Adsorption of maghemite nanoparticles at liquid/gas interfaces

M. Paulus[1], P. Degen[2], M. Maas[2], R. Kahner[2], S. Schmacke[1], S. Tiemeyer[1], S. Leick[2], M. Tolan[1], H. Rehage[2], and B. Struth[3]

[1]Fakultät Physik/DELTA, Technische Universität Dortmund, 44227 Dortmund, Deutschland

[2]Fakultät Chemie, Technische Universität Dortmund, 44227 Dortmund, Deutschland

[3]Deutsches Elektronensynchrotron, HASYLAB, Notkestr. 85, 22607 Hamburg, Deutschland

Nanoparticle materials are interesting candidates for the development of advanced materials with regard to magnetic, optic and electronic properties [1-3]. Because of the broad range of applications where nanoparticles are used for surface and interface modification a better knowledge about the arrangement of nanoparticles at these interfaces is of scientific interest. Thus, our study focuses on the adsorption of maghemite (γ-Fe_2O_3) nanoparticles at different gas/liquid interfaces. In order to study the effect of electrostatic interaction between the positively charged nanoparticles and the gas/ liquid interface differently charged Langmuir films (stearic acid, stearic alcohol and stearic amin) were prepared on the nanoparticle solution. Beside this, the adsorption of maghemite nanoparticles at the bare gas/water interface and at a laterally polymerized OTS (poly(organosiloxane)) network was studied.

The x-ray reflectivity technique was applied in order to resolve the vertical structure of the gas/liquid interface while grazing incidence diffraction was used to study the influence of adsorption on the crystallinity of Langmuir films. All experiments were carried out at beamline BW1 using the liquid surface scattering set-up at a photon energy of 9.5 keV. The γ-Fe_2O_3 nanoparticles were prepared at pH 3.5 leading to an average diameter of d = 8 nm and a zeta potential of ξ = +35 mV. Two different nanoparticle concentrations (0.07g/L and 0.7g/L) were used.

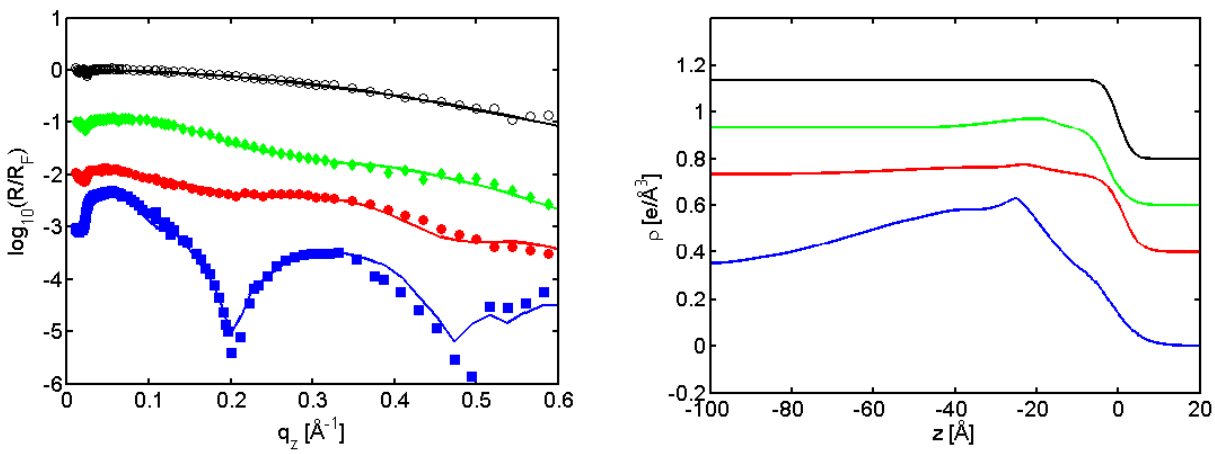

Figure 1: left: X-ray reflectivities of different gas/liquid interfaces normalized by the Fresnel reflectivity (symbols) as a function of the vertical wave vector transfer q_z. Black: pure water surface, green: stearic amin, red: stearic alcohol, blue: stearic acid (c=0.07g/L). The refinements are displayed as solid lines. Right: corresponding electron density profiles. For better visualization the curves are shifted vertically.

The effect of the electrostatic interaction on the adsorption process was revealed using negatively charged stearic acid, neutral stearic alcohol and positively charged stearic amin [4]. The reflectivites and resulting electron density profiles of the liquid/gas interfaces are shown in figure 1. It becomes clearly visible that the electrostatic attraction between the positively charged particles and the negatively charged Langmuir film leads to the formation of a dense particle film (blue line) while

the repulsive interaction between the particles and the positive charged stearic amin film prevents the layer formation (green line). The system consisting of a neutral stearic alcohol Langmuir layer shows only week adsorption (red line), which is conform to concentration dependent measurements at the bare liquid/gas interface which only exhibit nanoparticle adsorption when the nanoparticle concentration in the bulk liquid was raised significantly [5]. As visible in figure 1 the increase of electron density can be also observed in the Langmuir layer region, which points to a penetration of nanoparticles into the Langmuir film.

The effect of nanoparticle adsorption on the Langmuir films crystallinity is visualized in figure 2 were the [10] reflection of a hexagonal packed OTS layer is displayed in presence and absence of nanoparticles (green and red line). The peak width was used to determine the size *L* of the crystals using the Scherrer formula. It turned out that the nanoparticles reduced the average size *L* of the OTS crystals from *L*=113Å to *L* =57Å.

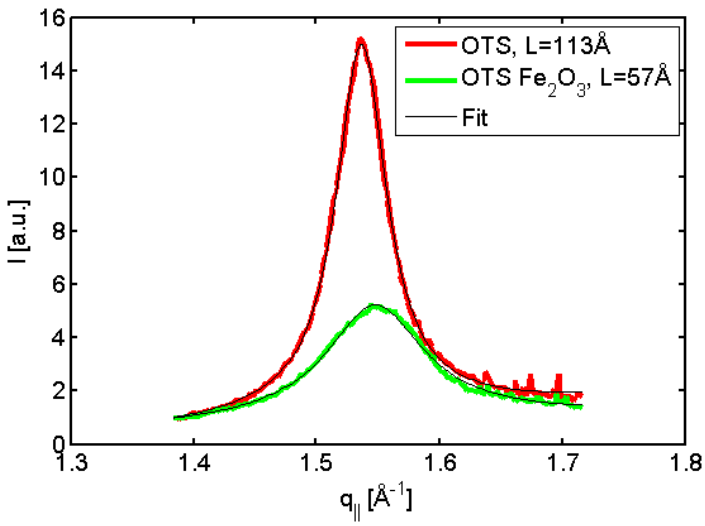

Figure 2: GID data of the [10] reflection of a hexagonal packed OTS layer. Red line: without nanoparticles, green line with nanoparticles. The black lines show the refinements to the data.

References

[1] B. Berkovskyl, V. G. Bashtovoy, *Magnetic Fluids Applications Handbook*, Begell House Inc, New York (1996).

[2] A. K. Gupta, M. Gupta, Biomaterials, **26**, 3995 (2005).

[3] Q. A. Pankhurst, J. Connolly, S. K. Jones, J. Dobson, J. Phys. D:Appl. Phys., **36**, 167 (2003).

[4] P. Degen, M. Paulus, M. Maas, R. Kahner, S. Schmacke, B. Struth, M. Tolan, and H. Rehage, Langmuir 24, 12958 (2008).

[5] M. Paulus, P. Degen, S. Schmacke, M. Maas, R. Kahner, B. Struth, M. Tolan, and H. Rehage, European Physical Journal Special Topics **167**, 133 (2009).