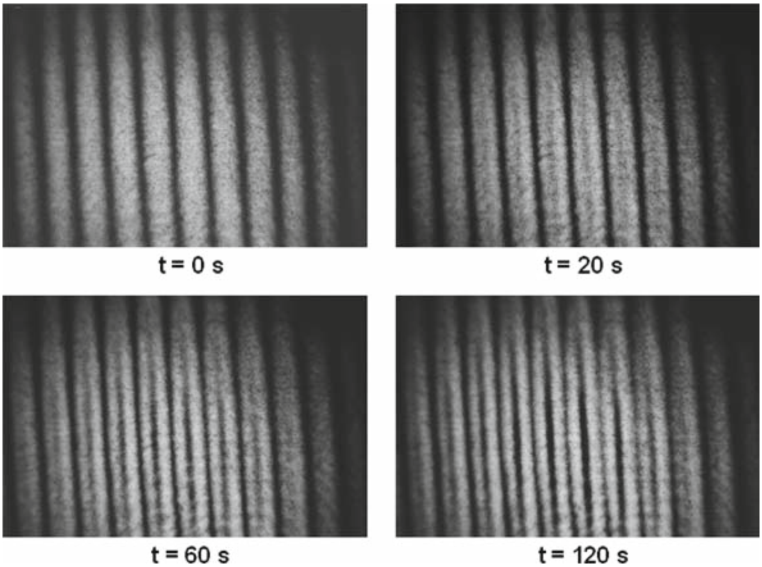


**Fig. 3** Shifted interference and concentration gratings in a kerosene-based magnetic fluid with negative thermodiffusion ($S < 0$)

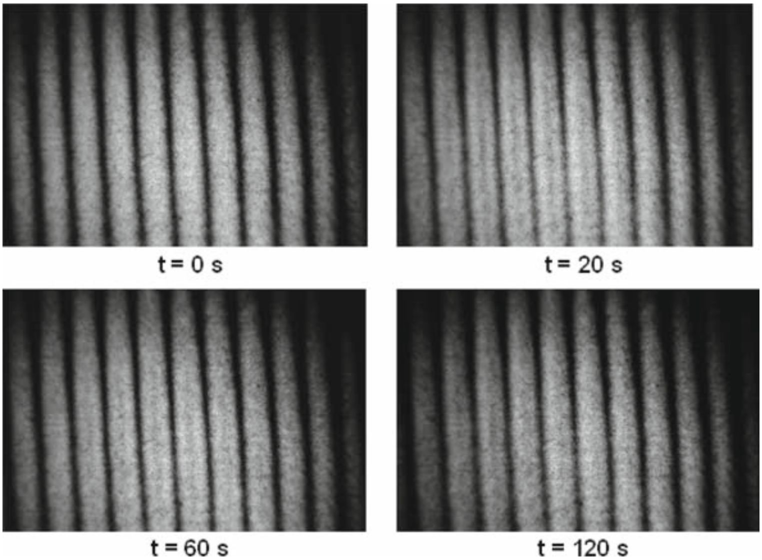


**Fig. 4** Overlap of interference and concentration gratings in a mineral oil-based magnetic fluid with positive thermodiffusion ($S > 0$)

diffusion and thermodiffusion of the nanoparticles, a concentration diffraction grating will be created. According to the behavior of the time dependence of the grating decay (after switching off the interference field and under the presence of additional lighting), it is possible to determine the sign of the thermodiffusion constant *S*. The additional illumination was provided by a homogeneous Ar laser with a power of $0.56\,\mathrm{W \cdot cm^{-2}}$.

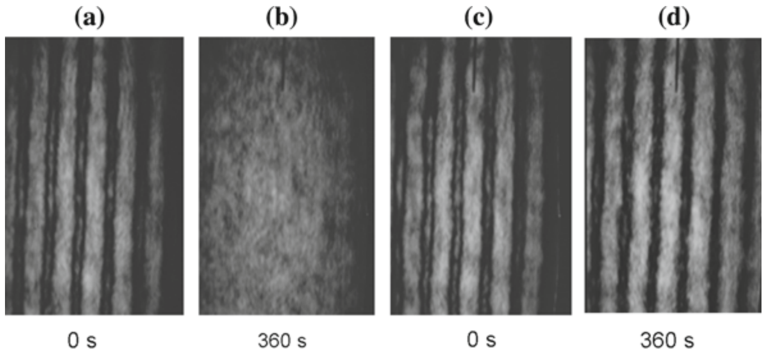


**Fig. 5** Grating decay in kerosene-based magnetic fluid (**a, b**) without and (**c, d**) with additional illumination

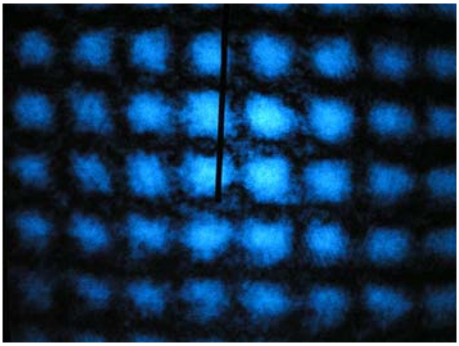

**Fig. 6** Planar square nanoparticle grating

The grating created in the mineral oil-based magnetic fluid with $S > 0$ will decay in the same way, independent of its additional illumination (see Fig. 5a, b), and the structure will decay 240 s after switching off the interference field. Another situation was observed for the kerosene-based magnetic fluid with $S < 0$. The grating decay without additional illumination is the same as in the case of the sample with $S > 0$. However, as it can be seen from Fig. 5c, d, the structure decay differs considerably under the presence of the additional illumination; the grating decay is slower, and the grating was still observed after 360 s. From Fig. 5, it is clear that without additional illumination, the structure disappeared completely at 360 s, whereas with illumination, the structure is observable up to higher values of time, what indicates a negative value of the Soret constant.

If the nanoparticle grating that points in one direction will be turned mechanically by 90 °, perpendicular to the interference field, then a new nanoparticle grating will be created in the sample. The new grating will be perpendicular to the previous one. The superposition of both gratings results in the creation of a planar square nanoparticle grating, which was observed in kerosene-based magnetic fluids (Fig. 6). If the same experiments were used for a mineral oil-based magnetic fluid, the square nanoparticle grating was not created. This observed effect also supports the possibility of a negative value of the Soret constant for kerosene-based magnetic fluids.

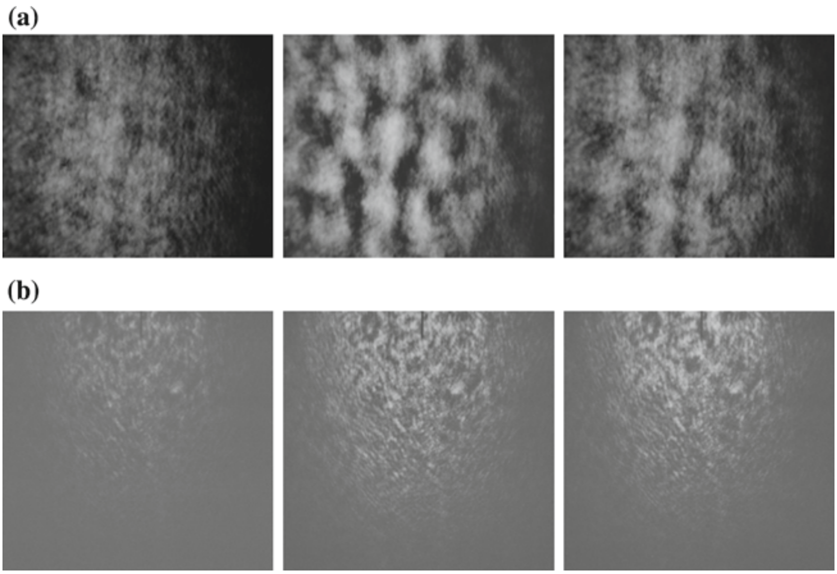


**Fig. 7** Development of the structure with "islands" of enhanced concentration: (**a**) in kerosene-based magnetic fluid and (**b**) in mineral oil-based magnetic fluid

The structuralization of magnetic particle concentration was observed in the kerosene-based magnetic fluid after the intensity of the illumination reached the value $I_0^c = 120\,\text{mW}$. Using this value and typical values of $\lambda \sim 10^{-1}\,\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $\alpha \sim 1\,\text{cm}^{-1}$, the value of $S$ was calculated to be $S \approx -10^{-2}\,\text{K}^{-1}$.

Figure 7 illustrates the situation in kerosene- and mineral oil-based magnetic fluids samples with increasing intensity. It is evident that, in kerosene-based magnetic fluids, a structure with "islands" of enhanced concentration has developed (Fig. 7a), if the illumination intensity was higher than a certain critical intensity. In mineral oil-based magnetic fluids, the same effect was not observed (Fig. 7b). This confirms the computer simulation illustrated in Fig. 1 and indicates a negative value of the Soret constant in the kerosene-based magnetic fluid.

## 5 Conclusions

The results obtained from our experiments could be regarded as evidence that negative thermodiffusion ($S < 0$) can be observed in a kerosene-based magnetic fluid with magnetite particles stabilized by a double layer consisting of oleic acid and DBS while in a mineral oil-based magnetic fluid stabilized by a monolayer of oleic acid, there is positive thermodiffusion ($S > 0$). This fact is in agreement with the Morozov prediction [8] where negative thermodiffusion can occur only in double-layer stabilized magnetic fluids. The development of the structuralization of magnetic particle concentration in an illuminated thin sample, after the illumination intensity reaches some critical value, was numerically simulated and then verified experimentally. The value of the negative Soret constant was estimated from the threshold laser intensity as $S \approx -10^{-2}\,\mathrm{K}^{-1}$ for the magnetic fluid under study. It was proved to be convenient to investigate the kinetics of the nanoparticles in magnetic fluids on a well-defined geometric structure such as a concentration diffraction grating.

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