Experimental report

13/01/2022

Proposal: **9-11-2027** **Council:** 10/2020

Title: Form factor and structure factor analysis of microgels with tailored density gradient.

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Kiran JATHAVEDAN**

Experimental team: Sylvain PREVOST

Local contacts: Sylvain PREVOST

Samples: $(C_6H_{11}NO)_n$

Instrument	Requested days	Allocated days	From	To
D11	3	1	07/06/2021	09/06/2021

Abstract:

Core-shell microgels with tailored softness and core-to-shell ratio are interesting candidates for new soft quasicrystals (QCs). Poly (N-isopropyl acrylamide) microgel is a well-known colloidal system which exhibit peculiar property called volume phase transition. PNIPAM undergoes a temperature-induced volume phase transition (VPT) in water at around 32°C and hence the particle volume fraction can be tuned by temperature. Moreover, the interaction potential of microgels changes from repulsive to attractive at VPTT. We make PNIPAM microgel with a core of highly crosslinked PNIPAM and fuzzy soft shell of less crosslinked PNIPAM chains. A deep understanding of the fuzziness of the shell and density profile of the core and shell is important in designing the QCs. The core-to-shell ratio and temperature can be used as tuneable parameters for the phase transition of the microgels. With SANS, we would like to study the form factor, the structure factor and density profile of PNIPAM particles of different core-shell ratios below and above VPTT to check the effect of fuzzy shell on the interaction between the particles and phase changes.

Experiment # **9-11-2027** INSTRUMENT **D11**

Experiment dates: **07/06/2021-09/06/2021**

TITLE

Form factor and structure factor analysis of microgels with tailored density gradient.

Abstract

Core-shell microgels with tailored softness and core-to-shell ratio are interesting candidates for new soft quasicrystals (QCs). Poly (N-isopropyl acrylamide) microgel is a well-known colloidal system which exhibit peculiar property called volume phase transition. PNIPAM undergoes a temperature-induced volume phase transition (VPT) in water at around 32°C and hence the particle volume fraction can be tuned by temperature. Moreover, the interaction potential of microgels changes from repulsive to attractive at VPTT. We make PNIPAM microgel with a core of highly crosslinked PNIPAM and fuzzy soft shell of less crosslinked PNIPAM chains. A deep understanding of the fuzziness of the shell and density profile of the core and shell is important in designing the QCs. The core-to-shell ratio and temperature can be used as tuneable parameters for the phase transition of the microgels. With SANS, we would like to study the form factor, the structure factor and density profile of PNIPAM particles of different core-shell ratios below and above VPTT to check the effect of fuzzy shell on the interaction between the particles and phase changes.

EXPERIMENTAL TEAM (names and affiliation)

Kiran Kaithakkal Jathavedan, Physical Chemistry I, Heinrich Heine University, Universitätstr. 1, 40225 Düsseldorf, Germany

Matthias Karg, Physical Chemistry I, Heinrich Heine University, Universitätstr. 1, 40225 Düsseldorf, Germany

LOCAL CONTACT: Sylvain Prevost

Date of report 21/12/2021

Small-angle neutron scattering (SANS) experiment was performed to determine the form factor and structure factor of microgels of different particle morphology. The particles were made of temperature sensitive polymer poly(N-isopropyl acrylamide) (PNIPAM) having highly crosslinked dense core and loosely crosslinked outer shell. This means that with the application of temperature, the volume fraction of microgels can be varied without changing the particle concentration. At higher volume fractions, the particles form ordered crystals. The crystalline behaviour can be observed with naked eye with the iridescence of the sample in the visible region. Furthermore, microgels typically feature a core-shell like structure with a denser and stiffer core and a softer, fuzzy shell thus meeting the prerequisite for the formation of soft quasicrystals.

Standard laboratory techniques like microscopy and light scattering cannot completely give the structural information of the particle internal morphology and fuzzy sphere character. Given the small radius of our particles, static light scattering is not suitable because of the much lower q. In this case, SANS is a robust tool. Due to the high flux and the lowest accessible q, SANS can be used to study colloids on nm to μm length scales. Here in our study, we used SANS to measure the scattering profiles over a broad ***q***-range under various conditions. In figure 1a, the scattering profiles for a dilute, a semi-dilute and a crystalline microgel sample at 20°C is shown. Slow evolution of structure factor is clearly evident from the low q profile. In the scattering profile of dilute sample, form factor is seen while in the crystalline sample, structure factor is dominated. Figure 1b shows the SANS intensity plotted versus q obtained by measuring a diluted suspension of microgel below and above the volume phase transition temperature (VPTT), at 20°C and 45°C respectively. The form factors are more prominent at temperatures above the VPTT. The data is fitted with a fuzzy sphere model. A detailed analysis of the data on the samples is currently in progress.

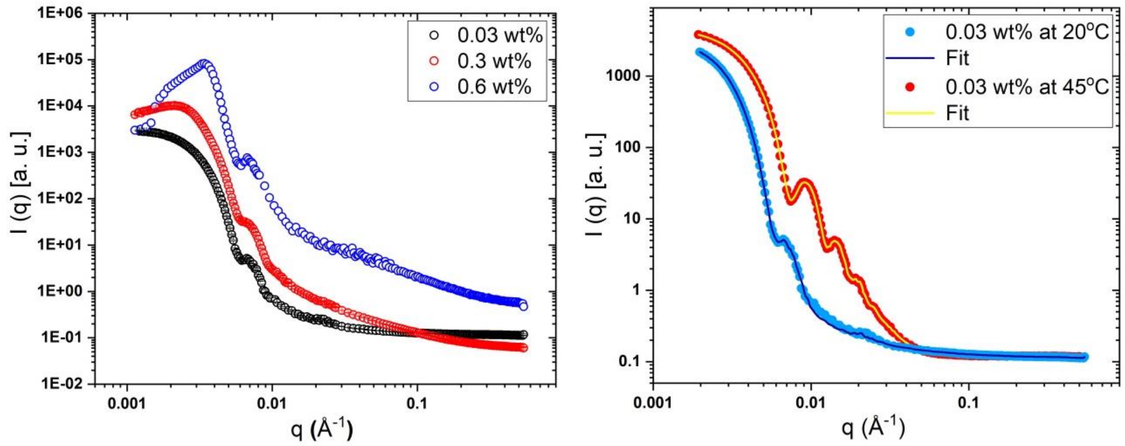

Figure1. SANS results measured on D11. 1a: SANS scattering spectra of a dilute (black circles), semi-dilute (red circles) and a crystalline (blue circles) dispersion of PNIPAM particles in quartz cell of 0.1 mm path length at 38m sample-to-detector distance. 1b: SANS form factor versus scattering vector PNIPAM microgels in dilute suspensions at 20 °C, blue circles, and 45 °C, red circles. The solid lines are fits with the fuzzy sphere model.

SANS measurements in the dilute regime were performed for all samples to investigate the particle form factor *P(**q**)* of the core-shell system. The D11 instrument at ILL with its unique range of momentum transfer and the high flux is ideal to resolve the internal morphology of microgel particles. In the proposed experiment, measured cores and core-shell of the two core-shell systems, a conventional microgel, and a microgel with homogeneous crosslink density. Spectra were recorded for three different concentrations and two temperatures using three sample-to-detector distances (1.7 m, 10.5 m and 38 m). The complete data analysis and the comparison of the spectra of particles with different morphology is in progress. The data will be analyzed in terms of the particle form factor, amount of fuzziness and the structure factor of the samples at higher concentrations.

We would appreciate to avail the D11 instrument of the ILL for SANS experiments particularly crystalline samples in the future.