

Structure analysis of aqueous ferrofluids at interface with silicon: neutron reflectometry data

I V Gapon^{1,2*}, V I Petrenko^{1,2}, L A Bulavin², M Balasoiu^{1,3},
M Kubovcikova⁴, V Zavisova⁴, M Koneracka⁴, P Kopcansky⁴,
H Chiriac⁵, M V Avdeev¹

¹ Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

² Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

³ National Institute of Physics and Nuclear Engineering, Bucharest, Romania

⁴ Institute of Experimental Physics, SAS, Kosice, Slovakia

⁵ National Institute of Research & Development for Technical Physics, Iasi, Romania

E-mail: gapon@jinr.ru

Abstract. Adsorption of nanoparticles from aqueous ferrofluids (FFs) on solid surface (crystalline silicon) was studied by neutron reflectometry (NR). Two kinds of FFs were considered. First kind was heavy water-based ferrofluids with magnetite nanoparticles coated by double layer of sodium oleate. Second one FF was cobalt ferrite nanoparticles stabilized by lauric acid/sodium n-dodecylsulphate layer and dispersed in water. It was obtained only a single adsorption layer for two types of ferrofluids. The impact of the magnetic nanoparticles concentration and geometry was considered in frame of the adsorption characteristic of FFs.

Introduction

Ferrofluids (FFs) or magnetic fluids (MFs) are unique systems combining magnetic properties and fluidity. They consist of magnetic nanoparticles (with a characteristic size of about 10 nm) placed in a liquid medium. To prevent aggregation, the particle surface is coated usually by a surfactant layer. Study of MFs is of great practical and fundamental importance (e.g. [1, 2]). Mainly papers devoted to the bulk structure of magnetic fluids, which is well observed by small-angle X-ray (SAXS) and neutron (SANS) scattering (e.g. see review in [3, 4]). However, ferrofluids have specific adsorption properties and the behavior of microstructure in MFs at interfaces with solids can be different from that in bulk, which is also important in respect of practical and fundamental point of view. are devoted The study structure organization of magnetic nanoparticles (MNPs) assembling into layer were done in recent few papers [5–7]. Using various methods it was shown that specific self-assembly of the nanoparticles occurs during the solvent evaporation, therefore interaction between the film and a substrate plays an important role in the ordering. Also an important point which should be considered is difference in the stability of MFs in bulk and at interfaces. It should be taken into account in the requirements for the stabilization of these systems with respect to their storage, namely to the interaction of the FFs particles with container walls under different conditions.

Thus, some kind of ordering into layered structures at the interface with silicon was reported [8] for a concentrated water-based MF (nanomagnetite coated by double layer of sodium oleate in



heavy water) with magnetic volume fraction $\varphi_m \sim 10\%$. Specular neutron reflectivity curve was analyzed and layers formation was found at the silicon substrate. It was shown that this ordering is strongly dependent on the particle concentration and sensitive to the external magnetic field. In a similar way, less concentrated analogue of the water-based MF ($\varphi_m \sim 1\%$) was compared [9] with the highly stable MF based on organic non-polar liquid carrier (nanomagnetite coated with oleic acid in deuterated benzene). In both cases, the formation of only one well-defined adsorption layer of nanoparticles on silicon surface was concluded. An interesting question is at what extent the bulk structure of MFs influences their adsorption properties. To clarify this point, in the given work we have performed similar kind of NR experiments applied to the various kinds water-based MFs. First kind of MFs was based on heavy water (D_2O) (nanomagnetite coated by double layer of sodium oleate) with concentration $\varphi_m = 2.1\text{ vol. \%}$ and $\varphi_m = 3.9\text{ vol. \%}$. Second kind FF was prepared on H_2O with cobalt ferrite nanoparticles (stabilization layer: lauric acid/sodium n-dodecylsulphate (DDS-Na)) with concentration of nanoparticles $\varphi_m \sim 3\text{ vol. \%}$. Heavy water was added to initial FF of the second kind to satisfy the condition of the total specular reflection of the neutron beam in the NR experiments.

Experimental

Preparation of first type aqueous magnetic fluid was based on the co-precipitation reaction to produce nanomagnetite (Fe_3O_4). MF was synthesized at the Institute of Experimental Physics, Slovak Academy of Sciences (IEP SAS), Slovakia, in accordance with the procedure described in [10]. To avoid aggregation between magnetite particles they were covered by a double layer of sodium oleate ($C_{17}H_{33}COONa$) with the following surfactant/magnetite mass ratio 0.73 to 1. Two ferrofluids with different volume of magnetite $\varphi_m = 2.1\text{ vol. \%}$ and $\varphi_m = 3.9\text{ vol. \%}$ were prepared. Magnetite concentration in the magnetic fluids was determined by the static magnetization analysis (MPMS SQUID magnetometer, IEP SAS).

Ferrofluid of the second kind was prepared at the Institute of Technical Chemistry (Perm) [11,12] by the co-precipitation of $Fe(OH)_3$ and $Co(OH)_2$, ferritisation of hydroxide mixture in 1M alkali aqueous solution, adsorption of lauric acid on ferrite particles and peptisation of hydrophobic precipitate in aqueous solution with sodium n-dodecyl sulphate.

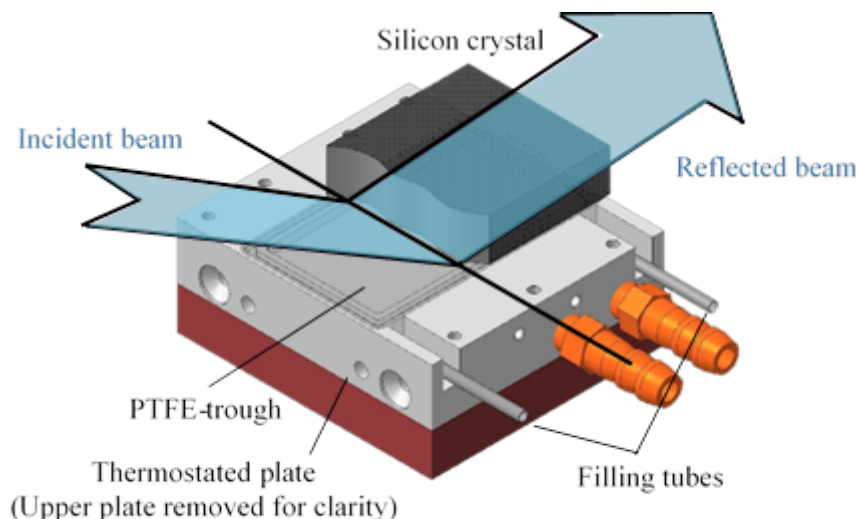


Figure 1. Schematic view of the neutron reflectivity cell for solid/liquid interface study

A principal scheme of the NR experiments with a solid-liquid interface was similar to that in our previous works [9,13]. The NR experiments were performed at the GRAINS reflectometer (Joint Institute for Nuclear Research, IBR2 reactor, Russia) with vertical scattering plane. Experiments at the GRAINS reflectometer were conducted in TOF (time-of-flight) mode with neutron wavelength range of $0.05 - 0.7 \text{ nm}$. For experimental with liquid/solid interface special cell was build. Principal scheme is presented on Fig.1. It is some kind modification of the extensively used liquid/solid cell from V6, BERII [14]. Here the neutron beam passes the front facet of a monocrystalline 111 oriented silicon block (dimensions: $80 \times 50 \times 15 \text{ mm}^3$). Reflection of the neutrons takes place at solid/liquid interface, a polished Si-surface with size $80 \times 50 \text{ mm}^2$ and roughness $\sigma_{Si} = 5 \text{ \AA}$ in contact with the ferrofluid. The required volume of liquid in a PTFE-trough is less than 10 ml. Holes in the edges of the trough allow changing the liquid volume bubble free. After leaving the backside of the Si-block the neutrons (reflected neutrons) are detected by the 2D position-sensitive detector. Before the measurements the polished Si-surface was cleaned and hydrophobized by applying the RCA-1 protocol. During the measurement a thermostat (Julabo F25-ME, JULABO GmbH, Germany) kept the sample under investigation at a constant temperature (20°C).

Results and discussion

The experimental reflectivity, R , for magnetite/sodium oleate/heavy water MFs at the silicon interfaces are represented at Fig.2a as $R Q_z^4$ to enhance the differences in the data from the samples under study and demonstrate the quality of the fits. The deviations of the curves in Fig.2 from Fresnel law (reflection from two semi-infinite homogeneous mediums) indicate that there are some layer formations at the interface caused by adsorption of particles from MFs. The curves were treated in the frame of the Parrat formalism [15] by using Motofit program [16]. For this type MFs the best fits (solid lines in Fig.2a) were obtained using a two layer model with an effective SLD (corresponding to the momentum transfer vector values, seen in the curves) on the silicon substrate. The corresponding SLD profiles along the surface normal are shown in Fig.2b. These SLD profiles might be interpreted similar to previous works [9,13]. The revealed two layers with significantly different SLDs can be considered as two sub-layers of one layer of colloidal core-shell particles adsorbed on the silicon substrate. The width ($\sim 5 \text{ nm}$) and SLD ($\sim 0 \text{ nm}^{-2}$) of the first sub-layer are close to the corresponding parameters of the surfactant shell (sodium oleate) around magnetite in MFs, while the width of the second sub-layer is well associated with the mean diameter of magnetite nanoparticles, $D \sim 6 \text{ nm}$. The mean SLD of this sub-layer is significantly lower than that of magnetite ($\rho = 6.9 \cdot 10^{-4} \text{ nm}^{-2}$) because of the large fraction of surfactant in it. In addition, it is found concentration dependence of the filling of the adsorption layer. More concentrated magnetic fluid more clear and sharp border was observed. This result is comparable with the paper [8] where multilayer adsorption structure for concentrated MFs was observed. It should be noted that in this case we have to mention that important parameter is the concentration of single magnetic particles as that individual non-aggregated nanoparticles are preferably adsorbed [9].

The experimental curves together with best fits and Fresnel law for second type MFs are presented on Fig.3a. This type of magnetic fluid was prepared in light water with MNPs consist from cobalt ferrite/lauric acid/DDS-Na. This liquid has a smaller SLD ($\rho \sim -0.52 \cdot 10^{-4} \text{ nm}^{-2}$) than silicon ($\rho = 2.07 \cdot 10^{-4} \text{ nm}^{-2}$) therefore we don't have total reflection. On Fig.3a. comparison of the experimental NR curve with Fresnel law are presented and additional structural organization as in previous case is concluded. But it was difficult to analyze the data in this case due to the high background from sample and small contrast between the solvent and the stabilizer shell of the particles. Obtained reflectivity data for such system after the addition of heavy water (about 50% D_2O in final MF) was used for analysis of the adsorption. With this contrast we have real critical momentum transfer vector (see Fig.3a) which was used to

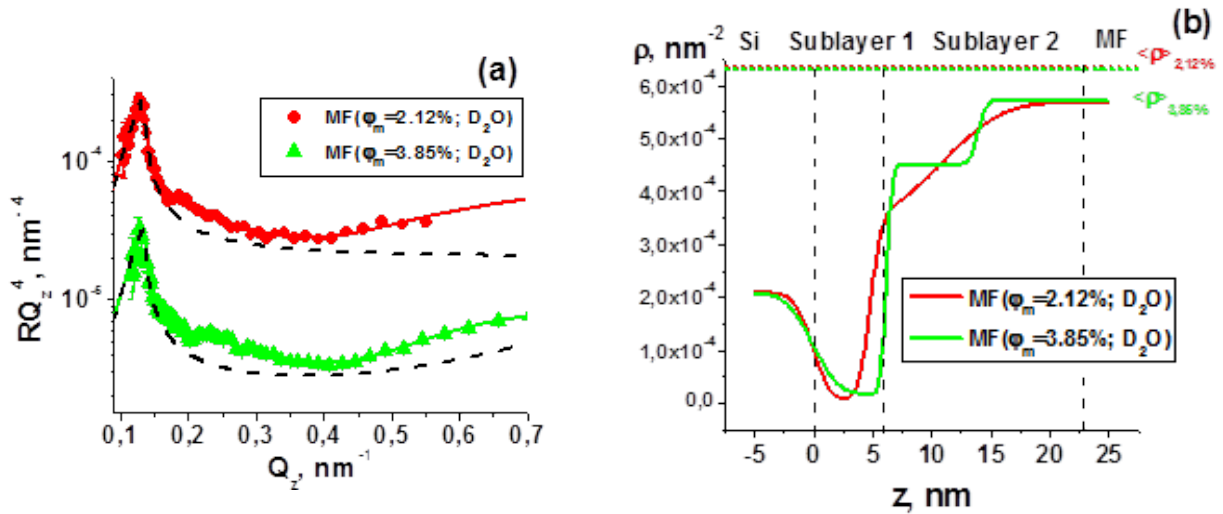


Figure 2. (a) Experimental reflectivity curves (points) together with fits (solid lines) for first type MFs with concentration: 2.1 % (red circles), 3.9 % (green triangles); black curve (dashed line) is correspond with Fresnel law (the curves for the two concentrations of MFs are shifted over the reflectivity axis for the convenient representation); (b) found from experimental data SLD profiles for two studied kinds of solid/liquid interfaces.

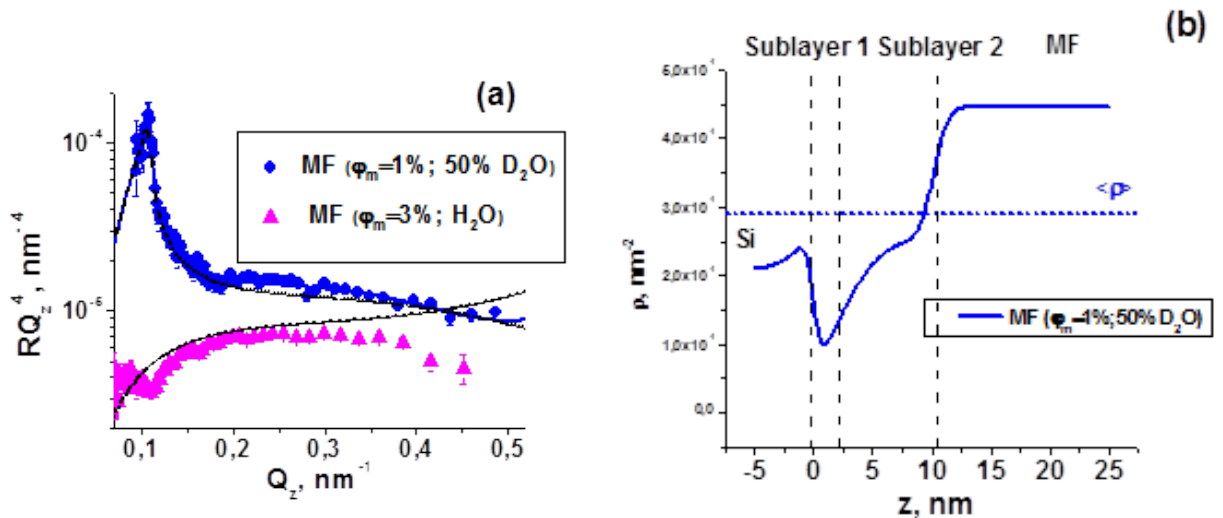


Figure 3. (a) Experimental reflectivity curves (points) together with fits (solid lines) for aqueous MF after dilution by D₂O (blue circles), initial aqueous magnetic fluids (magenta triangles); black dashed line is correspond with Fresnel law; (b) found from experimental data SLD profile for solid/liquid interface.

obtain bulk SLD. SLD profile which getting from best fit experimental data are show on Fig.3b. Model using to approximation is similar to previous case. The resulting fit was got first sublayer (consist of surfactant) has a size of about 2 nm. SLD of the second sublayer is 2.5 nm and the thickness of about 8 nm with large roughness (about 3 nm). This result is corresponding with bulk structure [17]. MNPs have ellipsoid forms with middle size about 8 nm. High roughness of second sublayer and low thickness of first sublayer correspondingly might be explained by disoriented ellipsoids of the MNPs.

Conclusions

Similar structural organizations of MFs at interface with silicon were concluded from NR experiments for two aqueous MFs with various bulk structures and chemical composition of magnetic nanoparticles and stabilization agents. It was obtained that individual non-aggregated nanoparticles are preferably adsorbed on the oxidized silicon surface from the aqueous MF to form a single adsorption layer. Values of the structural parameters of the adsorption layer are changed due to the different bulk structure of ferrofluids. Denser adsorption layer was observed at the increasing of the monomer concentration of magnetic nanoparticles in bulk of magnetic fluids.

Acknowledgments

The work is partially done in the frame of the RFBR grant # 14-22-01054 ofi_m. Also this work was supported by the VEGA 0045, Radiomag COST TD 1402, MERANET MACOSYS and by Ministry of Education Agency for Structural Funds of EU in frame of Projects 26220120005 and 26220120033. Authors acknowledge the grant of Romanian Plenipotentiary Representative No. 94/2016 item 16.

References

- [1] Odenbach S (ed) 2009 *Colloidal Magnetic Fluids* vol 763 (Berlin: Springer-Verlag)
- [2] Torres-Daz I and Rinaldi C 2014 *Soft Matter* **10** 8584–8602
- [3] Balasoiu M, Avdeev M and Aksenov V 2007 *Cryst. Rep.* **52** 505–511
- [4] Avdeev M V and Aksenov V 2010 *Phys. Uspekhi* **53** 971
- [5] Sun S, Murray C, Weller D, Folks L and Moser A 2000 *Science* **287** 1989–1992
- [6] Bodnarchuk M I, Kovalenko M, Pichler S *et al.* 2009 *ACS nano* **4** 423–431
- [7] Mishra D, Benitez M, Petravic O *et al.* 2012 *Nanotechnology* **23** 055707
- [8] Vorobiev A, Major J, Dosch H, Gordeev G and Orlova D 2004 *Physical Review Letters* **93** 267203
- [9] Avdeev M V, Petrenko V I, Gapon I V *et al.* 2015 *Appl. Surf. Sci.* **352** 49–53
- [10] Zavisova V, Koneracka M, Muckova M *et al.* 2011 *J. Magn. Magn. Mater.* **323** 14081412
- [11] Kaur-Rajput J and Kaur G 2013 *Chinese Journal of Catalysis* **34** 1697
- [12] Creanga D E, Iacob G, Ursache M, Nadejde C and Racuciu M 2008 *J. Optoelectron. Adv. Mater.* **10** 628
- [13] Gapon I V, Petrenko V I, Avdeev M *et al.* 2014 *J. Surf. Investigations.* **9** 320–325
- [14] Howse J H, Manzanares-Papayanopoulos E, McLure A *et al.* 2002 *Journal of Chemical Physics* **116** 7177
- [15] Parratt L G 1954 *Phys. Rev.* **95** 359–369
- [16] Nelson A 2006 *Journal of Applied Crystallography* **39** 273–276
- [17] Balasoiu M, Ivankov O I, Soloviov D, Lysenko S, Yakushev R, Balasoiu-Gaina A M and Lupu N 2015 *Journal of Optoelectronics and Advanced Materials* **17** 1114–1121