Experimental report

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Proposal: 9-11-1841 **Council:** 4/2017

Title: Off-specular neutron scattering from multilayer systems: destabilisedand stabilised interfaces

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Si
PMMA
PS

Instrument	Requested days	Allocated days	From	To
D17	5	3	28/05/2018	31/05/2018

Abstract:

With the increase in beam intensity, the use of off-specular neutron reflection (OS NR) to study interfaces is the next step in the evolution of reflectometry. In the case of ILL, the D17 is an ideal instrument to perform OS NR because of a good area detector. Recently we have started a research program with a focus on model soft matter systems for OS NR. One of such systems is a three layer system of immiscible polymers of a deuterated polymer (dPMMA) sandwiched between thick hydrogenated polymers (hPS) of the same kind. The thin layer in this case dewets via peristalsis process which gives a characteristic grating-like OS intensity. Scientifically, this kind of process is impossible to observe with any other experimental technique. We wish to explore the combined effect of the instabillity of the two interfaces by stacking five three layers on top of each other, creating multilayers for a combined signal from ten dewetting interfaces. We will vary the thickness of dPMMA sandwiched between hPS and measure the OS scattering. Additionaly we will measure reference samples which will not dewet to isolate the pure OS signal: inverse hPMMA/dPS/hPMMA and a miscible hPS/dPS/hPS.

9-11-1841: Off-specular neutron scattering from multilayer systems: destabilised and stabilised interfaces

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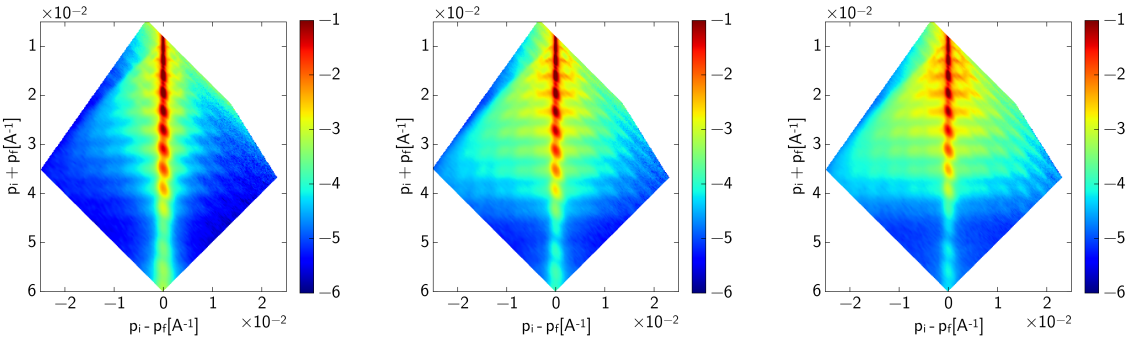
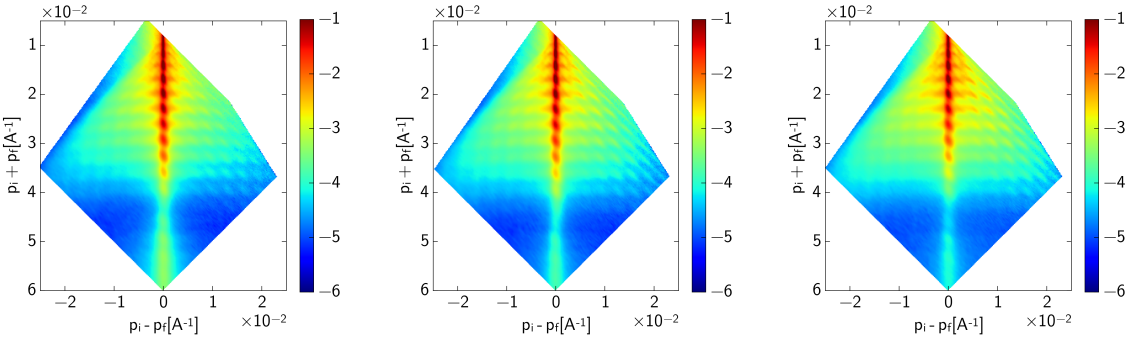
We have previously studied bilayer and trilayer thin polymer systems with the aim of understanding the rupture of a thin film between two thick polymer layers (dewetting process) as well as improving the analysis methods of the off-specular neutron scattering based on distorted wave Born approximation. The intensity of the off-specular signal could be significantly increased by stacking multiple unstable interfaces (multilayer systems).



(a) $t_{\mathrm{ann}} = 0\,\mathrm{min}$ (b) $t_{\mathrm{ann}} = 5\,\mathrm{min}$ (c) $t_{\mathrm{ann}} = 15\,\mathrm{min}$

Figure 1: Evolution of off-specular intensity in dependence of annealing time at $T = 160\,^{\circ}\mathrm{C}$ for the PF150 sample mentioned in the text.



(a) $t_{\mathrm{ann}} = 0\,\mathrm{min}$ (b) $t_{\mathrm{ann}} = 5\,\mathrm{min}$ (c) $t_{\mathrm{ann}} = 15\,\mathrm{min}$

Figure 2: Evolution of off-specular intensity in dependence of annealing time at $T = 160\,^{\circ}\mathrm{C}$ for the NF140 sample mentioned in the text.

We have prepared several samples of stacked protonated polystyrene (hPS) / deuterated poly methyl methacrylate (dPMMA) bilayers of different thickness on silicon substrates. Initially

the bilayers were prepared by spin coating the hPS on a glass substrate which was in some cases also coated with a sacrificial layer of polystyrene sulfonate (PSS). The dPMMA layer was the spin coated on top from an acetic acid solution which does not influence the existing PS layer. After that the samples were floated on top of each other in order to create a final multilayer.

Additionally we also prepared two bilayers with the inverted deuteration of PS and PMMA as reference samples. Here only one interface could be destabilised which should make the analysis more straightforward, as it is rather complicated to distinguish different contributions to the off-specular spectrum without references. The detailed composition of all the samples is shown in table .

Sample	1	2	3	4	5	6	7
Bilayer 1	dPS (60k)	hPMMA (310k)					
	106 Å	3500 Å					
Bilayer 2	dPS (60k)	hPMMA (230k)					
	120 Å	3100 Å					
PF150	hPS (526k)	dPMMA (264k)	hPS	dPMMA	hPS	dPMMA	hPS
	1350 Å	150 Å					
NF140	hPS (526k)	dPMMA (264k)	hPS	dPMMA	hPS	dPMMA	hPS
	1500 Å	140 Å					

As can be seen in figures 1 and 2 which represent measurements of multilayer two samples respectively, the off-specular signal is indeed very high and it increases with the annealing time, as the buried films rupture. Due to the interchanging deuteration, the most striking features are the lines at constant q_z which are caused by the interference of neutrons inside the sample, as several potential wells are created by the thin deuterated polymer acting as a barrier. The neutron is then free to propagate within the low scattering length density material (protonated polymer). During the 5 days on D17 we have measured several samples at several annealing steps, each time recording the specular as well as off-specular measurements, showing the potential for off-specular scattering in soft matter.