Experimental Report

17/09/2012

Proposal: **9-10-1225** **Council:** 10/2011

Title: Using Zero Average Contrast experiments to characterize temperature-dependent properties of microgels atultrahigh densities

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: poly(N-isopropylacrylamide) (PNIPAm) microgels, deuterated and hydrogenated, in D2O and H2O

Instrument	Req. Days	All. Days	From	To
D11	3	3	11/06/2012	13/06/2012
			20/11/2012	21/11/2012

Abstract:

Thermoresponsive cross-linked polymer microgel particles are a particularly interesting class of colloidal model particles. They possess a variable degree of softness and a tuneable interaction potential that can be varied between hard-sphere-like and very soft repulsive. Moreover, microgel suspensions can be driven into states with densities far above close packing, so-called squeezed states, with interesting structural and dynamic properties. We have already successfully demonstrated that we can use Zero Average Contrast (ZAC) experiments to eliminate the structure factor and characterize the size, shape and structure of microgels at very high effective volume fractions. We now propose to extend these measurements and study the effect of temperature on the structural properties of microgels at ultrahigh densities above close packing.

Using Zero Average Contrast experiments to characterize temperature-dependent properties of microgels at ultrahigh densities

Thermoresponsive cross-linked polymer microgel particles have recently attracted considerable attention from the soft matter community. They possess a variable degree of softness and a tuneable interaction potential that can be varied between hard-sphere-like and very soft repulsive. A particularly interesting feature of microgels is their ability to form suspensions with densities far above close packing, so-called squeezed states, with interesting structural and dynamic properties. It is intriguing to see that once the effective volume fraction $\phi_{eff} = nV_p$, where n is the number density and V_p the volume of an individual particle as obtained from DLS or SANS, reaches the value for close packing ϕ_{cp}, the characteristic distance $a_s = 2\pi/ q_{max}$, where q_{max} is the position of the interaction peak in the static structure factor S(q), follows a relationship $a_s \sim \phi_{eff}^{1/3}$. This indicates that it is the number density of particles only that determines the structure of these suspensions at ultrahigh densities, and not ϕ_{eff} that can vary with temperature, i.e., the degree of swelling. These findings by themselves do not allow for an unambiguous interpretation, as the $a_s \sim \phi_{eff}^{1/3}$ behavior and the underlying softness of the potential could be due to the ability of the particles to partially interpenetrate as well as because of a compression of the particles that will change the particle size in order to maintain a constant $\phi_{eff} = \phi_{cp}$.

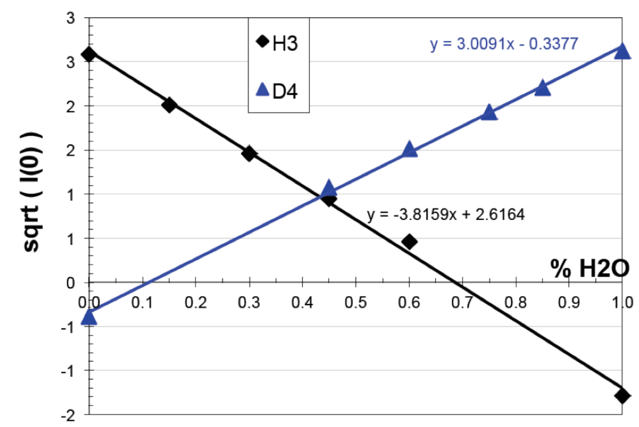

Fig. 1: Contrast determination for the hydrogenated (H3) and the deuterated (D4) microgels from an analysis of the intensity at q → 0, I(0), versus the percentage of H_2O in a mixture of H_2O and D_2O.

We have therefore used SANS with 50:50 mixtures of deuterated and hydrogenated microgel particles of identical composition and size under zero average contrast (ZAC) conditions in order to elucidate the concentration dependence of the particle size and structure at high densities at and above random close packing. We have in particular also looked at the temperature dependence of the particle size in order to see whether the temperature responsiveness is altered at high densities.

The particles where initially fully characterized and their contrast as well as the ZAC condition was determined (Fig. 1). Furthermore, the form factor of both the deuterated as well as the hydrogenated particles were determined at low concentrations far below ϕ_{cp} and the swelling curve of both particles was determined using dynamic light scattering (DLS) (Fig. 2). In a next step we have measured 50/50 mixtures under zero average contrast in order to resolve the temperature dependent form factor at high effective volume fractions above Φ_{cp}. Experiments were be done at different weight concentrations so that our effective volume fractions covered values below and above Φ_{cp}. Measurements were performed at two different temperatures of 16 °C and 27 °C, where the DLS experiments had shown that both the hydrogenated and deuterated particles have the same selling behavior. Over this temperature range both particles change their overall size by about 15%, which correspond to a change in effective volume of almost 40%. The results for 16°C are summarized in Figure 3, and those obtained at 27°C in Fig. 4.

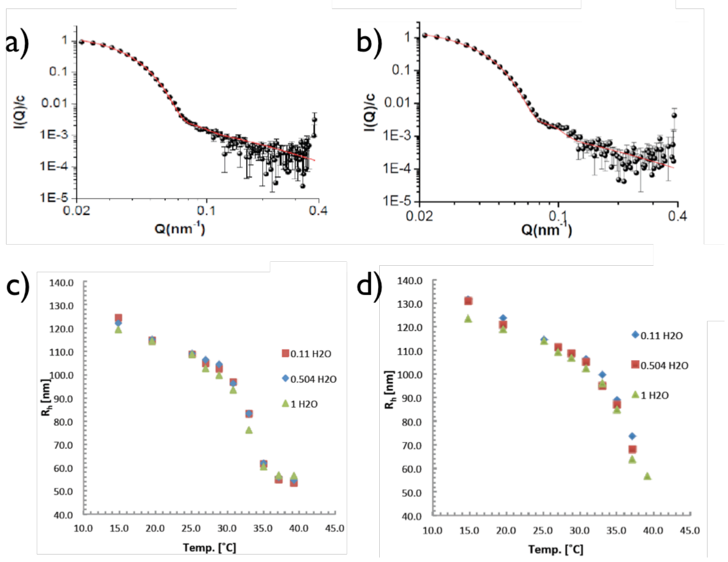

Fig. 2: Form factor for the hydrogenated (a) and deuterated (b) microgels measured under ZAC contrast condition as well as the swelling curves Rh vs. temperature for hydrogenated (c) and deuterated (d) microgels obtained from DLS for 3 different solvents

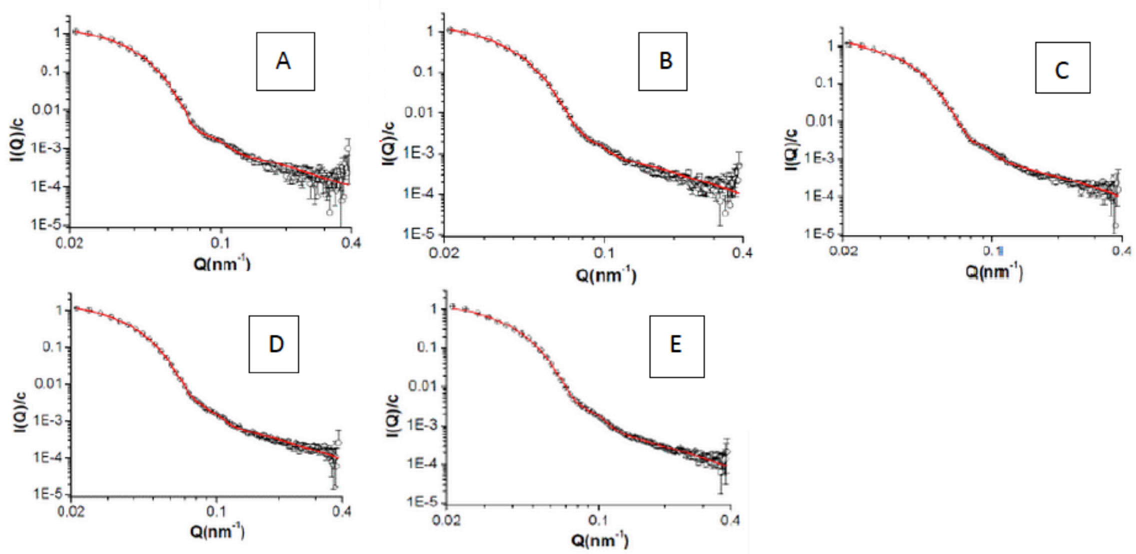

Fig. 3: Scattering data I(q)/C vs q for T = 16.4 °C and 5 different concentrations: A) 2 wt%; B) 4 wt%; C) 6 wt%; D) 8 wt%; E) 10 wt%. Also shown are fits using a fuzzy sphere model

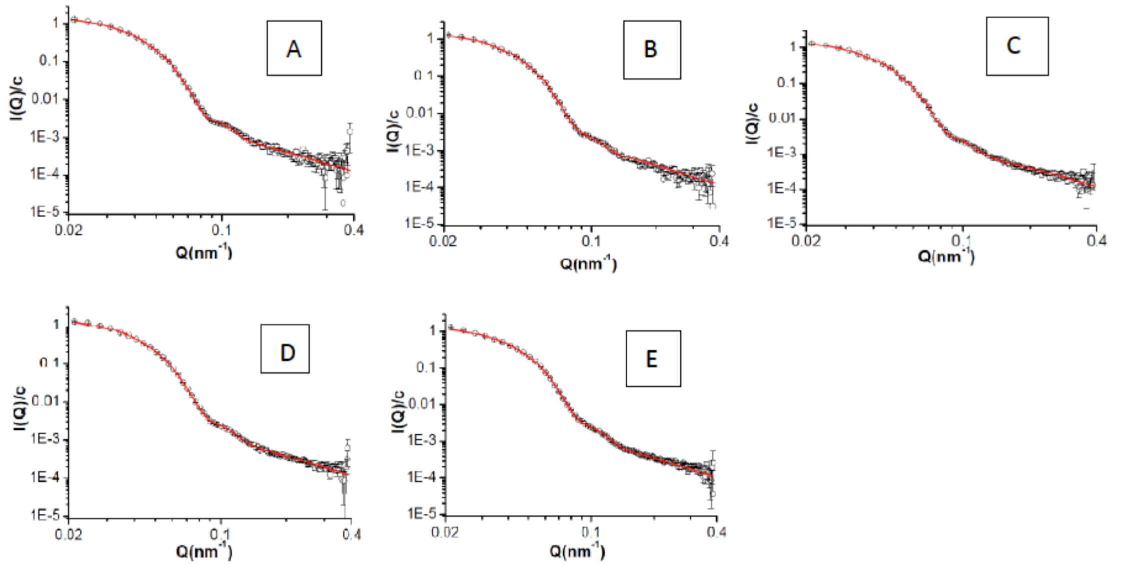

Fig. 3: Scattering data I(q)/C vs q for T = 27.4 °C and 5 different concentrations: A) 2 wt%; B) 4 wt%; C) 6 wt%; D) 8 wt%; E) 10 wt%. Also shown are fits using a fuzzy sphere model

Our data analysis reveals a weak concentration dependence of the overall particle size above Φ_{cp} only, indicating significant particle interpenetration under these conditions. However, the concentration dependence is more pronounced for T = 27.4 °C, presumably due to the fact that at the higher temperature the outer fuzzy shell is already partially collapsed, making it thus more difficult to interpenetrate than in the fully swollen state at 16.4 °C. These results are still based on a preliminary data analysis, and moreover we have not yet been able to measure the samples off ZAC so that we do not have simultaneous information on the structure factor as well. This is mainly due to the fact that we lost a day of beam time and will be able to perform the final measurements in November only.

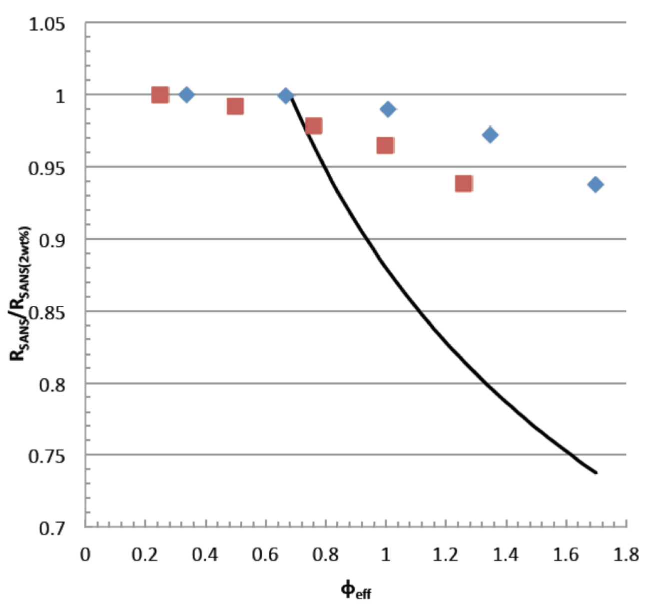

Fig. 3: Results from the analysis of the ZAC experiments for two temperatures (blue: 16.4 °C, red: 27.4 °C). Also shown is a $\Phi^{1/3}$ law that would hold for particle compression above Φ_{cp}