Dynamic scattering effects in grazing incidence small-angle X-ray scattering experiments

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Diblock copolymers are frequently used materials in thin film technology. Due the connectivity of two chemically different blocks they are able to undergo phase separation on a mesoscopic length scale and self assemble into highly regular structures of e.g. lamellae or cylinders with a repeat period of typically 10 – 100 nm. Due to the narrow polydispersity of the structures formed they can be used as membranes or templates in photolithography [1].
A major challenge is the control of the orientation of the mesoscopic structures formed, as lamellae or cylinders can either orient parallel or perpendicular to the film interfaces. Recently, grazing incidence small-angle X-ray scattering (GISAXS) has been developed as a nondestructive tool to investigate the orientation of diblock copolymers in thin films [2, 3]. In contrast to traditional SAXS, where the incident beam passes a bulk sample and the scattering of the transmitted intensity is probed, GISAXS experiments are carried out in reflection geometry on thin films on a reflective substrate. The incident beam impinges on the film surface under a grazing angle (typically 1° or lower), where most of the intensity is specular reflected. However, a small part of the intensity is also scattered off-specular, especially in the case of an internal structure of the film itself.
In the last few years this technique has been used mainly to investigate laterally structured films like perpendicular cylinders [1] or lamellae [2, 4], as in this case the momentum transfer parallel to the film plane $\mathbf{q}_{||}$ is directly related to the repeat period D by $\mathbf{q}_{||} = 2\pi/D$. This allows for a relative straightforward characterization of laterally structured films.
GISAXS investigations on films with a structure along the film normal – e. g. with lamellae parallel to the film normal – are rather scarce [4, 5]. This might be due to mainly two reasons. First of all the scattering along the film normal is affected by both refraction, when the incident beam enters the film surface and reflection from the substrate. In this case kinematic scattering theory fails to describe the scattering and approaches including dynamic scattering theories have to be applied. Second, many of the experiments performed so far were conducted at incident angles α_i close to the critical angles of the polymer film α_cP and the substrate α_cS in order to increase the off-specular scattered intensity or to vary the indentation depth by changing α_i. As it is difficult to vary α_i and adjust a circular beamstop with respect to the specular reflected beam, a rod like beamstop is usually used which covers most of the incident plane. However this has the drawback, that most of the intensity along q_z is blocked by the beamstop.
In a forthcoming publication we will present a dynamic scattering theory, which is able to explain the scattering at angles close to the critical angle of total reflection in the context of the distorted wave Born approximation [6]. In this theory it is expected, that the refraction and reflection effects are most pronounced at angles around the critical angle for total reflection and for large α_i kinematic scattering can be assumed. Experiments performed at low α_i confirm this approach, even though a rod like beamstop has been used and only the tails of rather broad peaks could be observed. In general the diffuse scattering at $\mathbf{q}_{||} = 0$ Å^{-1} contains the same information than the specular reflectivity. However, in specular reflectivity one has to scan over many incident angles which can be very time consuming, while in GISAXS the experiment can be performed in a single shot.
In order to test the theory developed in Ref. [6] we investigated the same film as in Ref. [6] at larger α_i. The lamellar Polystyrene-polybutadiene block copolymer had a molar mass of $\bar{M}_\mathrm{n} = 22.6$

kg/mol and a lamellar thickness of $D_{\mathrm{lam}} = 197$ Å. The film was prepared by spin coating from toluene solution and had a film thickness of 1570 Å, which is 8 times the lamellar thickness.
Fig. 1a shows the two-dimensional GISAXS-map at $\alpha_{\mathrm{i}} = 0.99°$. Several peaks can be observed in the scattering plane ($\mathbf{q}_{||} = 0$ Å^{-1}). This can also be seen in Fig. 1b, were a cut at $\mathbf{q}_{||} = 0$ Å-1 is shown. In Figure 1c the peak positions expected from the calculations in Ref. [6] are shown in dependence of the incidence angle α_{i} and the experimental peak positions from Figs .1a and b are drawn as circles. The two peaks at $q_z \approx 0.1°$ can be understood as the first and second order peaks, respectively. However, for the second order peak the q_z-position is highly affected by refraction and appears at nearly the same value as the first order peak. Thus, even at values of α_{i} which are much larger than α_{cP} dynamic scattering cannot be neglected for the length scales typically covered by diblock copolymers.

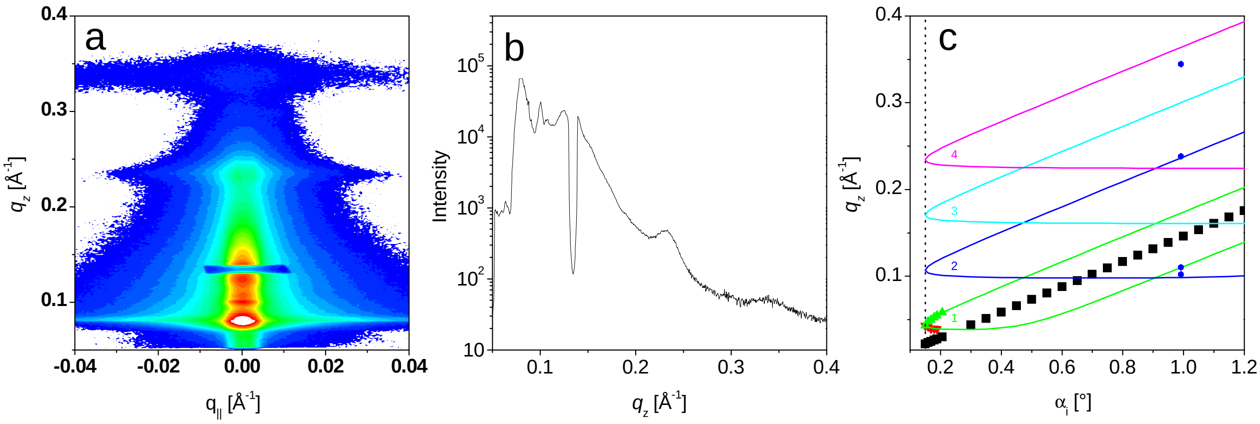

Figure 1: (a) GISAXS-map of a block copolymer film with lamellae oriented parallel to the films interfaces. (b) Vertical cut at $\mathbf{q}_{||} = 0$ Å^{-1} of the GISAXS-map in (a). (c) q_z-positions of the diffuse peaks in dependence on α_{i}. Squares: specular reflected beam, circles: $q_z$positions of diffuse peaks in (a), lines: peak positions predicted by Ref. [6], the orders are given as numbers in the graph. The vertical line denotes α_{cP}. For comparison, the peak positions observed in Ref. [6] are included as triangles.

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