# Experimental report

12/09/2017

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| **Proposal:** | **9-12-475** | **Council:** | 4/2016 |

**Title:** Study of the concentration dependence of the depletion length of freepolymer in highly concentrated microgel dispersions

**Research area:** Soft condensed matter

**This proposal is a continuation of 9-12-432**

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**Samples:** polystyrene / toluene / toluene-d8
fully deuterated polystyrene / toluene / toluene-d8

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D11 | 3 | 3 | 30/09/2016 | 03/10/2016 |

## Abstract:

The major part of the huge re-entry region of microgel colloids in mixtures with free polymer is located at effective polymer concentrations cP,Vfree above the overlap concentration. This suggests that the concept of the radius of gyration Rg becomes obsolete in semi-dilute polymer solutions and should be replaced by the screening length xs. Thus the depletion length should be defined by d=xs/Rcolloid and as xs<Rg the depletion length should decrease when entering the semi-dilute regime in the phase diagram. This could explain the large re-entry region in microgel-polymer-mixtures as compared to other systems with the same apparent depletion length. The extension of the fluid pocket increases significantly with a decrease of d as predicted by theory and verified in recent experiments. To obtain a complete picture of the size and the arrangement of the free PS polymer in the colloid-polymer mixture at different concentrations it is neccesary to determine the screening length xs and the structure factor of the free polymer. In addition the complementary structure factor of the microgel particles is also needed. To achieve the required q-range and resolution use of D11 is requested.

## 9-12-475: Study of the concentration dependence of the depletion length of free polymer in highly concentrated microgel dispersions

The addition of free polymer to a glassy colloidal dispersion leads to the creation of a fluid pocket in the phase diagram at high volume fractions between two glassy states - the "repulsive" and the "attractive" glass. This re-entry effect is extraordinarily strong for polystyrene (PS) microgel colloids in good solvent to which linear PS chains are added (cf. Fig.1) - a phenomenon which is still not understood [1]. A simple explanation via osmotic deswelling of the microgel particles can be ruled out as recent SANS measurements of the particle size in the re-entry region showed this to be only a negligible effect [2]. Therefore, we focused in this experiment on the size and the structure of the free polymer.

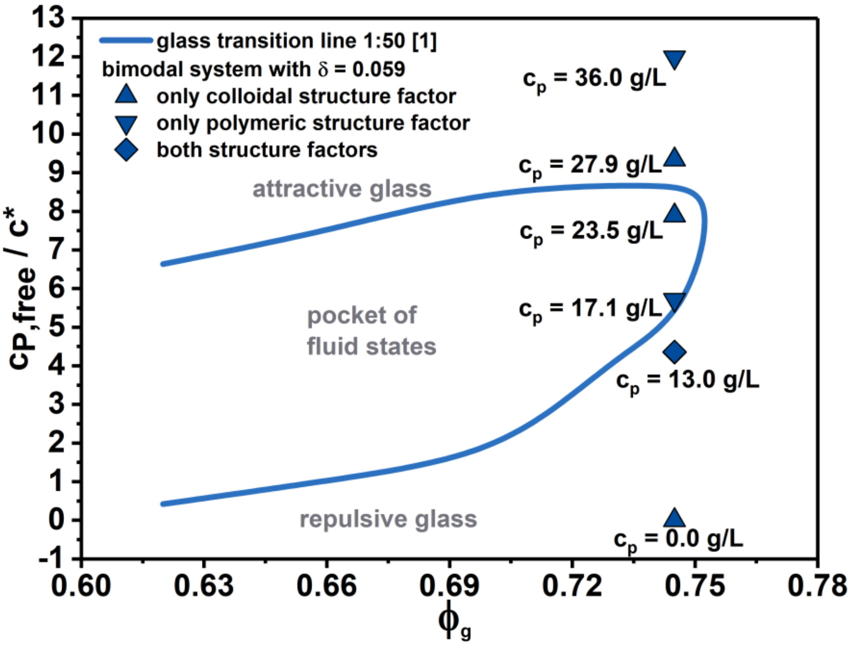

Fig. 1: Phase diagram of PS microgel – PS polymer mixture with size ratio δ = 0.059. Lines encircle fluid states [1]. Symbols indicate state points measured in this experiment.

$c_P$ = polymer concentration with respect to sample volume

$c_{P,free}$ = polymer concentration in the free volume available in the colloid dispersion [3]

c* = overlap concentration

The major part of the huge re-entry region of microgel colloids in mixtures with free polymer is located at effective polymer concentrations $c_{P,free}$ above the overlap concentration c*. This implies that the concept of the radius of gyration $R_g$ cannot be used to define the depletion length δ in semi-dilute polymer solutions and should be replaced by the screening length $\xi$, yielding $\delta = \xi / R_{colloid}$. As $\xi < R_g$ the depletion length should decrease when entering the semi-dilute regime in the phase diagram. The extension of the fluid pocket increases significantly with a decrease of $\delta$ as predicted by theory [4] and verified in recent experiments [1]. This could explain the large re-entry region in microgel-polymer-mixtures as compared to other systems with the same apparent depletion length. Another interesting question is the localization of the polymer inside the colloid-solvent-mixture and its potential influence on the phase behaviour.

Therefore, measurements of the screening length of a fully deuterated polystyrene polymer ($M_W$ = 80000g/mol; $R_g$ = 10.5 nm) were performed at the state points indicated in Fig.1. To eliminate the scattering contribution of the PS (protonated) microgel particles ($\langle R \rangle$ = 156 nm) the experiments were performed in a toluene / toluene-d8 mixture providing zero average contrast condition for the microgels at x(d8-Toluene) = 0.12 as determined in experiment TEST-2369. Additionally, samples with a zero average contrast of the deuterated polymer were prepared to enable the study of the structure factor of the colloids and to compare both systems with respect to Babinet's principle.

For the determination of the screening length the samples were measured at $\lambda$ = 10 Å with a detector distance of d = 8 m. The determination of the structure factor was performed at distances d = 28, 34 as well as 39m and at the same wavelength as before.To obtain the screening length from the measured intensity, 1/I was plotted against $q^2$. The square root of the slope divided by the intercept leads to the screening length according to [5]:

$$I^{-1}(q) = I^{-1}(0)\left(1+\xi^2 q^2+\cdots\right).$$

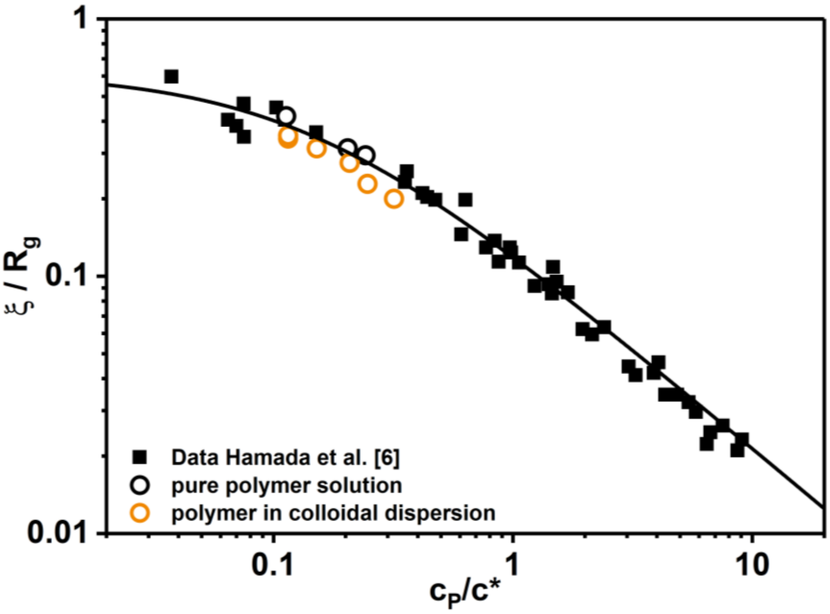

Fig. 2: Normalized screening length vs. normalized polymer concentration.
The obtained data from polymer in pure solvent and in a binary microgel mixture are shown together with literature data from Hamada et al [6].

Figure 2 shows the screening length normalized by the radius of gyration versus the concentration $c_P$ normalized by the overlap concentration c*. One can see that the data points of the polymer in the pure solvent mixture which were also measured follow the data obtained by Hamada et al. [6]. The data points for the polymer in the binary colloidal mixture show no deviation either. This would imply that the polymer is not restricted to the free volume but can penetrate the microgels. To test this hypothesis, we measured two samples at the same state point in the phase diagram (♦ in Fig.1) - under zero average contrast for polymer and microgels, respectively. A comparison between the two low-q measurements with same experimental parameters is shown in Fig. 3.

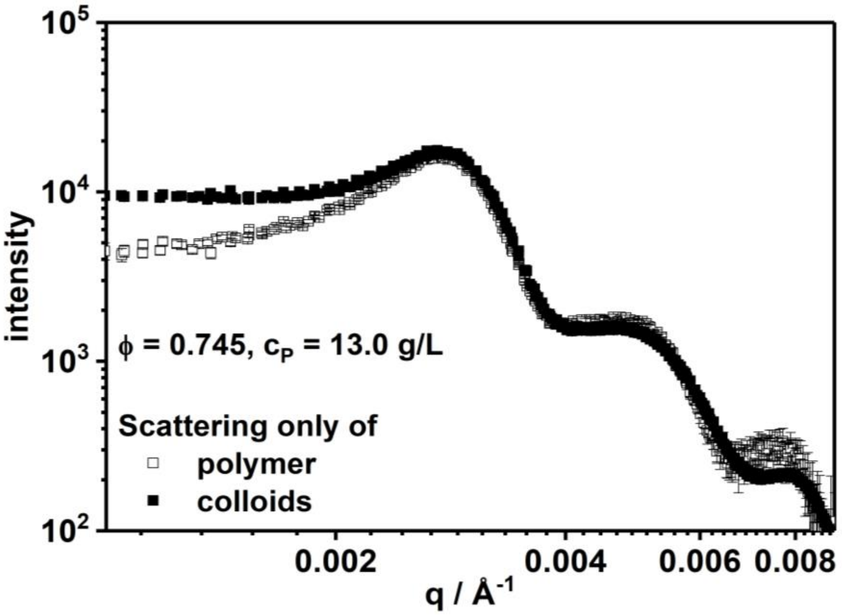

Fig. 3: Comparison of polymer and microgel scattering at the same state point in the phase diagram of Fig.1 ($\phi$ and $c_P$ as indicated in the figure)

Both scattering curves show the same distinct features, indicating that both experiments monitor the same structure. By virtue of Babinet's principle this implies that the polymer does not penetrate the colloids, but rather fills the voids between the microgel particles. This falsifies the hypothesis derived from Fig.2 and indicates that new descriptions for the polymer behaviour in a highly concentrated colloidal environment are needed.

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