

Thin polymer films on rough surfaces

M. Tolan^{a,*}, G. Vacca^b, J. Wang^b, S.K. Sinha^{b,1}, Z. Li^c, M.H. Rafailovich^c, J. Sokolov^c,
A. Gibaud^d, H. Lorenz^e, J.P. Kotthaus^e

^a*Institut für Experimentalphysik der Universität Kiel, Leibnizstraße 19, 24098 Kiel, Germany*

^b*Exxon Research and Engineering Company, Annandale, NJ 08801, USA*

^c*Department of Materials Science, State University of New York at Stony Brook, NY 11794-2275, USA*

^d*Faculté des Sciences, Université du Maine, 72017 Le Mans Cedex, France*

^e*Sektion Physik, Ludwig-Maximilians-Universität München, Geschwister-Scholl-Platz 1, 80539 München, Germany*

Abstract

X-ray diffraction measurements in the region of small incidence and exit angles on thin polystyrene (PS) films deposited on laterally structured surfaces are performed. From fits of the data we obtain how the Fourier-components of the substrates are damped by the adsorbed films. The results are compared with theoretical predictions for liquid films. It turns out that PS-films of low molecular weight ($\leq 300k$) behave like frozen liquids. Within films of a molecular weight of $1000k$ viscoelastic forces dominate over the substrate-adsorbate van der Waals-interactions so that even a 680 \AA thick film is not totally flat on top of a grating with a height of 130 \AA .

1. Introduction

The investigation of thin films deposited on rough surfaces is of great interest in basic research and in materials science. In most thin film preparation techniques an imperfection of one layer is transferred from a (solid) substrate through a thin film to the surface. This leads to the so-called conformal or correlated roughness [1–10].

Andelmann et al. [11, 12] have investigated theoretically how the Fourier-spectrum of an adsorbed thin film is influenced by a rough solid substrate and later Tidswell et al. [13] confirmed their results for thin liquid cyclohexane films with dominating van der Waals interactions between the adsorbate and the (statistically rough) silicon (Si) substrate. Deviations between theory and experiment were explained by the unknown influence of the capillary wave fluctuations on the substrate/adsorbate-interactions.

We have investigated polystyrene (PS) films with two different molecular weights ($M_w = 300k$ and $M_w = 1000k$)

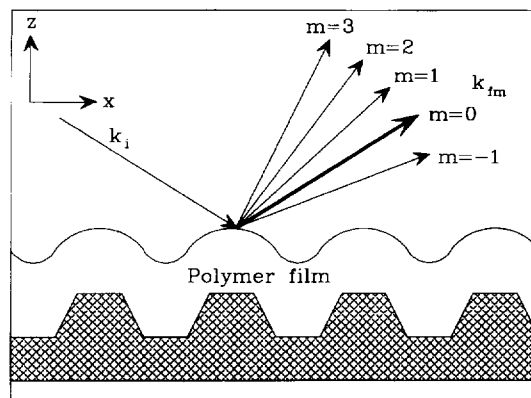


Fig. 1. Schematic drawing of a laterally structured surface with a polymer film on top. Due to the periodicity an incoming X-ray wave k_i is reflected ($m = 0$) as well as scattered into nonspecular diffraction orders ($m \neq 0$).

on top of surface gratings with a spacing of $d \approx 1 \mu\text{m}$ and heights of about $h \sim 150 \text{ \AA}$ (see Fig. 1). These surface gratings can be regarded as a special kind of “rough” substrates with only a few enhanced Fourier-components in the wave

* Corresponding author.

¹ Present address: XFD/APS Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA.

number spectrum. Therefore, a systematic study of the aforementioned problem and a quantitative comparison with existing theories becomes possible because the influence of the microscopic statistical part of the roughness (surface roughness of the gratings and capillary wave fluctuations of the films) is clearly separated from the periodic conformal part. X-ray scattering experiments in the region of small incidence and exit angles were performed to investigate the layer thicknesses and structures of the interfaces grating/PS and PS/air and Atomic Force Microscopy (AFM) was done to check directly the topmost surface.

2. Theory

In the following we consider a thin (liquid or polymer) film of thickness l on top of a rough surface. The two surfaces are described by the functions $f_S(x)$ (solid) and $f_L(x)$ (film), respectively. Then the question is: How does the particular shape of $f_S(x)$ influence the morphology of $f_L(x)$? Within a linear response approximation [11, 12] the result

$$\tilde{f}_L(q) = \chi(q, l) \tilde{f}_S(q) \quad (1)$$

can be obtained. The function $\chi(q, l)$ contains the physics of the system and connects the Fourier-transform $\tilde{f}_L(q)$ of the topmost surface with the Fourier-transform $\tilde{f}_S(q)$ of the underlying substrate. For a periodic surface the continuous variable q has to be replaced by discrete values $q_m = m \times 2\pi/d$ (m integer) and the Fourier-transforms have to be replaced by the respective Fourier-coefficients.

To explain the X-ray data we consider a system of N layers on top of a surface described by $f_{S_1}(x)$ with periodicity d (Si surface grating). In the particular case of our work two overlayers [a native oxide layer $f_{S_2}(x)$ and the PS film $f_{L_3}(x)$] are assumed.

The locations $z_k(\mathbf{r}_\parallel)$ of the interfaces are described by: $z_k(\mathbf{r}_\parallel) = f_k(x) + \delta f_k(\mathbf{r}_\parallel) + l_k$, where $f_k(x)$ is assumed to be the periodic part of the k th interface $f_k(x) = f_k(x + d)$, $\delta f_k(\mathbf{r}_\parallel)$ is a random part (microscopic roughness) with vanishing mean value $\langle \delta f_k(\mathbf{r}_\parallel) \rangle_{\mathbf{r}_\parallel} = 0$, and l_k denotes the baseline of $f_k(x)$.

Calculating the X-ray scattering intensity in Born approximation yields

$$\begin{aligned} I(\mathbf{q}_r, q_z) &\sim \frac{1}{q_z^4} \sum_m \sum_{j,k=1}^N \Delta \rho_k \Delta \rho_j e^{iq_z(l_k - l_j)} \\ &\times \mathcal{C}_{k,m}^*(q_z) \mathcal{C}_{j,m}(q_z) e^{-(\sigma_j^2 + \sigma_k^2) q_z^2} \\ &\times \left\{ 4\pi^2 \delta(\mathbf{q}_{r,m}) + \iint e^{-i\mathbf{q}_{r,m} \cdot \mathbf{r}_\parallel} \left(e^{iq_z A_{jk}(\mathbf{r}_\parallel)} - 1 \right) d\mathbf{r}_\parallel \right\}. \end{aligned} \quad (2)$$

The asterisk denotes a complex conjugate quantity and the electron density differences are given by: $\Delta \rho_k =$

$\rho_{k-1} - \rho_k$. Furthermore, $A_{jk}(\mathbf{r}_\parallel)$ is the height–height correlation function $A_{jk}(\mathbf{r}_\parallel) = \langle \delta f_j(\mathbf{r}_{k,\parallel}) \delta f_k(\mathbf{r}_{k,\parallel}) \rangle_{\mathbf{r}_{k,\parallel}}$ of the microscopic 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 $\mathcal{C}_{k,m}(q_z)$ are not the Fourier-coefficients of the periodic functions $f_k(x)$ but those of the function $\exp\{-iq_z f_k(x)\}$ [14–21].

The momentum transfer $\mathbf{q} := \mathbf{k}_f - \mathbf{k}_i$ (\mathbf{k}_i and \mathbf{k}_f are the wave vectors of the incident and scattered X-rays, respectively) is decomposed by: $\mathbf{q} = (\mathbf{q}_r, q_z)^\top$. The delta function $\delta(\mathbf{q}_{r,m})$ in Eq. (2) leads to resolution limited diffraction orders at the positions $\mathbf{q}_{r,m} = (q_x - q_m, q_y)^\top = 0$ in reciprocal space which are caused by the lateral periodicity (see Fig. 1). The diffuse scattering from the random fluctuations $\delta f_k(\mathbf{r}_\parallel)$ described by the integral in Eq. (2) is not considered in this paper. This will be done elsewhere [22]. In the present paper we concentrate on the q_z -dependence of the diffraction orders which contains the information about the periodic part of the interfaces. This does not mean that the rms-roughnesses σ_k can be neglected [see exponential in Eq. (2)]. Only the particular lateral structure of the microscopic part of the roughness is not considered [18, 23–27].

3. Samples

The substrates are symmetric trapezoidally shaped surface gratings (spacing d , width of the bars, grooves, and intermediate regions s , g , and b : $d = s + g + 2b$, grating height h) which were prepared using plasma-etching methods [28, 29]. For these gratings a calculation of the coefficients $\mathcal{C}_{S_1,m}(q_z)$ can easily be done (an analytic expression is given by Eq. (3.35) in Ref. [17], see also Ref. [15]).

Furthermore, we assume a very thin ($l_2 = 10 \text{ \AA}$), perfectly conformal [$\mathcal{C}_{S_2,m}(q_z) = \mathcal{C}_{S_1,m}(q_z)$] native oxide layer with the same parameters d , s , g , b , and h on top of the substrates [30]. The roughnesses of the Si/SiO₂- and SiO₂/PS-interfaces are denoted by σ_1 and σ_2 , respectively. This implies identical roughnesses of the bars and the grooves and is definitely *not* true for GaAs surface gratings which show a rather large rms-roughness within the grooves and a considerably smaller roughness of the bars [14–17]. However, X-ray investigations of the Si surface gratings which were used as substrates for the PS-films with a molecular weight of $M_w = 1000k$ yield equal rms-roughnesses of $\sigma_{1,2} = 5 \text{ \AA}$. For the other Si-substrates different roughnesses of the bars and grooves were obtained ($\sigma_{1,s} \approx 4 \text{ \AA}$ on top of the bars and $\sigma_{1,g} \approx 14 \text{ \AA}$ in the grooves). This renders the analysis of the data a little bit more complicated. The equation for the scattering amplitude slightly differs from Eq. (2) because now two roughnesses $\sigma_{s,k}$ and $\sigma_{g,k}$ for the bars and grooves, respectively, must be considered (for a detailed calculation see Refs. [14–17]).

The baseline of the PS film is given by l_3 and σ_3 denotes the rms-roughness of the PS/air interface. In this paper we always will call l_3 the PS-film thickness. Strictly speaking, $l_3 - l_2$ is the real PS-film thickness but due to the small value of $l_2 = 10 \text{ \AA}$ compared with those of l_3 this makes no difference.

AFM-measurements show that the adsorbed PS film $f_{L_3}(x)$ is nearly sinusoidal. Therefore a Fourier-expansion

$$f_{L_3}(x) = \sum_{n>0} \tilde{f}_{L_3}(q_n) \cos(q_n x),$$

with only one dominating Fourier-component, i.e. $|\tilde{f}_{L_3}(q_n)| \ll |\tilde{f}_{L_3}(q_1)|$ for $n > 1$, is straightforward and leads to the expression

$$\mathcal{G}_{L_3,m}(q_z) = i^{-m} J_m(u)$$

$$- \frac{1}{2} q_z \sum_{n>1} i^{n-m-1} \tilde{f}_{L_3}(q_n) \{J_{m-n}(u) + (-1)^n J_{m+n}(u)\} \quad (3)$$

with the argument $u = q_z \tilde{f}_{L_3}(q_1)$ in the Bessel-functions of integer order $J_m(u)$.

The PS films were first spun onto a glass substrate. Estimates of their thicknesses were obtained with ellipsometric measurements. Afterwards they were floated on a water surface. Finally, they were put on the surface of the gratings and then annealed for $2h$ at 185°C in a vacuum oven.

Before and after the X-ray experiments the surface of the deposited PS-films was checked with a commercial Nanoscope III AFM. Various places were investigated to guarantee a homogeneous and periodic PS layer. At the end of the experiments it was checked that a layer-by-layer growth, as done in this work, leads to the same surface structure as a growth of one thick layer. This test is crucial because it checks whether our results are independent from the preparation technique.

4. X-ray scattering experiments

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 setup was $\delta q_z = 3.5 \times 10^{-3} \text{ \AA}^{-1}$ without use of an analyzer crystal. The out-of-plane resolution is rather coarse and therefore needs not to be considered (integration over q_y).

We have performed q_z -scans in reciprocal space for fixed $q_x = q_m$ ($m = 0, \dots, 4$) along the diffraction orders

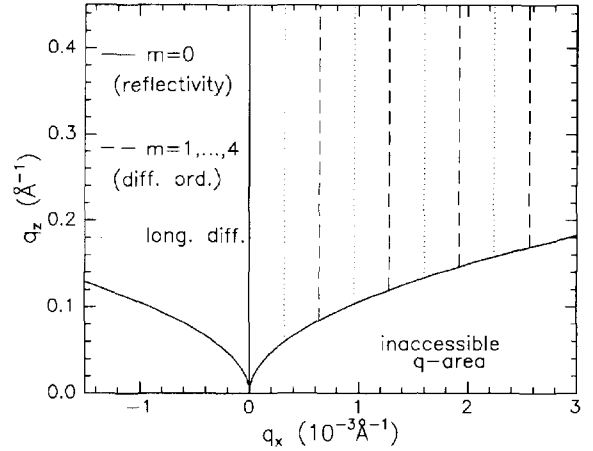


Fig. 2. The X-ray measurements were performed in reciprocal space (q_x, q_z). Due to geometrical restrictions the region below the solid parabolas is not accessible with the setup of this work. A measurement along the solid line at $q_x = 0$ yields the reflectivity and q_z -scans along the dashed lines (---) are scans along the respective diffraction orders ($q_x = m \times 2\pi/d$). The dotted lines (···) represent diffuse q_z -scans between the diffraction orders (for $q_x = m \times 2\pi/d + \pi/d$).

and additionally along $q_x = q_m + \pi/d$ to obtain the diffusely scattered intensity stemming from the random fluctuations $\delta f_k(r_1)$ (see Fig. 2). This diffuse intensity was subtracted from the data for $q_x = q_m$ to obtain the true specular reflectivity and true intensity of the diffraction orders, respectively. Therefore only the intensities from the periodic conformal part of the interfaces contribute to the signal which is explained by the fits of the data (see below).

Five PS films with $M_w = 1000k$ and thicknesses $l_3 = 275, 396, 498, 600, \text{ and } 680 \text{ \AA}$ on top of a Si-grating with $h = 132 \text{ \AA}$, $s = g = 4000 \text{ \AA}$, and $b = 900 \text{ \AA}$ were investigated. Additionally, one more $M_w = 1000k$ film with $l_3 = 179 \text{ \AA}$ on a second grating with a height of $h = 105 \text{ \AA}$ was measured. As examples Figs. 3 and 4 show measurements (open circles) and fits (solid lines) of the X-ray data for the $l_3 = 275 \text{ \AA}$ and $l_3 = 600 \text{ \AA}$ PS films. All five curves in each figure were fitted simultaneously (for clarity the curves were shifted by three orders of magnitude on the intensity scale) using the above-mentioned parameters for the substrate, the values for the electron densities of Si, SiO₂, and PS from literature [31] and from previous experiments [30, 32], the measured resolution, and correction factors due to the small incidence and exit angles. Therefore only six free fit parameters were introduced: The rms-roughnesses σ_2 and σ_3 , the height of the baseline of the PS film l_3 , and three Fourier-coefficients $\tilde{f}_{L_3}(q_1)$, $\tilde{f}_{L_3}(q_3)$, and $\tilde{f}_{L_3}(q_5)$. Note that due to $s = g$ only odd Fourier-coefficients occur.

It turns out that all fits are extremely sensitive to the parameters σ_2 , σ_3 , l_3 , $\tilde{f}_{L_3}(q_1)$, and $\tilde{f}_{L_3}(q_3)$, and less sensitive

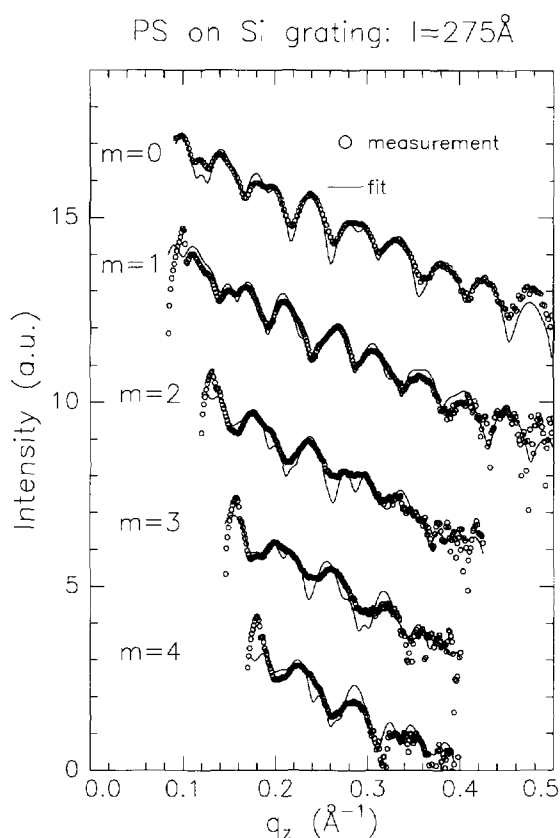


Fig. 3. Measurements (open circles) and fits (solid lines) of the reflectivity ($m = 0$) and the first four diffraction orders ($m = 1, \dots, 4$) for the $M_W = 1000k$ PS film with $l_3 = 275 \text{ \AA}$. For clarity, all curves are shifted three orders of magnitude against each other.

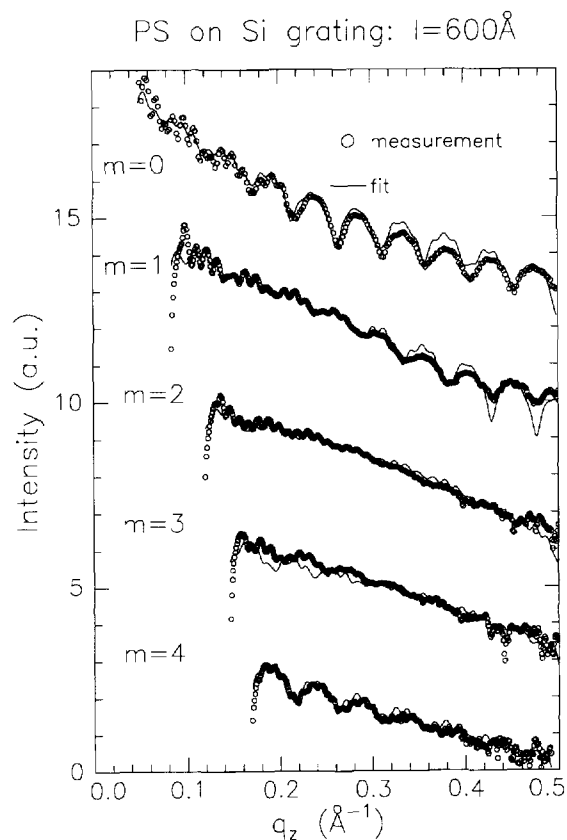


Fig. 4. Measurements (open circles) and fits (solid lines) of the reflectivity ($m = 0$) and the first four diffraction orders ($m = 1, \dots, 4$) for the $M_W = 1000k$ PS film with $l_3 = 600 \text{ \AA}$. For clarity, all curves are shifted three orders of magnitude against each other.

to the coefficient $\tilde{f}_{L_3}(q_s)$. This means that a determination of $\chi(q_1, l)$ and $\chi(q_3, l)$ is possible.

The fits in Figs. 3 and 4 yield $\sigma_2 = 4.0 \text{ \AA}$ and $\sigma_3 = 4.5 \text{ \AA}$ for both cases. These numbers for the roughnesses are nearly the same for all investigated $M_W = 1000k$ films. The Fourier-coefficients are: $\tilde{f}_{L_3}(q_1) = 58.7 \text{ \AA}$, $\tilde{f}_{L_3}(q_3) = -6.0 \text{ \AA}$, and $\tilde{f}_{L_3}(q_s) = -1.3 \text{ \AA}$ for the $l = 275 \text{ \AA}$ film and $\tilde{f}_{L_3}(q_1) = 8.6 \text{ \AA}$, $\tilde{f}_{L_3}(q_3) = -0.7 \text{ \AA}$, and $\tilde{f}_{L_3}(q_s) = 0.3 \text{ \AA}$ for the fit shown in Fig. 4 (errors are given by the last digit). Higher-order coefficients do not improve the quality of the fits significantly. Due to the Born approximation which is used to explain the data, the first part 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 [18, 25–27, 33, 34]).

Fig. 5 shows the reflectivities (solid lines) together with the scans along the first diffraction orders (broken lines) for the $M_W = 300k$ samples. The upper two curves are the

measurements for the bare grating whereas the other curves show the results for $l_3 = 230 \text{ \AA}$ and $l_3 = 390 \text{ \AA}$. The reflectivity of the bare substrate only shows weak oscillations stemming from interferences of scattered X-rays from the top of the bars and the bottom of the grooves. This is a clear hint that the roughnesses are not identical. A fit yields the values $\sigma_{2,s} = 4.0 \text{ \AA}$ and $\sigma_{2,g} = 14.0 \text{ \AA}$. The modulations which are present in the other reflectivities are caused by the PS-overlayers. If the scans along the diffraction orders for $l_3 = 230 \text{ \AA}$ and $l_3 = 390 \text{ \AA}$ are compared with those of the bare grating (see Fig. 5) one can see that they are nearly unaffected by the $300k$ PS films. This means that all Fourier coefficients are very small; in other words: The film is totally flat on its surface. Here a fit of the data yields the values: $\tilde{f}_{L_3}(q_1) = 4.4 \text{ \AA}$, and $\tilde{f}_{L_3}(q_3) \approx 0 \text{ \AA}$ for the $l_3 = 230 \text{ \AA}$ film and $\tilde{f}_{L_3}(q_1) = 2.4 \text{ \AA}$, $\tilde{f}_{L_3}(q_3) \approx 0 \text{ \AA}$ for $l_3 = 390 \text{ \AA}$. Both numbers for $\tilde{f}_{L_3}(q_1)$ are of the order of the microscopic roughnesses $\sigma_{2,s}, \sigma_{3,s}$ and much smaller than $\sigma_{2,g}, \sigma_{3,g}$.

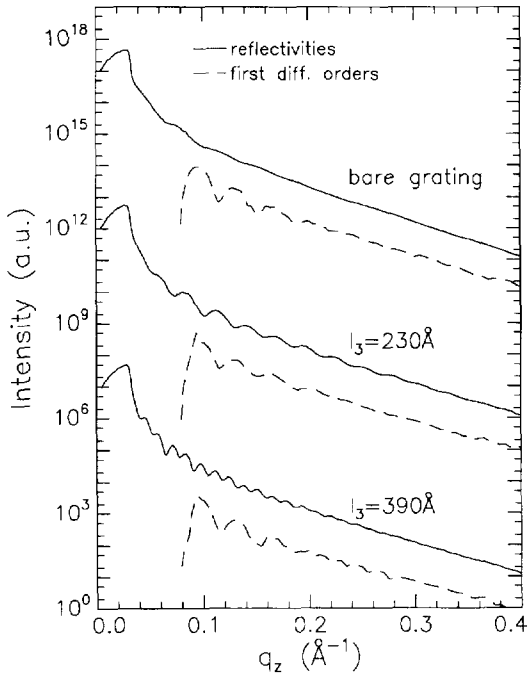


Fig. 5. Measurements of the reflectivities ($m = 0$, solid lines) and the first diffraction orders ($m = 1$, broken lines) for the $M_w = 300k$ PS films with $l_3 = 230 \text{ \AA}$ and $l_3 = 390 \text{ \AA}$. For clarity, the curves for different film thicknesses are shifted four orders of magnitude against each other.

5. Results

5.1. PS films of $M_w = 1000k$

The investigated film thicknesses cover the interesting region: For $l_3 = 179 \text{ \AA}$ and $l_3 = 275 \text{ \AA}$ the fits to the data and the AFM-pictures yield that the film follows the substrate. The dominating Fourier-coefficient $\tilde{f}_{L_3}(q_1)$ nearly fulfills the condition $2\tilde{f}_{L_3}(q_1) \sim h$ which means that $\chi(q_1, l)$ is close to 1 (here 0.86, see Fig. 6). But the shape of the film is not trapezoidal any more. Higher-order Fourier-coefficients are much smaller (see inset of Fig. 6). On the other hand, the analysis of the data of the thickest film ($l_3 = 680 \text{ \AA}$) shows that the surface has become nearly (but not totally!) flat and therefore $\chi(q_1, l) \ll 1$. The inset of Fig. 6 shows the calculated real structure of the systems for the investigated PS films. The damping of the amplitude and the loosing of the higher-order Fourier-coefficients with increasing film thickness can clearly be seen.

Assuming non-retarded van der Waals interactions between the substrate and the molecules of the film yields the following prediction for the response function $\chi(q, l)$ in

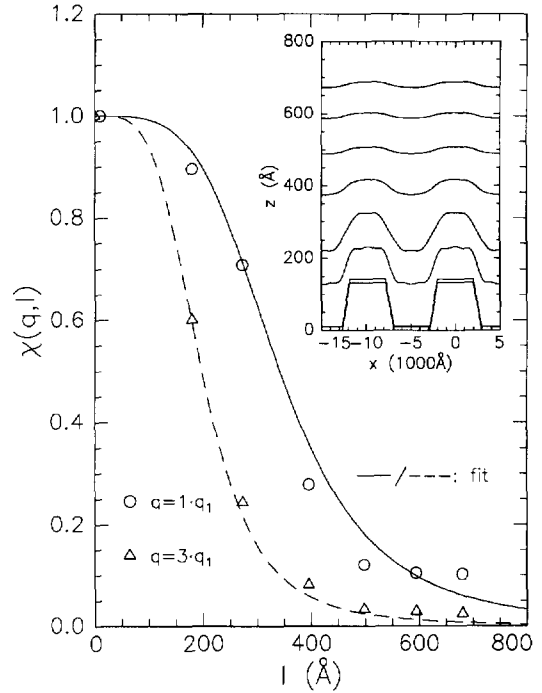


Fig. 6. The function $\chi(q_m, l)$ ($m = 1, 3$) for the $M_w = 1000k$ PS films obtained from the X-ray data (open circles: $q = q_1$, triangles: $q = q_3$). The solid and dashed lines are fits which yield $a = 75 \text{ \AA}$. The inset shows the calculated real structures of the PS films. Note, that even the 680 \AA thick PS film is not totally flat.

Eq. (1) (for details see Andelmann et al. [11, 12]):

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

with the length $a = (A_{\text{eff}}/2\pi\gamma)^{1/2}$ (effective Hamaker constant A_{eff} of the system Si–SiO₂–PS, surface tension γ of PS) and $\tilde{K}(q) \approx 1$ (Deryagin approximation [35], which is valid in our case because $l_3/d \ll 1$). The solid and dashed lines in Fig. 6 are fits of the data for $q = q_1$ and $q = q_3$, respectively [the symbols are obtained via: $\chi(q_m, l) = \tilde{f}_{L_3}(q_m)/\tilde{f}_{S_2}(q_m)$ with $\tilde{f}_{S_2}(q_m) = 8h \sin[q_m(s+b)/2] \sin(q_m b/2)/(q_m^2 b d)$].

The fit yields a number of $a = 75 \text{ \AA}$ whereas a value of only $a \approx 5 \text{ \AA}$ is typical [$A_{\text{eff}} \sim 5 \times 10^{-13} \text{ erg}$ for the system Si–SiO₂–PS, $\gamma \sim (25\text{--}35) \text{ erg/cm}^2$] if only van der Waals interactions are taken into account [32, 36]. The difference between this number and the measured value of $a = 75 \text{ \AA}$ is rather large which leads to suspect that on one hand the principal assumption of pure van der Waals interactions between the PS film and the substrate may not be valid or on the other hand that the linear response theory may break down for our particular system [37].

For our data the discrepancy between the measured value of $a = 75 \text{ \AA}$ and the theoretical predicted $a \approx 5 \text{ \AA}$ can be

explained in the following way which fully bases on the linear response theory but with modified interactions. The free energy per area of a thin polymer film of thickness l , n chains/unit area, and constant volume is [38, 39]:

$$F = \gamma + \gamma_{sl} - \gamma_{so}^d + \frac{A_{\text{eff}}}{12\pi l^2} + \frac{\pi^2}{6} k_b T n \left[\frac{R_0^2}{l^2} - 1 \right]. \quad (5)$$

Ordering the terms of Eq. (5) in another way leads to

$$F = \tilde{\gamma} + \gamma_{sl} - \gamma_{so}^d + \frac{\tilde{A}_{\text{eff}}}{12\pi l^2}.$$

using the definitions $\tilde{\gamma} = \gamma - \pi^2 k_b T n / 6$ and $\tilde{A}_{\text{eff}} = A_{\text{eff}} + 2\pi^3 k_b T n R_0^2$. This equation is similar to the free energy of a liquid with surface tension $\tilde{\gamma}$ and van der Waals-like interactions described by \tilde{A}_{eff} . Therefore we replace in the theory of Joanny et al. [11, 12] simply γ by $\tilde{\gamma}$ and A_{eff} by \tilde{A}_{eff} . This means that the length a now has to be replaced in Eq. (4) by $\tilde{a} = \sqrt{\tilde{A}_{\text{eff}} / 2\pi\tilde{\gamma}}$. With $R_0 = 6.7 \text{ \AA} \sqrt{N}$ (N is the number of monomers), $n = l / (163N) \text{ \AA}^{-3}$, and $T \sim 300k$ we obtain for a thickness of $l \sim 300 \text{ \AA}$ the value $\tilde{a} \approx 100 \text{ \AA}$ which is in rather good agreement with the experimental data of $a = 75 \text{ \AA}$.

5.2. PS films with $M_w = 300k$

The $300k$ PS films behave quite differently. As already mentioned one can conclude from Fig. 5 that even for the thinnest film the surface is flat. This means that the PS films with lower molecular weight seem to behave like a frozen liquid after they are annealed for two hours. A number of $a = 5 \text{ \AA}$ (see above) inserted into Eq. (4) yields $\chi(q_1, l) = 0.02$ and $\tilde{f}_{L_1}(q_1) \approx 3 \text{ \AA}$. This value is close to the result of 4.4 \AA which was obtained from the fit of the X-ray data. Therefore the theory of Andelmann et al. [11] is able to explain the data without modification of the substrate–adsorbate interactions (pure van der Waals interactions).

6. Summary and conclusions

In summary, we have presented a systematic study of the behaviour of polymer films on “rough” surfaces. X-ray scattering experiments were performed and fits of the data yield the Fourier-coefficients of the adsorbed PS films. The basic result is that for polymers with a rather large molecular weight (here $1000k$) the Fourier components of the substrate are damped much slower by the adsorbed films than expected from a theory which bases on pure van der Waals substrate–adsorbate interactions. A simple inclusion of viscoelastic forces into the theory can explain the data satisfactorily within the model.

Films with $M_w = 300k$ are quite different. They seem to behave according to the theory for liquids given by Eq. (4).

This was also confirmed after the X-ray measurements by various AFM-investigations of PS films of lower M_w using gratings with depths up to $h \approx 300 \text{ \AA}$. The pictures reveal that the polymer simply fills up the grooves which means that the Fourier-components of the adsorbed films are damped very quick with increasing film thickness.

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