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NEUTRON INVESTIGATIONS OF FERROFLUIDS

A review of neutron scattering researches of various magnetic fluids (ferrofluids) is made. Advantages and disadvantages of other complementary methods for the structure characterization of ferrofluids are discussed. The small-angle neutron scattering (SANS) method with a wavelength of 0.1–1 nm is a classic example of applying radiation to the determination of a structure in liquid nanosystems on a scale of 1–100 nm. The capabilities of the SANS method for the analysis of a magnetic fluid structure are illustrated by real examples.

Keywords: ferrofluids, magnetic fluids, small-angle neutron scattering, structure investigation, aggregation, ferrofluid stability.

1. Introduction

Magnetic fluids, or ferrofluids, are liquid dispersions of magnetic nanoparticles with a typical dimension of 10 nm. The latter corresponds to the single-domain magnetization state in every particle and governs the superparamagnetic behavior of those systems on the whole [1, 2]. In order to compensate the dipole-dipole attraction between magnetic particles, the latter are covered with a stabilizing layer, in particular, consisting of surfactants. The volume fraction of magnetic particles in highly stable ferrofluids can reach 25%.

The variety of unusual properties of the systems concerned, in particular, the combination of magnetism and fluidity, determines both fundamental and applied interest in ferrofluids. For instance, if ferrofluids undergo the action of external magnetic fields, a specific aggregation of nanoparticles into linear chains oriented along the field can take place. Such an aggregation drastically changes all properties of ferrofluids and makes them anisotropic with respect to the magnetic field direction, which stimulates the spatial modification of almost all physical properties in ferrofluids, including the density, viscosity, surface tension, conductivity, inductance, *etc.* [1, 2]. Therefore, the properties of ferrofluids can be controlled by applying a magnetic field. Ferrofluids are widely used

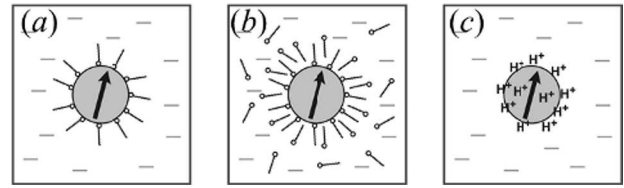
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in practice in various technical devices [1–4]. Their medical and biological applications are also developed intensively [2, 4–6].

Nowadays, the method of small-angle neutron scattering (SANS) is effectively used in structural researches of bulk ferrofluid specimens [7]. The method makes it possible to analyze the ferrofluid structure on the microscopic scale and, accordingly, relates it to macroscopic properties. It should be noted that, since recently, the method of neutron reflectometry has also been actively used for studying the adsorption of ferrofluid nanoparticles on the solid surface [8–10].

Let us classify the main types of ferrofluid stabilization. The structures of corresponding particles are schematically shown in the figure. The stabilization of ferrofluids on the basis of organic nonpolar solvents (benzene, hexane, decalin) occurs by means of the formation of a single surfactant layer on the surface of magnetic particles (Figure, *a*) owing to the surfactant chemisorption [1, 11–13]. A classical surfactant for this purpose is oleic acid $C_{18}H_{34}O_2$, the unsaturated monocarboxylic acid. The length of an oleic acid molecule (1.8 nm) and its bend at the middle-point owing to the double bonds provide a sufficient noncharge (steric) repulsion between the shells of different particles.

In polar liquid bases, including water, the interaction between the lyophobic head of a surfactant molecule and the liquid competes with the adsorption of the surfactant head on the magnetic particle surface. In order to prevent the surfactant desorption, the double steric stabilization is used [14–19]; namely, the particles described above with one layer of surfactants are covered with another layer due to its physical adsorption on the first one (Figure, *b*). This procedure requires that an excess of the second surfactant should be in the solution. Such a stabilization cannot be completely steric because of the polarity of solution components (both the solvent and the surfactant). At the interface between the shell and the solvent, there is always a certain induced charge, which makes an additional contribution to stabilization by forming an electric double layer around the particles [20, 21]. In the case of water basis, a purely charge stabilization (Figure, *c*) can be implemented owing to the presence of H^+ and OH^- ions, or ion-containing groups (e.g., citrate) located on the surface of magnetic particles [22, 23]. This class of ferrofluids



Main types of ferrofluid stabilization. Single steric stabilization (*a*), double steric/electrostatic stabilization (*b*), and ionic (electrostatic) stabilization (*c*)

is characterized by a high sensitivity to the pH and ionic strength of the liquid basis [24, 25].

2. Comparison of SANS with complementary methods for the structural analysis of highly dispersed systems

Today, the development of various structural analysis methods allows a complex approach to be used, while studying complicated nanosystems. This approach combines some methods complementing one another. Ultimate conclusions about the structure of examined objects are drawn on the basis of the results obtained by several methods, each of which permits one to specify the unique features in the internal system organization to that or another extent. On the one hand, each method has its “obvious” advantages, which, first of all, stimulate its application. At the same time, the interpretation of the data obtained using any method requires, to that or another extent, special tricks and simplifications. Let us consider the structural methods, which are most actively used together with the SANS for the determination of the dimensional parameters of nanoparticles and their clusters.

Analysis of static magnetization (magnetic granulometry) in systems with magnetic nanoparticles. A system containing superparamagnetic monodisperse nanoparticles is magnetized in an external magnetic field with strength H in accordance with the Langevin function. The magnetization of a particle is unambiguously determined by its radius R . For polydisperse systems, the averaging over the distribution function $D_n(R)$ is required [26].

As an “obvious” advantage of the magnetic granulometry, we may regard its capability to directly measure the magnetic sizes of particles, by analyzing the magnetization curve. However, this method

requires that the system should be purely superparamagnetic. Difficulties arise if the dipole-dipole interaction between the particles manifests itself to some extent owing to a high specific magnetization of particles (e.g., when pure metals rather than oxides are used), a high concentration of particles, and clustering. A broad polydispersion of nanoparticles substantially complicates the interpretation and is practically not analyzed. Special approaches are also required in the case where particles, under the influence of an external magnetic field, begin to aggregate into small nonchain clusters [27]. Note that, in certain cases, the applied external magnetic field can change the internal organization of the system (reorientation, appearance, and rearrangement of clusters). The method is valid for the diluted systems of nanoparticles (a volume fraction of about 1%) with a sufficiently weak aggregation.

Electron Microscopy. Electron microscopy, transmission (TEM) or scanning (SEM), proposes a variety of techniques for the analysis of the interaction between electron irradiation and nanoparticles in various optical modes. However, the overwhelming majority of applications are aimed at determining the dimensions of nanoparticles located on special substrates, by analyzing patterns created by the beams of electrons transmitted through the specimen or reemitted from its surface. The corresponding experiments are carried out in vacuum.

The representation of EM results in the coordinate space is the most illustrative from the viewpoint of finding the dimensions of individual nanoparticles. However, this procedure depends on the pattern sharpness. The latter, in turn, is determined by the electron beam parameters (for modern installations, there are more than 20 control parameters) and the substrate properties. The influence of sharpness becomes especially important in strongly polydisperse systems, where it actually determines the interval of method sensitivity. The latter, in turn, can affect the magnitudes of parameters determined for the sought size distribution function. Taking a probable nonspherical shape of particles into account is also a certain problem. As involved problems for electron microscopy, one may regard the consideration of particle aggregation and the analysis of the internal structure in inhomogeneous particles with hydrogen-containing components. In essence, the method does not allow one to look into complex particles and ag-

gregates. Moreover, when the specimens on the substrates are dried out, there may appear the additional aggregation, which directly or indirectly (the modification of size distribution for separate nonaggregated particles) changes the measured density distribution function.

Dynamic light scattering. Dynamic light scattering (DLS), or quasi-elastic light scattering, aimed at finding the hydrodynamic radius, R_H , of particles fluctuating in liquid (the Brownian motion) is a standard method used to study liquid colloidal solutions. It should be noted that the parameter R_H is determined indirectly. A directly measured quantity, on the basis of the autocorrelation function for Doppler frequency shifts, is the diffusion coefficient of particles D . The latter, under certain assumptions, is used to calculate R_H . Since this method is based on the application of light, the measurement interval includes aggregates less than 500 nm in diameter, which is an undoubted advantage of the method, because it allows one to monitor the clustering in real (not dried up) solutions and in a wide interval of dimensions.

At the same time, an extremely high dissolution required in the standard light-transmission experimental setup (to one millionth percent of the particle volume fraction) may give rise to the violation of the solution stability, i.e. to the appearance of new aggregates and the development of initial ones. A principal difficulty consists in the determination of a relationship between the dimensions of "loose" or fractal clusters and their diffusion coefficient. If the sensitivity interval is sufficiently wide and large clusters (more than 100 nm in dimensions) are present, the signal of the latter prevails. Therefore, the restoration of the size distribution function for small particles and aggregates (less than 10 nm in dimensions) becomes unstable. Finally, it is basically impossible to analyze the internal structure of particles and aggregates making use of DLS.

X-ray (synchrotron) and neutron diffraction. The determination of crystalline nanoparticle size from the width of diffraction peaks is a standard way to characterize disperse systems. The size of the coherent distribution region, which is related to a crystallite size, is determined from the Lorentzian peak broadening at the angle θ according to the Debye-Scherrer formula. Here, an important point consists in that we have information concerning the size of a structural crystalline unit irrespective of the aggrega-

tion degree in the system! However, in this case, only one size, averaged over the volume, can be obtained, as a rule. In the literature, the restoration procedure for the size distribution function by simulating the profiles of diffraction peaks can be found [28]. However, the unambiguity and the accuracy of the solutions obtained for polydisperse systems with a broad size distribution raise doubts. Neutron diffraction allows one to say, in principle, about the restoration of the magnetic size in systems with magnetic crystalline nanoparticles [28]. However, for the statistics to be sufficient, systems with rather large volumes (about 1 cm³ and more) are required.

Small-angle x-ray (synchrotron) and neutron scattering. Small-angle scattering of X-rays (SAXS) and neutrons (SANS) covers rather a large interval of particle sizes from 1 to 100 nm. The main specific feature of the method in comparison with the previously discussed scattering methods (electrons and light) consists in ample possibilities to study the internal nanoparticle structure. This is especially true for neutrons, because the method allows the scattering length densities of the components in analyzed systems to be varied in a wide interval by means of the isotope substitution.

An important specific feature of small-angle scattering researches is the closeness of experimental conditions to real ones. A large enough penetration depth of those radiations allows unmodified and concentrated systems to be dealt with. A shift of the sensitivity interval toward smaller dimensions makes the restored size distribution function in polydisperse systems more stable. At the same time, the influence of polydispersion is comparable with the effects of shape anisotropy [29] and aggregation, which raises an issue concerning their joint simulation in complicated systems. A special place in the application of neutron scattering is occupied by magnetic systems. As was mentioned above, the magnetic component of scattering becomes substantial in this case. On the one hand, this circumstance extends the capabilities of neutron scattering. On the other hand, owing to a more complicated scattering scenario, there emerge a number of issues that demand the utmost carefulness, while interpreting the experimental results. The magnetic component of scattering is resolved at the magnetic saturation of the examined system in the external magnetic field. The latter can insert modifications into the system structure (e.g., it

can initiate the additional aggregation in liquid systems). New appearing features make their own contribution to scattering, and, in certain cases, this contribution is difficult to be distinguished from the contribution of purely magnetic scattering. The situation becomes more complicated for polydisperse and initially clustered systems. If, additionally, the particle concentration is not low enough to reduce the particle-to-particle interaction (both atomic and magnetic), the problem of the scattering intensity interpretation cannot be solved. In other words, for today, there is no possibility to quantitatively analyze atomic and magnetic correlations of corresponding structural factors in real polydisperse systems [30].

3. Application of the Method of Modified Basis Functions for Small-Angle Neutron Scattering in Ferrofluids

In this section, the application of the method of modified basis functions [31] to three classes of ferrofluids is considered.

Low-polarity organic ferrofluids with steric stabilization. The structure of the systems concerned is the closest to the concept illustrated in Figure, *a*. In works [32, 33], a substantial difference between the characters of scattering changes in specimens stabilized by myristic (MA) and oleic (OA) acids as a consequence of the difference between the corresponding size distribution functions for dispersed magnetite particles was demonstrated. The characteristic radius, which determines both the average radius and the polydisperse distribution width, is more than twice larger for the OA specimen in comparison with the MA one. By comparing the given basis functions, the surfactant shell thickness was determined, which turned out identical for both specimens and equal to about 1.4 nm.

Aqueous ferrofluids with electrostatic stabilization. Let us consider ferrofluids belonging to the class of charge-stabilized fluids prepared following the Massart method [22]. In the course of stabilization, magnetite nanoparticles adsorb small charged molecules (in this case, these are C₃H₅O(COO)₃³⁻ citrate ones), a typical dimension of which (less than 0.5 nm) is much less than the characteristic dimension of particles (more than 10 nm). The description of and the control over the interaction potential in such ferroflu-

ids are extremely difficult. The potential depends on the pH, ionic force, and particle size (especially in the case of large particles with dimensions exceeding 12 nm).

A weak influence of the stabilizing shell around nanoparticles on scattering was found. In work [34], the following conclusions were made: (i) the main contribution to nuclear scattering is given by the magnetite “core”, the radius of which is considerably larger than the surfactant shell thickness; (ii) the thickness of the nonmagnetic layer manifests itself extremely weakly with respect to the determination of the shell thickness δ ; therefore, it plays no appreciable role in the analysis of the data on contrast variation; and (iii) the determined small effective thickness of the stabilizing shell testifies that citrate molecules do not cover the entire magnetite surface, so that one may say about the shell only conditionally. For this reason, the determined effective thickness of the shell is less than the size of a stabilizing molecule (about 0.5 nm).

Hence, an almost homogeneous structure of magnetite nanoparticles with respect to the nuclear scattering length density in the charge-stabilized ferrofluids made it possible to separate information on the nuclear and magnetic radii of particles with the help of contrast variations. A considerable difference between those radii was confirmed in independent experiments carried out in the magnetic field making use of polarized neutron scattering.

Aqueous ferrofluids with double stabilization. An alternative to the charge stabilization in aqueous ferrofluids is the application of a stabilizing double layer, where the steric repulsion is the main component of the stabilizing interaction. Such ferrofluids are extremely promising for biomedical applications, because their structure changes rather weakly with the variation of the pH and ionic force of the medium. However, the synthesis of such systems without aggregation remains a problem till now [21, 35, 36]. Even in relatively stable specimens of aqueous ferrofluids with double stabilization, in which the volume fraction of a dispersed magnetic material does not exceed a few percent, a complicated multilevel aggregation of particles was revealed (the corresponding examples can be found in works [15, 17, 19, 21, 35, 37, 38]). As was shown in work [18], such systems are not free from aggregation; nevertheless, they are stable both in the absence and in the presence of an external magnetic field.

A considerable difference between the aggregate organizations in two ferrofluids was detected. For the LA+LA specimen (the double layer of lauric acid (LA)), an appreciable distinction was observed between the functions $p(r)$ calculated from the basis function and from the curve obtained in the H₂O case. At the same time, for the MA + MA specimen, those functions are practically identical. In the MA + MA specimen, the surfactant shell weakly affects the maximum size of aggregates. A scenario was proposed, in which the content of surfactants in MA + MA aggregates is lower than in LA + LA ones. A conclusion was also drawn that magnetite particles in the aggregates of the MA + MA specimen are not covered entirely with the surfactant. Nevertheless, this circumstance weakly affects the stability of ferrofluids. Summarizing, we may say that the contrast variation allowed the issue concerning the structure of rather aggregated systems to be substantially elucidated. The direct simulation, which would simultaneously describe the structure of separate particles and aggregates, is highly complicated in this case because of the strong polydispersion of initial particles.

4. Small-Angle Neutron Scattering in Complex Structural Researches of Ferrofluids

Effect of size selectivity for nanomagnetite at ferrofluid stabilization by monocarboxylic acids in nonpolar organic solvents. It was found that, despite a low stabilization efficiency, stable nonpolar organic ferrofluids prepared in decalin and stabilized by acids from a series of saturated acids with the alkyl chain length within the interval C12–C18 – these are lauric (LA), myristic (MA), palmitic (PA), and stearic (SA) acids – can be obtained [13, 39]. In the relevant studies, a complex structural analysis of indicated ferrofluids was used, including X-ray diffraction (in order to determine the average size of crystalline magnetite nanoparticles), the analysis of static magnetization, transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and SANS (polarized and nonpolarized neutrons). On the one hand, the static magnetization curves showed that all specimens demonstrated rather a good superparamagnetic behavior. On the other hand, numerical data for the magnetic size testified to a considerable dis-

crepancy between the specimen with OA stabilization and the specimens with stabilization by saturated acids. The distinctions also manifested themselves in the TEM patterns obtained after drying up the diluted (by a factor of 1000) specimens. The functions $D_n(R)$ obtained by both methods agreed with the results of X-ray diffraction. Moreover, besides a reduction of the average dimension, one may also say that, in the case of saturated acids, the radial distribution of magnetite nanoparticles was characterized by a smaller width and asymmetry. The structure, including the function $D_n(R)$, and the composition of particles in ferrofluids were determined with the help of a combined SAXS (synchrotron radiation) and SANS (nonpolarized neutrons) application. The parameters of the function $D_n(R)$ obtained from SAXS data are well reproduced in SANS experiments (the nonpolarized mode) for ferrofluids prepared with ordinary (nondeuterated) solvents. Those parameters also agree with the magnetometry and TEM data. In addition, the SANS data for ferrofluids with the mainly deuterated solvent demonstrate a pronounced modulation of scattering, as the length of a surfactant molecule changes. As one could see above, the revealed variation of the magnetite size also manifests itself in the SANS data on the contrast variation when comparing OA and MA stabilizations.

On the basis of the obtained information about the structure of particles in ferrofluids, the physical principles aimed at the stabilization of those systems can be substantially specified. On the one hand, distinctions between the effective thicknesses of surfactant layers, when linear saturated surfactants are applied, are well demonstrated, which, however, do not affect the stabilized size of magnetite. On the other hand, this parameter strongly changes, when saturated acids are used instead of OA. From whence, it follows that the shell thickness does not play an essential role in the stabilization of magnetite particles with a certain dimension in the case of acids, the alkyl chain length of which falls within the considered interval. The main factor is the different organization of OA and saturated acids on the magnetite surface, which manifests itself in different elastic and solvation [40] shell properties.

Influence of surfactant excess on the structure of nonpolar magnetic fluids. A number of researches were carried out concerning the factors that govern the stability of ferrofluids [41–45]. One of those fac-

tors is the content of surfactant molecules in the system. It is known that there is an optimum ratio between the contents of a magnetic material and a surfactant in ferrofluids, at which the system state is the most stable. If we suppose that the amount of a surfactant in the system is not enough for coating the whole surface of every magnetic particle, the deterioration of the magnetic fluid stability becomes quite clear. At the same time, the excess of a free surfactant in ferrofluids has a more complicated effect. In the case of polar ferrofluids, such an excess is required (its optimum value is known from practice) for the formation of a second layer around magnetic particles. However, in the case of nonpolar organic magnetic fluids with a single layer of acid around the magnetic particles, such an excess also results in the deterioration of the system stability. At the moment, there is no complete understanding of the mechanism of this phenomenon. It can be emphasized that this problem is common for colloidal solutions [46–50].

The influence of the surfactant excess in classical ferrofluids with a single surfactant layer was studied for ferrofluids with magnetite particles stabilized by monocarboxylic acids in benzene and decalin [41, 44, 51–53]. In some experiments, the surfactant excess exceeding 25% resulted in a drastic deposition of magnetic particles from the solution. Repulsion dominates in the system oleic acid/benzene; however, a rather strong attraction is also observed [42, 54]. For the studied colloidal particles in a magnetic fluid, it is possible to conclude that, although the surfactant excess does not give rise to an appreciable particle aggregation, nevertheless, the effective attraction between OA molecules grows. Seemingly, this factor becomes essential, when the excess increases to 25%. For a more detailed study of the features in the behavior of surfactant molecules in the solution, the method of molecular dynamics [45, 55–57] is actively used in addition to SANS.

Change in the cluster state of aqueous ferrofluids at the stabilizing shell modification. As was said above, for medical and biological purposes, the double stabilization of aqueous ferrofluids prevails over the ionic stabilization owing to its lower sensitivity to the pH and ionic force of medium. However, it is impossible to exclude the appearance of a charge on the surface of the stabilizing shell in a polar solvent. For instance, at the magnetite stabilization in water by creating a double layer of sodium oleate

[8, 20], there appears a charge on the shell, affecting the system stability. Therefore, in this case, a combined steric/electrostatic stabilization of ferrofluids is dealt with. In biocompatible ferrofluids, the chemical composition of the particle surface should also suppress the reaction of immune system (reticuloendothelial system, RES). For this purpose, magnetic particles in ferrofluids are covered with compounds that are neutral for the given system, such as polyethylene glycol (PEG) [59–61]. This trick prolongs the lifetime of particles in organisms of animals from minutes to hours. PEG is widely used in various applications [62], including the coating of colloidal particles [64–66]. A substantial decrease of the fraction of dispersed magnetite in ferrofluids was revealed after the introduction of PEG, which testifies to a worse stability of the modified system. It should be noted that, in the framework of this effect consisting in the influence of PEG on the ferrofluid structure, the aqueous solutions of pure PEG [67, 68] and the PEG mixture with sodium oleate [69] were also studied. A technique to evaluate the fraction of micelles in the ferrofluid volume was proposed in work [70], while carrying out the structural analysis of the micelle formation in aqueous commercial ferrofluids with double stabilization by dodecylbenzene sulfonic acid.

A model was proposed [71] for the aggregate restructuring, when PEG is added into the system. Initially, the ferrofluid mainly consists of separate magnetite particles covered with a double layer of sodium oleate and their small associates. If there is an excess of a free surfactant in the liquid carrier, which is required for the stabilization, micelles are formed from the nonadsorbed surfactant. The added PEG partially substitutes the surfactant on the accessible particle surface and modifies the shell, leaving its thickness approximately the same. However, separate particles are not as stable as before, and they form new large aggregates of the fractal type. The initial aggregates, as well as separate particles, become unstable because of the PEG penetration into the stabilizing shell. They grow and precipitate in the course of preparation, which explains a reduction of the magnetite volume fraction in the final system. It is important to note that the amount of added PEG is, to some extent, crucial for the observed transition. If the concentration of added PEG is half as high, the described transition is not observed, and

the structural properties of the fluid differ insignificantly from those of initial ferrofluid, despite that the substitution and the adsorption of PEG on magnetite is registered [70]. Therefore, it should be said about a certain optimum between the biocompatibility (the amount of PEG) and the stability (the amount of sodium oleate) of ferrofluids on the basis of mixed stabilization.

5. Conclusions

In this work, on the basis of real examples, the capabilities and advantages of the method of modified basis functions in the contrast variation were demonstrated for three types of ferrofluids. The results of integrated studies (a combination of a number of complementary methods) of ferrofluids, which are important from the viewpoint of technical and biomedical applications, were reported. The role of the SANS method (with polarized and nonpolarized neutrons) in the restoration of a ferrofluid structure was shown. A number of effects observed at the stabilization of oxide magnets in solvents with various polarities was revealed and explained.

Summarizing the researches discussed in this work, a conclusion can be drawn that, when the matter concerns highly disperse nanosystems, the results obtained by one method should be used very carefully, when interpreting the results obtained by the other method. In special cases, e.g., polydisperse multicomponent systems, for the structure analysis to be adequate, experiments should be carried out by consecutively varying the system parameters and analyzing the “relative” variations of quantities rather than their magnitudes.

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НЕЙТРОННІ ДОСЛІДЖЕННЯ ФЕРОРІДИН

Резюме

Огляд присвячений нейтронним дослідженням різного типу магнітних рідинних систем (ферофлюїдів). Розглянуто переваги і недоліки інших комплементарних методів структурного аналізу рідинних наносистем. Метод малокутового розсіювання нейтронів (МКРН) з довжиною хвилі 0,1–1 нм є класичним прикладом використання випромінювань при визначенні структури наносистем на рівні розмірів 1–100 нм. На реальних прикладах показані можливості МКРН методу при дослідженні структури ферорідин і ефектів у них.