Crystalisation of aqueous ferrofluids at the free liquid interface investigated by specular and off-specular x-ray reflectometry

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Abstract. Structural organization of nanoparticles from aqueous ferrofluids on free liquid surface was studied by X-ray reflectometry. The observed layered structure at interface is associated with the evaporation of the solvent. By orienting an external magnetic during evaporation of the aqueous ferrofluids their structural organization can be manipulated. For a magnetic field applied perpendicular to the surface a more pronounced ordering along the surface normal is observed as in the case of a parallel field. Independent on the orientation of the magnetic field a ~ 20 µm thick surface layer of depleted nanoparticle concentration is found at the interface.

1. Introduction
Ferrofluids (FFs) are fine stable dispersions of magnetic nanoparticles in liquids and belong to the class of advanced nanomaterials. To ensure the long-term stability of FFs the magnetic nanoparticles are coated with some stabilization layers, which prevent the particle coagulation induced by attractive van der Waals forces and magnetic interactions. FFs have been widely used in various industrial and technical fields. The present-day interest to these systems is also associated with their prospects in actively developing medical applications such as drug targeting, magnetic resonance imaging (contrast medium), magnetic hyperthermia for cancer treatment, etc. [1, 2]. For this purpose, many efforts are concentrated to the synthesis of highly stable, reproducible and controllable water-based ferrofluids. Structure characterization of FFs in last two decades focused mainly on the organization of bulk solutions, which is well accessible via small-angle X-ray (SAXS) and neutron (SANS) scattering (e.g., see review [3, 4]). At the same time, because of specific adsorption properties, the behavior of magnetic nanoparticles and surfactants in FFs at interfaces with solids and gases differs significantly from that in bulk, which is to be also considered with respect to application purposes [5–7]. An additional point is that a possible difference in the stability of FFs in bulk and at interfaces should be taken into account in the requirements for the stabilization of these systems with respect to their storage, namely
their destabilization at hydrophilic and hydrophobic interfaces like functionalized container walls or the free liquid surface under varying storing conditions (temperature, humidity etc.).

In our previous works [8–11] we investigated the structure organization of ferrofluids at a silicon wall by neutron reflectometry. We found that a single layer of sodium oleate stabilized FFs, dissolved in polar as well as non-polar solvents, arranges at the interface as a transition zone [8, 10]. Additionally we proved that the specific adsorption properties of ferrofluids at interfaces is independent on their core material but can be manipulated by the stabilizing shell [11]. According to neutron reflectometry and small-angle neutron scattering experiments we found a clear correlation between the bulk and its structure at the solidliquid interface for initial aqueous ferrofluids and after PEG polymer modification of water-based FFs[9].

Recently, several works were published in which behavior of ferrofluids at interface with air is investigated. Thus, in [6, 7] formation of the specific layers from surfactant and magnetic particles on free surface of aqueous FFs was reported. Such a structural organization was observed irrespective of the concentration of particles (volume fraction of magnetite 2% and 7%) and after repeated cleaning of the surface. Therefore, the authors concluded [6] that this structure is a characteristic structural organization of magnetic particles near the free surface for aqueous FFs with steric stabilization. This result was verified in [7]. In order to obtain a more homogeneous and controlled surface of the FFs, the authors attempted to exclude the specific layered organization of FFs components in two different ways. However, in both cases, such a structural organization was observed on the surface, but with a slightly different concentration of particles and the thickness of the layer. At the same time, the dependence of this effect on the concentration of magnetite in volume was not detected. The authors concluded [7] that the described two-layer material can be assumed as an essential equilibrium feature inevitably existing at the interface of water-based ferrofluids with gas. For organic FFs only one layer of magnetic nanoparticles was observed [6].

In the present work we investigate the free surface of ferrofluids using X-ray reflectometry. From the data obtained, we can conclude that the self-organization of FFs nanoparticles at the interface with gas is depended on concentration of nanoparticles and the direction of the applied external magnetic field. An additional particles organization near the surface is observed for perpendicular magnetic field.

2. Experimental

Preparation of magnetic fluid was based on the co-precipitation reaction to produce nanomagnetite ($Fe_3O_4$). The FFs were synthesized at the Institute of Experimental Physics, Slovak Academy of Sciences (IEP SAS), Slovakia, in accordance with the procedure described in [12]. To avoid aggregation between magnetite particles they were covered by a double layer of sodium oleate ($C_{17}H_{33}COONa$) with a surfactant/magnetite mass ratio ranging from 0.73 to 1. Two FFs with magnetite volume fractions of $\varphi_m = 0.4$ vol. % and $\varphi_m = 6.6$ vol. % were prepared. The exact magnetite concentrations in the FFs were determined by the static magnetization analysis (MPMS SQUID magnetometer, IEP SAS).

The free surface of FFs was investigated at the NREX instrument (Garching, Germany) using the X-ray reflectometer mode. The scans were either done in $\theta - \theta$ geometry, i.e. the sample position was fixed and only detector and source were moved or a series of detector scans for fixed incidence angles to map the reciprocal space. In both cases the sample was not moved during the experiment. To study the surface of the the liquid system in a reflectometer, a bath of inert material is used. To reduce the evaporation, the bath is placed in a closed casing, which allows to create additional pressure and maintain a certain temperature and to provide the surroundings of the bath with an inert gas. Fig. 1 shows the details of the experimental set-up. While on the left side the magnetic field is applied vertically with respect to the liquid interface it is parallel oriented on the right picture. Between the steel plates, which are separated by
permanent magnets, a trough made of PTFE is placed. In this setting magnetic fields of 100 Oe at the trough position and in the respective orientations were achieved. It should be noted that it is necessary to provide a special sample holder for the reduction of any mechanical vibrations during the study of free surfaces of liquid systems. For this purpose, specific anti-vibration platforms are used, which can extinguish even significant fluctuations.

3. Results and discussion
During the measurement of the magnetic fluid with concentration of 0.4 vol. % the solvent was evaporating from ferrofluid. For correct interpretation of the data, the reflectometry curves were taken during and after the complete evaporation of the solvent. The data are presented in fig. 2a. Scattering map for this system after solvent evaporation is shown in fig. 2b. Complex structural organization on the free surface of the ferrofluid was concluded from the resulting curve. The

Figure 1. Photographs of the working chamber of the reflectometer NREX for the study of liquid systems using X-rays.

Figure 2. (a) Experimental reflectometry dependences for the free surface of the aqueous ferrofluids before (black circles) and after evaporation of the solvent (red squares). Arrows show correspondent Brag peaks at reflectivity curves. (b) Scattering map for ferrofluids after evaporation of the solvent. Specular reflection is presented by dashed line. Diffuse scattering are shown by arrows.
found Bragg-peaks at reflectivity curves (fig. 2) indicate a periodic structure in both cases. In addition, after the evaporation we investigated the formed layered structure using off-specular reflectivity. Since the evaporation is an ongoing process during a x-ray scan it is hopeless to model the reflectivity curves. Instead we make use of the position of the characteristic Bragg-peaks. According to the rule $D = 2\pi/q$, where is the wave vector transfer between the maxima on the curve. The resulting size is about 4 nm. This is twice less than the average diameter ($D \sim 8 \text{ nm}$) of the magnetic particles in the ferrofluid. This means that when the solvent is completely evaporated from a magnetic fluid, the magnetic particles are packed in a layered structure with a dense packing. On reflectometry curves (see fig. 2a), obtained before and after evaporation of the solvent, we see the coincidence of the position of the Bragg-peaks. From this fact, it can be assumed that during the investigation of the free surface of the ferrofluid there is a process of evaporation of the solvent from the near-surface layer of the liquid system, which increases the concentration of nanoparticles in the near-surface layer. An increase in the concentration of particles in this layer leads to their aggregation. Therefore, to exclude effect of solvent evaporation on reflectometry data, special cell for magnetic fluid should be used in future experiments. Form the off-specular measurement (fig. 2b) we have to conclude that the NP arrangement seems to be isotropic in 3D. Since the probed lateral $q$-space is rather small, additional scans under grazing incidence at larger $q$-values are necessary to prove this hypothesis.

Figure 3. Experimental data of the X-ray reflectometry experiment for the free surface of ferrofluid with a volume fraction of magnetite of 0.4% (a) and 6.6% (b) under the application of the magnetic field in parallel (blue squares) and perpendicularly (red circles) to the surface of the ferrofluids

The additional investigation of the structural reorganization of nanoparticles at the free surface was carried out for two concentrations of magnetite in the ferrofluids under application of an external magnetic field. The experiment was done at two direction of field (perpendicular or parallel to the surface of the ferrofluids) and constant magnetic field with an induction of 0.01 T. Ferrite magnets with two metal plates were used for creation magnetic field at the sample, as is presented on fig. 1. In fig. 3a the reflection as function of the scattering vector $q$ is shown for both magnetic orientations for the free surface of the magnetic fluid with a $\varphi_m = 0.4 \text{ vol. \%}$. In the investigated system, with the perpendicular direction of the magnetic field, we can see the additional structural organization of the magnetic particles. This corresponds to the creation of a layer of particles near the surface. Obviously the orientation of the magnetic field has an impact on the resulting NP arrangement. Due to technical reasons the liquid sample is instable during the measurements and these results have only preliminary character. Nevertheless for higher NP-concentration ($\varphi_m = 6.6\%$) two critical edges are observed for both field directions.
The lower one at $q = 0.023 \ \text{Å}^{-1}$ corresponds well with the expected value for pure sodium oleate ($q_{\text{crit}, C_{18}H_{33}NaO_2} = 0.0229 \ \text{Å}^{-1}$ at $\rho = 1.2 \ \text{g/cm}^3$) and the higher at $q = 0.047 \ \text{Å}^{-1}$ with the one for magnetite $q_{\text{crit}, Fe_3O_4} = 0.0444 \ \text{Å}^{-1}$ at $\rho = 5.2 \ \text{g/cm}^3$). The steep step between both plateaus of total external reflection ($\sim$ 97\% attenuation) can serve as a rough estimate for the thickness of the absorbing layer. Since the $k$-absorption of iron (7.11 keV) is close to the one for $Cu$ (8.14 keV) strong x-ray fluorescence is expected. Indeed the mass attenuation coefficient for $Fe_3O_4$ exceeds for photons with 8 keV a value of $\mu = 2400 \ \text{cm}^{-1}$. Using the Lambert-Beer absorption law one calculates a thickness of roughly 20 $\mu$m.

4. Conclusions
As a result of the work, it was discovered that the evaporation of the solvent from the free surface of the ferrofluid leads to the aggregation of its nanoparticles and the creation of the layered structure. It was found that structural organization of nanoparticles at the air/FFs interface dependent on concentration of magnetite in initial FF. The highest effect on additional particles organization near surface is observed for perpendicular to the surface magnetic field.

Acknowledgments
The work was financed via Russian scientific foundation (project 14-12-00516). Also this work was supported by the VEGA 0045, Radiimag COST TD 1402, MERANET MACOSYS and by Ministry of Education Agency for Structural Funds of EU in frame of Projects 26220120005 and 26220120033.

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