NEEDLE-LIKE MAGNETIC CLUSTERS IN MAGNETIC FLUID AND THEIR BEHAVIOR IN MAGNETIC FIELD

O.A. ANTONYUK, V.F. KOVALENKO, B.M. MOLDOVAN, M.V. PETRYCHUK

Taras Shevchenko Kyiv National University, Faculty of Radiophysics
(2, Academician Glushkov Prosp., Kyiv 03122, Ukraine)

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The application of a magnetic field with gradient to a magnetic fluid put into a round capillary allows us to experimentally create the periodic structures of needle-like clusters composed of magnetic particles. The period of such a structure can be varied in some boundaries under the influence of a magnetic field. Needle-like clusters are free to rotate in the external magnetic field by repeating its direction. With increase in the magnetic field, the periodical structure transforms into a hexagonal lattice of clusters. The fact of coincidence of the experimental results with the results of analytic description within the model we suggest to explain the behavior of magnetic clusters in magnetic fields proves the legitimateness of such a model.

Introduction

Magnetic fluids (MF) are the colloid solutions of small magnetic particles in a fluid-carrier which have recently attracted a considerable attention (see, e.g., [1]). This is related, in particular, to the studies in the field of photonic crystals [2], but the range of applications of MF is significantly wider [3].

One of the peculiarities of MF is the cohesion of its particles in clusters which can be considered as the initial stage of the transition of MF to the solid state or of the precipitation of magnetic particles. The appearance of clusters (the agglomeration of particles) and the mechanisms of the interaction of particles в MF have been comprehensively studied (see, e.g., [4]). The appearance of clusters in MFs is undesirable in a number of their applications. This concerns the usage of MF as lubricants, printing inks, damping fluids, coolers, and thickeners and other cases where the stability of MF's characteristics is important for the preservation of its hydrodynamic parameters. Therefore, a great attention was always paid to the methods of elimination of the phenomenon of agglomeration of particles. However, just the presence of clusters in MF allows one to use MF, in some cases, for the other purposes. The visualization of magnetic force lines, magnetic inhomogeneities in a material, and magnetic domains, the operation of optical shutters, the use of MF for the creation of photonic crystals, and a number of other applications of MF gain ground due to such a "nonideal" behavior of MF. We also note that the design of photonic crystals is also based on the use of MF's clusters, namely on the phenomenon of their spatial ordering which appears most frequently under the action of an external magnetic field [14].

The creation of clusters is based on the dipole-dipole interaction of magnetic nanoparticles and is hampered by thermal oscillations of molecules of the fluid-carrier. Therefore, the greater the size of magnetic particles, the stronger the clusterization. The threshold size of nanoparticles, at which the probability of creation of clusters becomes significant, is about 10 nm [3]. Upon the switching-on of an external magnetic field, the probability of clusterization grows. In this case, the created cluster is a magnetic dipole, whose magnetization direction coincides with the field direction.

The mechanisms of creation and the parameters of spatially ordered clusters in thin films of magnetic fluids were studied in a number of works [8, 11—13]. Their authors considered mainly the case where a magnetic field is applied normally to the film area, and clusters are positioned, analogously to cylindrical magnetic domains in thin magnetic films, at sites of a 2D hexagonal lattice. Such a distribution is most dense.

Here, contrary to the above-mentioned works, we study needle-like clusters freely growing in MF. To ensure the free growth of clusters and to arrange them in a series, we used glass capillaries with round cross-section as reservoirs for MF.

A goal of our studies was to determine the conditions, under which the magnetic clusters of MF are arranged in a capillary according to a prescribed order.

1. Theory

Here, we take into account the dipole-dipole interaction of clusters and their interaction with an external magnetic field and consider the dipoles to be point-like.

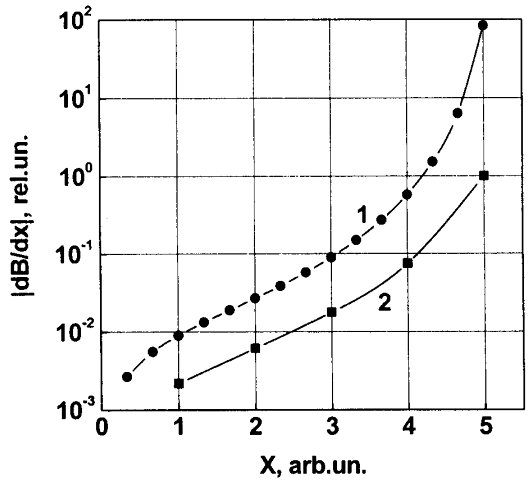

Fig. 1. Sum (3) (at $n = N$) vs the coordinate x for two cases: $2N + 1 = 31$, $n = 1, ..., 15$, (curve *1*) and $2N + 1 = 11$, $n = 1, ..., 5$ (curve *2*)

We analyzed the static case, therefore the viscosity of MF was omitted.

The mutual position of magnetized clusters in a magnetic field is defined by the dipole magnetic interaction of clusters one with another and by the action of the boundary between the magnetic fluid and the nonmagnetic glass wall of a capillary on clusters. Of a great interest is the periodic arrangement of clusters. To determine the conditions for the creation of similar structures, we used a model analogous to that describing a periodic structure of cylindrical magnetic domains in the 1D case.

The interaction energy of two point-like magnetic dipoles with magnetic moments $\vec{m}_1$ and $\vec{m}_2$ is

$$V_{12} = \frac{\vec{m}_1 \vec{m}_2}{\left|\vec{R}_{12}\right|^3} + \frac{3\left(\vec{m}_1 \vec{R}_{12}\right)\left(\vec{m}_2 \vec{R}_{21}\right)}{\left|\vec{R}_{12}\right|^5},$$

where $\vec{R}_{12}$ is the displacement between a dipole with moment $\vec{m}_2$ and a dipole with moment $\vec{m}_1$, and $\vec{R}_{21} = -\vec{R}_{12}$.

Consider the system of $2N + 1$ magnetic dipoles with identical magnetic moments $|\vec{m}_i| = m$ positioned on the Ox axis at the points with coordinates x_i, where $i = 1, ..., 2N + 1$. The dipoles are in a constant inhomogeneous magnetic field $\vec{H}(x)$ directed along the Oy axis, and m is the magnetic moment of a saturated cluster. Therefore, m does not depend on H. If we consider only the interactions of each dipole with the inhomogeneous magnetic field $\vec{H}(x)$ and with the other $2N$ dipoles, the total energy of the system is

$$E = \sum_{j=1}^{2N+1} \left(\sum_{\substack{i=1 \\ i<j}}^{2N+1} \left(\frac{\vec{m}_i \vec{m}_j - 3\left(\vec{m}_i \vec{e}_x\right)\left(\vec{m}_j \vec{e}_x\right)}{\left|x_i - x_j\right|^3} \right) \right) - \sum_{j=1}^{2N+1} \vec{m}_j \vec{H}\left(x_j\right), \quad (1)$$

where $\vec{e}_x$ is a unit vector along the Ox axis.

Assuming that all dipoles are directed along the magnetic field $\vec{H}||Oy$ $(\vec{m}_i \vec{e}_x = 0)$, we get the system of equations for the coordinates of dipoles x'_s, $s = 1, ..., 2N + 1$, which correspond to an equilibrium state of the dipole system:

$$\left(\frac{\partial E}{\partial x_s}\right)_{x_s = x'_s} = -\sum_{\substack{i=1 \\ s \neq i}}^{2N+1} \left(3\vec{m}_i \vec{m}_s \frac{(x'_s - x'_i)}{\left|x'_s - x'_i\right|^5} \right) + \vec{m}_s \left(\frac{\partial \vec{H}(x_s)}{\partial x_s}\right)_{x_s = x'_s} = 0, \quad s = 1, ..., 2N + 1. \quad (2)$$

Consider the case of a uniform distribution of clusters along the Ox axis. The requirement of periodicity of the equilibrium structure, $x'_s = na$, and system (2) yield the necessary values of $(\partial \vec{H}/\partial x)_{x'_n}$ $(n = s - N - 1, \quad n = -N, ..., N)$:

$$\left|\frac{\partial \vec{H}}{\partial x}\right|_{x'_n} = \frac{3m}{a^4} \sum_{\substack{i=1 \\ i \neq n+N+1}}^{2N+1} \frac{(n - (i - N - 1))}{\left|n - (i - N - 1)\right|^5},$$

$$\left|\frac{\partial \vec{H}}{\partial x}\right|_{x'_n} = \frac{3m}{a^4} \sum_{t=-n+1}^{n} \frac{1}{(N + t)^4}, \quad n > 0. \quad (3)$$

In the last sum, we omitted the terms which are mutually nullified and correspond to the forces affecting the n-th dipole from the side of the dipoles symmetrically positioned relative to it.

The results of calculations of sum (3) as a function of the coordinate x are given in Fig. 1. There, we present the dependences for $x \geq 0$. At $x < 0$, the plot is symmetric relative to $x = 0$. The coordinates of points correspond to the positions of clusters.

The results of calculations allow us to conclude that, in order to create a prescribed spatial distribution of magnetic clusters, it is necessary to apply a field with the corresponding distribution of its intensity over the coordinate along the series of clusters. As a peculiarity of such a distribution, we mention the presence of a gradient which sharply increases in the absolute value on the periphery of a group of clusters. It is obvious that only in this case is created a force counteracting the force of mutual repulsion of magnetic dipoles.

For nonpoint-like dipoles with a constant length h identical for all dipoles, we can estimate a correction to sum (3).

The exact formula for the interaction force of two parallel dipoles with length h, which are positioned on the line normal to their dipole moments, looks as

$$F = 2\left(\frac{q^2}{R^2} - \frac{q^2}{(R^2+h^2)}\frac{R}{\sqrt{R^2+h^2}}\right) =$$

$$= \frac{3q^2h^2}{R^4} - \frac{15q^2h^4}{4R^6} + O\left[h^6\right], \quad h \to 0. \tag{4}$$

Since $m = qh$, we get

$$F = \frac{2m^2}{h^2}\left(\frac{1}{R^2} - \frac{R}{(R^2+h^2)^{3/2}}\right) \tag{5}$$

for magnetic dipoles with length h. Substituting $R = (N+t)\,a$ in (5), we obtain that (3) becomes

$$\left|\partial\vec{H}\big/\partial x\right|_{x'_n} = \frac{2m}{h^2a^2}\times$$

$$\times\sum_{t=-n+1}^{n}\left(\frac{1}{(N+t)^2} - \frac{1}{\left((N+t)^2+(h/a)^2\right)^{3/2}}\right). \tag{6}$$

Such a substitution will not considerably influence the plots in Fig. 1, because the value of the sum is essentially defined by remote dipoles which can be considered as point-like ($(N+t)\,a >> h$). In particular, the influence of the adjacent dipole ($N+t=1$) is not compensated by the influence of the symmetrically positioned dipole only upon the calculation of the gradient of the field acting on the end dipole ($n = N$).

Here, we consider the magnetization of clusters to be constant. However, the experiment testifies to that clusters grow with the magnetic field induction and reach the saturation at its certain value.

Let's consider the dependence of the cluster form on the applied magnetic field, by using the condition of minimization of the energy of a single cluster. In this case, we assume that the external magnetic field is not considerably varied at distances comparable with the cluster size.

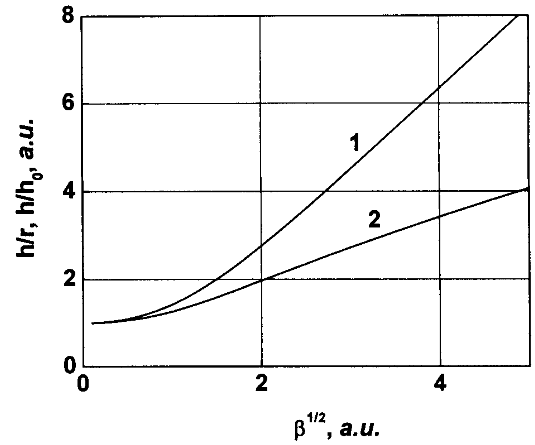

Fig. 2. Ratios of the cluster length to its diameter (curve *1*) and to the initial length (in the zero field) (curve *2*) vs $\beta^{1/2}$

Let σ be the energy necessary to create a unit area of the cluster surface, and let M be its magnetization. We assume that σ is an invariable value. Then the total energy of the cluster is

$$E = 2\pi\left(1-\varepsilon^2\right)\frac{\mathrm{arth}\varepsilon - \varepsilon}{\varepsilon^3}M^2V + \frac{\pi}{2}\left(\frac{6V}{\pi}\right)^{2/3}\times$$

$$\times\sigma\left[\left(1-\varepsilon^2\right)^{1/3} + \frac{\arcsin\varepsilon}{\varepsilon}\left(1-\varepsilon^2\right)^{-1/6}\right]. \tag{7}$$

The first term is the energy of the field of demagnetization of a spheroid magnetized along the axis of revolution, $\frac{1}{2}n_zM^2V$, where $n_z = 4\pi\left(1-\varepsilon^2\right)\frac{\mathrm{arth}\varepsilon-\varepsilon}{\varepsilon^3}$ is the demagnetization coefficient of the ellipsoid [15] with regard for its elongation (two equal semiaxes of the ellipsoid are less than the third one, $b < a$).

The second term is the cluster surface energy equal to the specific energy σ multiplied by the spheroid area. Such a contribution to energy (7) is defined by the fact that particles appearing on the cluster surface lose a half of their "neighbors". In the above formula, the ellipsoid area is written in terms of its eccentricity ε with regard for the relations $\varepsilon = \sqrt{1-\frac{b^2}{a^2}} = \sqrt{1-\frac{3V}{4\pi a^3}}$, $V = \frac{4}{3}\pi b^2 a = \mathrm{const}$. Under this condition, an increase in the ellipsoid eccentricity leads to an increase in the area of its surface and, hence, to an increase in the surface energy.

In Fig. 2, we show the relative length of a cluster calculated with regard for the energy minimum condition (7) versus $\beta^{1/2} = \left(\frac{4\pi}{3}\right)^{1/3}\frac{MV^{1/6}}{\sigma^{1/2}}$ which is proportional to magnetization M. The obtained result foresees that the cluster length depends almost linearly on its magnetization.

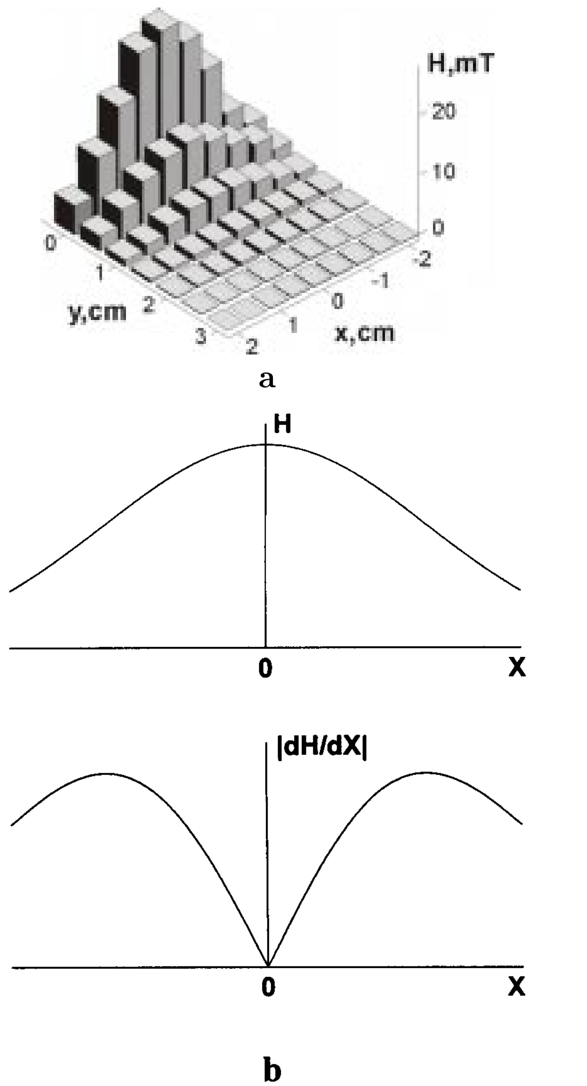

Fig. 3. Distribution of the magnetic field intensity in the capillary area (a) and the scheme of the creation of the field gradient symmetric relative to the point $x = 0$ (b)

2. Experiment Conditions

As a working material, we chose a monodispersed magnetite powder which is a constituent, along with polymers and a black dye, of the composition of a toner for laser printers. The mean size of magnetic particles was 1.5 μm. As a fluid-carrier, we took ethyl alcohol. The magnetic powder concentration in MF was 100 mg/cm^3. We did not use any anticoagulants. In the absence of a magnetic field, the powder lay as a precipitate on the container bottom.

As the containers for a magnetic fluid, we chose glass capillaries with inner diameters of 120, 200, and 370 μm.

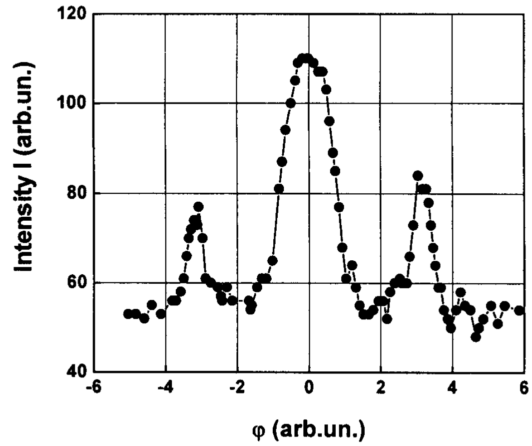

Fig. 4. Distribution of the intensity of diffraction maxima in the experiment on the diffraction of light on a structure of uniformly arranged clusters

The external magnetic field was created by Helmholtz coils or by a constant magnet. The induction of an external magnetic field with any direction was varied from 0 to 30 mT.

The experimental distribution map of the induction of an inhomogeneous magnetic field in the capillary area was measured with a Teslameter at the points located in 0.5 cm and is given in Fig. 3,a. Fig. 3,b shows the distribution of its gradient.

3. Experimental Results

Upon the switching-on of a magnetic field, we observe the appearance of magnetic clusters of needle form in a capillary. They are growing from the magnetic powder precipitated in the bottom part of the horizontally positioned capillary. In a homogeneous (without gradient) magnetic field, clusters are arranged in the series at an arbitrary distance one from another. In the case where the clusters are in the region of the maximum of an inhomogeneous magnetic field (i.e., there is a symmetric gradient of the field), the arrangement of the clusters becomes periodic. The degree of periodicity is rather high, which is testified by the small blur of the first diffraction maxima in the experiment on the diffraction of light on the derived ordered structure of clusters (Fig. 4).

At relatively small gradients, clusters are arranged in one series at the same distance one from another. With increase in the gradient [when the capillary approaches the magnet (see Fig. 3)], the period decreases (Fig. 5),

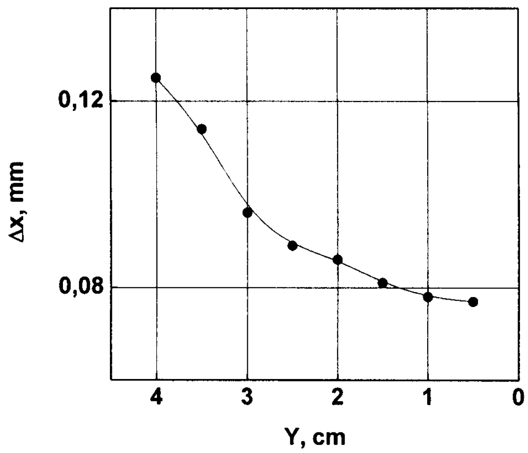

Fig. 5. Period of a linear structure of clusters Δx vs the distance between a capillary and the constant magnet at $x \approx 0$

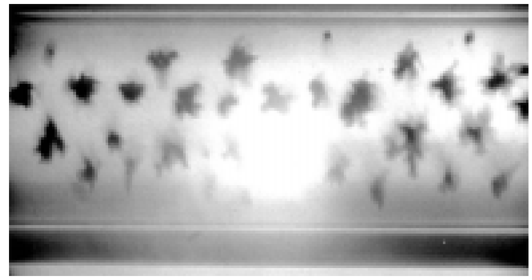

Fig. 6. Photo of needle-like clusters ("to the end") after the separation of a $1D$ structure into several series in an inhomogeneous external magnetic field (the direction of the magnetic field is normal to both the capillary axis and the photo area)

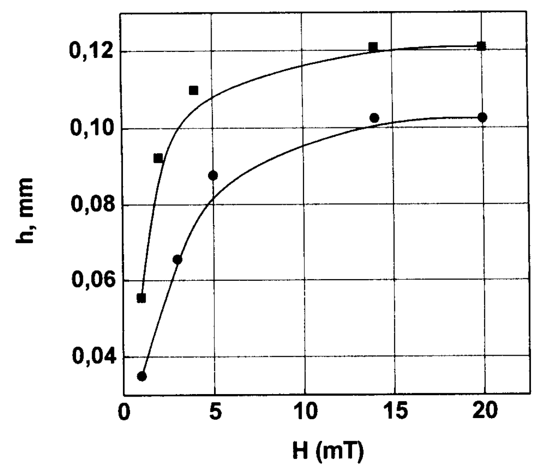

Fig. 7. Length of growing clusters vs the external magnetic field induction

and then the number of series grows (Fig. 6). In the last case, clusters form a hexagonal structure.

A change in the direction of the magnetic field leads to the corresponding rotation of the axis of clusters. In the case of a uniform magnetic field, the rotation occurs synchronously around the centers of clusters without displacement along the capillary axis.

The length of clusters in a magnetic field with induction greater than 20 mT is constant and equal to about 110 μm. For this reason, clusters in a capillary of 120 μm in diameter are practically positioned from wall to wall.

As seen in Fig. 5, the greater the field gradient modulus $|dH/dx|$ (upon a decrease in the distance from the magnet to the container with a magnetic fluid), the lesser the lattice constant of clusters. This observation agrees qualitatively with the results of theoretical calculations (3).

As mentioned above, clusters become to grow from the precipitate upon the switching-on of a magnetic field. The theoretical calculation foresees the almost linear growth of the cluster length with its magnetization (Fig. 2). The experimental dependence of the length of a growing cluster on the applied field induction is given in Fig. 7 for two different clusters. The presence of the saturation of these curves reflects, most likely, the saturation of the magnetization of clusters. The saturation field is close to 15 mT, and the length of clusters under saturation is $h = (0.11 \pm 0.01)$ mm.

Conclusions

The proposed method of application of a gradient magnetic field to the magnetic fluid filling a round capillary allowed us to experimentally create the periodic structures of the needle-like clusters of magnetic particles.

The peculiarities of the behavior of the magnetic fluid filling a capillary under the action of an external magnetic field with gradient at the capillary ends are as follows:

— there appears a periodicity in the arrangement of clusters;

— the period of this structure can be varied in some limits (up to 60% in our case) by changing the value of the magnetic field;

— needle-like clusters freely rotate in the external magnetic field repeating its direction;

— beginning from a certain value of the magnetic field, the ordered structure is divided into several series, which yields the formation of a hexagonal structure of clusters.

Thus, we have developed a model of the observed peculiarities of the behavior of needle-like clusters, given the analytic description of this model, and confirmed its correctness.

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ГОЛЧАСТІ МАГНІТНІ КЛАСТЕРИ В МАГНІТНІЙ РІДИНІ І ЇХ ПОВЕДІНКА В МАГНІТНОМУ ПОЛІ

О.А. Антонюк, В.Ф. Коваленко, Б.М. Молдован, М.В. Петричук

Р е з ю м е

Прикладання до магнітної рідини, розміщеної в круглому капілярі, градієнтного магнітного поля дозволило експериментально створити періодичні структури із голкоподібних кластерів магнітних частинок. Період утвореної структури можна змінювати в деяких межах, змінюючи величину магнітного поля та його просторовий розподіл. Голкоподібні кластери вільно обертаються у зовнішньому магнітному полі, повторюючи його напрямок. Починаючи з деякого значення магнітного поля, відбувається розпад упорядкованої структури на декілька рядів, в результаті чого утворюється гексагональна гратка з кластерів. Порівняння результатів аналітичного опису запропонованої в роботі моделі, яка пояснює поведінку голкоподібних кластерів в магнітному полі, з результатами експерименту свідчить про правомірність її застосування.