

X-ray diffraction from mesoscopic systems: thin films on 'rough' surfaces

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Received 5 September 1994, in final form 27 October 1994

Abstract. In this work x-ray diffraction measurements on thin polystyrene films deposited on laterally structured surfaces are reported. The experiments were performed in the region of small incidence and exit angles. The x-ray data are compared with the results of atomic force microscopy investigations, both being performed to obtain the morphology of the polymer film on top of the surface grating. Our results do not confirm existing theoretical predictions assuming pure van der Waals interactions between the substrate and the film.

1. Introduction

The morphology of thin films deposited on rough surfaces is of great interest, both in basic research and in materials science. In particular, the question of how the roughness propagates from a substrate through a thin film to the surface is important for investigations concerning the growth of films and multilayers.

In the present work we concentrate on the growth of polymer films on laterally structured surfaces (namely surface gratings, see figure 1). These substrates can be regarded as a special kind of 'roughness' with only a few enhanced Fourier components in the wavenumber spectrum, which may be damped by an adsorbed film. Andelmann *et al* [1, 2] have investigated theoretically a system with van der Waals interactions between the rough substrate and a thin film. Tidswell *et al* [3] confirmed their results for thin liquid cyclohexane films on rough silicon (Si) substrates: Very thin ($< 60 \text{ \AA}$) cyclohexane films are conformal (the roughness spectrum follows the substrate), thicker films ($> 60 \text{ \AA}$) are not conformal.

We have investigated polystyrene (PS) films on top of surface gratings with a lateral spacing $d = 9800 \text{ \AA}$ and a height $h \approx 130 \text{ \AA}$. In this system, van der Waals interactions between the substrate and the polymer chains dominate and render the system ideal for investigation of the aforementioned problem.

Our experiments were performed using (i) x-ray scattering in the region of small incidence angles to investigate the layer thicknesses and structures of the

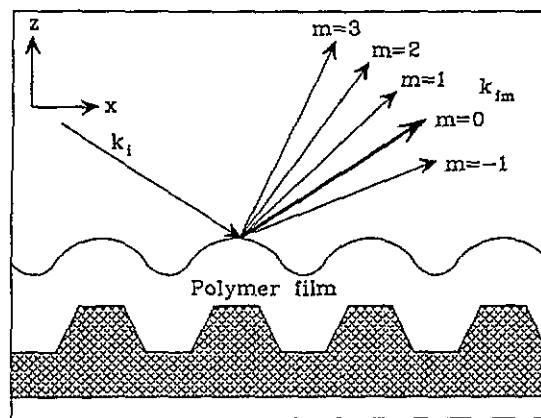


Figure 1. A schematic drawing of a laterally structured surface with a polymer film on top. Owing to the lateral periodicity an incoming x-ray wave k_i is reflected ($m = 0$) as well as scattered into non-specular diffraction orders ($m \neq 0$).

interfaces grating/PS and PS/air and (ii) atomic force microscopy (AFM) to examine directly the topmost surface.

The paper is structured as follows. After the introduction, a brief description of the theory of Andelmann *et al* [1, 2] and of the x-ray scattering theory is given. Then the samples and the measurements are presented. The results are discussed and a conclusion finishes this paper.

2. Theory

2.1. The propagation of roughness in thin films

In this section the basic result of the theory of Andelmann *et al* [1, 2] is discussed. We consider a thin (liquid) film of thickness l on top of a rough surface. The two surfaces are described by the functions $f_1(x)$ (solid) and $f_2(x)$ (liquid), respectively. Then the question is that of how the particular shape of $f_1(x)$ influences the morphology of $f_2(x)$. A free-energy minimization within a linear response approximation leads to the following result [1, 2]:

$$\tilde{f}_2(q) = \chi(q, l) \tilde{f}_1(q). \quad (1)$$

Assuming non-retarded van der Waals interactions between the substrate and the molecules of the liquid (or the polymer) yields the following expression for the function $\chi(q, l)$, which connects the Fourier transform $\tilde{f}_2(q)$ of the liquid surface with the Fourier transform $\tilde{f}_1(q)$ of the solid substrate:

$$\chi(q, l) = \frac{a^2}{a^2 + q^2 l^4} \tilde{K}(q) \quad (2)$$

with $a = [A_{\text{eff}}/(2\pi\gamma)]^{1/2}$ and $\tilde{K}(q) \approx 1$ (the Deryagin approximation [4]). The length a contains the physics of the system. If the liquid–vapour surface tension γ dominates over the van der Waals interaction described by the effective Hamaker constant A_{eff} , then $qa \ll 1$ results and equations (1) and (2) lead to a flat surface of the absorbed film ($f_2(q) \approx 0$). The other extreme case (small surface tension γ and strong substrate interactions) yields $qa \gg 1$ and $\chi(q, l) \approx 1$, which means that the film follows the substrate perfectly ($f_2(q) \approx f_1(q)$).

For a laterally periodic structured surface the continuous variable q in equation (1) has to be replaced by discrete values $q_m = 2\pi m/d$ (m is an integer) and the Fourier transforms $\tilde{f}_{1,2}(q)$ have to be replaced by the respective Fourier-coefficients $\tilde{f}_{1,2}(q_m)$ of the periodic surfaces $f_{1,2}(x) = f_{1,2}(x + d)$.

2.2. X-ray scattering

We consider a system of layers on top of a laterally structured surface described by $f_1(x)$ with periodicity d . In the particular case of our work two layers (a native oxide layer and the polymer film) are assumed, which are on top of a Si surface grating with a spacing of $d = 9800$ Å.

The locations $z_k(\mathbf{r}_{\parallel})$ of the interfaces are described by the expressions $z_k(\mathbf{r}_{\parallel}) = f_k(x) + \delta f_k(\mathbf{r}_{\parallel}) + l_k$, where $f_k(x)$ is assumed to be a periodic function $f_k(x) = f_k(x + d)$, $\delta f_k(\mathbf{r}_{\parallel})$ is a random part (roughness) with vanishing mean value $\langle \delta f_k(\mathbf{r}_{\parallel}) \rangle_{\mathbf{r}_{\parallel}} = 0$ and l_k denotes the baseline of $f_k(x)$, which equals the film thickness (note that $l_1 = 0$).

Calculating the x-ray scattering intensity within the Born approximation for this system yields

$$I(q_r, q_z) \simeq \frac{1}{q_z^4} \sum_m \sum_{j,k=1}^N \Delta \rho_k \Delta \rho_j \exp[iq_z(l_k - l_j)] \\ \times C_{k,m}^*(q_z) C_{j,m}(q_z) \exp[-(\sigma_j^2 + \sigma_k^2)q_z^2/2] \\ \times \left(4\pi^2 \delta(q_{r,m}) + \iint \exp(-iq_{r,m} \cdot \mathbf{r}_{\parallel}) \right.$$

$$\left. \times [\exp(q_z^2 \Lambda_{jk}(\mathbf{r}_{\parallel})) - 1] d\mathbf{r}_{\parallel} \right). \quad (3)$$

The asterisk denotes a complex conjugate. A system consisting of N components ($k = 1$ is the substrate) with electron densities ρ_k and density differences $\Delta \rho_k := \rho_{k+1} - \rho_k$ is assumed. In the particular case of a PS film of density ρ_{PS} on top of a Si grating with a native oxide layer, these quantities are $\Delta \rho_1 := \rho_{\text{SiO}_2} - \rho_{\text{Si}}$, $\Delta \rho_2 := \rho_{\text{PS}} - \rho_{\text{SiO}_2}$ and $\Delta \rho_3 := -\rho_{\text{PS}}$. Furthermore, $\Lambda_{jk}(\mathbf{r}_{\parallel})$ is the height–height correlation function $\Lambda_{jk}(\mathbf{r}_{\parallel}) := \langle \delta f_j(\mathbf{r}_{k,\parallel}) \delta f_k(\mathbf{r}_{k,\parallel}) \rangle_{\mathbf{r}_{k,\parallel}}$ of the roughnesses between interfaces j and k and $\sigma_k^2 := \langle [\delta f_k(\mathbf{r}_{k,\parallel})]^2 \rangle_{\mathbf{r}_{k,\parallel}}$ is the square of the RMS roughness of interface k . Note that the quantities $C_{k,m}(q_z)$ do not directly yield the Fourier coefficients of $f_k(x)$ but rather the Fourier coefficients of $\exp(-iq_z f_k(x))$:

$$C_{k,m}(q_z) = \frac{1}{d} \int_0^d \exp(-iq_z f_k(x)) \exp(-iq_m x) dx \\ q_m = 2\pi m/d.$$

The momentum transfer $q := k_f - k_i$ (k_i and k_f are the wavevectors of the incident and scattered x-rays, respectively) is decomposed by $q = (q_r, q_z)^T$. Owing to the lateral periodicity, the delta function $\delta(q_{r,m})$ in equation (3) leads to resolution-limited diffraction orders at the positions $q_{r,m} = (q_x - q_m, q_y) = 0$ in reciprocal space.

The diffuse scattering caused by the random fluctuations $\delta f_k(\mathbf{r}_{\parallel})$ and described by the integral in equation (3) is not considered in this paper. This will be done elsewhere. In the present paper we only concentrate on the diffraction orders and their q_z -dependence. Of course, the RMS roughnesses σ_k of the interfaces have an influence on the intensities of the diffraction orders and cannot be neglected (see equation (3)).

The substrates are trapezoidally shaped surface gratings (spacing d , widths of the bars, grooves and intermediate regions s , g and b : $d = s + g + 2b$, grating height h). For these gratings, a calculation of the coefficients $C_{1,m}(q_z)$ yields [5, 6]:

$$C_{1,m}(q_z) = \begin{cases} \frac{s+g}{d} - 2 \exp(-iq_z h/2) \\ \times \left[i \frac{s}{d} - \frac{b}{d} \frac{2}{q_z h} \right] \sin(\frac{1}{2} q_z h) & m = 0 \\ \exp(-i(q_m x_0 + q_z h/2)) \\ \times \left(\exp(iq_m(g+b/2)) \right. \\ \times \frac{\sin[\frac{1}{2} q_z h(1 - \varepsilon_m)]}{\frac{1}{2} q_m d(1 - \varepsilon_m)} \\ \left. - \exp(-iq_m b/2) \right. \\ \times \frac{\sin[\frac{1}{2} q_z h(1 + \varepsilon_m)]}{\frac{1}{2} q_m d(1 + \varepsilon_m)} \left. \right) & m \neq 0 \end{cases} \quad (4)$$

with $\varepsilon_m := q_m b/q_z h$ and a phase x_0 , which controls the position of the adsorbed layer in relation to the underlying substrate.

The oxide layer of thickness l_2 on top of the Si surface grating is treated in the same way. We assume a very thin ($l_2 \approx 10$ Å), perfectly conformal ($C_{2,m}(q_z) = C_{1,m}(q_z)$)

native oxide layer with the same parameters d , s , g , b and x_0 . Furthermore, the roughnesses of the Si/SiO₂ and SiO₂/PS interfaces are denoted by σ_1 and σ_2 , respectively. Note that this implies identical roughnesses of the bars and the grooves. This is definitely *not* true for GaAs surface gratings, which show a rather large roughness within the grooves and a considerably smaller roughness of the bars [5, 6]. For the Si surface gratings used as substrates in this work, roughnesses of the order of $\sigma \approx 5 \text{ \AA}$ are expected so that this approximation is not crucial.

The AFM measurements show that the structure of the surface of the polymer film $f_3(x)$ is nearly sinusoidal. Therefore a Fourier expansion

$$f_3(x) = \sum_{n>0} \tilde{f}_3(q_n) \sin(q_n x)$$

with only one dominating Fourier component, namely $|\tilde{f}_3(q_n)| \ll |\tilde{f}_3(q_1)|$ for $n > 1$, is straightforward and leads to the expression

$$C_{3,m}(q_z) = J_{-m}(u) - \frac{1}{2} q_z \sum_{n>1} \tilde{f}_3(q_n) [J_{n-m}(u) - J_{-n-m}(u)] \quad (5)$$

with the argument $u := q_z \tilde{f}_3(q_1)$ in the Bessel functions of integer order $J_m(u)$. Furthermore l_3 denotes the thickness of the polymer film (strictly speaking, the mean value of the interface $z_3(\mathbf{r}_{\parallel})$) and σ_3 is the RMS roughness of the PS/air interface.

Equations (3)–(5) were used to fit the x-ray data. Additionally the q_z resolution of the diffractometer as well as geometrical correction factors due to the small incident and exit angles were taken into account.

3. Experiments

3.1. Samples

As already mentioned, we have used a Si surface grating with a lateral spacing of $d = 9800 \text{ \AA}$ and a height of $h = 130 \text{ \AA}$ as substrate [7, 8]. This substrate was prepared using plasma-etching methods. X-ray investigations of similar bare gratings show that they are covered by a native oxide layer of thickness $l_2 \approx 10 \text{ \AA}$ of roughness about $\sigma_1 \approx 5 \text{ \AA}$ of the Si/SiO₂ interface [9]. Before the PS films were deposited on the surface, the bare grating was measured with an AFM and the values $s \approx 3300 \text{ \AA}$, $g \approx 5100 \text{ \AA}$ and $b \approx 700 \text{ \AA}$ were obtained.

The PS films were first spun onto a glass substrate to determine the thickness with an ellipsometer. Then they were floated on a water surface. Finally, they were put on the surface of the grating and they were annealed for 2 h at 185 °C in a vacuum oven.

Before the x-ray experiments were started, the surface of the sample was checked for each film by AFM measurements using a commercial Nanoscope III instrument in the contact mode. Various points on the surface were investigated to guarantee a homogeneous and periodic PS layer. At the end of the experiments it was checked that layer-by-layer growth, as done in this work, leads to the same surface structure as growth of one thick layer.

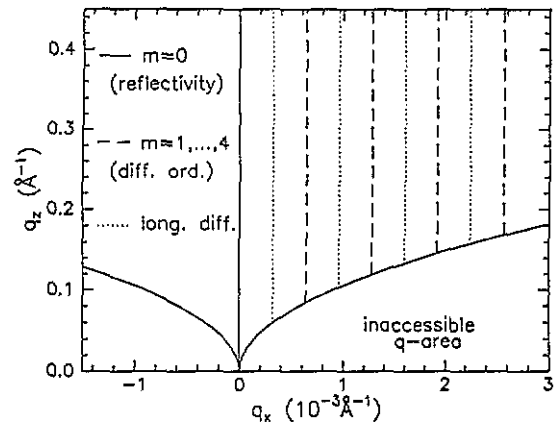


Figure 2. The x-ray measurements were performed in reciprocal space (q_x , q_z). Owing to geometrical restrictions, the region below the full parabolae is not accessible with the set-up of this work. A measurement along the full line at $q_x = 0$ yields the reflectivity and q_z scans along the broken lines are scans along the respective diffraction orders ($q_x = 2\pi m/d$). The dotted lines represent diffuse q_z scans between the diffraction orders (for $q_x = 2\pi m/(d + \pi/d)$).

3.2. X-ray measurements

The x-ray measurements were performed at the National Synchrotron Light Source (Brookhaven National Laboratories) on the Exxon beamline X10B using a wavelength of $\lambda = 1.131 \text{ \AA}$. The measured q_z resolution for our set-up was $\delta_{q_z} = 3.5 \times 10^{-3} \text{ \AA}^{-1}$ without using an analyser crystal. The out-of-plane resolution is rather coarse and therefore need not to be considered (integration over q_y).

Figure 2 shows the region in reciprocal space (q_x , q_z) that is of interest for this paper. q_z scans for fixed $q_x = q_m$ along the diffraction orders (broken lines for $m \neq 0$, full line for $m = 0$ in figure 2) or between two orders for $q_x = q_m + \pi/d$ (broken lines) are performed. For each film the reflectivities and four diffraction orders were measured. The diffuse scattering was monitored with q_z scans in the middle between two orders and afterwards it was subtracted from the data to obtain the true specular reflectivity and true intensity of the diffraction orders, respectively.

The reflectivities (full lines) and first diffraction orders (open circles) for five different film thicknesses $l_3 = 230, 390, 490, 590$ and 690 \AA are shown in figure 3 (curves I–V). Here the thicknesses obtained by ellipsometry before the film was put on the structured surface are given; as we shall see, the more accurate values obtained from the x-ray data differ from these numbers.

From figure 3 it can be seen that the period of the oscillations in the first part of the curves is reduced with increasing film thickness. For large q_z values only the modulation of the underlying grating is present which indicates that the microscopic roughness σ_2 of the SiO₂/PS interface is a little smaller than the roughness σ_3 of the interface PS/air.

The same qualitative discussion holds for the first diffraction orders. Owing to geometrical restrictions, they start at $q_z = 0.084 \text{ \AA}^{-1}$ (see figure 2). The q_z intensity of the first diffraction order for film I almost follows the reflectivity with a phase shift of $\pi/2$. This is an indication of a nearly conformal PS layer on top of the

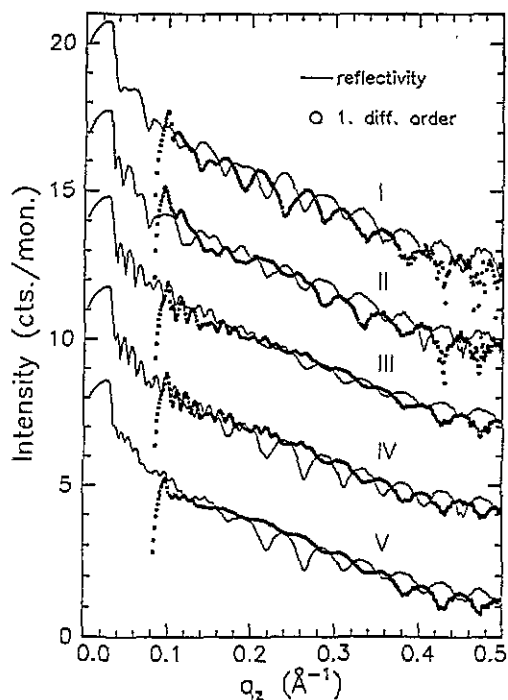


Figure 3. Reflectivities (full lines) and first diffraction orders (open circles) for the films I–V with the thicknesses $l_3 = 230, 390, 490, 590$ and 690 Å.

surface, which means that the amplitude of the modulation of the topmost layer is approximately the grating height h . This was also confirmed by the AFM pictures. They yield a sinusoidal shape of the surface with an amplitude of $2\tilde{f}_3(q_1) \approx 140$ Å. Thicker layers II–V do not show the above-mentioned behaviour. The intensity of the first diffraction order does not follow the reflectivity. This means that the amplitude of the modulation of the PS layer decreases more and more. Again the AFM measurements confirm these qualitative discussions of the data.

To obtain more accurate values of the parameters and additional information about the interfaces, the x-ray data of the film I were fitted with the model presented in section 2.2. Owing to the fact that a kinematical model was used, for small incidence or exit angles the theory failed and the data were not fitted within these regions.

Figure 4 shows the measurement and the best fit of the reflectivity and the first four diffraction orders for layer I. Note that all curves were fitted simultaneously and therefore only one normalization factor was introduced (for clarity, in figure 4 all curves were shifted by three orders of magnitude). The fit yields a layer thickness of $l_3 = 270$ Å and $2\tilde{f}_3(q_1) = 120$ Å for the modulation amplitude of the topmost layer. These values differ from the numbers determined with the ellipsometer and the AFM. However, it should first be stated that the ellipsometry was performed for a film on a flat surface and before the annealing, and second, it is well-known that AFM pictures can suffer from possible contaminations of the tip. In contrast to these measurements, it turns out that the fit of the x-ray data is very sensitive to the parameters l_3 and $\tilde{f}_3(q_1)$. Nevertheless, both the AFM and the ellipsometer yield rather good estimates for these parameters. For the roughnesses,

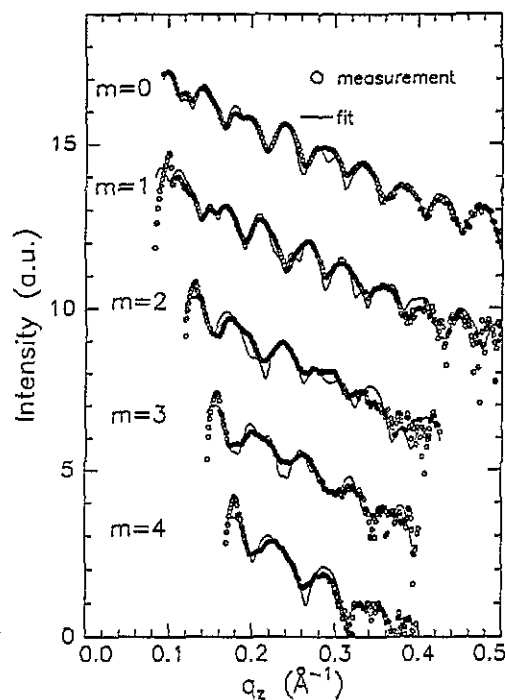


Figure 4. Measurements (open circles) and fits (full lines) of the reflectivity ($m = 0$) and the first four diffraction orders ($m = 1, \dots, 4$) for film I with the thickness $l_3 = 270$ Å. Owing to the Born approximation, which is used to explain the data (see text), the first parts of the curves of the diffraction orders cannot be explained by the theory (very small incidence angles, here the dynamical transmission functions dominate the scattering). For clarity, all curves are shifted by three orders of magnitude relative to each other.

the fit yields $\sigma_2 = 4.5$ Å and $\sigma_3 = 6.2$ Å. Furthermore, non-vanishing higher order Fourier components are also obtained from the fit ($\tilde{f}_3(q_3) = 5$ Å, $\tilde{f}_3(q_5) = 2$ Å and $|\tilde{f}_3(q_n)| \leq 0.5$ Å for $n > 5$).

As yet only the data for the first film have been fitted. The analysis of the whole data set is in progress.

4. Results and discussion

For the quantity a in equation (2) a value of $a \approx 5$ Å is typical ($A_{\text{eff}} \approx 5 \times 10^{-13}$ erg for the system Si–SiO₂–PS, $\gamma \approx 25$ – 35 erg cm⁻²). Inserting this number into equation (2) and calculating the function $\chi(q_1, l_3)$ leads to the curve in figure 5 which is given by the full line. The open circles are obtained from the five different films by analysing the data.

It can be clearly seen that the full line (the theory of Andelmann *et al* [1, 2] with $a = 5$ Å) is not able to explain the x-ray measurements of film I ($l_3 = 270$ Å) and the AFM and ellipsometer data of the films II–V ($\chi(q_1, l_3) = \pi \tilde{f}_3(q_1)/(4h)$).

The difference between the measurement and the theory is rather large, which leads us to suspect that a fundamental assumption of the theory is not valid. Maybe the assumption of simple van der Waals interactions does not hold for the polymer used or the linear response approximation breaks down. The broken line in figure 5 is a

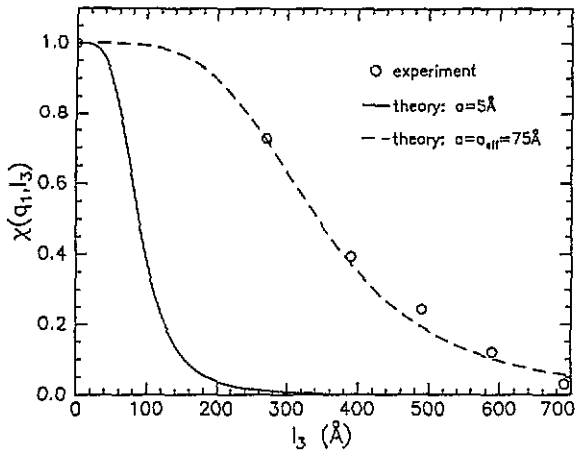


Figure 5. The function $\chi(q_1, l_3)$ obtained from the theory (full line) with a value of $a = 5 \text{ \AA}$. The broken line is a fit to the data (open circles) with $a = a_{\text{eff}} = 75 \text{ \AA}$. Note that only the point for $l_3 = 270 \text{ \AA}$ is obtained from the x-ray data. All other points are measured with the atomic force microscope and the film thicknesses are determined with an ellipsometer. Therefore, for these points, errors of about 30% might have to be taken into account.

fit of the data with $a = a_{\text{eff}} = 75 \text{ \AA}$, which is 15 times larger than expected (this means an effective Hamaker constant 225 times larger than the nominal value!). Therefore equation (2) seems to describe the behaviour of the PS film on top of the grating correctly, but the constant a has to be considered in another way.

In summary, we have shown x-ray and AFM measurements of thin PS films that had been deposited

on a laterally structured Si surface. The basic result is that the theory of Andelmann *et al* does not explain the data quantitatively if simple van der Waals interactions between the PS layer and the substrate are assumed.

Acknowledgments

We thank B Zhang (Exxon), W Zhao and Y Liu (SUNY at Stony Brook) for their help during the experiments and W Press, OH Seeck, and V Nitz (Universität Kiel) for discussion, a critical reading of the manuscript and the help with computer problems. MT is indebted to the surface x-ray scattering group at Brookhaven National Laboratory for their hospitality.

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