X-RAY SCATTERING STUDIES OF MOLECULAR ORDERING PHENOMENA IN CONFINED FILMS

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ABSTRACT

A knowledge of the structural behavior of molecules confined in thin liquid films and the way in which they differ from bulk behavior is of great importance to a variety of technological applications. We discuss X-ray scattering studies of the conformation of liquid polymer wetting layers on laterally structured substrates in order to test theories of the conformality of the wetting layer to the substrate. Recent work on guided X-ray beams confined to the thin film opens up the possibility of detailed studies of ordering phenomena in molecular layers adjacent to solid surfaces. Recent experiments are discussed.

In this article, we take "confined geometries" to mean situations where all interfaces present have an effect on determining the structure or morphology of the fluid confined between them, as opposed to purely two-dimensional or surface behavior. Thus, thin films which have thickness comparable to or smaller than a typical interaction or correlation length in the material of the film are candidates for discussing the behavior of fluids in confined geometry, as opposed to much thicker films which reflect simply the sum of the behavior at each of the film interfaces.

Wetting of solid surfaces by liquid films is an example of such confined behavior until bulk liquid behavior is reached at large film thicknesses. A problem of continuing interest is the wetting of laterally structured (e.g., rough or periodically modulated) surfaces and the conformality to the substrate of the wetting layer. This is a problem which can be probed conveniently and accurately by X-ray scattering studies, and a few such studies have been carried out on wetting films on rough substrates by studying off-specular scattering of synchrotron X-rays [1,2]. In the first part of this paper, we discuss the use of periodically structured substrates to study the conformation of liquid polymer wetting layers. Some preliminary results have been presented earlier [3].

According to a theory proposed by Robbins, Andelman, and Joanny [4] the fluctuations of the top of a (liquid) wetting film are correlated with those on a (solid) substrate below via the relation

$$\delta z_2(\vec{q}) = \chi(\vec{q}, \ell)\delta z_1(\vec{q}) \tag{1}$$

where $\delta z_1(\vec{q})$ is the (two-dimensional) Fourier transform of the height fluctuations $\delta z_1(x, y)$ of the substrate and $\delta z_2(\vec{q})$ is the corresponding function for the top surface of the film. ℓ is the film thickness and Eq. (1) is valid in the linearized theory [4]. We may define a length given by

$$a = \left(A_{eff} / 2\pi\gamma\right)^{1/2} \tag{2}$$

where A_{eff} is the effective Hamaker constant for the Van der Waals interaction between the liquid and the substrate and γ is the surface tension between the liquid and the overlying vapor. In terms of a, we can define another length ξ given by

$$\xi = \ell^2 / a \tag{3}$$

In terms of this, the response function $\chi(q, \ell)$ is given by

$$\chi(q, \ell) = \frac{\tilde{K}(q)}{1 + q^2\xi^2} \tag{4}$$

where $\tilde{K}(q)$ is a function which can be taken as $\simeq 1$ in the so-called Deryagin approximation [4], valid when $q\ell \ll 1$.
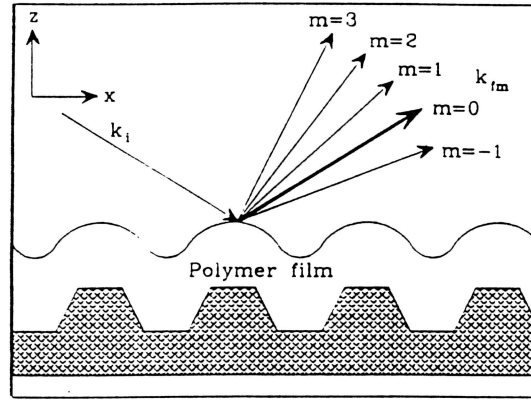
Fig. 1. Laterally structured Si diffraction grating schematic.

For a laterally structured substrate such as the diffraction grating structure indicated in Fig. 1, the relation in Eq. (1) can be tested for a discrete one-dimensional set of q-vectors, given by $q_n = n \cdot 2\pi / d$ ($\vec{q}$ normal to the strips of the diffraction grating) where d is the grating spacing. The present experiments were carried out on nanofabricated silicon gratings of spacing $d \sim 1\mu$ while the polymer films had thicknesses of ~ 100 Å so that the condition $q\ell \ll 1$ was satisfied for the experiments.

Consider a set of interfaces of area A given by $z_n(x)$ (n = 1, 2, 3; n = 1 corresponding to the silicon substrate height, n = 2 to the height of the oxide film on the substrate (assumed to be perfectly conformal with it), and n = 3 to the height of the top surface of the polymer film), where x is the direction normal to the grating strips. In the Born Approximation, the X-ray scattering intensity for wavevector transfer q_x in the plane and q_z normal to the surface is given by [5,6]

$$S(q_x, q_z) = \frac{4\pi^2 A}{q_z^4} \sum_m \sum_{j,k=1}^{3} \Delta\rho_k \Delta\rho_j e^{iq_z(\bar{z}_k - \bar{z}_j)}$$

$$(x)\, e^{-(\sigma_j^2 + \sigma_k^2)q_z^2/2} C_{k,m}^*(q_z) C_{j,m}(q_z) \delta(q_x - m \cdot 2\pi/d) \qquad (5)$$

where (a) we have assumed that open detector slits in the out-of-scattering-plane direction have integrated over all q_y (b) $\bar{z}_n$ is a reference height for interface n (e.g. for n = 1, $\bar{z}_1 = 0$) (c) σ_n is the rms roughness for interface n (d) $\Delta\rho_k$ represents the difference in scattering length density (proportional to electron density difference) across interface k and

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$$C_{k,m}(q_z) = \frac{1}{d}\int_0^d dx\ e^{-iq_z\delta z_k(x)}\ e^{-im\cdot(2\pi/d)x} \tag{6}$$

where $\delta z_k(x)$ is the height of interface k relative to its reference height $\bar{z}_k$. In Eq. (5), we have neglected the diffuse scattering from random roughness fluctuations, so that the scattering exists only on "truncation rods" ($q_x = m\cdot2\pi/d$) as a function of q_z, corresponding to the various orders of diffraction from the grating (m = 0 corresponds to the specular reflectivity).

If the top surface $\delta z_k(x)$ (k = 3) follows the lower two interfaces perfectly (conformal film), then the phase relations between the coefficients $C_{k,m}(q_z)$ will be such that modulations of $S(\vec{q})$

with period $(2\pi/\ell)$ in q_z will exist for all m. (For the specular reflectivity (m = 0), these would give the usual "Kiessig fringes" superimposed on another set of fringes arising from the height of the grating strips themselves [5,6].) As the top film surface loses conformality with the substrate these fringes will "wash out" for the rods corresponding to higher m values.

The measurements were done at the X10B beamline of the NSLS Synchrotron Source at Brookhaven, using a wavelength of 1.131 Å. Data were taken along rods corresponding to the orders m = 0 through m = 4 for the bare grating (Si + oxide overlayer) plus various thicknesses of overlaid polymer films, the diffuse background (corresponding to roughness scattering) being subtracted off by measuring it along q_z-rods slightly displaced from the rod positions $q_x = m\cdot(2\pi/d)$. From these scans, using Eq. (5) and the shape of the diffraction grating strips shown in Fig. 1, the geometrical parameters for the grating, the rms roughness of its surface and the thickness and roughness of the oxide layer and the parameters corresponding to the upper film surface (see below) were determined by least squares fitting. (Note that the Born Approximation expression (Eq. (5)) works only for values of q_z larger than those corresponding to the critical angle for total external reflection.) From these, the lateral periodicity d of the grating was determined to be 9800 Å, the height of the strips to be 132 Å, the width of the grooves and bars to be 4000 Å, the thickness of the oxide layer to be 10 Å and the roughness of the Si/SiO$_2$ and SiO$_2$ surfaces to be 5 Å. These parameters are in semiquantitative agreement with those obtained from AFM studies of the substrate using a commercial Nanoscope III instrument in the contact mode. The polystyrene films were first spun onto a glass substrate to determine the thickness of the films with an ellipsometer. Afterwards, they were floated on a water surface and then picked up on the surface of the grating. Finally they were annealed for 2 hours at 185°C in a vacuum oven during which time it was assumed the liquid polymer film achieved equilibrium with the substrate. The thickness was built up by adding several such polymer films in succession and annealing each time to melt them into one film. For the top surface of the polymer film a Fourier series expansion was used for $\delta z_3(x)$, i.e.

$$\delta z_3(x) = \sum_{p>0} f_p Sin\left(p\frac{2\pi}{d}x\right) \qquad (7)$$

and only the terms $p = 1, 3$ were taken as non-zero. (From AFM studies of the top surfaces of these films, it was qualitatively seen that the surfaces became rapidly sinusoidal for increasing ℓ.)

Substituting Eq. (7) in Eq. (6), and using Eq. (5), the data along all the rods were fitted (after diffuse background subtraction) for each film thickness ℓ, and from the ratios of the f_p to the corresponding Fourier coefficients of $\delta z_1(x)$ for the grating, the values of $\chi(q_p, \ell)$ ($q_p = p.2\pi/d$) determined. Some representative data sets for the rod scans for the thinnest and thickest films and the corresponding films are shown in Figs. 2. It may be seen for the larger
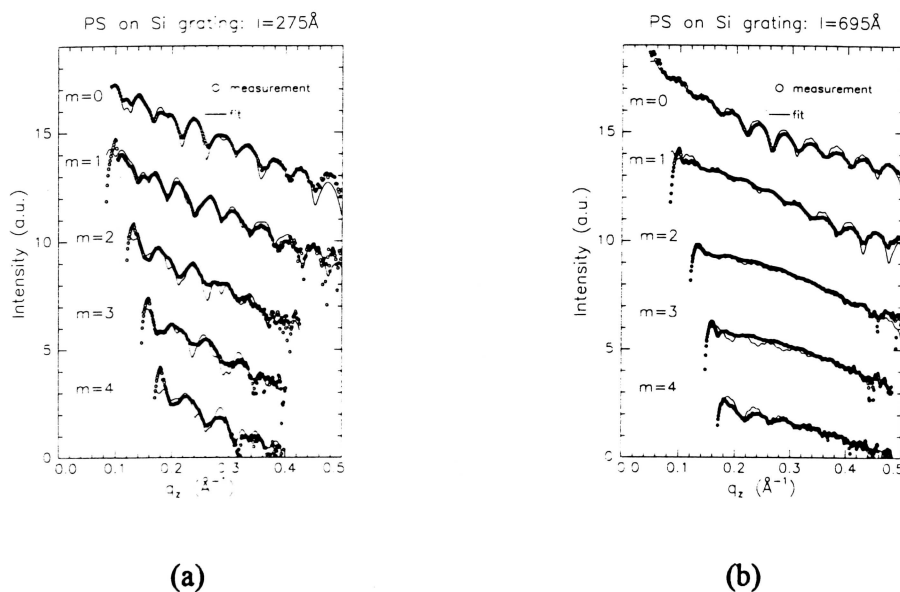

(a)   (b)

Fig. 2. Background-subtracted q_z (rod) scans corresponding to the various diffraction orders (m) for the 275 Å polymer film (a) and the 695 Å polymer film (b). The solid curves are the model fits.

thickness that the modulations in q_z are eliminated for the higher order rods showing a loss of conformal modulation of the top film surface. Fig. 3 shows the quantities $\chi(q_1, \ell)$ and $\chi(q_3, \ell)$ as a function of ℓ along with the theoretical result in the linear Deryagin approximation given by Eq. (4). The solid curve is calculated with the length $a = 5$ Å as expected from Eq. (2) with the known values of A_{eff} and η, and clearly does not explain the data. The expression (4) can, however, be made to fit the data if a is chosen as $a_{eff} = 75$ Å as seen in Fig. 3. The reasons for

this somewhat unrealistic value for the length a are not clear at present. One possible explanation could be that with the (relatively deep rectangular grooves of the grating, the linear theory of Eq. (4) is not valid and must be replaced by a full non-linear calculation, of the type done by Robbins et al. [4]. Another explanation could be that the film equilibrium is determined not purely by surface tension but by viscoelastic forces upon solidification [7]. At any rate the degree of conformality for thick films is quantitatively far greater than the simple theory would predict. In particular, the first harmonic modulation of the top film surface appears to become almost constant in amplitude (or decay very slowly) at large film thicknesses.
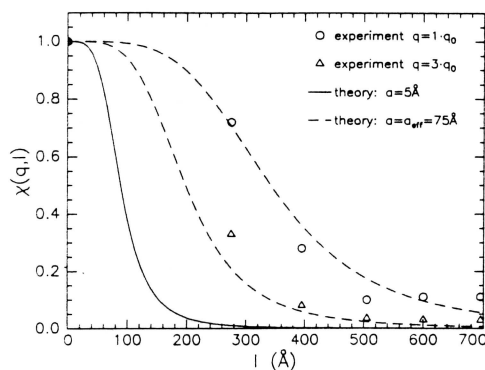

Fig. 3. Comparison of measured $\chi(q,\ell)$ for $q = q_0$ and $q = 3\ q_0$ as a function of ℓ with the theory of Eqs. (2)-(4).

In the second part of this paper, we discuss methods of using X-ray scattering to determine in-plane molecular ordering in confined thin films. Recently, several experimental and computer simulation studies of liquid films of the order of tens of molecular diameters thick and confined between two solid walls have suggested both layering and lateral ordering of the molecules in the film, particularly adjacent to the solid surfaces. Very little direct confirmation of such ordering is available by diffraction techniques, although some X-ray scattering studies of 4000 Å thick liquid crystal films between mica plates have been recently reported by Idziak et al. [8]. The problem one faces in X-ray scattering studies of very thin films between solid surfaces is the problem of getting the X-ray beam in and out of the surrounding solid medium and still being able to distinguish the relatively weak signal of a single or few layers ordering above the diffuse background from the solid. We shall outline here a possible method for doing this by utilizing the film itself as an X-ray wave guide or resonant beam coupler [9,10]. Consider a thin film of lower electron density bounded by media of higher electron density as shown in Fig. 5. Since the refractive index for X-rays (neglecting absorption effects) is given by

$$n = 1 - \left(\frac{e^2}{mc^2}\right)\frac{\lambda^2 \rho}{2\pi} \tag{8}$$

where ρ is the electron density of the medium, the film can sustain modes which correspond to constructively interfering totally reflected beams from each surface, since the film has a higher refractive index than its bounding media. Now consider the case where the overlayer is very thin so that a wave incident on the top surface from air and totally reflected from it has an evanescent component in the overlayer which can tunnel into and excite one of the resonant modes in the underlying film. The situation is analogous to a one-dimensional potential well illustrated in Fig. 4, since for the direction normal to the film (z-direction) the wave equation for the X-rays maps on to the one-dimensional Schrodinger equation for particles of mass m in a potential V given by $\frac{\hbar^2}{2m}(e^2/mc^2)4\pi\rho$. The "particle energy" then stands for $\frac{\hbar^2}{2m}k_z^2$, k_z being the normal component of the incident X-ray wavevector in free space. The film with a dense overlayer then maps on to the square well potential shown in Fig. 4, which has bound states that correspond to
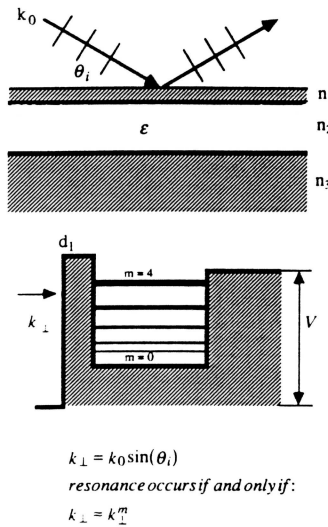

$$k_\perp = k_0 \sin(\theta_i)$$
resonance occurs if and only if:
$$k_\perp = k_\perp^m$$

Fig. 4. Illustration of resonant tunnelling of X-rays into a thin film of refractive index (n_2) greater than those of its substrate (n_3) and overlayer (n_1).

the guided modes of the film. If the incident k_z is such that it matches one of these resonances, a wave of very large amplitude can be built up in the film. Physically this means that a plane wave of width W incident on the top overlayer can couple most of its energy into the film of thickness ℓ, achieving a flux enhancement of ~ (W/ℓ) before this energy is either absorbed in the film or leaks out through the overlayer (or it can stay trapped in the film by having the overlayer become thick in the region beyond the incident beam footprint). This is the basis for optical beam thin film coupling devices developed in the 1970's [11]. The theory of this coupling and flux compression was worked out by R. De Wames and the present author around that time [12]. It should be noted that similar resonance effects in thin films were also discussed independently by Croce and Pardo [13] for both X-rays and neutrons in terms of a Fabry-Perot interferometer. Guided X-ray waves in thin films were independently demonstrated by Spiller and Segmuller in the 1970's [14]. However, it is with the advent of highly brilliant synchrotron sources and coherent beams from these that one has the hope of realizing the potentially large flux compressions with such a device (since W above cannot be larger than a coherence width of the incident beam which is also assumed to be highly collimated and monochromatic). Such flux enhancement with resonant beam couplers have been demonstrated by Feng et al. [9,15] at the NSLS and ESRF synchrotron sources. Wang et al. have also demonstrated a similar "quasi-resonant" enhancement of the flux in a thin film <u>without</u> an overlayer [16]. Fig. 5 shows the device used which utilized a Si substrate, a polyimide film (thickness ~ 1200 Å), and a SiO_2 overlayer. Fig. 6 shows dips in the reflectivity from the overlayer below the critical angle (i.e., in the totally reflected region) corresponding to the various resonant guided modes in the film, and Fig. 7 shows the angular distribution of intensity emerging from the decoupling region corresponding to the various guided modes excited when the incident beam is set for exciting a single resonance, this being due to mode mixing effects [17]. Finally, Fig. 8 shows the far field diffraction pattern from a guided beam emerging from a truncated waveguide (i.e., exiting form the edge of the film itself instead of from a decoupling thin overlayer) together with the calculated pattern based on the field distribution for the particular modes excited [15]. With such a device to enhance the flux inside a thin film and minimize scattering from the bounding solid media (in which the field is evanescent away from the film) it should be possible to study molecular ordering conveniently and elegantly in thin confined liquid films. Such experiments are planned for the near future. In closing, we should also point out that the technique can also be used with neutrons, although the flux gain in the film is much lower due to the lower brilliance and coherence of neutron sources. Guided neutron wave propagation and resonance effects have recently been demonstrated by several groups [18-22] and remain to be explored more fully for studying confined films.
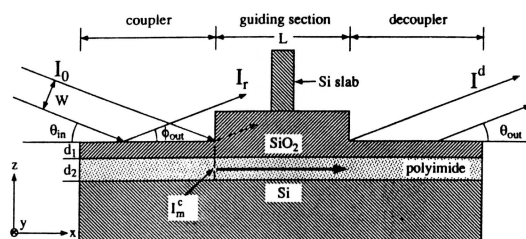
Fig. 5. Illustration of waveguide device showing the Si substrate, thin polymer film and the thin SiO$_2$ overlayer (with the thick overlayer in the guided region in the middle).
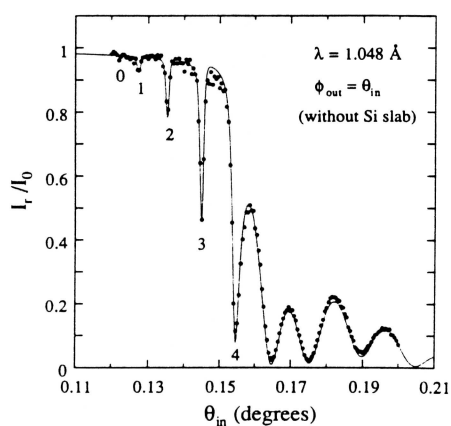

Fig. 6. The reflectivity of the Resonant Beam Coupler from the coupling region. The five dips for $\theta_{inc} < 0.16°$ signify the five TE modes. The solid line represents a fit using the standard EM theory for multilayers (from Ref. [9]).
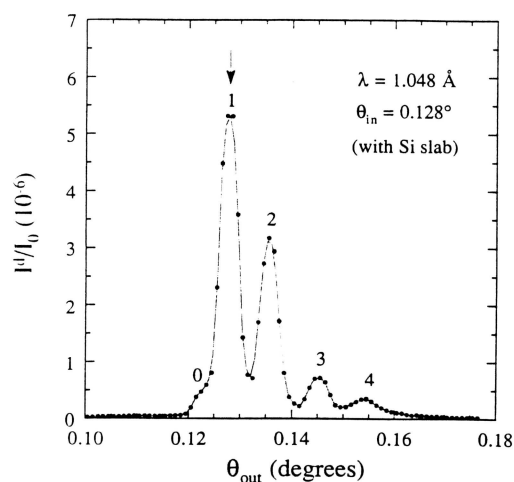
Fig. 7. The X-ray intensity exiting the decoupler with $\theta_{inc} = 0.128°$ to excite the TE1 mode only. The four peaks and the shoulder correspond to all 5 guided TE modes excited in the guide due to mode mixing. The small magnitude of I_d is primarily due to absorption in the guide (from Ref. [9]).
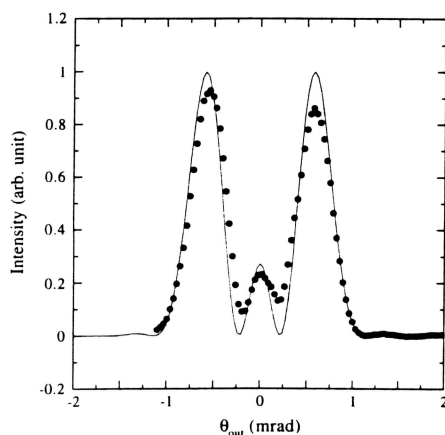

Fig. 8. Far-field intensity as a function of angle θ_{one} out of the plane of the waveguide for a guided X-ray beam exiting the truncated end of a 600 Å thin-film polymer waveguide with Si substrate and SiO_2 overlayer. The calculated curve is obtained from the Fourier transform of the electric field distribution in the guide in an excited symmetric TE mode (from Ref. [15]).

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