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The behavior of magnetic nanoparticles in liquid in magnetic field

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The behavior of magnetic nanoparticles in a liquid free of anti-coagulants in magnetic field has been studied in two container types (round and flat). Application of a specifically configured gradient magnetic field to the magnetic nanoparticles in a round capillary makes it possible to form a periodic structure consisting of needle-like clusters of the magnetic particles. In a flat container, a fairly homogeneous distribution of clusters is observed. In some conditions, clusters of larger size (mega-clusters) appear within a two-dimensional ensemble of the needle-like clusters. The mega-clusters are of dumbell-like shape with asymmetric (presumably spiral) constriction.

Изучено поведение магнитных наночастиц в жидкости без использования антикоагулянтов в магнитном поле в двух типах контейнеров: круглом и плоском. Приложение градиентного магнитного поля определенной конфигурации к магнитным наночастицам в жидкости в круглом капилляре позволяет создавать периодическую структуру из игольчатых кластеров магнитных частиц. При использовании плоского контейнера распределение кластеров характеризуется их относительно равномерным распределением. При некоторых условиях в двумерном массиве игольчатых кластеров наночастиц появляются кластеры увеличенных размеров (мегакластеры). Форма мегакластеров — гантелевидная с несимметричной (предположительно — винтовой) перетяжкой.

Magnetic liquids (ML) are colloidal solutions of tiny magnetic particles in a liquid carrier. Those attract last years an intense attention due to their technical applications (see, e.g., [1]), and are also considered to be a material of good promise for functional electronics and, in particular, for obtaining so-called "photon crystals" [2]. Coupling of the magnetic particles into clusters is a specific property of magnetic liquids prepared without adding of anti-coagulants; that can be interpreted as the initial state of transition to gel phase (sedimentation of the particles). The fact of such a coupling (agglomeration) and the interaction mechanisms of the particles in ML were investigated in detail [3, 4]. Appearance of clusters in ML is considered not to be desirable for its applications. This concerns the usage of ML as lubricants, printing inks, damper liquids, coolants, seal materials, and other cases where stability of the ML hydrodynamic parameters plays an important role. That is the reason of a great attention paid to the methods reducing agglomeration. However, the cluster formation mentioned above is a necessary condition for practical usage of ML in some cases. Visualization of magnetic field lines, magnetic irregularities and magnetic domains; operation of optical valves, and other applications require such a non ideal state of ML. Note that spatial ordering of the clusters in magnetic field underlies the development of ML-based photon crystals [5].

The cluster formation mechanism is based on dipole-dipole interaction between magnetic nanoparticles and counteracting thermal oscillations of the liquid carrier

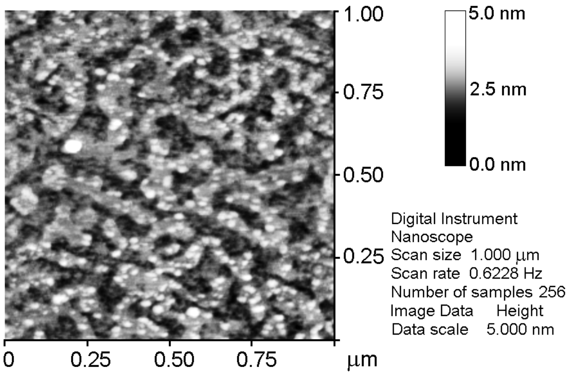

Fig. 1. Magnetite nanoparticles AFM-image. The average particle size is 17.5 nm. The scale of gray gradations correspondence to the surface geometry is shown at right-hand side of the Figure.

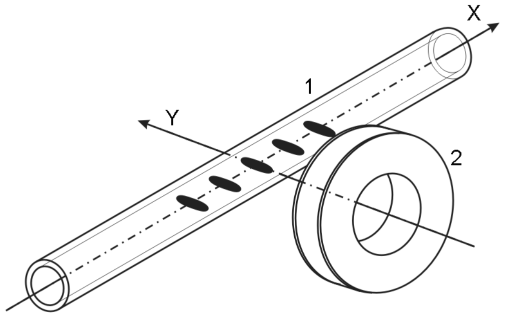

Fig. 2. Scheme of experimental setup used to study the magnetic field gradient influence on cluster distribution in the magnetic liq-

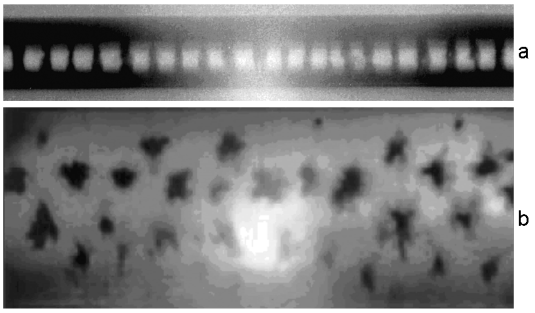

Fig. 3. Needle-like clusters in magnetic field gradient: one-dimensional (a) and two-dimensional distribution (b).

molecules. That is why clusterization is the more intensive, the larger the particles are. The critical dimension of nanoparticles at which coupling probability becomes appreciable is about 10 nm [1]. The clusterization probability increases when an external magnetic field is applied; in this case, the cluster itself arises as magnetic dipole with magnetization directed along the external field.

Numerous investigations are devoted to the properties and formation process of ordered clusters in thin ML films [6–11]. In those works, analyzed is mainly the case of external magnetic field perpendicular to the film surface and clusters arranged like cylindrical magnetic domains in thin magnetic films in the sites of two-dimensional hexagonal lattice. Such an arrangement is the closest. In this work, in contrast to those mentioned above, the clusters are studied which grow freely in ML prepared without using anticoagulants. Cylindrical glass capillaries were used in order to provide necessary conditions for such growth and clusters arrangement along a straight line. Furthermore, studies concerning behavior of ML in a flat container are continued.

Monodispersed powder of magnetite was selected as the initial material (Fig. 1). Ethyl alcohol was selected as the carrier liquid. The powder content in the liquid was 100 mg/cm^3. No anticoagulants were used. In absence of magnetic field, the powder formed a precipitate at the capillary bottom. Glass capillary tubes of 120, 200 and 370 µm inside diameter were used as the round containers for a magnetic liquid. The external magnetic field was generated either by Helmholtz coils (Fig. 2) or by permanent magnet. The external magnetic field intensity could be varied from 0 to 260 Oe and its direction could be arbitrary.

Switching on the magnetic field results in needle-like clusters growing from the precipitate. The clusters are almost of the same height; their growing stops at a certain size (about 100 µm) even when the capillary diameter is sufficient for further growth. Magnetic field induction at which the growing process stops is about 15 mT. In a homogeneous magnetic field, the clusters are arrange into one row on arbitrary spacings from each other, while staying in the same plane passing through the capillary tube axis. If there is a bell-shaped magnetic field distribution, the clusters are arranged near its maximum in a periodic fashion (Fig. 3). The periodicity rather regular, what is testified by a small spot size of the diffraction peaks in light diffraction experiment with the obtained ordered cluster structure [14]. The dependence of field gradient on coordinate is quadratic in the case of bell-shaped field distribution.

The structure period can be reduced by moving the magnet near to a capillary tube what causes gradient increase (Fig. 4). The structure period can be changed by up to 60 % as the field increases from 0 to

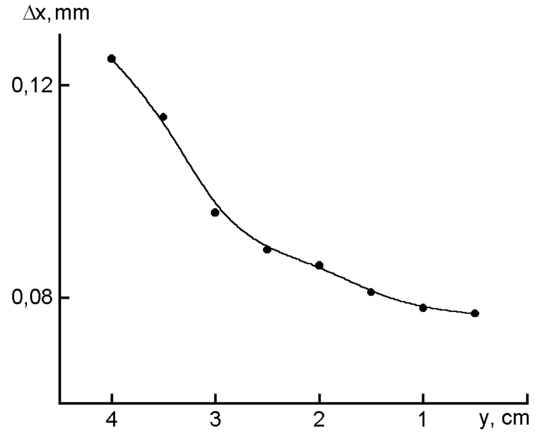

Fig. 4. One-dimensional clusters structure period Δx as a function of distance between the capillary and the permanent magnet measured near the point of zero gradient ($x = 0$). The capillary diameter 120 μm.

15 mT. The single-row arrangement of clusters in the capillary of 120 μm inside diameter is maintained till the field induction in the maximum of its bell shaped distribution does not exceed 15 mT. A further field increase results in the structure rearrangement into a multi row one. In this case, the clusters form a structure close to hexagonal (Fig. 3). The distance between clusters remains stable in such a structure, too.

The capability of period control is shown at Fig. 4. Here, the dependence of structure period Δx on distance between the magnet and the capillary with ML is presented. The period change obtained in experiment reaches 60 %. Further period decrease is hindered by appearance of extra rows of clusters.

We have considered the theory of cluster behavior in the cylindrical capillary in [14]. The results testify to a high stability of the cluster structure against the field gradient profile deviation from the optimal one. The second important conclusion shows that to obtain periodic structure, a high gradient value is required at the edges of the clusters group. Theoretical calculations in [14] and in present work are based on equality (1) obtained on the energy balance condition.

$$\frac{\partial E}{\partial x_i} = -\sum_{ij,j=-N}^{N}\left(3\mathbf{m_i m_j}\frac{x_i - x_j}{|x_i - x_j|^5}\right) - \mathbf{m_i}\frac{\partial H(x_i)}{\partial x_i} = \tag{1}$$
$$= 0, i = -N \ldots N.$$

Here, $\mathbf{m}_i$, $\mathbf{m}_j$ are magnetic moments of interacting clusters; $\partial H(x_i)/\partial x_i$, the external field gradient in the point of i-th cluster location (cluster with coordinate x_i); ($2N + 1$), number of clusters.

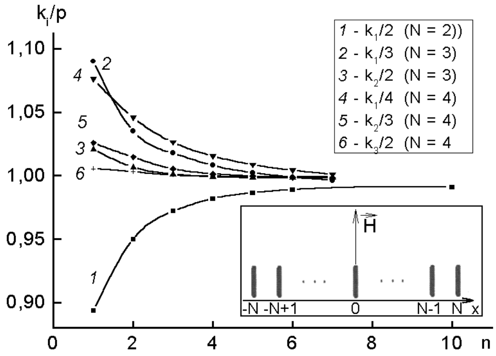

Fig. 5. Calculated dependences of relative cluster coordinate deviation from the points corresponding to their uniform arrangement on n (p-normalizing factor) for groups of $2N + 1 = 5$, 7 and 9 clusters. The scheme of clusters arrangement is shown at the bottom of the Fig-

Let us consider how the gradient dependence on coordinate x influences the cluster structure disorder extent. Let the field gradient be presented as a power function: $\partial H(x_i)/\partial x_i \sim (x_i)^n$. The disordering extent will be defined as $k_i = x_i/x_N$. Solving the combined equations (1), the dependence of k_i on n can be obtained for various amount of clusters ($N = 2$, 3, 4) (Fig. 5).

Consideration of the curves presented shows that the period deviation from regularity less than 5 % is approached when n is as small as 2 and for $n \geq 6$, the cluster distribution is almost ideally regular. Thus, the theoretical calculations show that a regular cluster distribution is the most energy favourable when the field has a gradient at the structure edges. Hence, a trend of the cluster ensemble to self-organization must manifest itself in those conditions.

Solving the combined equations (1) and assuming that magnetic moments are equal for all clusters, we get an expression for cluster coordinate x_i relatively to the center of the cluster ensemble:

$$x_i = \lambda_i\left(\frac{|\mathbf{m}|}{\partial H(x_i)/\partial x}\right)^{1/4}, \tag{2}$$

where λ_i is a calculation coefficient depending on cluster coordinate and number of clusters. The cluster distribution remains uniform when magnetic field intensity profile does not change in its shape but only in absolute value. Changing field intensity by a factor of p results in the structure period

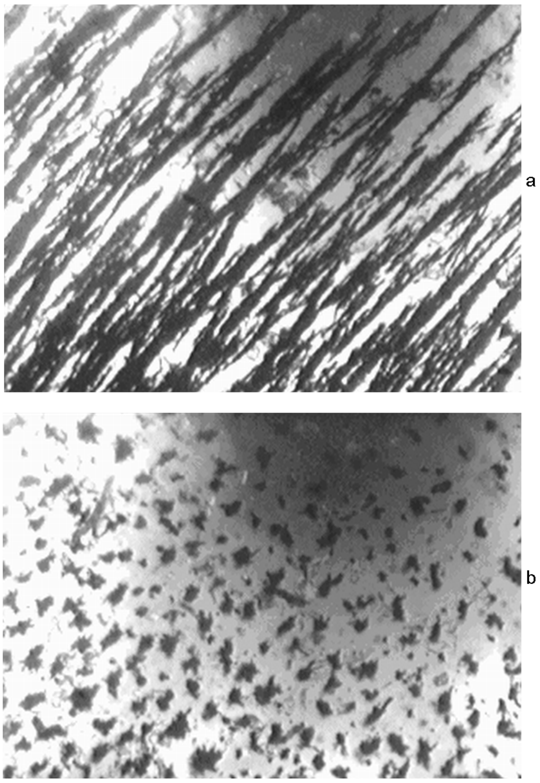

Fig. 6. Magnetic clusters in magnetic liquid in homogeneous magnetic field. a, magnetic field direction in the figure plane; b, perpendicularly to it.

change. The period relative change $\Delta x/\Delta x_0$ in the case $\partial H/\partial x \sim x^n$ is

$$\frac{\Delta x_0}{\Delta x} = (p)^{n+4}, \tag{3}$$

where Δx and Δx_0 are final and initial values of the uniform structure period, respectively. Eq.(2) allows to define cluster magnetic moment m, and Eq.(3) testifies to opportunity of uniform distributed clusters period to be controlled by varying the external magnetic field intensity (parameter p) and/or its spatial distribution (parameter n).

In this work, the magnetic cluster behavior in a flat glass container was also studied. The ML composition and magnetic field magnitude were the same as in the case of cylindrical capillary. The flat container thickness was 100 μm.

In external magnetic field magnetic particles form needle-like clusters (Fig. 6). A trend to their uniform distribution over the area is observed in the region of field maximum. Under a disturbance (periodic magnetic field direction rotation by 10–20°), the uniform cluster ensemble (Fig. 6) produces clusters of larger size (Fig. 7). More precise examination shows that those are dumbbell shaped with a constriction (Fig. 8). The constriction is unsymmetrical and arranged at an angle to the field direction. Such a cluster form is rather stable to the external influences: changes in magnetic field intensity or direction do not result in evident cluster shape changing, except for its poles. The poles are supplied by extra particles which form "tails" if it is located in the plane of the container. Such an unsymmetrical constriction is observed in all mentioned large clusters. Basing on symmetry conditions, the observed constriction can be assumed to be of spiral shape and appears to be a visible part of complex internal structure of the cluster. The revealed peculiarities of ML behavior in the flat container require a further research.

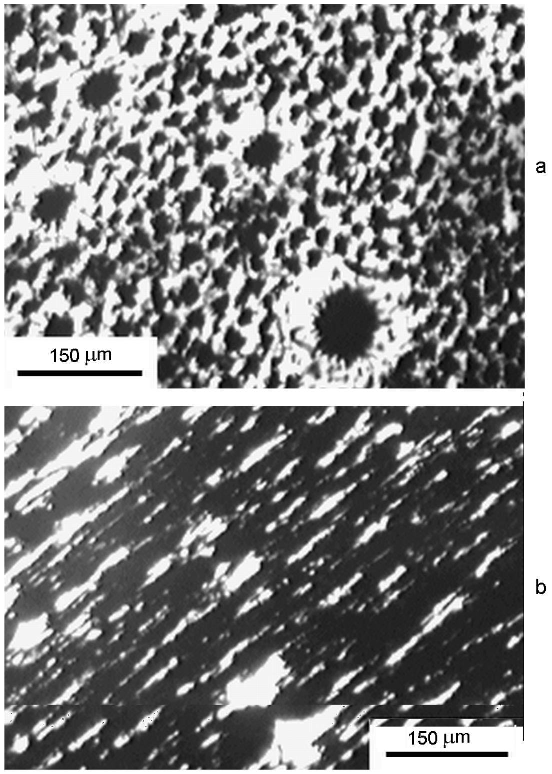

Fig. 7. Micro photo of large size clusters in the flat container. Magnetic field is applied perpendicularly to the figure plane (a) and nearly to the figure plane (b). The dumbbell shape of the cluster can be seen (cluster with constriction).

To conclude, application of magnetic field of a specified configuration allows to create periodic structures of magnetic nanoparticles clusters in a cylindrical capillary. The clusters formed in such a way show the following properties: clusters form peri-

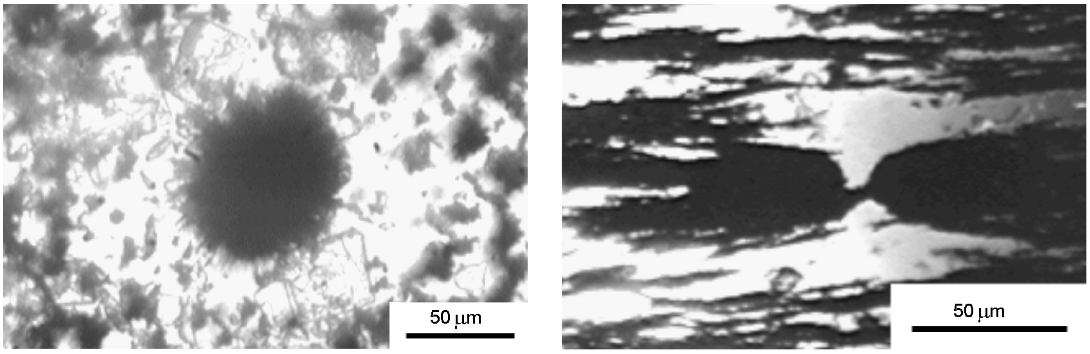

Fig. 8. A large cluster microphoto in the flat container. Magnetic field is applied perpendicularly to the figure plane (a) and in the mentioned plane (b).

odic structure along the capillary axis; the structure period can be varied within some limits (in our case, up to 60 %) by changing the field intensity and gradient; at certain value of field intensity, the single-row structure in reorganized into multi row one. Calculations show that uniform (to within 5 %) cluster distribution can be reached at quadratic character of the field gradient dependence on coordinate. The cluster distribution can be characterized by relatively uniform arrangement over the area of flat container. Cluster of large size occur in two-dimensional cluster ensemble under certain conditions. The shape of this type of clusters is dumbell-like with unsymmetrical constriction.

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Поведінка магнітних наночастинок у рідині у магнітному полі

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Досліджено поведінку магнітних наночастинок у рідині без використання антикоагулянтів у магнітному полі у двох типах контейнерів: круглому і плоскому. Прикладання градієнтного магнітного поля визначеної конфігурації до магнітних наночастинок у рідині у круглому капілярі дозволяє створювати періодичну структуру з голчастих кластерів магнітних частинок. При використанні плоского контейнера розподіл кластерів характеризується їх відносно рівномірним розподілом. При деяких умовах у двовимірному масиві голчастих кластерів наночастинок з'являються кластери збільшених розмірів (мегакластери). Форма мегакластерів — гантелеподібна з несиметричною (орієнтовно — гвинтовою) перетяжкою.