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# Self-organization of micro- and nanoparticles in ferrofluids

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**Abstract. The principles of specific self-organization of particles with formation of chains, layers or three-dimensional structures in ferrofluids under the action of external magnetic field are considered. It is shown that interactions between the particles depend on the magnetic field magnitude, and this fact can be utilized to control parameters of the self-assembled structures. The changes in the optical properties of ferrofluids upon the formation of such structures are discussed. The bibliography includes 118 references.**

## I. Introduction

Magnetic fluids are colloidal suspensions of ferromagnetic particles dispersed in liquids. Their behaviour and functional properties can be controlled by varying the parameters of the external magnetic field.[1–4]

There are two main types of magnetic fluids, ferrofluids (FF) and magnetorheological fluids (MRF). The first type of magnetic fluids represents stable colloids containing ~10 nm nanoparticles, they practically do not age and do not decompose; they remain liquid in a magnetic field and fully restore their characteristics when the field is disabled. Magnetorheological fluids contain ferromagnetic particles of larger size (up to several micrometres), they are prone to sedimentation and aggregation, but have an important property, namely, the ability to sharply change their viscosity (right up to solidification) under the influence of an external magnetic field.

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Magnetic fluids found wide use in technology in the second half of the 20th century, and since then, the interest in such fluids has not faded (Fig. 1). They are used for dynamic sealing of valves, heat dissipation and vibration damping, and for fabrication of magnetic coatings.

At present, new areas of application of magnetic fluids, mainly FF, are intensively developed, they are used in medicine for drug delivery, electromagnetic hyperthermia, as contrast agents in MRI diagnosis, for magnetic separation of cells, subcellular structures and proteins, in magnetic optics for the control of light intensity and wavelength and for construction of magnetic field sensors. In view of prospects for new applications of ferrofluids, it becomes necessary to use not only single-phase ferromagnetic particles as the dispersed phase of colloids, but also composite particles containing a magnetic material.

This review considers the processes of self-organization of magnetic micro- and nanoparticles in ferrofluids. Particular attention is paid to the effect of these processes on the optical properties of FFs. This review complements earlier publications devoted to various aspects of studies of magnetic fluids such as methods for synthesis of magnetic nanoparticles,[5] studies of magnetic and hydrodynamic

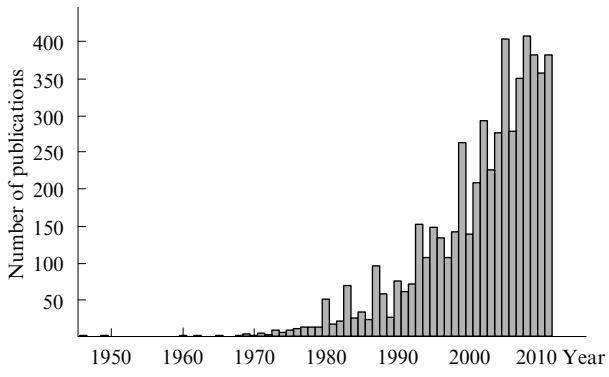



**Figure 1.** Diagram of variation in the number of publications devoted to magnetic fluids in the period from 1950 to 2010 (Web of Science data).

properties of magnetic fluids,[1] their structure,[6] fundamental properties and applications [3,7] as well as publications that discuss properties of FFs based on superparamagnetic particles,[8] their magneto-optical characteristics [9,10] and phase equilibria.[11]

## II. Composition, methods of synthesis and stability of ferrofluids

The behaviour of magnetic particles in colloid solutions is mainly determined by three types of interactions related to repulsion forces between the shells of magnetic particles or their charges, van der Waals attraction and magnetic dipole–dipole interaction, which may occur as either attractive or repulsive force.[11] The problems of increasing the stability of colloid solutions against sedimentation and aggregation are typical of colloid chemistry. In this review, the problem of stabilization of FFs is considered through the lenses of the magnetic dipole–dipole interaction inherent in them. For conventional (without specific interaction) colloid solutions, phenomena such as van der Waals interaction, Brownian movement and electrostatic interaction have been described in detail.[12,13]

As in the case of conventional colloid solutions, surfactants are utilized and/or electrostatic charges are created on particle surfaces to stabilize FFs. In addition, magnetic dipole–dipole interaction, which can result in particle aggregation, should be weakened in FFs. The energy of this interaction is inversely proportional to the cubed distance between the particles.[14] To keep the particles away from each other, it is possible to either coat them by a non-magnetic shell or embed them into a polymer.[15] If the particles are charged, they are repelled due to Coulomb interaction.

Thus, stable FF should resist the sedimentation in gravitational field, should not be concentrated under the action of magnetic field gradient, and its particles should not aggregate due to magnetic dipole–dipole or any other interactions. These requirements are usually fulfilled for sufficiently small ($\sim$10 nm) particles,[14] often existing in the superparamagnetic state. In this state, the dipole–dipole interaction energy is insignificant in comparison with the thermal energy, which determines intensive Brownian motion and flipping of magnetic moment vector inside the particles.

The magnetic dispersed phase is usually comprised of metals and intermetallic compounds (Fe, Co, Ni, FePt, CoPt), iron oxides ($Fe_3O_4$, $\gamma$-$Fe_2O_3$) and ferrites ($CoFe_2O_4$, $BaFe_{12}O_{19}$). The dispersed phase in FFs can form stable colloid solution due to electrostatic or steric stabilization, or their combination.[3]

The stability of FFs depends on the composition of the dispersion medium. In the case of electrostatically stabilized FFs, addition of an electrolyte results in weakening of the electrostatic repulsion because of shielding of the magnetic particles by ions.[16] The repulsion weakening in sterically stabilized FFs with nonpolar solvents occurs upon the addition of a polar solvent.[17] When repulsive forces are reduced to a certain level, a gas–liquid type phase separation occurs in the colloid system: the gas-like phase is depleted of magnetic particles, whereas the liquid-like phase is enriched with them.

The size of magnetic particles in FFs is usually $< 100$ nm; in contrast to macroparticles, they do not break up into several magnetic domains, but form one domain, in which all atomic magnetic moments are oriented in the same direction. Superparamagnetic and hard-magnetic particles with non-zero intrinsic coercive force can be distinguished among these ferromagnetic particles.

The magnetic moment vector in superparamagnetic particles does not retain its direction relative to the particle but randomly rotates due to thermal fluctuations. In a magnetic field, the average direction of the magnetic moment vector of such particles is along the field. Supraparamagnetic particles can be easily stabilized in a colloid solution because magnetic dipole–dipole interactions between them are slight and do not cause aggregation. This is why superparamagnetic particles are used most often for preparation of FFs.

Hard-magnetic particles are microscopic permanent magnets. Their magnetic moments are directed along easy magnetic axes or planes. Hence, in external magnetic field, floating particles are oriented in such a way that their easy magnetic axes coincide with the magnetic field direction. If the particles are secured (*i.e.*, if there is no rotational diffusion), reorientation of magnetic moments occurs only in large magnetic fields, with coercive force being up to hundreds of kiloamperes per meter. Single-domain particles have maximum coercive force at a non-zero energy of magnetic anisotropy energy composed of the energy of magnetocrystalline anisotropy and magnetostatic energy, the latter being determined by the particle shapes. The utilization of particles with strong shape anisotropy makes it possible to detect magnetic moment relative to the particle even in materials with low magnetocrystalline anisotropy. In comparison with superparamagnetic particles, hard-magnetic particles have larger volume and therefore larger spontaneous magnetic moment; this hampers stabilization of FFs due to strong dipole–dipole interactions.

Composite particles in which the magnetic component is embedded in a non-magnetic matrix represent more sophisticated items forming a dispersed phase. The size of such particles can vary widely. According to their structure, the composite particles (taking magnetic polymers as an example) [18] are classified into three groups:

— non-magnetic core coated by a shell of magnetic particles (Fig. 2 *a*);

— magnetic core coated by a non-magnetic shell (Fig. 2 *b*);

— magnetic particles evenly distributed in a larger non-magnetic particle (Fig. 2 *c*).

Additional functional properties can be introduced to FFs by a dispersion medium or inserted non-magnetic (paramagnetic or diamagnetic) particles to which the effect of an external magnetic field is transferred. Ferronematics [19–21] and ferrosmectics [22,23] can serve as examples.

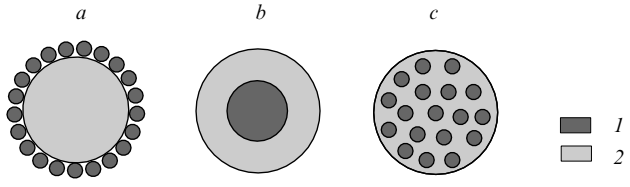



**Figure 2.** Typical structures of magnetic composite particles.[18] (*a–c*) See text; (*1*) magnetic phase, (*2*) non-magnetic phase.

The idea of using magnetic particles to improve magneto-orientational response was stated back in the 1970s.[24, 25] Because of the diamagnetism of liquid crystals, a rather strong magnetic field ($> 1$ T) must be applied to align them; however, if FF is introduced into liquid crystals, ordering occurs even in a $\sim 1$ mT field.[19] The magnetic particles whose shape reproduced the shape of the liquid crystal molecules turned out to be most effective.[26] The magnetic properties of thus obtained materials can be controlled by varying their electrical properties and *vice versa*.[27]

To prepare FFs, magnetic particles should be synthesized and stabilized in a liquid carrier. A classical method for the synthesis of magnetite FFs is co-precipitation from iron salt solutions in an alkaline medium.[28–31]

$$Fe^{2+} + 2\,Fe^{3+} + 8\,OH^- \longrightarrow Fe_3O_4 + 4\,H_2O$$

This method producing particles of $\sim 10$ nm size was studied in details using various iron salts and alkalis. Its drawbacks are the difficulty of preparing particles of $> 20$ nm and broad particle size distributions.[32] After the synthesis, the particles are usually modified by adsorption of surfactants on their surfaces followed by separation of surfactant-coated particles and washing away of the surfactant excess by magnetic decantation and centrifugation, and, finally, re-dispersing of particles in a liquid.[33] The use of non-toxic high-molecular-mass humic acids as surfactants[34, 35] afforded magnetic fluids that contained separate iron oxide nanoparticles or their aggregates enclosed into an organic shell.

An emulsion method was applied to prepare superparamagnetic nanoparticles of iron oxides and ferrites.[36] Oxide particles were dispersed in water and coated with citrate ions. The average size of the magnetic particle cores was 3–6 nm, and the mean standard deviation of the size was 20%–30%. The resulting FFs were stored without oxidation and aggregation for a week.

Hard-magnetic nanoparticles are microscopic permanent magnets with strong magnetic dipole–dipole interaction existing between them; therefore, their stabilization in FFs requires additional effort.

Barium and strontium hexaferrites are most widely used hard-magnetic materials. The authors of a series of studies[4, 37–42] attempted to obtain FFs on the basis of barium hexaferrite. With this aim, they synthesized nanoparticles of $BaFe_{12-2x}Ti_xCo_xO_{19}$ ($x = 0.8$ and 1.2) with a 8 nm size using the glass-ceramic method based on thermal crystallization of oxide multicomponent glass. The partial replacement of iron atoms by titanium and cobalt atoms was performed to decrease the magnetocrystalline anisotropy and to form particles with properties resembling the properties of superparamagnetic particles. To prepare the magnetic fluid, the nanoparticles were treated in a ball mill in the presence of oleic acid. Then a carrier liquid (dodecane or Isopar M, which is a mixture of aliphatic hydrocarbons) was added to the particles, and FF was separated by centrifugation. A stable magnetic fluid was formed only by particles with coercive force of $< 12$ kA m$^{-1}$.

For electrostatic stabilization of a colloid solution of hexaferrite particles, it is necessary to create a significant charge on their surface; this corresponds to high zeta-potentials (a few tens of millivolts). The potential was increased, as compared with the values observed for aqueous solutions of acetic acid,[43] by using dodecylbenzenesulfonic acid as a surfactant and alcohols as a dispersion medium.[44] The zeta-potential increased following decrease in the solvent polarity to reach a maximum (104 mV) in hexyl alcohol. Despite that, the particles precipitated quite fast due to magnetic interactions. Nevertheless, the stability of the colloids was sufficient to carry out electrophoretic coating by hexaferrite particles.

Hard-magnetic particles can efficiently be stabilized directly during their synthesis using, for instance, surfactants. For example, sterically stabilized disk-shaped $BaFe_{12}O_{19}$ nanoparticles 9–12 nm in diameter and $\sim 3$ nm thick were prepared by hydrothermal synthesis in the presence of oleic acid.[45] Ferrofluids were obtained by dispersing these nanoparticles in decane. However, the saturation magnetization of the magnetic nanoparticle ensemble was at most 1 A m$^2$ kg$^{-1}$ and coercive force did not exceed 30 kA m$^{-1}$. Thus, in fact, the stability of the FFs obtained was achieved by the decrease in magnetic dipole–dipole interaction.

In a series of studies,[41, 46–60] the glass-ceramic method was successfully applied to the synthesis of superdispersed strontium hexaferrite $SrFe_{12}O_{19}$. By varying the conditions of heat treatment of multicomponent glasses of various composition, ensembles of non-aggregated single-crystal nanoparticles of hexaferrite with the mean particle size from a few to hundreds of nanometers and rather narrow size distribution were formed. A specific feature of such particles was preservation of magnetic hardness even in particles of minimum size, while the coercive force varied from tens of kiloamperes per meter to record-breaking values exceeding 800 kA m$^{-1}$ (Ref. 54). To prepare FFs, the glass ceramics containing $SrFe_{12}O_{19}$ particles of $< 100$ nm in size was treated with an acid solution.[56, 59, 61] This treatment resulted in dissolution of matrix phases, while magnetic nanoparticles acquired a positive charge due to proton adsorption and formed a stable colloid solution. After performing coagulation and peptization, a pure aqueous solution of hard-magnetic hexaferrite nanoparticles was isolated. It should be noted that stable FFs containing rather large nanoparticles of $SrFe_{12-x}Al_xO_{19}$ (platelets with a thickness of 7 nm and a length of 50–100 nm) with strong coercive force (up to 445 kA m$^{-1}$) were prepared by this method.[61]

Magnetic fluids based on nanoparticles of magnetic metals and intermetallic compounds are usually prepared by reduction of derivatives of desired metals in high-boiling organic solvents in the presence of a surfactant with subsequent dispersion in aqueous or organic medium. Thus FFs based on spherical FePt particles of diameter 2–3 nm[62] and metallic cobalt nanoparticles of diameter 3–6 nm[36] were synthesized; the latter were extracted with oleic acid and dispersed in hexane. Highly anisotropic rod-like metal nanoparticles can be prepared by electrolysis of metal salts in an anodized alumina matrix.[63, 64] This method was successfully applied to form nickel nanorods, which were isolated after dissolution of the matrix in alkali solution in the presence of a surfactant with subsequent washing and dispersion in a liquid carrier.[65, 66]

Composite particles of the non-magnetic core–magnetic shell type can be obtained by polymerization of the Pickering emulsions in which a thin layer of solid nanoparticles is formed at the interface between a microdroplet of the dispersed phase and the surrounding medium.

To prepare composite particles with magnetic core and non-magnetic shell, magnetic particles can be coated with a polymer layer. This requires that a polymerization initiator be located on the surface of magnetic particles suspended in a monomer solution. In addition, by controlling the surface tension and phase separation effects, one can form shells of different shape coating the magnetic cores (Fig. 3).[67]

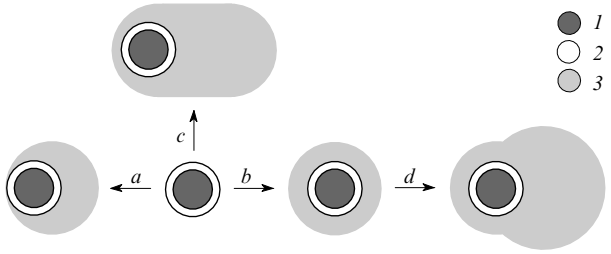



**Figure 3.** Scheme of the synthesis of the $Fe_3O_4-SiO_2$–polystyrene composite particles by emulsion polymerization.[67]
The morphology of the final product was controlled by changing the surface tension (*a*), replacing the cross-linking agent (*b*) and by performing simultaneous (*c*) or separated (*d*) stages of swelling and phase separation; (*1*) $Fe_3O_4$, (*2*) $SiO_2$, (*3*) polystyrene.

Composite particles consisting of non-magnetic matrix and small magnetic particles evenly distributed in its bulk are formed upon emulsion polymerization where the dispersion medium is a colloid solutions of magnetic particles in the monomer.

During emulsion polymerization, an internal structure can be formed in each composite particle under the action of an external magnetic field. Particularly, upon polymerization of an aqueous FF emulsion in the presence of a magnetic field,[68] chains of magnetic nanoparticles were detected in each polymeric microparticle.

The Stober process[69] is often used to obtain composite particles. For example, $Fe_3O_4$ particles coated by a $SiO_2$ layer were synthesized by hydrolysis of tetraethoxysilane (TEOS) in the presence of ammonia. The shell thickness was controlled by varying the relative amounts of magnetic particles and TEOS.[70] To attach a fluorescence marker to the composite particle surface, a dye containing the isothiocyanate group is first made to react with (3-aminopropyl)triethoxysilane; this leads to the formation of a covalent bond and opens a way for embedding the dye molecule into the silica shell upon hydrolysis. By carrying out hydrolysis in an emulsion, one can obtain spherical composite particles whose cores are aggregates of magnetic nanoparticles.[71]

Another interesting example of synthesis of composite particles includes the use of amorphous red selenium as a non-magnetic matrix.[72] By varying the temperature, it is possible to obtain both core–shell type particles and magnetic particles distributed in a matrix by the same reaction (Fig. 4).

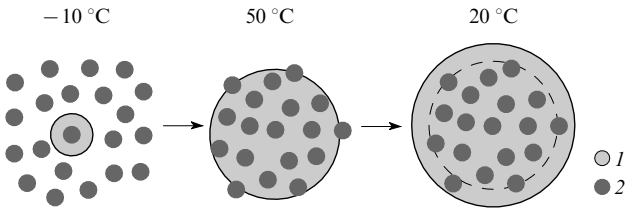



**Figure 4.** Scheme of the synthesis of composite particles from magnetite and selenium nanoparticles.[72]
Structures obtained at different temperatures are shown; (*1*) Se, (*2*) $Fe_3O_4$.

## III. Self-organization of magnetic nanoparticles in ferrofluids

In a magnetic field, a single particle is oriented in such a way that its magnetic moment is directed along the magnetic field. If the applied magnetic field is not uniform, the particle experiences a force directed along the magnetic field gradient. The dipole–dipole interactions arise between the particles. Depending on the relative orientations of the magnetic moments and the particles, these interactions can be attractive or repulsive (Fig. 5).

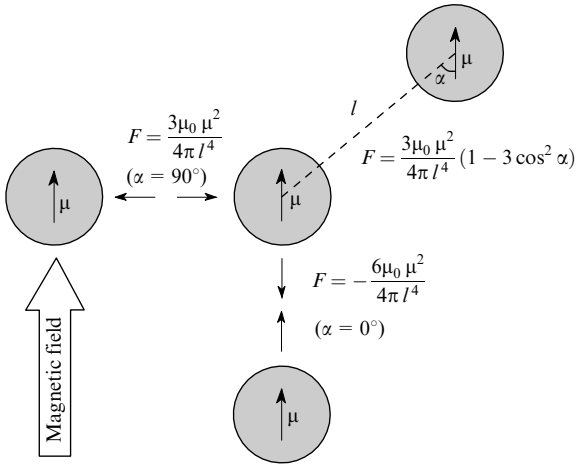



**Figure 5.** Magnetic dipole–dipole interaction between magnetic particles depending on their relative positions.
$\mu$ is the magnetic moment of a particle, $\mu_0 = 4\pi \times 10^{-7}$ H m$^{-1}$, $F$ is the interaction force between the particles (positive and negative values correspond to repulsion and attraction, respectively).

The magnetic dipole–dipole interactions between the particles of the dispersed phase may give rise to self-organized structures such as chains, layers or three-dimensional objects.[73] If a superparamagnetic substance, in which interaction between the particles depends on the magnitude of the applied magnetic field, is used as a magnetic phase, it becomes possible to control characteristics of the self-organized structure. Organization of paramagnetic and diamagnetic particles in FFs is also observed, in addition to the self-organization of magnetic particles. This process depends on the magnetic susceptibility of FFs, an additional parameter which can be set by changing the concentration of magnetic particles in the solution.

### 1. Self-organization at the macro level

The interaction of concentrated solutions of magnetic nanoparticles with a magnetic field results in surface instability of magnetic fluid[1] and gives rise to the Rosensweig effect

consisting in that the surface of a magnetic fluid is curved toward the magnetic field lines to form spikes. This effect can be observed for both aqueous magnetic fluids [74] and those based on organic solvents [75] (Fig. 6). Using a magnetic field of a complex configuration, one can form surfaces of magnetic fluids of different shape consisting of spikes of different size. Usually, a 50 mT magnetic field (which can easily be obtained using a permanent magnet or a moderate electromagnet) is sufficient to resist gravitation and to cause the spike formation.[7]

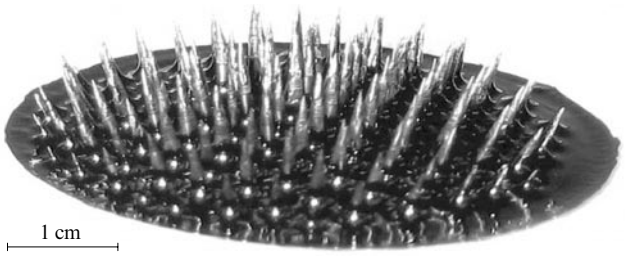



**Figure 6.** Ferrofluid surface curved in a magnetic field.[75]

If a magnetic fluid is placed in a uniform magnetic field, the spikes form a hexagonal structure, the distance between them (the parameter of the structure) can be controlled by changing the applied magnetic field.[76] If a magnetic fluid is placed together with an immiscible non-magnetic liquid between two parallel plates to restrict its surface changes, then, in addition to the hexagonal [77] and double hexagonal [78] structures, one can obtain a multi-point star shape or a labyrinth structure [76, 79] (Fig. 7).

In a rotating magnetic field, dissipative self-organization takes place [80, 81] leading to formation of dendrite structures with the centre at the magnetic field rotational axis. If a field rotating in the horizontal plane and a constant vertical field are applied simultaneously, structures representing the combination of the dendrite and labyrinth structures are formed.

The deformation of magnetic fluid surfaces under the influence of a magnetic field is suggested to use to create mirrors with a variable surface shape.[82] According to authors' opinion, such mirror composed of a magnetic fluid coated by a layer of silver nanoparticles would be free from aberrations and could substitute gallium and mercury mirrors employed in telescopes.[82]

## 2. Self-organization at the level of particle ensembles

Under the influence of an external magnetic field, droplets of a concentrated magnetic fluid in an aqueous emulsion are aligned along the magnetic field lines and form chains.[83, 84] Parameters of this structure depend on the magnetic field magnitude.

The formation of three-dimensional ordered structures composed of layers of hexagonally packed particles was detected in a cobalt nanoparticle-based magnetic fluid in a $\sim 1$ T magnetic field by small-angle polarized neutron scattering and X-ray-based method using synchrotron radiation.[85] The magnetization vector of each particle in the layers is aligned along the magnetic field. The distance between the layers depends on the concentration of magnetic particles in the magnetic fluid.

Chain and labyrinth structures extended along the magnetic field lines can be formed in a thin layer (several tens of micrometers) of FFs depending on the magnetic field magnitude.[86–89] For instance, disk-like structures characterized by rather broad size, shape and interparticle distance distributions were formed in FFs based on cobalt nanoparticles in a magnetic field ($\leqslant 0.01$ T) orthogonal to the substrate.[36] In the magnetic field in the range of 0.01 – 0.47 T, an ordered hexagonal structure of rods composed of magnetic particles is formed (Fig. 8 *a*), the rod

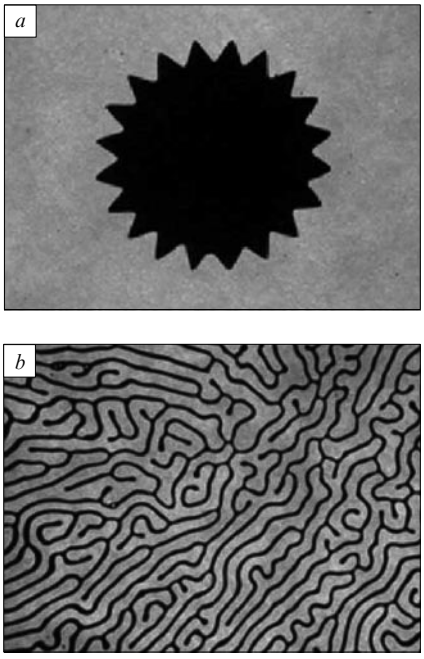



**Figure 7.** Star-shaped ferrofluid droplet in a 120 mT magnetic field (*a*) and a labyrinth structure in a 25 mT field (*b*).[76]

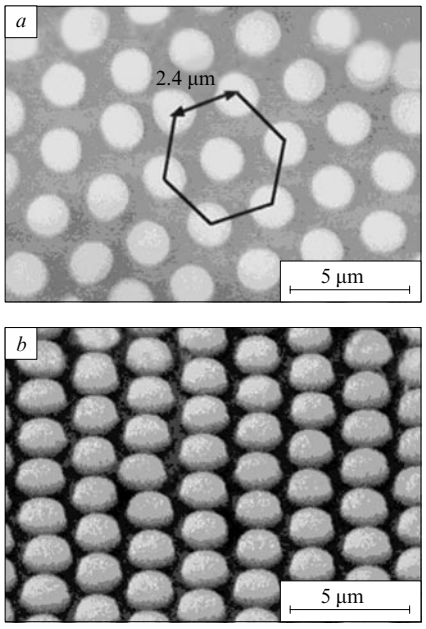



**Figure 8.** Superlattice formed upon evaporation of a ferrofluid based on cobalt nanoparticles in a magnetic field (0.27 T) orthogonal to the substrate.[36]

diameters and the distances between them decreasing with the increase of the magnetic induction (Fig. 8 *b*). Worm-like and labyrinth structures are formed in the magnetic field below 0.47 T (Fig. 7 *b*). In a field of 0.78 T and above, the formation of an ordered labyrinth structure is observed.[36]

The phenomenon of self-organization of magnetic nanoparticles in the thin layers of magnetic fluids was suggested for lithography applications.[90] An FF layer was placed in a magnetic field oriented orthogonally to the substrate. This gave vertical rods consisting of magnetic nanoparticles. The rods played the role of mask upon UV irradiation. As a result, a lithographic imprint was obtained which represented the projection of these rods on the substrate plane. The distance between the rods and hence their imprints depended on the magnetic field magnitude and the thickness of the magnetic fluid layer and was between 2 and 6 μm. In addition, the formation of imprints in the form of rings, rather than circles was observed.

In addition to self-organization of ferromagnetic particles, self-organization of non-ferromagnetic (paramagnetic and diamagnetic) particles can be observed. The interactions of non-ferromagnetic particles in FFs can be described by ascribing to them some effective magnetic moments relative to FF.[91] In this case, a diamagnetic particle would have quite a large effective magnetic moment directed against the magnetic field. Consequently, an appreciable interaction arises between such particles, and it can be calculated like the conventional magnetic dipole–dipole interaction, but with the use of the effective magnetic moment of the particle relative to FF.[91] Diamagnetic particles in FFs can be attracted or repelled depending on the angle between the line connecting the centres of the particles and the magnetic field direction.

Under the action of a magnetic field directed orthogonally to the FF layer containing non-magnetic particles, the latter form a hexagonal structure.[8] If the field is directed along the layer, the chains of non-magnetic particles are formed.

It was suggested[92] to use the self-organization of non-magnetic particles in FFs for the synthesis of photonic crystals. In strong magnetic fields with large magnetic induction gradient, three-dimensional photonic crystals of high quality were obtained. Because of large gradient, diamagnetic particles are concentrated in the areas with the weakest magnetic field. Efficiency of such self-assembly can be explained by that the diamagnetic particles initially form linear chains, which then form three-dimensional structures.

If FFs are dried up on a substrate, two- and three-dimensional structures arise.[93,94] Two-dimensional structures of magnetic nanoparticles are promising as media for data storage. If FFs are dried in the presence of the magnetic field directed along the substrate, fibres aligned along magnetic field lines are formed.[95] The fibre thickness decreases with increasing magnetic field. By utilizing particles with non-magnetic shells, one can obtain one-particle-thick chains due to a decrease in the interaction forces between neighbouring particles.[96] In the absence of a magnetic field, these chains are closed up, the length of the chains depends on the concentration of particles in the ferrofluid.

Applying a magnetic field during vertical deposition of ellipsoidal magnetic particles, a colloidal crystal can be obtained from FF (Fig. 9). In a magnetic field, ellipsoidal particles are oriented along the field; therefore, they are oriented uniformly in the formed structure; this cannot be achieved without a magnetic field.[97]

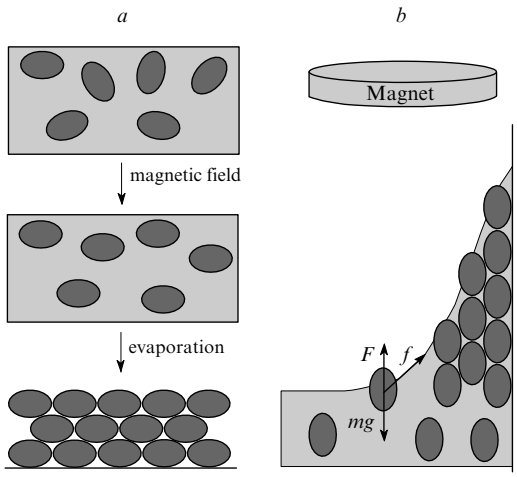



**Figure 9.** Schematic representation of the assembly of photonic crystals from a magnetic fluid based on magnetic composite ellipsoidal particles under the action of a magnetic field by horizontal (*a*) and vertical (*b*) deposition techniques.[97]
*F* ia the interaction force between the magnet and a particle; *mg* is the particle gravity force; *f* is capillary force.

### 3. Self-organization at the level of individual particles

The effective magnetic moment of a paramagnetic (weakly magnetic) particle dispersed in a ferrofluid depends on the effective magnetic susceptibility of the ferrofluid, which is determined by the concentration of magnetic nanoparticles and their magnetic properties.[98] When the concentration of magnetic particles changes, the magnitude and sign of the effective magnetic moment of the non-ferromagnetic particles also change, and this leads to changes in interaction between them. Therefore, it is possible to change the 'apparent behaviour' of paramagnetic particles from paramagnetic to diamagnetic by increasing the concentration of magnetic particles in FFs. By combining this approach with the use in FFs of paramagnetic particles of several types differing in their size and magnetic susceptibility, one can obtain certain structures consisting of several particles.[99] For example, let a fluid contain particles of two types, *viz*., particles A, large particles with high magnetic susceptibility, and particles B, small particles with insignificant magnetic susceptibility. When the concentration of FF is low, the particles of both types exhibit paramagnetic properties, particles B being attracted to the poles of particles A. If the concentration of FF is increased so that its magnetic susceptibility becomes higher than that of particles B, the latter become diamagnetic relative to FF and will be attracted to the equators of particles A The use of particles of several types extends the range of possible structures.

## IV. Magnetooptical characteristics of ferrofluids

Considerable attention has been paid to the study of the birefringence effect in FFs.[9,100] Below we will consider the effects related to changes in light transmission in a magnetic field, such as linear dichroism, diffraction and formation of non-transparent aggregates.

A magnetic field changes both reflection and transmission spectra of FFs. The reflection spectra can be affected by diffraction in the FF structure or in the structure of an individual composite particle as well as by ordering of diamagnetic micromirrors in FFs. If a dispersed phase is formed by anisotropic magnetic particles, a uniform orientation of these particles occurs under the influence of a magnetic field, resulting in anisotropy of the dielectric permittivity tensor and appearance of linear dichroism. Depending on the magnetic field magnitude, the parameters of the FF structure which define its optical properties change.

## 1. Anisotropy of optical properties of ferrofluids related to the particle shape

A magnetic field applied to FFs containing dispersed nonmagnetic micromirrors can align the latter along the field.[101] Therefore, if the magnetic field is oriented along the light direction, the micromirrors almost do not reflect it; when the magnetic field is orthogonal to to the light direction, micromirrors reflect the light, and the FF becomes virtually non-transparent. A model of a monochrome monitor was designed on the basis of such FF.[101] Plates of metallic aluminium of thickness 40 nm and 1–15 μm in diameter were used as micromirrors. The resulting ferrofluid contained magnetite (0.016 mass %) and micromirrors (0.06 mass %). To prevent the aluminium particles from sedimentation, a high-density liquid, a mixture of toluene with diiodomethane, was used. Under the influence of a magnetic field, a 20% increase in optical transmission of a 200 μm layer of this FF occurs virtually in the whole visible region.

Another mechanism of interaction with light is implemented in FFs based on magnetic particles with a shape anisotropy. In a magnetic field, the anisotropic particles are aligned; thus, the preferential direction arises in the FF and determines the anisotropy of its optical properties.[102] Since the wavelength of the commonly used electromagnetic radiation exceeds, as a rule, the typical particle size, FFs represent practically homogenous media for the light. The optical anisotropy occurs due to anisotropy of dielectric permittivity tensor resulting from the difference in depolarization factors[103–105] along different directions in a particle. When polarized light goes through a layer of oriented particles, the transmission depends on the orientation of the electric component of the electromagnetic wave relative to the anisotropic particle. The maximum absorption occurs when the plane of polarization is parallel to the direction along which the particle has the largest size, whereas the minimum absorption occurs if the vector of electric field strength of the electromagnetic wave is parallel to the direction along which the particle has the minimum size.

For instance, under the influence of a magnetic field, nickel nanorods in FF are aligned along the field.[65] The nanorods obtained by electrodeposition into the pores of anodized aluminium templates were 13 nm in diameter and and 40 to 160 nm in length. These nanorods are single-domain particles and have spontaneous magnetization directed along the longer axis. In the case of parallel orientation of the applied magnetic field relative to the electromagnetic wave electric vector, the minimum transmission was observed, whereas, if the orientation was perpendicular, the maximum transmission was obtained.[65] The ratio of the maximum transmission of the polarized light to the minimum transmission depended on the aspect ratio of the nanorods; for the incident light at 632.8 nm, this ratio reached 12. For comparison, the relative change in the optical density for conventional FF (magnetite in kerosene) in a 80 mT field was only several percent.[106] The transmission anisotropy increased with increasing aspect ratio.

When non-polarized light was used, transmission was maximized for parallel orientation of the light and the magnetic field vector, because in this case, the electric vector of the incident light was orthogonal to the external magnetic field. Depending on the particle size, saturation of the optical anisotropy occurred in the fields from 10 to 40 mT. These experimental data are described with a good precision by a theoretical model[65, 104, 105] considering polarizability of prolate ellipsoids in the quasi-static approximation and alignment of the magnetic moments of particles fastened along the longer axes of nanorods in an external magnetic field. The study of the transmission dynamics on switching-off the magnetic field showed that it can be described by an exponent with the time constant of 0.38 ms. This value is related to the constant of rotational diffusion of the nanorods, which is 439 $s^{-1}$. Due to lower viscosity of water in comparison to glycerol and by using smaller nanorods, the time constant was lowered by four orders of magnitude with respect to the value found in the previous study.[66]

## 2. Diffraction by self-organized structures

The diffraction by structures formed upon self-assembly induced by a magnetic field is considered in detail in a recent review.[107]

The formation of the hexagonal packing of rods in a thin layer of a magnetic fluid brings about diffraction of the transmitted electromagnetic radiation. Because of interference of the diffracted radiation, only light of a certain wavelength arrives at the detection point.[108] By varying the parameters of the hexagonal packing by changing the magnetic field, it is possible to select the desired wavelength of the incident beam, which may comprise waves from UV to microwave region. A change of the colour of the back-scattered radiation was observed when an aqueous emulsion of FF was used.[84]

The dependence of the reflection spectrum on the direction of the applied magnetic field is observed in magnetic fluids based on composite microparticles containing chains of magnetic nanoparticles extended in one direction.[68] It occurs because the composite particles are rotated by the magnetic field so that the chains become parallel to the magnetic field. If the magnetic field is directed along the light beam, a peak appears in the reflection spectrum; if the field is orthogonal to the beam, the peak disappears (Fig. 10). The position of the reflection peak depends on the size of magnetic nanoparticles and changes from the blue to red region of the spectrum.

This effect is due to light diffraction by the particle chains (Fig. 11). Upon light reflection from two neighbouring magnetic nanoparticles, a path difference $(\delta_1 + \delta_2)$ arises, its magnitude determines the position of the reflection peak. The path difference depends on the distance between particles ($d$), which is equal to the particle diameter if the particles are in contact.

Such effect was observed in FFs based on superparamagnetic nanoparticles of magnetite, which were submicron spherical aggregates $\sim$120 nm in diameter.[109–112] Under the influence of a magnetic field, a photonic structure was

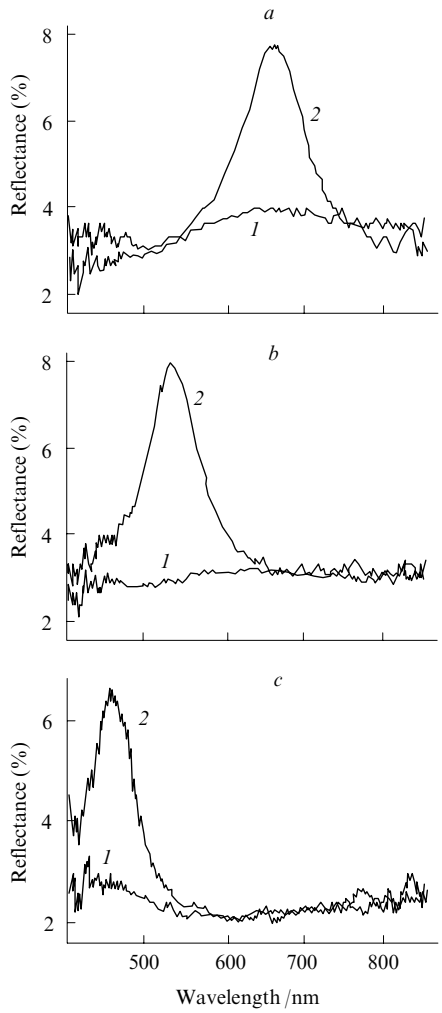



**Figure 10.** Reflection spectra of magnetic fluids on the basis of composite microparticles containing chains of magnetic nanoparticles extended in one direction with sizes of 197 (*a*), 154 (*b*), 127 nm (*c*).[68]
The magnetic field is orthogonal (*1*) and parallel (*2*) to the incident light.

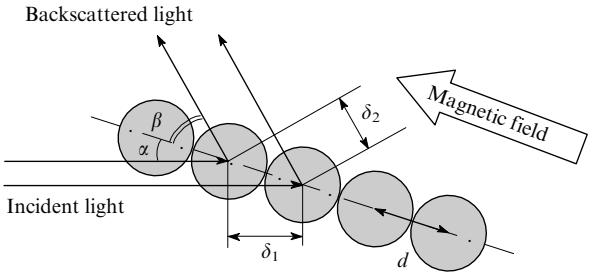



**Figure 11.** Schematic representation of the interaction of light with an assembly of ordered magnetic nanoparticles inside a composite microparticle.[68]
$\delta_1 = d\cos\alpha$, $\delta_2 = d\cos\beta$.

formed, which was characterized by a high regularity in the aggregate positions in chains along the magnetic field lines. The structure parameter decreased with increasing magnetic field. Particularly, with an increase in the magnetic induction from 8.8 to 35.2 mT, the distance between the aggregates decreased from 274 to 169 nm, resulting in changes in the reflection spectra of the FF. The colour of the magnetic fluid changed in the whole visible region with the change in the applied magnetic field. The reflection intensity depended on the wavelength and was 8%–42%. The maximum reflection was observed in the wavelength range of 570–640 nm . Alternating switching on and off of the magnetic field with a frequency of 2 Hz induced periodic changes of the reflection spectrum. Therefore, the self-organization process lasted a split second.

Another approach was used by He *et al.*;[92] it was based on self-assembly of non-magnetic polymeric particles in FF under the influence of a magnetic field. Utilizing an aqueous FF with concentration of superparamagnetic magnetite particles of 4 vol.%, the authors succeeded in self-assembling polystyrene particles of diameter 185 nm in a photonic crystal. When a non-uniform magnetic field was applied to the sample, a small peak at 563 nm first appeared in the reflection spectrum due to the formation of polystyrene particle chains. As soon as a minute later, the peak shifted to 533 nm, the reflection maximum was 25%. Subsequently, during the formation of the photonic crystal, the peak intensity grew to reach 83% within 6 min after the magnetic field was switched on.

Magnetic fluids based on spherical aggregates of superparamagnetic nanoparticles were proposed for the use as colour inks.[113, 114] The printing process consists in polymerization of FF areas under UV laser irradiation in the presence of a magnetic field determining the colour. This process affords high-resolution full-colour images, utilizing only one material as the ink.

## 3. Self-assembly of non-transparent particle aggregates in a magnetic field

The optical transmission of a thin layer (0.3 mm) of a magnetite-based FF strongly changed under the influence of a magnetic field;[115–117] this fact is attributable to microstructural changes in the FF. Initially, magnetic particles are evently distributed in the FF (Fig. 12). When a weak (2 mT) magnetic field is applied, short chains aligned along the magnetic field are first formed. Since the cross-sectional

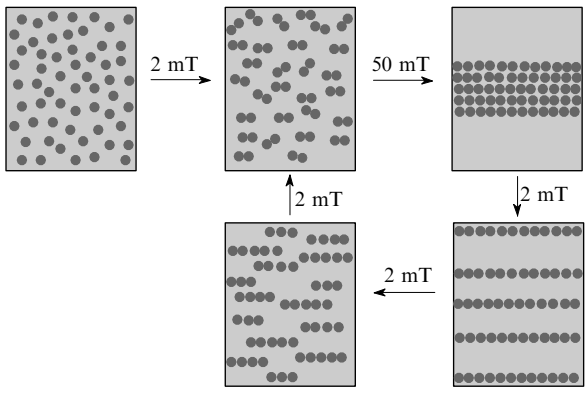



**Figure 12.** Schematic representation of microstructural changes in a ferrofluid film.[115]
A magnetic field is applied along the optical path (from left to right).

area of the solution decreases being covered by the particles, the optical transmission of the solution increases. Upon further strengthening of the magnetic field, the short chains are assembled into larger aggregates. Probably, due to significant scattering of light on these aggregates, the transmission strongly decreases. Then, if the magnetic field is switched off, the chins dissipate due to thermal motion, and the system returns to the state characterized by the presence of short chains in the solution.

The transmission depends on both the FF concentration and the applied magnetic field strength. In the case of FFs with the concentration of magnetic particles of 0.1 vol.%, transmission decreases by a factor of 3 (50 mT) to 5 (130 mT). With the increase of the concentration to 0.3 vol.%, transmission in the magnetic field decreases virtually to zero. In the case of a strong structural rearrangement (necessary to change the optical transmission), the characteristic time of the FF response to the magnetic field action is $\sim 10$ s. Apart from the rather long response time, the system behaviour depends on its prehistory. With each new cycle of the field switching, transmission in the absence of the field increases, that in the presence of the field decreases, and the time of switching between these states increases.

A change in the absorption coefficient was observed [118] in an aqueous FF based on 6 nm magnetite particles stabilized by a double lauric acid layer. An increase in the absorption coefficient up to 70% occurred in a magnetic field. In contrast to the previous system, the system rearrangement time upon the the field switching on was much longer, about 100 s, while the system relaxation time upon switching off the field was again 10 s.

* * *

The considered studies of self-organization processes in magnetic fluids under the influence of an external magnetic field indicate that considerable progress has been achieved in the synthesis of optical FFs, in understanding of their functional properties and in their practical applications. The greatest advance was made in the creation of magnetically controlled photonic structures based on isotropic particles or their aggregates, they are promising materials for the use as optical switches, detectors of magnetic field, magnetic inks and displays. At the same time, FFs based on anisotropic nanoparticles demonstrate more interesting and faster optical effects occurring in weaker magnetic fields and depending on the light polarization. These FFs can be magnetic analogues of liquid crystals. However, to implement this idea, it is necessary to synthesize monodisperse magnetic nanoparticles with maximum anisotropy and large magnetic moments and prepare stable FFs based on them.

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