Experimental report

21/05/2024

Proposal:	**9-11-2099**	**Council:**	10/2022

Title: Influence of core size and compression on the conformation and vertical position of plasmonic core-shellmicrogels at air/water interfaces

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: gold nanoparticles
Poly(N-isopropylacrylamide)

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	3	3	22/05/2023	25/05/2023

Abstract:

We want to study plasmonic core-shell microgels confined at air/water interfaces using neutron reflectometry. Through this we want to gain knowledge on the influence of the size of the gold cores and uniaxial compression on the conformation and vertical position at the interface. This information is crucial for understanding the optical response of the monolayers and thus for development of new colloid-based materials with applications in colour-tunable materials, sensing and lasing. We propose to use gold-PNIPAM core-shell microgels with two differently cross-linked shells. Through postmodification of the gold cores we will be able to study monolayers of the same two microgel systems but with significantly overgrown cores. The scattering contrast will be varied through the subphase, i.e. by mixing D2O and H2O. The obtained results will be compared to ex-situ results from microscopy after transfer of the monolayers to solid substrates. Furthermore, we will use in-situ and ex-situ spectroscopy to investigate the plasmonic properties of the monolayers. Through this we will generate a comprehensvie understanding of the structure, arrangement and optical properties of such monolayers.

Neutron reflectometry was performed to analyze the behavior of plasmonic core-shell microgel systems at the air/water interface under uniaxial compression. The objective of the experiment was to study how variations in core size and compression affect not only the conformation, but also the vertical position of the plasmonic microgels. We investigated small and large gold nanoparticle (AuNP) cores, with radii of 7 nm and 46 nm, respectively, encapsulated in a poly(*N*-isopropylacrylamide) (PNIPAM) shell with crosslinker densities of 16.5 mol% and 8 mol%, respectively.

The behavior of the core-shell microgels was already analyzed in bulk using the standard techniques such as light scattering and extinction spectroscopy. Additionally, monolayers were transferred from the air/water interface onto solid substrates for *ex situ* analysis of their structure and properties. However, limited knowledge exists regarding their behavior and vertical profile at the interface. Therefore, neutron reflectometry with the FIGARO instrument is a perfect tool to study the systems under different contrast situations assembled at the air/water interface. During the experiment, we used two subphases to match the AuNP core and the air, respectively. All four sample batches were spread at the interface of both subphases at a temperature of 20 °C. We could measure the reflectivity of each sample at different surface pressures. Thus, we could collect a great set of data to describe the microgels at the interface in detail. Currently, data analysis and comparison between the different samples are in progress. We compare the reflectivity in dependence of crosslinker densities and core sizes.

The isotherm of Au-PNIPAM microgels with small cores (R = 7 nm) and a crosslinker density of 16.5 mol% is shown in Figure 1a. The dots mark the surface pressure at which neutron reflectivity with air contrast matched water was measured. The corresponding neutron reflectivity curves are depicted in Figure 1b with an increase in surface pressure from dark red to dark green.

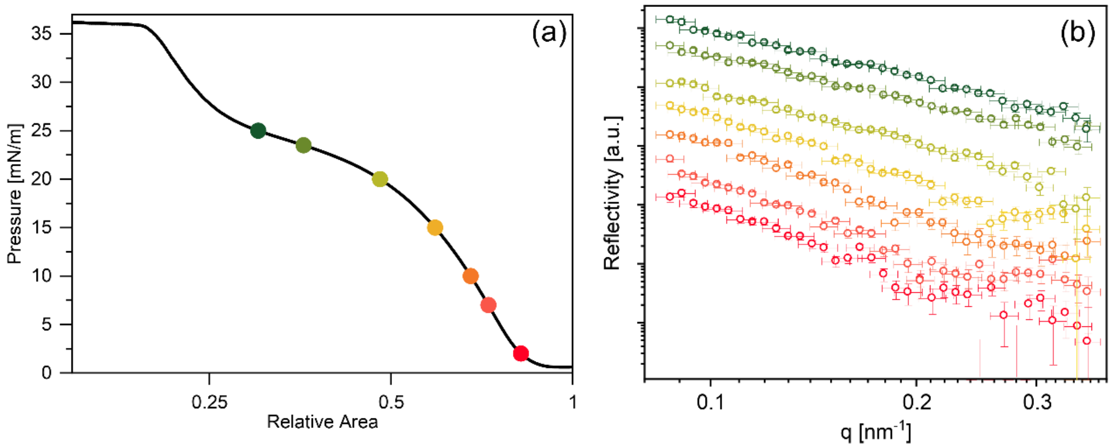

Figure 1: Data of Au-PNIPAM microgels (R_{core} = 7 nm, crosslinker density = 16.5 mol%) (a) Isotherm and surface pressures at which neutron reflectivity with air contrast matched water was measured marked as dots. (b) Neutron reflectivity R as a function of the exchanged wave-vector Q at the corresponding surface pressures. The surface pressure increases from dark red to dark green.

During our experiment, we could not record the complete isotherm in one run. After reaching maximum compression, it was necessary to expand our monolayer. We then added more sample and restarted compression to reach higher surface pressures. We would value the availability of a Langmuir trough with a larger area and consequently a higher compression ratio at FIGARO in the future. Such an enhancement would result in time savings, as there would be no need for expansion and additional sample additions to fully record the isotherm. We would highly appreciate the use of FIGARO instrument for future neutron reflectometry measurements on microgels at the interface.