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TECHNICAL PHYSICS

Self-Assembly of Superparamagnetic Ferrihydrite Nanoparticles

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Nowadays, a large number of types of nanoparticles that are able to form one-, two-, and three-dimensional ensembles with extremely high functional characteristics can be obtained. Among them, a wide class of nanoobjects is represented by magnetic nanoparticles. When aggregating, they form chained structures, which are of great interest.

As a rule, when considering the formation of chains of magnetic nanoparticles, one restricts oneself to taking into account their dipole interaction [1–4]. For forming steady pairs of anisotropic particles, the energy of dipole–dipole interaction should be much higher than the energy of thermal fluctuations. This condition corresponds to ferromagnetic and superparamagnetic nanoparticles of cobalt, iron, magnetite, or maghemite with reasonably large sizes and magnetic moment. For obtaining nanoparticles forming steady chained structures, various chemical and physical methods of synthesis are developed: coprecipitation from solutions, pyrolysis of carbonyl compounds of cobalt and iron, reduction of nickel ions by hydrazine, etc. [4–7]. For stabilizing the chains, one uses an external magnetic field with an intensity of 0.2–1.8 T and higher and the modification of the surface of nanoparticles by surfactant species [5, 7, 8].

Nevertheless, the chained aggregates of superparamagnetic nanoparticles with sizes less than 10–20 nm are unstable and disintegrate with removing the external field [6, 9]. In this connection, we note that, when a system of nanoparticles passes from the disperse structure to aggregates of one or another form, its magnetic characteristics [9] vary. In particular, the degaussing field and the stray fields of a chain also vary as its length increases. The effect of exchange-interaction forces on the magnetic properties of nanoparticles and their aggregates is known [10]. However, their participation in the self-assembly of nanoparticles in aggregates of certain shapes was not considered. The role of these fields in forming chained structures is also the subject of analysis in this study.

The purpose of this study is to estimate the possibility of formation of chains of superparamagnetic nanoparticles of iron oxyhydroxides synthesized in a bacteria culture. The self-assembly of biogenic nanoparticles distinguished by low values of magnetization and small sizes is assumed to proceed due to the forces of magnetic dipole–dipole interaction as an initial mechanism of aggregation and exchange-interaction forces, which provide the stability of chains.

Our experimental data are the basis for carrying out the calculations and estimates of the possibility of self-assembly of superparamagnetic ferrihydrite. We singled out ferrihydrite nanoparticles from the *Delftia tsuruhatensis* bacteria culture in the form of a colloidal solution after removing bacteria and rinsing in distilled water. They represent superparamagnetic two-line ferrihydrite and have an average radius of 1.6–2.3 nm according to the small-angle x-ray scattering [11, 12]. For microscopic observation, drops of the colloidal solution were deposited on copper grids dried at room temperature in a weak magnetic field (0.02–0.03 T). No other external conditions for favoring the aggregation were provided.

The microphotographs demonstrate the self-assembly of anisotropic cobalt-doped ferrihydrite nanoparticles in aggregates of ellipsoidal shape with sizes of about 550 × 300 nm (Fig. 1a) and a platelike shape of 50–100 nm thick (Fig. 1b). The aggregates, in turn, are combined from blocks, which include a restricted number of nanoparticles of about 5 nm in

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diameter and have the shape of rods of 50–100 × 12 nm in size. The observed assemblies differ from the known ones by the fact that they are formed from biogenic nanoparticles with a diameter that is much less than 10 nm and as a result of imposing an external magnetic field with a much lower intensity.

The structures with the sizes of about several hundred nm cannot be obtained by simply increasing the number of nanoparticles in aggregates. It is logical to assume that the process of assembling aggregates has a stage character. First, chains are formed of nanoparticles with sizes of about the length of sticks or thickness of plates, which can be seen in Fig. 1. Then there is the assembly of two- and three-dimensional structures. In this study, we calculated the magnetic energy of aggregates of nanoparticles in the form of chains, which are frequently observed in experiments.

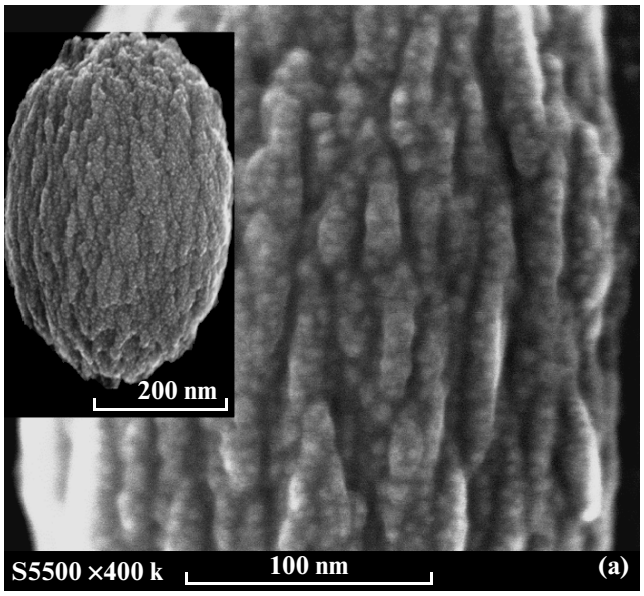
It is known that the six-line ferrihydrite is an antiferromagnet [13]. However, owing to the small size, the nanoparticles have an uncompensated magnetic moment caused by the near-surface decompensation of magnetizations of antiferromagnetic sublattices [14]. The two-line ferrihydrite belongs to ferrimagnets [13]. Biogenic particles have a radius of 2–3 nm. The presence of the magnetic moment results in the magnetodipole interaction, which is relatively long-range and serves as the cause of the association of particles. As the magnetic nanoparticles are approached, their magnetic moments are mutually arranged. This process has two paths: the particle rotation as a whole and the rotation of the magnetic moment in a sample. The first motion is universal, and the second is typical for soft magnetic materials, i.e., the materials having a low value of magnetic anisotropy. The last property favors the orientation of magnetic moments of particles in the direction of even a weak external magnetic field. If the particles approach at a small distance between them or have a contact, short-range forces, which stabilize the structure that has arisen as a result of the dipole interaction, are switched on. For the contacting nanoparticles with magnetic moments, such forces can be caused by the exchange interaction.

Let us consider the system of n identical spherical ferromagnetic particles contacting among themselves and placed in an external magnetic field $\mathbf{H}$, which are oriented along the line of contact points. The magnetic moment of each spherical particle of radius R is directed along $\mathbf{H}$. We present the free energy of such a system as the sum

$$F = F_1 + F_2 + F_3, \tag{1}$$

where F_1 is the ferromagnet free energy

$$F_1 = \frac{V_n}{2} M^2 (\beta + 4\pi N_z) - V_n \mathbf{H}\mathbf{M}, \tag{2}$$



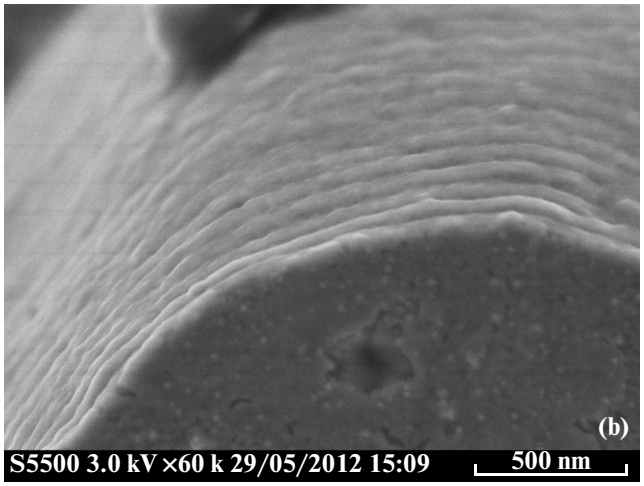


Fig. 1. Microphotographs of (a) two- and (b) three-dimensional assemblies of ferrihydrite nanoparticles.

F_2 is the energy of stray fields in the space outside a ferromagnetic sample

$$F_2 = \frac{1}{8\pi} \int H_s^2(\mathbf{r}) d\mathbf{r}, \tag{3}$$

and F_3 is the energy of the dipole–dipole interaction of the nanoparticles forming the system under consideration

$$F_3 = \sum_{\substack{i,j \\ i \neq j}} \frac{(\mathbf{m}_i \mathbf{m}_j) - 3(\mathbf{m}_i \mathbf{n}_{ij})(\mathbf{m}_j \mathbf{n}_{ij})}{2r_{ij}^3}. \tag{4}$$

In Eqs. (2)–(4), $V_n = \frac{4}{3}\pi R^3 n$ is the ferromagnetic-sample volume, $\mathbf{M}$ is the vector of ferromagnet magnetization, $M = |\mathbf{M}|$, β is the parameter of single-axis anisotropy of the particle, N_z is the degaussing factor

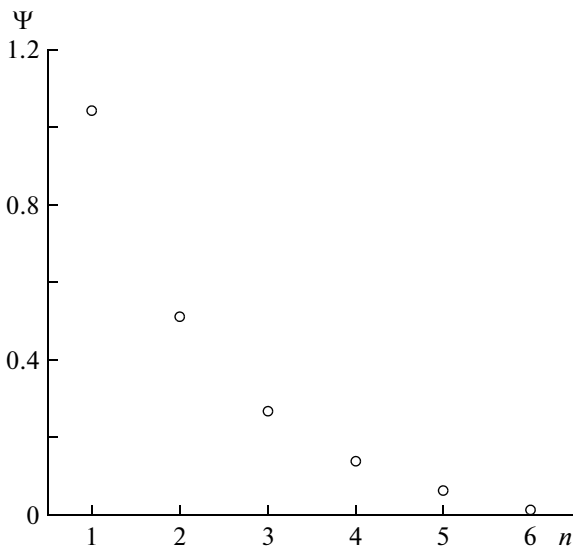


Fig. 2. Variation of free energy of the linear system of nanoparticles depending on the chain length.

of the ferromagnet in the direction of its magnetization (the axis z), $H_s(\mathbf{r})$ is the stray field (the integration in Eq. (3) is carried out over the entire space except for the volume occupied by the ferromagnet); $\mathbf{m}_i$ is the magnetic moment of the spherical particle with the number i, and $\mathbf{n}_{ij} = \dfrac{\mathbf{r}_{ij}}{r_{ij}}$, $r_{ij} = |\mathbf{r}_{ij}|$, where r_{ij} is the distance between the points in which the magnetic dipoles $\mathbf{m}_i$ and $\mathbf{m}_j$ are located.

We calculate the degaussing field and the stray field approximating the structure by an ellipsoid with the principal axes R and nR. We note that the volume of such an ellipsoid is V_n. In the chosen approximation, N_z is set [15] by the expression

$$N_z = \frac{1-e^2}{2e^3}\left(\ln\frac{1+e}{1-e} - 2e\right), \qquad (5)$$

where $e = \sqrt{1-\dfrac{1}{n^2}}$ is the eccentricity of the ellipse lying in the ellipsoid cross section along the larger principal axis (the axis z). It is important that N_z is the function of the number n of particles.

Numerically, we determine the free energy of the system of ferromagnetic particles, which also depends on the number n of particles and is caused by the stray fields. Finally, the energy of dipole–dipole interaction, which is determined with taking into account the nearest neighborhoods and those following them, we write in the form

$$F_3 = -V_n M^2 \frac{\pi}{6}\left(\left.\frac{n-1}{n}\right|_{n>1} + \left.\frac{n-2}{8n}\right|_{n>2}\right). \qquad (6)$$

Substituting Eqs. (3), (5), and (6) into Eq. (1), we have

$$F = V_n M^2\left[\frac{\beta}{2} - \frac{H}{M} + \pi\Psi(n)\right], \qquad (7)$$

where the dimensionless function $\Psi(n)$ represents the system free-energy fraction dependent on n:

$$\Psi(n) = 2N_z + \frac{F_2}{\pi V_n M^2} - \left.\frac{n-1}{6n}\right|_{n>1} - \left.\frac{n-2}{48n}\right|_{n>2}. \qquad (8)$$

The function $\Psi(n)$ is shown in Fig. 2 at the integer values of n. The monotonic dependence $\Psi(n)$ is determined by decreasing the energy density of the degaussing fields and stray fields with increasing chain length. Each subsequent connection of a nanoparticle to the chain decreases its energy; however, this gain, as can be seen from Fig. 2, becomes lower as the chain length increases. In other words, it is energetically favorable for a particle to join a shorter chain thus providing a decrease in the energy of the entire system. From here, it follows that the formation of chains of a certain and approximately identical length depends on the nanoparticle concentration.

The energy of degaussing fields of chains is reasonably high, which forces them to form two- and three-dimensional structures in which the compensation of such fields is provided. In particular, it becomes probable that the ellipsoids and disks shown in Fig. 1 appear, which are composed of magnetic chains forming 180-degree neighborhoods of the type of the domain structure in massive ferromagnets.

In summary, it should be noted that the self-assembly of superparamagnetic nanoparticles of biogenic ferrihydrite distinguished in the small sizes and the saturation magnetization into the one-dimensional chained and two-, and three-dimensional structures due to the forces of magnetic dipole–dipole interaction becomes possible if the exchange-interaction forces for aggregates as a whole are simultaneously taken into account.

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