ESRF	**Experiment title:** Study of the structure and alignment of magnetic nanoparticle embedded in hydrogels in dependence of the magnetic field	**Experiment number**: SC 2990
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Report:

The aim of this experiment was to investigate the phase behavior of thermosensitive hydro-ferrogels, which consist of Pluronic (35 wt% PEO-PPO-PEO) and magnetite nanoparticles (0, 0.5, 1 or 2 wt% Fe_2O_3) to demonstrate, that the self-assembly of the Pluronic template determines the structure of the hydro-ferrogel. After literature, these smart hydrogels can easily be shear aligned. The self-assembly structure of the systems are investigated without shear (steady state condition), under shear (steady shear) or in presence of an external magnetic field (0-1 T, parallel and perpendicular to the incidient beam, no shear). Depending on that conditions, we found pronounced differences in the self-assembly/lattice structure behavior of the systems. It turned out, that the scattering contribution of the polydisperse magnetite particles contributed mainly to the scattering of the hydro-ferrogels (q^{-4} power law) and superimpose the signals steming from the pluronic matrix. For concentrations over 0.5 wt% magnetite it was not possible to obtain reliable signals from the matrix structure as well. Therefore the results can only be presented for pure pluronic and for a hydro-ferrogel with 0.5 wt% magnetite.

Rheo-SAXS and magnetic experiments showed that the magnetite particles are constrained to the remaining interstitial spaces between the template micelles. The magnetite nanoparticles are aligned in the gel phase and therefore distinct clusters of Fe_2O_3 are ruled out. The phase transition is observed during the first heating circle of matrix and hydro-gel and occurs under similar conditions. The transitions before melting seems to pass from cubic phase (fcc, bcc) over hexagonal phase (p6/mm) to lamellar arrangement. The cooling cycles indicates that the investigated systems show hysteresis.

<u>Rheo-SAXS experiments:</u>

The structure of the samples was most pronounced when obtained under shear conditions (cf. fig. 1). Directly after cessation of the shear the structure relaxated and more complicated 2D SAXS pattern were obtained. The analysis of the data still revealed the same lattice structure and lattice unit cell, pointing to the fact that microdomains aligned by shear forces exists over the whole cell. The microdomains reorient themself after abruped cessation of the shear (spatial dependence of shear flow profile). Additionally, deformation relaxation modes like layer sliding may occur. This way, for example fcc twins can be formed.

The results of the Rheo-SAXS experiments are summarized in table 1. As unit cell dimension the values "under shear" are noted. The unit cell dimensions after stopping the shear were similar, but with a significant higher error.

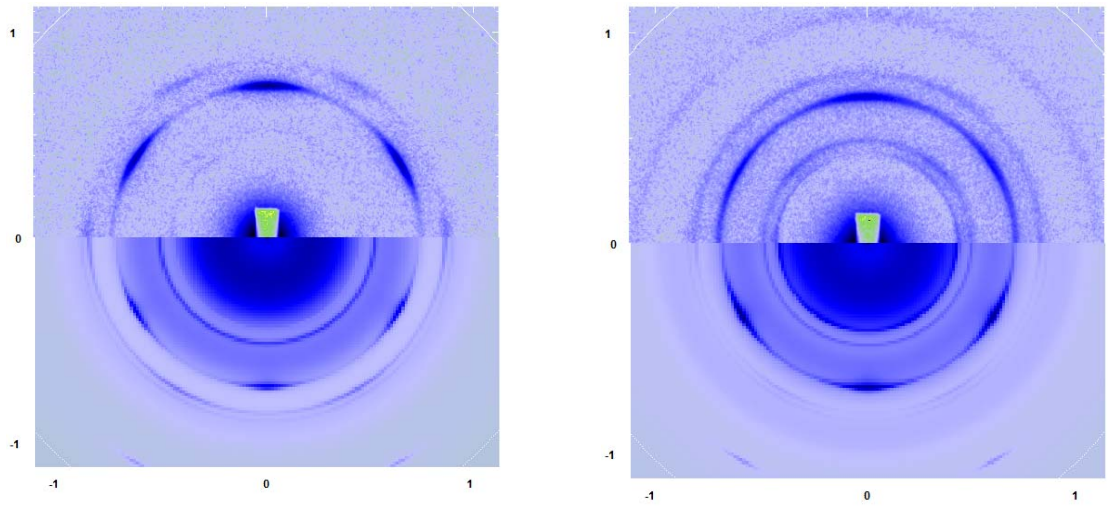

Fig. 1: Measured (top) and simulated (bottom) 2D-SAXS pattern of a pluronic gel (35 wt% in water) in the fcc phase. Left: during shear, 12°C, unit cell dimension = 24.1 nm. Right: directly after cessation, 45°C, unit cell dimension = 25.6 nm.

Table 1: Results of the Rheo-SAXS experiments.

Pluronic (35 wt%)				**pluronic (35 wt%) + 0.5 wt% magnetite**		
T [°C]	lattice	unit cell [nm]		T [°C]	lattice	unit cell [nm]
4	none			4	none	
10	fcc	24.1		10	fcc	23.6
12	fcc	24.1		12	fcc ?	23.8
14	fcc	24.2		14	fcc	24.1
20	fcc	24.5		20	fcc	24.2
45	fcc	25.6		45	fcc + p6/mm	ca. 25.7 + 17.9
55	fcc ?	27.5		55	p6/mm	18.4
60	p6/mm	18.8		60	p6/mm	19.2
				75	p6/mm	19.7 ?
				80	none	

Experiments with external magnetic field

The next part of the study focused on the influence of an magnetic field. The measurements were done in standard glas capillaries with 1 mm diameter, where no good shear alignment of the micro-crystalline domaines could be obtained during the filling. The structural changes seen in the 2D SAXS patterns observed under the influence of an external magnetic field (parallel and perpendicular to the incidient beam) were not easy to simulate, propably due to multidomain structures. Therefore, mainly the 1D data were analysed. The results are shown in table 2.

Table 2: Results of SAXS experiments during heating and following cooling of the samples in precence of an external magnetic field.

Pluronic (35wt%)			**pluronic (35wt%)+ 0.5 wt% magnetite**		
T [°C]	lattice	unit cell [nm]	T [°C]	lattice	unit cell [nm]
25	hcp ?	18.2	25	hcp ?	18.4
30	hcp ?	18.4	30	hcp ?	18.8
35	hcp ?	19.0	35	hcp ?	19.2
40	hcp ?	19.5	40	hcp ?	19.5
42	hcp ?	19.7	42	hcp ?	19.7
45	bcc	22.4	45	bcc+ p6/mm	22.5 + 18.0
50	bcc	22.7	50	bcc+ p6/mm	22.56 + 18.9
55	bcc	23.0	55	p6/mm	18.9
60	p6/mm	19.2	60	p6/mm	19.2
62	p6/mm	19.2	62	p6/mm	19.5
65	p6/mm	19.6	65	p6/mm	19.7
70	p6/mm	19.8	70	p6/mm	20.1
75	p6/mm	20.8	75	p6/mm	20.6
80	none	none	80	Lamellar ?	18.0
75	Lamellar ?	18.0	75	p6/mm	20.1
70	p6/mm?	20.5	70	p6/mm	19.8
65	p6/mm?	19.6	65	p6/mm	19.7
62	p6/mm?	19.8	62	p6/mm	19.6
60	p6/mm?	19.6	60	p6/mm	19.5
55	p6/mm?	19.4	55	p6/mm	19.3
50	p6/mm?	19.2	50	p6/mm	19.1
45	p6/mm?	18.9	45	p6/mm	18.8
42	p6/mm?	18.7	42	p6/mm	18.6
35	p6/mm?	18.2	35	p6/mm	18.1
30	p6/mm?	17.8	30	p6/mm	17.7
25	p6/mm?	17.1	25	p6/mm	17.1