

# Surface Layers of Maghemite Nanoparticles with Oleic Acid Shells

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Polymer nanocomposites are intensely investigated because nanoparticles improve polymer properties already at very low volume fractions and because they provide additional functionalities that would otherwise not be available for polymeric materials [1,2]. Tailoring the structure of nanocrystal superlattices is an important step toward controlled design of novel nanostructured materials and devices. Here, we study the self-assembly in two dimension of cubic maghemite ( $\text{Fe}_2\text{O}_3$ ) nanoparticles with a shell of oleic acid. The layers are prepared at the air/water interface [3].

Three different batches of nanocubes are investigated. Electron microscopy shows that they differ in their side length: sample (a): 8.4 nm, (b) 8 nm, (c) 5.5. The lateral structure of the monolayer is measured with X-ray GID (Grazing Incidence Diffraction) and reflectometry at BW1, in the liquid surfaces set-up [4]. Isotherms of the lateral pressure vs the nanoparticle area indicate structural rearrangements. However, even before the lateral pressure increases, diffraction peaks are observed (cf. Fig. 1). On monolayer compression, up to the onset of the lateral pressure increase, the peaks increase in intensity, yet the peak position does not vary. Apparently aggregates form spontaneously, their surface coverage increases on monolayer compression. The peak width indicates that an aggregate consists of about 10 nanocubes. Up to nine diffraction peaks are measured. Note that almost all peaks have a maximum at  $Q_z=0$ , indicated that the cube faces are aligned parallel to the water surface (yet one peak of sample (a) deviates). The peak at the lowest  $Q_{xy}$ -value shows a very pronounced rod scan. It allows to determine the thickness of the monolayer, and amounts to 8.1, 7.2 and 5.5 nm for samples (a), (b) and (c), respectively. These values are consistent with the diameters of the nanocubes determined with electron microscopy.

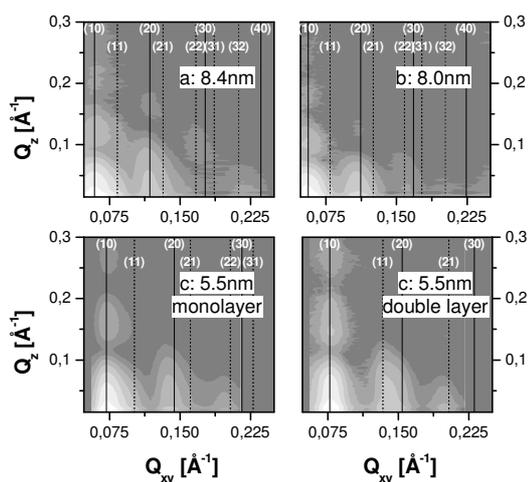


Figure 1: Small angle GID data obtained from Langmuir layers of laterally ordered cubic maghemite nanocubes with an oleic acid shell. Monolayers of different nanocubes (edge length indicated) are investigated at the onset of the increase of the lateral pressure. Additionally, data from a double layer (bottom right) are shown (for the isotherm, see Fig. 2). For the monolayer (double layer) the peak positions corresponding to a square (hexagonal) lattice are indicated by lines. Straight lines symbolize (h0) peaks, dotted lines (hk) peaks with  $k \neq 0$ .

The superstructure parallel to the water surface determines the peak positions at specific  $Q_{xy}$ -positions. For all monolayers, the data are consistent with a quadratic lattice (cf. Fig. 1). However, we do not observe all peaks expected for a quadratic lattice. This is due to systematic extinctions, which can be explained qualitatively by the very large form factor of the maghemite nanoparticles. We performed model calculations, and found that (h0) peaks are less likely to suffer systematic extinction. Therefore, the first peak is indexed (10), and the second (20). Then, the side length of the quadratic superlattice of samples (a), (b) and (c) is 11 nm, 11 nm and 9.2 nm, respectively. For all three samples, the lattice parameter exceeds the side length of a nanocube by 3 – 3.7 nm, suggesting a bilayer of oleic acid between the faces of the nanocubes.

In the next step, the monolayer of sample (c) is compressed (cf. isotherm in Fig. 2), and characterized by both X-ray reflectivity (cf. Fig. 2) and GID. X-ray reflectometry shows a double layer of nanocubes. The two nanocube layers are separated by 3 – 3.2 nm of organic material. Again, this value is consistent with the thickness of a bilayer of oleic acid. The GID data (cf. Fig. 1) indicate a hexagonal structure. As for the diffraction pattern of the quadratic lattice, systematic extinction is also prominent for the hexagonal lattice. If the rod scans of the respective lowest order peak of monolayer and double layer are compared, one realizes that the second maximum in  $Q_z$  direction is very asymmetric, suggesting (partial) vertical alignment of the two nanocube layers. Interestingly, the area per nanocube is the same in the quadratic and the hexagonal lattice.

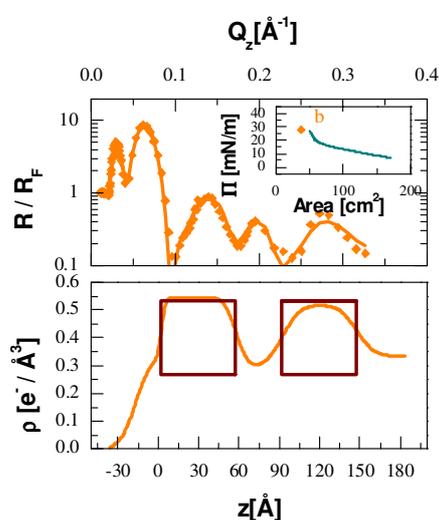


Figure 2: Top: Normalized X-ray reflectivity of a highly compressed layer of sample (c) measured at high lateral pressure as indicated by the isotherm in the inset. Bottom: deduced electron density profile along the surface normal (air/film interface:  $z=0$ ). The squares indicate the position of the nanocubes.

To summarize: the self-organization of maghemite nanocubes with an oleic acid shell is investigated with GID and reflectometry at the air/water interface. Little compressed monolayers have a quadratic superlattice. For one strongly compressed sample, a double layer with a hexagonal lattice is observed. All lattice parameters measured are consistent with a double layer of oleic acid between the faces of the nanocubes.

## References

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