

LIGHT INDUCED THERMODIFFUSION IN MAGNETIC FLUIDS

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The influence of intensive periodic illumination of a magnetic fluid upon the temperature distribution and consecutive creation of diffraction gratings due to the temperature dependence on the refractive index, or the redistribution of colloidal particles (in colloidal liquids) due to the temperature gradient, is studied. The parameters of rise and decay of such gratings are calculated under a linear approximation and are compared with the parameters of gratings observed in magnetic fluids after intensive periodic illumination. The work presents also a simplified description of the phenomenon of structuralisation of the colloidal particles' concentration, which is caused by a nonlinearity present at intensive illumination of a colloidal fluid with a negative Soret constant. The existence of this phenomenon is documented by observation of structuralisation of optical transmittance caused by intensive illumination. The presented results of the second diffraction maximum observation indicate to the anharmonicity of created gratings, and so, to the presence of a non-linearity in the grating building process.

Introduction. The light induced heating of fluids can give various results in dependence on the illumination character and the character of the illuminated fluid. When two intense coherent beams pass through an absorbing fluid, the periodic heating and following periodic modulation of the refractive index occurs in their interference field. This manifests itself in diffraction of the light beams passing through the fluid (selfdiffraction on phase grating [1]). When a colloidal fluid is illuminated in this way, not only the refractive index space modulation, but also, through the thermodiffusion (the Soret effect), a redistribution of colloidal particles appears. This is connected with the space modulation of the absorption coefficient and thus with the diffraction of the light on a created amplitude grating [2, 3]. At intensive illumination another interesting phenomenon can occur in colloidal fluid with negative Soret coefficient: in such a case a fluctuation of absorption may spontaneously increase what can give rise to a self-structuralisation of the particles density. Self-diffraction as well as self-structuralisation phenomena were studied in magnetic fluids containing Fe_3O_4 particles dispersed in various media. Trying to explain the observed phenomena, we have attempted to give a more detailed description of the thermodiffusion process in colloidal fluids. The results following from this description and their comparison with those obtained in experiment are presented in the next paragraphs.

1. The periodic illumination (linear approximation).

1.1. The temperature distribution. Let us suppose that a magnetic fluid sample is illuminated with an intensity harmonically changing in the direction normal to the light propagation direction and that the fluid absorption coefficient is large enough to cause noticeable medium heating. At the same time the sample

thickness is supposed to be smaller than the inverted value of the absorption coefficient, so the sample volume can be considered to be lighted independently on the light propagation in the z -direction. To express the temperature distribution in the studied system, the calorimetric equation will be used. Supposing only a weak light absorption in the sample, it can be written as

$$\alpha I_0(1 + \sin \Omega x) - \lambda \frac{\partial^2 T}{\partial x^2} - \lambda'(T - T_{\text{sur}}) = c\rho \frac{\partial T}{\partial t}, \quad (1)$$

where I_0 is the amplitude of the space dependence on illumination, varying with a period $2\pi/\Omega$ in the x -direction, Ω is the intensity distribution space frequency, α is the light absorption coefficient of a studied liquid, λ is its thermal conductivity coefficient, λ' is the heat outlet coefficient (supposed to be the same at each point of the sample) and T_{sur} is the temperature of the surrounding. Searching the solution of Eq. (1) in form $T(x, t) = A(t) \sin(\Omega x) + B(t)$, the expression for the temperature modulation amplitude was found as

$$T(x, t) = T_0 \left[1 - \exp\left(-\frac{\lambda\Omega^2 + \lambda'}{c\rho} t\right) \right] \sin(\Omega x) + \frac{I_0\alpha}{\lambda'} \left[1 - \exp\left(-\frac{\lambda'}{c\rho} t\right) \right] + T_{\text{sur}} \quad (2)$$

where

$$T_0 = \frac{I_0\alpha}{(\lambda\Omega^2 + \lambda')} \quad (3)$$

Eq. (2) shows that in case of small heat outlet and space period of the temperature distribution of tenth's micrometers order, the time constant of the thermal relaxation is of a few milliseconds order for fluids with the temperature conductance and specific heat close to those of water. In any case the steady temperature distribution (relative to the temperature of the surrounding) will be achieved in a time shorter than the time given by the heat conductivity in the x -direction only.

1.2. The distribution of the colloidal particles concentration. The temperature space modulation affects the distribution of the colloidal particles' concentration (via thermodiffusion) in colloidal fluids and therefore, the absorption coefficient, so after periodic illumination the sample behaves as an amplitude optical grating.

The influence of the periodic temperature distribution upon the distribution of colloidal particles can be determined by the continuity equation. In the case of zero external force and sample temperature varying only in the x -direction it can be supposed that the concentration and consequently the particle flow density will also depend only on the x -coordinate. Then the continuity equation can be used in the form

$$\frac{\partial \tilde{n}}{\partial t} = D_{\text{dif}} \frac{\partial^2 \tilde{n}}{\partial x^2} - S D_{\text{dif}} T_0 n_0 \Omega^2 \sin(\Omega x) \quad (4)$$

where D_{dif} is the particle translation diffusion coefficient and S is the thermodiffusion coefficient (Soret constant). In this equation the colloidal particles' concentration n is expressed as a sum of a constant mean value n_0 and a value \tilde{n} varying in space, which is so small that it can be neglected if compared with n_0 in heat intensity calculations. The solution of Eq. (4) was found to be

$$\tilde{n}(x, t) = -n_0 S T_0 (1 - \exp(-D_{\text{dif}} \Omega^2 t)) \sin(\Omega x) \quad (5)$$

As seen, the particle concentration modulation amplitude, after reaching the steady state, is equal to

$$n_a = |n_0 S T_0|. \quad (6)$$

Regarding Eq. (3), this equation shows that the concentration modulation is proportional to the light intensity I_0 . As Eq. (5) shows, when used the assumptions are satisfied, the amplitude of the concentration periodic space modulation increases in time after switching-on the periodically distributed heating, or after its switching-off, decays exponentially with the time constant

$$\tau = \frac{D^2}{D_{\text{dif}} 4\pi^2}. \quad (7)$$

Here expression $\Omega = 2\pi/D$ was used. Eq. (7) shows that the concentration relaxation is characterized by a time constant, which depends upon the space period of the created grating, analogically as the time constant of the temperature distribution relaxation (Eq. (2)). However, the particular values for thermal and concentration relaxation may strongly differ from each other.

Using the Einstein–Stokes formula $D_{\text{dif}} = k_B T / 3\pi \eta d_H$, where η is the medium viscosity and d_H is the hydrodynamic diameter of a moving particle, the time constant of the concentration relaxation can be written as

$$\tau = \frac{3\eta d_H D^2}{4\pi k_B T}. \quad (8)$$

This formula holds for spherical or nearly spherical colloidal particles with uniform diameters. When the diameters cannot be considered the same for each particle, the concentration relaxation will not be monoexponential.

In magnetic fluids with a real particle size distribution the relaxation phenomena are multiexponential and can be expressed as

$$I(t)/I(0) = \int \exp(-t/\tau_d) p(\tau_d) d\tau_d, \quad (9)$$

where $p(\tau_d)$ is the distribution of the time constants corresponding to the particle size distribution. The diffracted beam intensity I is proportional to n^2 , so its relaxation time $\tau_d = \tau/2$. In this sense the relaxation measurements of the diffraction intensity curves allow to determine the particle size distribution function. Substituting the values of the water viscosity $\eta = 1$ centipoiss ($0.001\text{N} \cdot \text{s}/\text{m}^2$) and of the space frequency of the optical (temperature) grating $\Omega \sim 6 \cdot 10^4 \text{m}^{-1}$ (corresponding to the space dependence with a period of 100 nm order) into Eq. (8), the relaxation time constant τ for a liquid with particles 10 nm in diameter will be of seconds order. So it can be said that the colloidal particles' concentration relaxation is slower by few orders than the temperature distribution relaxation.

1.3. The influence of the temperature distribution upon the optical parameters of the medium. The temperature distribution affects also the refractive index of the medium, both due to its direct temperature dependence and due to the theoretically allowed dependence upon the particle concentration. The periodic heating of a colloidal liquid layer induces a space modulation of the sample optical thickness, that manifests itself in diffraction of the light passing through the sample. The diffracted beam amplitude depends upon the difference between the transmitted light wave phases at points with maximal and minimal temperature (i.e. upon the temperature modulation amplitude and the sample thickness).

If the phase difference between the places of maximal and minimal temperature is much smaller than 2π , the amplitude of the diffracted beam is the same as if the diffraction were caused by an amplitude grating with a relative modulation of transparency equal to the phase modulation. It follows from this that the amplitude of the diffracted beam created by a sample with a small amplitude of periodical temperature space modulation is

$$a_{\text{diffr}} = a_0 \Delta\phi = 2\pi a_0 n^{(T)} \frac{T_0 h}{\lambda},$$

where a_0 is the amplitude of the primary beam, $n^{(T)}$ is the temperature derivation of the refractive index at the wave-length λ and h is the sample thickness. So the diffracted beam intensity can be expressed by the relation

$$I_{\text{diffr}} = \left(2\pi n^{(T)} \frac{T_0 h}{\lambda} \right)^2 I_0. \quad (10)$$

The effect of the phase modulation due to the temperature dependence on the refractive index is combined with the effect of the transparency dependence on the particle concentration. So a simple observation of the diffracted beam amplitude cannot answer the question what role play the phase and the amplitude modulations at diffraction. However, the difference between the time dependencies of the temperature relaxation and the particle concentration relaxation allow to answer this question, but only if the phase modulation is supposed to be dominantly caused by the refractive index temperature dependence. Thus, the time dependence of the rise or decay of the grating after putting on or off the temperature space modulation allows to determine important values of the parameters of self-diffraction and in such a way to verify the adequacy of the used description.

1.4. The experimental set-up and results. The experimental set-up used for the self-diffraction investigation consists of a Zeiss Ar laser ILA (120 working with 0.514 or 488 μm), a beam splitter, a mechanical shutter, a sample of magnetic fluid consisting of Fe_3O_4 -nanoparticles dispersed in various media (kerosene, water, mineral oil), and a photo detector connected to PC. The beam splitter gives two coherent beams providing an interference field in the place of the sample. It allows to adjust the angle between the beams in the range 0.002 – 0.1 rad, the distance between the beams can be 0.5 – 5 cm. The space period of the interference field used in the experiments ranges 5–200 μm . The shutter is able to interrupt one of the primary beams in 0.1 ms that allows to determine the time constants of signal decay in the range from fractions of millisecond up to long periods of time.

The used magnetic fluid samples were thin films bounded by two planparallel glass plates. Their thicknesses ranged from cca 5 to 50 μm , depending on the concentrations of used magnetic fluids. Typical curves of the diffracted beam intensity decrease, observed after interrupting one of the interfering primary beams, are presented in Fig. 1. These curves correspond to different illumination space periods. They include a fast exponential component with the time constant of the millisecond order corresponding to the decay of the periodic temperature distribution, and a slow exponential component with the time constant of the second order, corresponding to the diffusion relaxation of the colloidal magnetic particles distribution.

The majority of fluids have $n^{(T)}$ equal approximately to 0.0005 grad^{-1} (except water, where $n^{(T)} = 0.00008 \text{ grad}^{-1}$), so Eq. (10) can be used for estimating the periodic temperature distribution amplitude T_0 according to the relative amplitude of the diffracted beam fast component at known h and λ (if the temperature

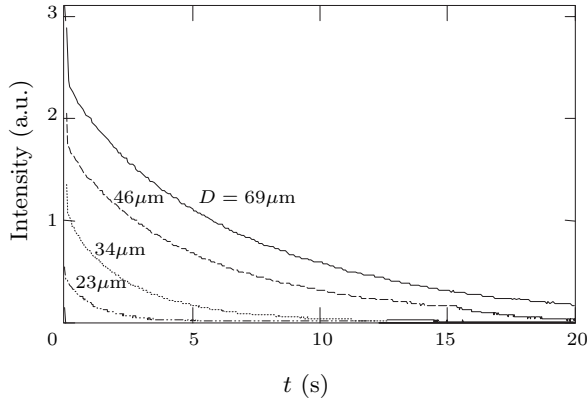


Fig. 1. Time dependencies of the diffracted beam intensity for different illumination space periods.

distribution relaxation is dominantly caused by the thermal conductivity between the points with maximal and minimal illumination). To estimate if the thermal conductivity (λ) or the heat outlet (λ') are crucial for the temperature distribution, the dependence of the fast component time constant upon the space period can be used.

The particle size distributions, obtained from relaxation measurements by Eq. (8) and Eq. (9) are presented in Fig.2. The dependencies of the slow and fast component decay time constants upon the space period D are presented in Fig.3.

It demonstrates that the experimentally obtained slow component dependence corresponds to a quadratic dependence following from Eq. (8), the fast component dependence does not match the quadratic dependence although its values are of the same order as the values following from the temperature distribution relaxation analysis. Thus, it can be said that the thermal conditions in the sample correspond to a semi-case, when the temperature relaxation is accomplished through both the thermal conductivity of the fluid and the heat outlet into the surrounding.

2. The influence of the heating process non-linearity.

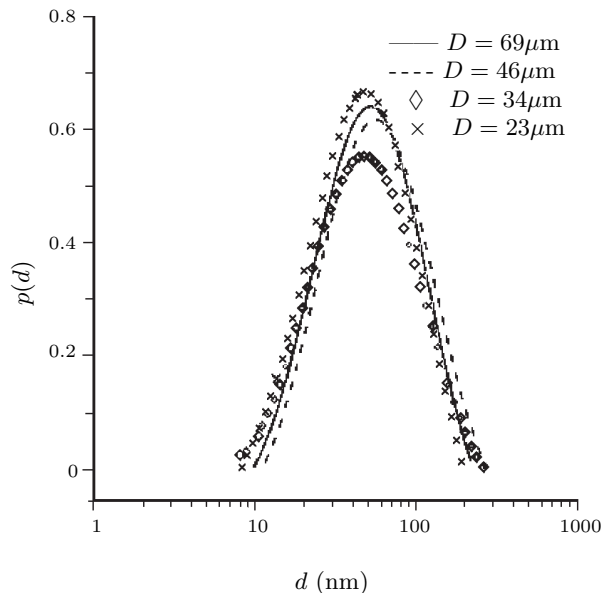


Fig. 2. Corresponding particle size distributions.

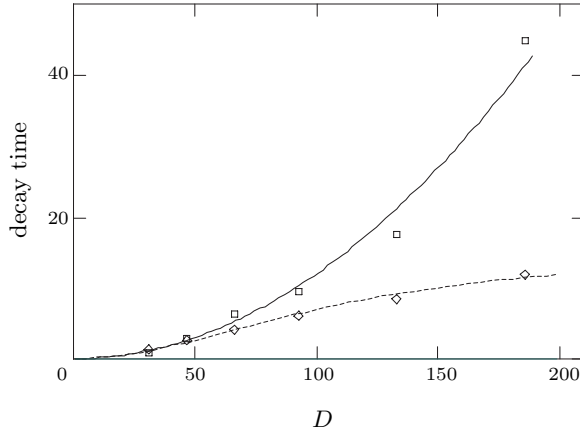


Fig. 3. Dependencies of the slow (\diamond) and fast (\square) component decay time constants upon the space period D .

2.1. The self-structuralization of the colloidal particles' concentration. At calculating the colloidal particles concentration distribution in the previous sections the temperature distribution was supposed to stay constant during the whole redistribution process. Such assumption is valid for low-intensity or short-time illuminations, when the concentration changes are small comparing to the initial values. However, large changes of the particle concentration influence the light absorption coefficient and hence the heating distribution also. Thus, the results of the previous chapter are no more valid. To estimate the influence of such non-linear process upon a thin film of a colloidal fluid, the following consideration can be made. Regarding the previous results, the time constant of temperature relaxation is much slower than that of concentration relaxation. It means that during the time needed to achieve an equilibrium temperature corresponding to a particle distribution, the changes of the particle distribution are negligibly small. Consequently, for slow changes of the particle concentration, the equilibrium temperature value corresponding to the particle distribution at the actual moment can be considered as an "instantaneous temperature". Thus, in equations describing the influence of the temperature distribution upon the distribution of particle concentration at intensive illumination, the equilibrium temperature may be used as expressed by Eq. (2). However, the space and time dependence of the colloidal particles concentration have to be considered here. Thus, at a harmonic distribution of heating, the formula

$$T_0 = \frac{I_0 \alpha_{n0}}{2(\lambda \Omega^2 + \lambda')} n(x, t)$$

may be written, where α_{n0} denotes an absorption coefficient corresponding to the unit concentration. If the heating perturbation is not harmonic, instead of the heating distribution space frequency Ω the space frequency value Ω_m , for which the Fourier projection of the considered non-homogeneity reaches its maximum, can be considered as a valid approximation of the real situation.

To simplify the next expressions, substitution of $K = \alpha_{n0}/2(\lambda \Omega^2 + \lambda')$ may be used, then the continuity equation gets the form

$$\frac{\partial n}{\partial t} = D_{\text{dif}}(1 + S K n I_0) \frac{\partial^2 n}{\partial x^2} \quad (11)$$

Although no exact solution of Eq. (11) will be given in this paper, this equation is useful for the description of the processes connected with intensive illumination of a colloidal liquid. For example, if there is a spot with a locally enhanced concentration n (and thus with locally enhanced heating at a constant light intensity



Fig. 4. An example of structuralization of the particle concentration in ionic water based ferrofluid, $pH = 2.9$.

I), according to Eq. (11), the time derivation of n will be non-zero in the spot. The sign of this derivation is given by the sign of the coefficient at the right site of the equation. The second derivation of n is negative in a maximum of n . Consequently, at a positive Soret constant the time derivation of n will be negative, because D , K , n and I_0 are always positive. It means that the locally enhanced concentration value will spontaneously decrease in time. Similarly at a point with a minimal concentration the concentration will spontaneously increase in time, so the concentration perturbation will vanish. However, if the Soret constant fulfils the inequality

$$S < -\frac{1}{K n I_0} \quad (12)$$

then an accidentally occurred concentration maximum will increase and a minimum – decrease. It means that a structure with "islands" of enhanced concentration can arise in a colloidal liquid with a negative Soret constant though the initially particle distribution is uniform because an instant fluctuation (which is always present) is amplified.

Eq. (11) not only explains (surprisingly easy) the self-structuralization observed in a colloidal liquid at intensive illumination (Fig. 4), but it also enables to express the character of the relation between the parameters of the structure creation process. This enables to estimate the characteristic dimension of the created structure.

In order to find the connection of the characteristic dimension of the structure with other parameters, the incident "incipient" concentration (or intensity) fluctuation can be expressed as the sum (or integral) of harmonic functions with different space frequency Ω values. Condition (Eq. (12) shows, after expressing K , that the harmonic component of the incident fluctuation will spontaneously increase if

$$\frac{1}{2}(-S) \alpha_0 I_0 > \lambda \Omega + \lambda' \quad (13)$$

where $\alpha_0 = \alpha_{0n} n_0$. This condition is easier fulfilled the smaller is Ω (the larger is the period of the corresponding harmonic component). However, Eq. (11) shows that for smaller Ω the spontaneous concentration changes much slower. So the generation of observable structures with smaller Ω needs a longer time.

To give an idea of the dependence of the time needed for development of the fluctuation upon its space frequency, let us consider the concentration fluctuations only for the case when the changes of concentration are much smaller than

the mean value n_0 . Using Eq. (12), this approximation enables to express the amplitude of the harmonic component \tilde{n} as

$$\frac{\partial \tilde{n}}{\partial t} = D_{\text{dif}} \left(1 + \frac{S \alpha I_0}{2(\lambda \Omega^2 + \lambda')} \right) \Omega^2 \tilde{n} \quad (14)$$

where α is $\alpha_0 n$. Eq. (14) shows that \tilde{n} will exponentially increase (or decrease) with the time constant

$$\tau = \frac{2(\lambda \Omega^2 + \lambda')}{\Omega^2 D_{\text{dif}} [2(\lambda \Omega^2 + \lambda') + S \alpha I_0]} \quad (15)$$

The character of dependence τ on illumination intensity and space frequency Ω given by Eq. (15) is illustrated in Fig. 5. The values τ are there multiplied by the diffusion coefficient and frequency ω and Ω is divided by ω , where ω is the space frequency, at which $\lambda \omega^2 = \lambda'$. The curve, corresponding to I_1 , shows the τ -dependence at so small illumination intensity, at which condition Eq. (13) is not fulfilled. The curves drawn for I_2 and I_3 gain negative values in regions, where condition Eq. (13) is fulfilled. It means that in these regions the structuralization of particle concentration may occur. It can be seen that for a more intensive illumination the region of space frequencies, at which the bond between the concentration fluctuation and its increase is positive, is larger and the time constant of the fluctuation increase is smaller.

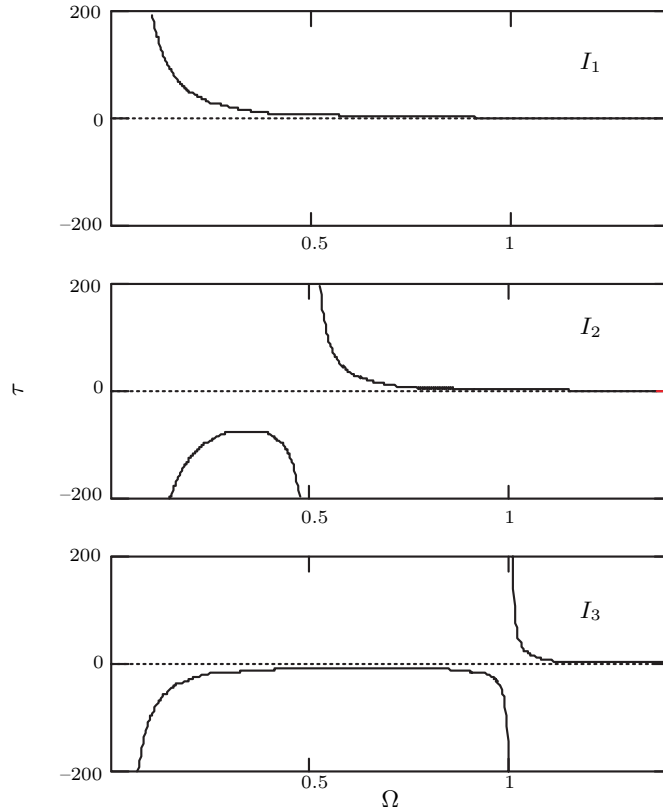


Fig. 5. The illustration of the τ -dependence on the space frequency Ω for three different illumination intensities $I_1 < I_2 < I_3$ ($f = 0.05$).

3. Conclusion. As a conclusion it can be said, that the results following from the presented description of the influence of the illumination caused fluid heating upon the refractive index and absorption coefficient are at least in semi quantitative agreement with the experimentally observed illumination consequences. Thus, it can be supposed that the change of the optical parameters of magnetic fluids induced by their heating is the real cause of the observed self-diffraction and self-structuralization of the colloidal particles' concentration. The existence of the fast and slow self-diffraction relaxation component shows that both the refractive index change caused by the temperature modulation and the absorption change caused by the change of the magnetic fluid particles' concentration take place in the performed experiments. The observed self-structuralization of the colloidal particles' concentration, as well as the existence of the higher orders maxima with a long time constant, created by intensive illumination, support evidence to the assumption about the negative value of the Soret constant in these fluids.

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