Experimental report

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Proposal: 9-11-1873 **Council:** 4/2018

Title: Resonance-enhanced off-specular scattering from unstable polymer/polymer interfaces

Research area: Soft condensed matter

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Samples: Si
PMMA
PS

Instrument	Requested days	Allocated days	From	To
D17	5	0		
SUPERADAM	0	5	26/09/2018	01/10/2018

Abstract:

Lately we have been developing off-specular neutron scattering for the study of soft buried interfaces on two model systems: an immiscible polymer bilayer with a single interface, destabilised by van der Waals forces and a three layer system where a polystyrene layer is sandwiched between two thick poly-methyl methacrylate layers. In order to improve the signal coming from these systems, we propose an optimised system of a "soft neutron guide" with the system of interest on top. A potential well will be created (Fabry-Perot configuration) by putting a polymer of low scattering length density between two deuterated polymers of high scattering density. By varying the thicknesses of the barriers and the well we will optimise the probability density for a neutron to tunnel through the barrier and then propagate in the low density material. System will then be annealed above glass transition temperature in order to observe dewetting of the lowest layer. Because of the resonance effect in the potential well, the off-specular signal should improve considerably.

9-11-1873: Resonance-enhanced off-specular scattering from unstable polymer/polymer interfaces

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It has previously been shown [1, 2] that an equivalent of a neutron "waveguide" can be made by placing a thin barrier of high scattering length density (SLD) on top of a thick low-SLD layer, placed on a high-SLD substrate. In such case, the neutrons tunnel through the top barrier ($d < 200$ Å) and propagate in the thick layer. Depending on the thickness of the thick layer, the probability for constructive (destructive) resonance can be tuned to occur at different depths in the sample. This means that the signal coming from those areas is higher (lower) than elsewhere. Off-specular neutron scattering is a powerful technique, which, in combination with specular reflectivity, yields 3D information about buried structure in the sample. However, scattering in out-of-specular direction is much weaker and requires longer measuring times. Furthermore, if the scattering is coming from a small volume, it might not exceed background levels.

The phenomenon of thin dewetting polymer layer buried under the surface can be investigated using a technique such as off-specular scattering. Due to the polymer/polymer interfacial region, where the onset of dewetting would be visible, being very small ($d_{\text{interface}} \sim 30$ Å), such process is hard to detect. We have speculated that preparing the sample as a neutron waveguide, enhancing the scattering probability in the said region, would yield significantly higher signal, improving the signal-to-noise ratio and reducing the measuring time [3].

It is relatively easy to prepare a "soft" waveguide of such type, since deuterated polymer acts as the high-SLD material and vice-versa, the protonated polymer as the low-SLD material. They can then be spin coated onto a solid substrate. We have prepared two different sample types of several different thicknesses of deuterated and protonated polystyrene (d-PS, h-PS) and poly methylmethacrylate (d-PMMA, h-PMMA) on silicon (Si) substrates. The first series has the following composition: Si / 130 Å d-PS ($M_w = 627$ kDa) / 800 Å to 1200 Å h-PMMA ($M_w = 317$ kDa) / 100 Å d-PS ($M_w = 627$ kDa), and the second: Si / 800 Å to 1200 Å h-PS ($M_w = 541$ kDa) / 130 Å d-PMMA ($M_w = 230$ kDa) / 3000 Å h-PS ($M_w = 541$ kDa). In the first trilayer, the thickness of the middle layer was chosen such that the scattering probability is concentrated at the bottom d-PS/h-PMMA interface. In the second trilayer, the scattering is concentrated throughout the thin d-PMMA layer, which also acts as the tunneling barrier.

The resonance can properly be exploited only if the incoming wavevector q_z fulfills the resonance conditions. Meaning that it is aligned with the location of the resonance dip which is seen in specular reflectivity, below the critical angle. In order to check whether the resonance indeed helps with enhancing the signal, the measurements were repeated twice, once in the resonant condition and once outside.

For this preliminary experiment we have prepared and measured three samples described above (Si / 130 Å d-PS / 1000 Å h-PMMA / 100 Å d-PS, Si / 130 Å d-PS / 1200 Å h-PMMA / 100 Å d-PS and Si / 1000 Å h-PS / 130 Å d-PMMA / 3000 Å h-PS). However, the systems showed a

wide specular reflection (as seen in figure 1), probably connected to sample preparation or the characteristic of the silicon substrate. Further analysis will show whether qualitative comparison would be possible.

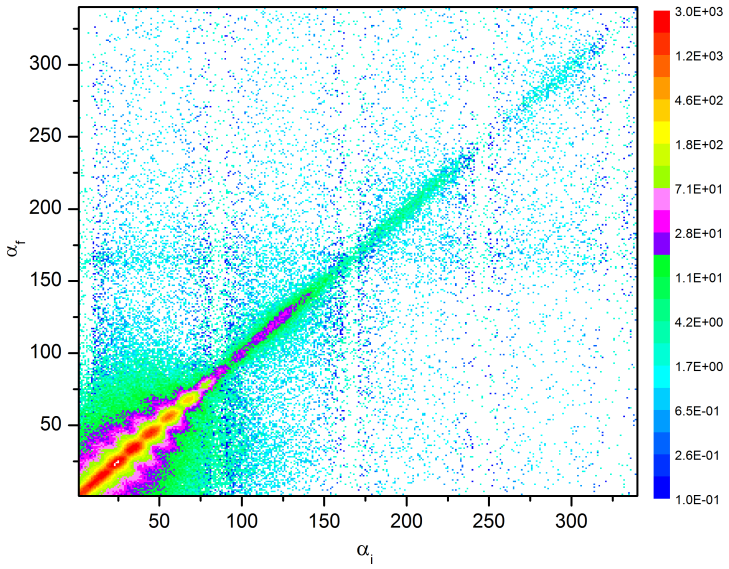

Figure 1: An example off-specular scattering pattern recorded during the measurement, with clearly visible specular reflection ($\alpha_i = \alpha_f$) and the off-specular part around.

Bibliography

[1] L. J. Norton, E. J. Kramer, R. A.L. Jones, F. S. Bates, H. R. Brown, G. P. Felcher, and R. Kleb. Resonantly enhanced neutron intensity in a surface segregated polymer blend. *Journal de Physique II*, 4(2):367–376, 1994.

[2] S. V. Kozhevnikov, F. Ott, A. Paul, and L. Rosta. Resonances and off-specular scattering in neutron waveguides. *The European Physical Journal Special Topics*, 167(1):87–92, 2009.

[3] Zhang Jiang, Dong Ryeol Lee, Suresh Narayanan, Jin Wang, and Sunil K. Sinha. Waveguide-enhanced grazing-incidence small-angle x-ray scattering of buried nanostructures in thin films. *Physical Review B*, 84(7), 2011.