Experimental report

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Proposal: 9-11-1855 **Council:** 4/2017

Title: Hollow microgel in highly packed samples: SANS with contrast variation study.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: suspensions of pNIPAM / D7-pNIPAM microgels in D2O/H2O

Instrument	Requested days	Allocated days	From	To
D11	3	3	20/04/2018	23/04/2018
D22	0	0		
D33	0	0		

Abstract:

Hollow microgels are particles where a silica core, surrounded by a polymeric crosslinked shell, is dissolved leading to soft particles with a cavity at their center. We have verified that, in diluted suspensions, the cavity is present both in the swollen and deswollen state. No information about this system in concentrated suspensions are available. We have performed rheological measurements covering a wide range of concentration, from loosely packed up to highly overpacked suspensions. For the same sample we have investigated their phase behavior at different concentrations. We propose to study the deformation of these particles in response to an increase of the sample concentration. To do this we have made samples at different concentrations where few protonated hollow microgel are dispersed in a matrix of deuterated particles that are matched with the solvent. In this way SANS allows to study the form factor of hollow particles in concentrated suspensions. This is the only scattering technique able to do this. We will fit the data with our model for hollow fuzzy spheres. We will use this information to rationalize both the phase behavior and the flow priorities of this system.

Our goal was to use SANS with contrast variation to directly study the response of pNIPAM hollow microgel to the increase of the particle concentration in a matrix of normal D7-pNIPAM-based microgels, $(C_6D_7H_4NO)_n$, synthesized with 5% of crosslinking.

Fig. 1(a) shows the SANS scattered intensities of the hollow protonated microgels at $\zeta = 0.08 \pm 0.01$ below (light blue empty circles) and above (red upside empty triangle) the volume phase transition temperature (VPTT), at 20 and 40C respectively. The data are fitted (solid lines) with a core-fuzzy-shell model previously used to fit SANS data obtained from similar systems.

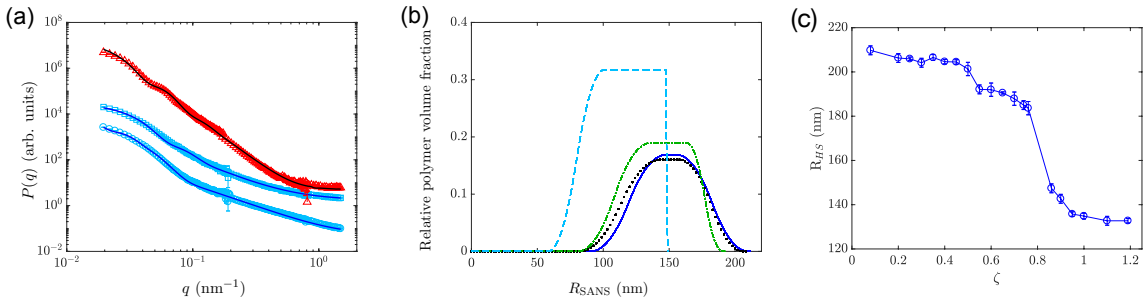

Figure 1 (a) Small-angle neutron scattering form factors, P(q), versus scattering vector, q of hollow microgels at: $\zeta = 0.08 \pm 0.01$, T = (20.0 ± 0.01) C (light blue empty circles); : $\zeta = 1.19 \pm 0.03$, T = (20.0 ± 0.01) C (light blue empty squares); $\zeta < 0.08 \pm 0.01$, T = (40.0 ± 0.01) C (red upside empty triangle). The solid lines are fit of the data with the hollow sphere model. (b) Relative polymer volume fraction within the microgel versus distance from the microgel center, R_{SANS}, for: $\zeta = 0.08 \pm 0.01$ (solid blue line); $\zeta = 0.20 \pm 0.01$ (dotted black line); $\zeta = 0.65 \pm 0.01$ (dash-dotted green line); $\zeta = 0.86 \pm 0.02$ (dashed light blue line). (c) Radius measured with SANS, R_{SANS}, versus total generalized volume fraction, ζ, for: hollow microgels (light blue empty circles).

From the data fit, the radial profile of the relative polymer volume fraction within the microgels are obtained and plotted in Fig. 1(b). Below the VPTT, the data fit leads to a radial distribution (solid blue line) showing that there is a cavity of (91±4) nm in the center of the microgels. The hollow microgels present fuzziness both internal and external. Between these two regions a volume with constant polymer concentration is obtained. In the swollen state, the total radius of the microgels is (210 ± 5) nm with a size polydispersity equal to (14 ± 1)%.

Once the temperature is increased to 40C, above the pNIPAM VPTT, the microgels collapse to (88 ± 2) nm maintaining the internal cavity with a radius of (25.9 ± 0.8) nm, as already reported in literature both from SANS and molecular dynamics experiments. Since the mass of the polymer within the microgels remain constant we choose to use the radial distribution of the polymer volume fraction above the VPTT to normalize all the obtained distributions in Fig. 1(b). The light blue empty squares in Fig. 1(a) are the data relative to the hollow protonated microgels embedded in a matrix of deuterated hollow microgels at (20.0 ± 0.01)C; the total volume fraction of the sample is $\zeta = \zeta_{HS} + \zeta_D = 0.86 \pm 0.02$, with $\zeta_{HS} = 0.08 \pm 0.01$. At ζ above the limit of random close packing for hard incompressible spheres ($\zeta_{rcp} = 0.64$), the external shell is completely collapsed with a decrease of the radius to a value of (147 ± 4) nm, dashed light blue line in Fig.1(b). Also the cavity is further compressed to a size of 58 ± 2 nm. The course of the outer radius of the hollow micro-gels as a function of the generalized volume fraction is reported in Fig. 3, empty blue circles. At $\zeta > 0.50 \pm 0.01$ there is a first decrease in the size; (ii) at $\zeta > 0.86 \pm 0.02$ a further steep decrease is observed. Notably the first decrease happens at concentration beyond the value for the direct contact between microgels. This deswelling before direct contact has already been observed for regular microgels and hollow micro-gels embedded within a matrix of regular one. It has been explained in terms of the overlapping of the counter-ion clouds surrounding the microgels

that leads to a significant increase in the suspension osmotic pressure. In contrast, the second step in the decrease of the radius is mainly due to a collapse of the external fuzzy shell and the rearrangement of the polymer within the cavity.

The present data are the core of an upcoming manuscript within the next months.