

Partial structure factors in star polymer/colloid mixtures

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Abstract. Addition of polymer to colloidal suspensions induces an attractive part to the colloid pair potential, which is of purely entropic origin (“depletion interaction”). We investigated the influence of polymer branching on depletion forces by studying mixtures of hard sphere colloids and star polymers with increasing arm number $f = 2–32$, but constant $R_g \approx 500 \text{ \AA}$. We found a pronounced effect of branching on the position of the gas/liquid demixing transition. Using small angle neutron scattering (SANS) we were able to measure partial structure factors in star polymer/colloid mixtures. The relative distance to the demixing transition is reflected in our scattering data.

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Typically, soft matter systems almost always occur in the form of mixtures. Thus, the inherent features of mixtures, like structure, dynamics, phase behaviour and non-equilibrium properties, independent from their detailed chemical structure are one prominent topic of present research. The understanding of well defined model systems would therefore provide profound progress for many areas of soft matter science. Recently we investigated the phase behaviour of star polymer/colloid mixtures, where we found an excellent agreement between theory and experiment for the position of the gas/liquid demixing transition [1]. Moreover, theory predicts that the unusual star polymer structure factor $S_{ss}(Q)$ [2, 3] should be mediated to the colloid structure factor $S_{cc}(Q)$. Small angle neutron scattering (SANS) combined with contrast variation should enable us to measure partial structure factors $S_{ij}(Q)$ in star polymer/colloid mixtures and verify the expected effect.

1 Experimental

We studied star polymer-colloid mixtures consisting of poly(methylmethacrylate) (PMMA) particles and poly(buta-

diene) (PB) star polymers with size ratio $R_g/R_c \approx 0.49$. PMMA particles were synthesized following a standard procedure [4]. Stock suspensions were prepared in cis-decahydronaphthalene (cis-decalin). These systems have been established as hard sphere models [5]. The colloid volume fraction $\eta_c = \frac{N_c}{V} \frac{4\pi}{3} R_c^3$ was calibrated using the onset of the hard sphere freezing transition, taken to be at $\eta_c = 0.494$ and observed as the nucleation of iridescent colloidal crystals. PB star polymers were prepared by anionic polymerization. The result of the synthesis are star polymers with a near-monodisperse distribution in functionality and molecular weight [6]. For contrast matching either PMMA particles or PB star polymers, we used h/d-solvent mixtures given in Table 1.

SANS experiments were performed at D11, ILL (Grenoble), using detector settings of 3, 13 and 35.7 m with wavelengths $\lambda = 7$ and 10 \AA , giving a Q -range of $1.09 \times 10^{-3} \leq Q \leq 1.07 \times 10^{-1} \text{ \AA}^{-1}$. All data were corrected for background/solvent scattering and normalized to water using standard ILL procedures. For data analysis resolution effects have been taken into account according to Pedersen et al. [7].

Sample	ρ^a [cm ⁻²]	Φ_{d-cis}^b [%]
h-PMMA	1.06×10^{10}	14.91
h-PB	4.12×10^9	6.06
h-PHS	4.54×10^8	1.08
h-cis-decalin	-3.36×10^8	/
d-cis-decalin	7.30×10^{10}	/

^{a)} scattering length density, ^{b)} volume fraction

Table 1. Match points of PMMA and PB in d/h-cis-decalin

2 Results and discussion

In a first step, we investigated the pure components before studying star polymer/colloid mixtures. Figure 1 shows star polymer form factors obtained in d-cis-decalin. At low Q -vectors, $Q \leq 8 \times 10^{-3} \text{ \AA}^{-1}$, our data could be modelled using the Benoit form factor [8] for a Gaussian star, which

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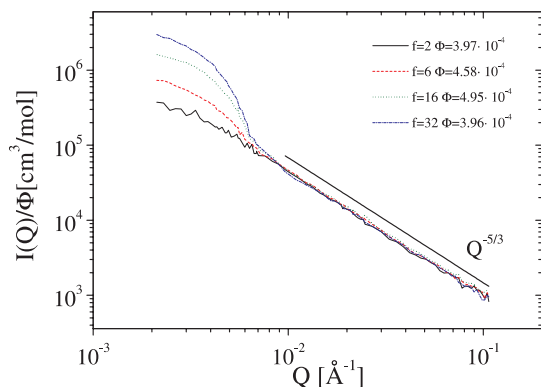


Fig. 1. $I(Q)$ in absolute units (normalized to polymer volume fraction η_c) versus scattering vector Q for PB star polymers with increasing functionality f , but constant radius of gyration R_g , in d-cis-decalin. Extrapolation to zero concentration gives molecular form factors with parameters listed in Table 2

Table 2. Molecular characteristics of PMMA particles and PB star polymers from SANS experiments

Monomer	f	$M_w \times 10^{-6}$ [g/Mol]	R_c [Å]	R_g [Å]
PMMA	—	—	1040 ± 25	—
PB	2	0.86 ± 0.36	—	510 ± 35
PB	6	1.51 ± 0.06	—	521 ± 6
PB	16	3.45 ± 0.27	—	511 ± 5
PB	32	5.11 ± 0.39	—	514 ± 5

gives the explicit dependence on functionality f . For describing the complete data sets we used the Beaucage form factor [9], which describes also the observed power law at high Q -vectors. One should note that this power law extends over more than one order of magnitude in Q and starts at the same Q -value of $\approx 8 \times 10^{-3} \text{ \AA}^{-1}$ for all f . The observed power law slope of $\approx -5/3$ reflects the good solvent quality of cis-decaline for PB and decreases slightly with increasing f , indicating increasing arm stretching. All molecular parameters are summarized in Table 2. PMMA colloids behave as hard spheres as shown in Fig. 2. For steric repulsion each PMMA particle has a small shell consisting of poly(hydroxystearic acid) (PHS), thus analysing

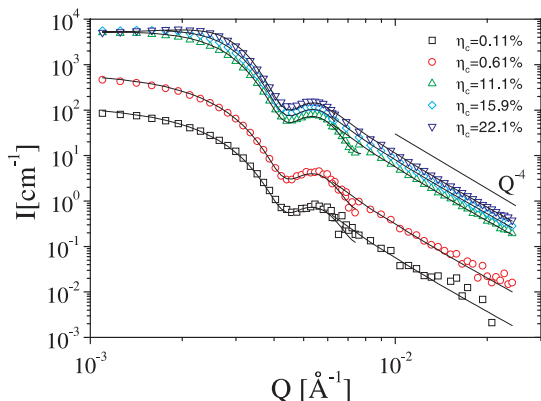


Fig. 2. $I(Q)$ in absolute units versus scattering vector Q for PMMA colloids with increasing colloid volume fraction η_c . *Solid line:* core-shell form factor plus Percus-Yevick structure factor, see text

dilute solution data we obtained the following parameters using a core-shell form factor: Radius of PMMA core $R_c = 1042 \text{ \AA}$ with a polydispersity $\sigma = 9.5\%$, radius of PHS shell $\Delta R = 80 \text{ \AA}$.

Both, core and shell are swollen by solvent, thus using the corresponding scattering length densities as an additional fit parameter we got a degree of swelling of 26.3% for core and 87.4% for shell. At high η_c our scattering data can be described by multiplying the particle form factor with the appropriate Percus-Yevick (PY) structure factor [10]. We emphasize that for all samples η_c was not used a fitting parameter, but taken from calibration procedure described above. All results are in reasonable agreement with previously reported experiments [11].

Addition of star polymer has a pronounced effects on the scattering intensity $I(Q)$, see Fig. 3. This becomes even more obvious, when we compare the experimental structure factors $S_{cc}(Q) = I(Q)/P(Q)$, with $P(Q)$ the experimental particle form factor obtained from dilute solution. The addition of even a small amount of star polymer increases the peak heights considerably. Following Ye et al. [12], we tried to estimate $S_{cc}(Q)$ by a mean spherical approximation (MSA) approach using the Asakura-Osawa (AO) depletion potential [13]: Only the amplitude of the depletion part is used as a free parameter, whereas all other parameters are given by experiment. To adjust peak heights we obtained an amplitude value of $1.2k_B T$, which is surprisingly small. The

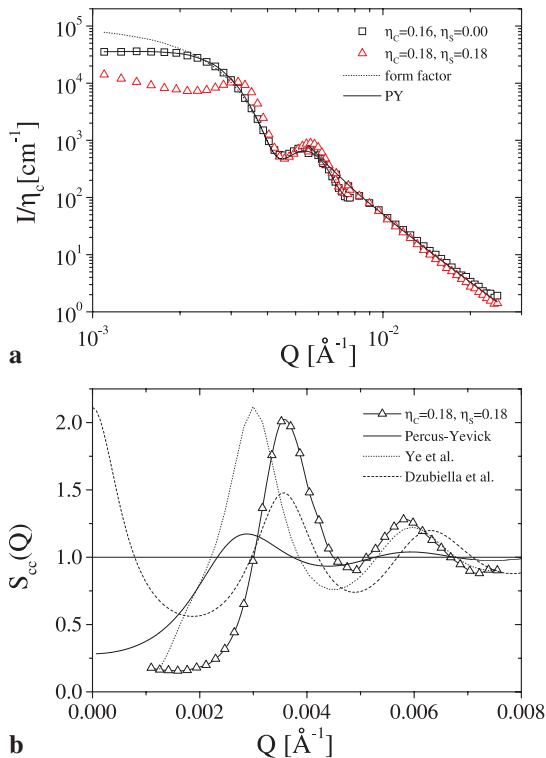


Fig. 3a,b. Comparison of pure colloid solution and 32-arm star polymer/colloid mixture at approximately constant colloid volume fraction η_c . **a** Scattering intensity $I(Q)$ in absolute units (normalized to η_c) versus scattering vector Q , *dotted line:* particle form factor $P(Q)$, *solid line:* $P(Q)S(Q)$, with $S(Q)$ calculated Percus-Yevick structure factor. **b** Experimental structure factor $S_{cc}(Q) = I(Q)/P(Q)$, *solid line:* PY $S(Q)$, *dotted line:* calculated $S_{cc}(Q)$ following Ye et al. [12], *dashed line:* $S_{cc}(Q)$ obtained directly from star polymer-colloid interactions as calculated by Dzubiella [14, 15]

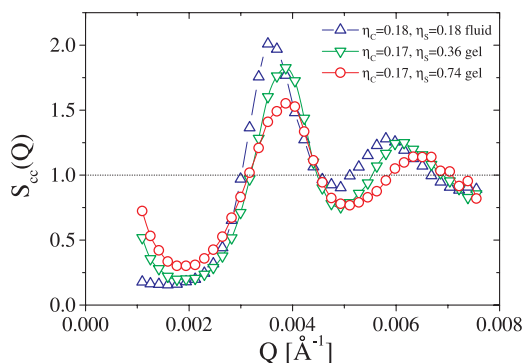


Fig. 4. Experimental colloid structure factor $S_{cc} = I(Q)/P(Q)$ vs. scattering vector Q , for star polymer/colloid mixture at approximately constant colloid volume fraction η_c , but increasing star polymer volume fraction η_s ; $R_c = 104$ nm, $R_s = 51.4$ nm, $f = 32$

result is also shown in Fig. 3b (dotted line), but one clearly sees that the position of the main peak is not described correctly. The dashed line in Fig. 3b, on the other hand, gives $S_{cc}(Q)$ obtained by using the microscopic interaction potential given in [1, 14, 15] without any adjustable parameter. Here the position of the main peak agrees much better with our experimental data.

Figure 4 shows $S_{cc}(Q)$ obtained from mixtures with increasing star polymer volume fraction $\eta_s = \frac{N_s}{V} \frac{4\pi}{3} R_s^3$, but approximately constant η_c . Increasing the star polymer concentration further results in i) a decreasing peak height and ii) an increasing excess scattering at low Q -vectors. These effects resemble the well known behaviour of $S_{cc}(Q)$ when approaching the critical point [10] and indeed, at high star polymer concentrations we are in the metastable gel phase/slowly demixing fluid, whereas at the lowest star polymer concentration we are slightly below the demixing binodal. But similar effects were also observed experimentally for $S_{ss}(Q)$ in pure star polymer solutions around their overlap concentra-

tion c^* [3]. Thus, due to this merging of colloidal phase separation, gelation and special star polymer feature at the moment it is not completely discernible, what is the real origin of the observed unusual scattering behavior of star polymer/colloid mixtures. Nevertheless, these preliminary results corroborate the effects expected from theory and are a promising approach for explaining the structural properties of star polymer/colloid mixtures starting from a microscopic interaction potential.

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References

1. J. Dzubiella, A. Jusufi, C.N. Likos, C. von Ferber, H. Löwen, J. Stellbrink, J. Allgaier, D. Richter, A.B. Schofield, P.A. Smith, W.C.K. Poon, P.N. Pusey: *Phys. Rev. E* **64**, 10401R (2001)
2. M. Watzlawek, H. Löwen, C.N. Likos: *J. Phys.: Condens. Matter* **10**, 8189 (1998)
3. J. Stellbrink, J. Allgaier, M. Monkenbusch, D. Richter, A. Lang, C.N. Likos, M. Watzlawek, H. Löwen: *Prog. Colloid Polym. Sci.* **115**, 88 (2000)
4. L. Antl, J.W. Goodwin, R.D. Hill, R.H. Ottewill, S.H. Owens, S. Papworth, J.A. Waters: *Coll. Surf.* **17**, 67 (1986)
5. S.M. Ilett, A. Orrock, W.C.K. Poon, P.N. Pusey: *Phys. Rev. E* **51**, 1344 (1995)
6. J. Allgaier, K. Martin, H.J. Raden, K. Müllen: *Macromolecules* **32**, 3190(1999)
7. J.S. Pedersen, D. Posselt, K. Mortensen: *J. Appl. Cryst.* **23**, 321 (1990)
8. H. Benoit: *J. Polymer Sci.* **11**, 507 (1953)
9. G. Beaucage: *J. Appl. Cryst.* **29**, 134 (1996)
10. C.A. Croxton: *Introduction into liquid state physics* (J. Wiley & Sons, New York 1975)
11. P. Bartlett, R.H. Ottewill: *J. Chem. Phys.* **96**, 3306 (1992)
12. X. Ye, T. Narayanan, P. Tong, J.S. Huang, M.Y. Lin, B.L. Carvalho, L.J. Fetters: *Phys. Rev. E* **54**, 6500 (1996)
13. S. Asakura, F. Osawa: *J. Chem. Phys.* **22**, 1255 (1954)
14. J. Dzubiella: private communication
15. A. Jusufi, J. Dzubiella, C.N. Likos, C. von Ferber, H. Löwen: *J. Phys.: Condens. Matter* **13**, 6177 (2001)