Evidence of Self-Affine Rough Interfaces in a Langmuir-Blodgett Film from X-Ray Reflectometry

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A Langmuir-Blodgett multilayer film of tricosenoic acid with a cadmium-substituted headgroup has been studied by x-ray reflectometry. The *diffuse or off-specular scattering* close to the positions of the 20 observed Bragg peaks in the reflectivity profile has been studied. Its line shape has been found to be Lorentzian and the half-widths of the peaks vary according to the *square* of the longitunal wave vector q_z. This suggests that the film is characterized by self-affine rough interfaces, with no cutoff length, corresponding to a roughness texture $h = 0.5$.

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An important feature of surfaces is that they are rarely flat. In the past ten years, a large amount of work has been devoted to the study of surfaces by techniques such as electron microscopy, atomic force microscopy, and x-ray scattering (particularly reflectometry). The reflectivity profile for a homogeneous sample with a perfectly smooth surface is characterized by a *longitudinal* ridge of intensity, the specular reflection, which decays according to the Fresnel law as $1/q_z^4$ and which has a *transverse* width which is resolution limited. This scattering contains information on the variation of refractive index normal to the surface of the specimen (we will assume in the following that the subscripts x and y relate to quantities in the plane of the surface and z perpendicular to the surface of the sample). However, any departure from a smooth surface leads to the appearance of some diffuse, off-specular scattering transverse to the specular ridge. This is the signature of the roughening and it also causes the decay of intensity along the ridge to depart from Fresnel's law. The theoretical and experimental work of Sinha *et al.* [1] and of Andrews and Cowley [2] in the field of x-ray scattering has shown how information on the structure within a surface or at interfaces can be obtained by the analysis of *transverse scans* through the specular reflectivity. For a rough surface in which the roughness is saturating at a fixed value $\sigma = \sqrt{\langle z(x,y)^2\rangle}$, a lateral correlation length ξ (called a cutoff length in [1]) characterizes the height-height correlation function in the surface. The quantity which governs the scattering cross section for an isotropically rough surface [1] is the average value of the square of the difference between the heights of two arbitrary points within the surface. Specifically, this quantity is

$$g(X,Y) = \langle [z(x',y') - z(x,y)]^2 \rangle ,$$

where $X = x' - x$ and $Y = y' - y$.

If there is no cutoff length ξ, then the reflectivity curve does not display any true specular reflectivity but only diffuse, nonspecular scattering. In the isotropic case, the function $g(X,Y)$ does not depend on X and Y separately and diverges as

$$g(X,Y) = AR^{2h},$$

with $R = \sqrt{X^2 + Y^2}$ and h is an exponent which determines the texture of the surface. The scattering cross section at small angles is then given by [1,2]

$$S(\mathbf{q}) = \frac{2\pi}{q_z^2} \int_0^\infty dR\, e^{-(A/2)q_z^2 R^{2h}} J_0(q_r R),$$

where $q_r = \sqrt{q_x^2 + q_y^2}$ and $J_0(u)$ denotes the Bessel function of order zero. When there is no cutoff length ξ, the transverse reflectivity profile does not display any true specular component but only diffuse scattering, as there are no delta functions in the transverse wave vectors q_x and q_y. However, for longitudinal q_z scans the shape of $S(q)$ is unaffected by the value of ξ. It is also possible to show that the cross section in this case is the Fourier transform of an effective [3] correlation function

$$C(R) = e^{-(A/2)R^{2h}q_z^2}.$$

The experimental study of rough surfaces has been well developed for the case of the so-called roughening transition in metals [4,5] and for liquid surfaces [6–8] in which there is a thermal population of propagating capillary waves. However, much less has been done, so far, on the experimental investigation of isotropically rough surfaces. The use of multilayer samples can be particularly helpful in the study of the roughness texture of surfaces and interfaces [9,10], because the specular reflectivity profile exhibits intense Bragg peaks located every $q_z = 2\pi/\Lambda$, where Λ is the periodicity of the layers. It is not unusual to find that the interface roughness in such systems presents a degree of conformality, i.e., the fluctuations of one interface are correlated to some degree with the neighboring interfaces. Recently, Yan and Egami [11] have shown that if the roughness in a multilayer is perfectly correlated among the interfaces (conformal roughness), then the scattering cross section follows the same functional form as the one given above, only at the location of the Bragg peaks. Our aim in this Letter is to show that rough interfaces with a high degree of conformity can be encountered in Langmuir-Blodgett (LB) films.

The experiments were performed on a Langmuir-Blodgett film consisting of eight bilayers of cadmium-substituted tricosenoic acid ($C_{22}H_{45}COOH$). The sample was deposited in the *Y* configuration from a water subphase onto a 2 in. diameter silicon wafer, using an alternate layer LB trough under computer control. A deposition speed of 1 cm/min and a surface pressure of 25 $mN\,m^{-1}$ were adopted. In this substituted sample, the two hydrogen atoms belonging to adjacent carboxylic heads (COOH) are replaced by a doubly charged Cd^{2+} ion. The resultant cross linking confers some rigidity to the film, and the *presence* of these Cd ions is more significant for an x-ray scattering experiment, owing to the high contrast of electron density between the head and the tail of the molecule. The x-ray experiments were performed with a horizontal Huber diffractometer mounted on a Philips PW 1130 x-ray generator equipped with a Cu $K\alpha$ target running at 40 kV and 30 mA. The incident beam was tightly collimated by slits, to 100 μm in the horizontal plane but relaxed in the vertical direction with a slit aperture of 4 mm. The reflected beam was analyzed with a PG002 monochromator, in front of which was located a set of two slits collimated to 200 μm in the horizontal plane. The resolution of the instrument in the transverse direction was found to be consistent with the HWHM (half width at half maximum) of the direct beam, and was measured prior to the experiment on a perfectly smooth silicon wafer from the same batch as used for the sample.

Figure 1 shows the specular reflectivity profile measured directly along the ridge of intensity (see Gibaud, Vignaud, and Sinha [12] for details of the different ways of measuring the reflectivity profile and for details of the instrumental resolution). More than 20 Bragg peaks, located at multiples of $q_z = 2\pi/\Lambda = 0.1$ Å^{-1}, can clearly be seen in the profile out to a maximum value of $q_z = 2$ Å^{-1}. These show unambiguously that the bilayer periodicity of the LB film is 62.8 Å, in agreement with (twice) the estimated molecular length, and this confirms that the multilayer structure has the *Y* configuration of LB films, as shown in the inset of Fig. 1. However, a preliminary analysis of the Bragg peak *intensities* does not rule out a small admixture of the *X* configurations (see Fig. 1). Since our aim is to make a timely presentation in this Letter of our evidence that an LB film can provide an example of conformal roughness, we will report a fuller analysis of the specular and nonspecular reflectivity data at a later date [13].

Figure 2 shows a three dimensional graph of a selected part of the specular and off-specular reflectivity covering the region of the third and fourth Bragg peaks over q ranges of $0.25 < q_z < 0.45$ Å^{-1} and $-0.003 < q_x < 0.003$ Å^{-1}, respectively. This figure shows clearly how the off-specular intensity is developed transversely to the longitudinal ridge and that it is intense only at the Bragg peak positions and is absent between them. This observation is in agreement with the findings of Yan and Egami [11]. Careful analysis of these transverse features

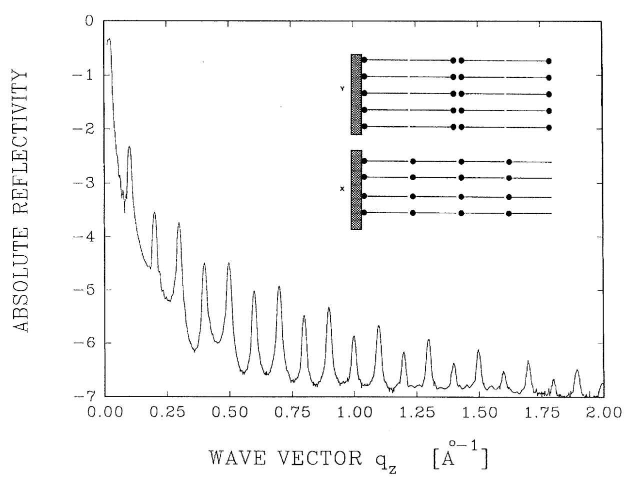

FIG. 1. The reflectivity curve of the LB film measured directly along the longitudinal ridge is shown on a logarithmic scale as a function of the wave vector q_z. The regularly spaced Bragg peaks arising from the multilayer structure can be seen up to a value $q_z = 2$ Å^{-1}. The *X* and *Y* multilayer configurations of an LB film are shown in the inset.

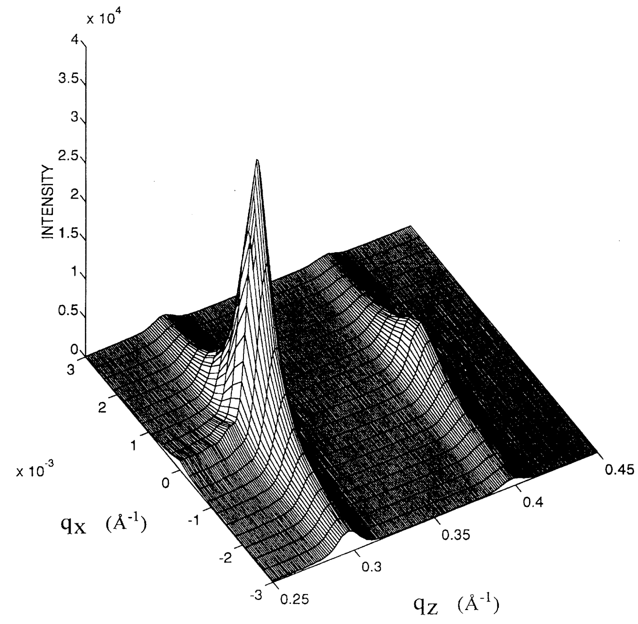

FIG. 2. A three dimensional representation of a selected part of the reflectivity profile is shown. It covers the region of the third and fourth Bragg peaks positions over q ranges of $0.25 < q_z < 0.45$ Å^{-1} and $-0.003 < q_x < 0.003$ Å^{-1}, respectively. The intensity scale is linear and it is clear that the transverse, nonspecular reflectivity is located exclusively about the Bragg peak positions.

shows that their profile is Lorentzian, except below $q_z \approx 0.3$ Å^{-1} where a weak narrow resolution-limited Bragg peak is superimposed on a broad Lorentzian. The width of these Lorentzian peaks, which can be fitted with a high degree of confidence, depends strongly on the value of the longitudinal wave vector q_z as shown in Fig. 3.

We will show below that this dependence is consistent with the reflection from a self-affine surface for which the exponent h has the value $h = 0.5$. In such a case, the scattering cross section at the Bragg peak positions has the following analytical form [1]:

$$S(\mathbf{q}) = \frac{A\pi F^2(\mathbf{q})}{[q_r^2 + (A/2)^2 q_z^4]^{3/2}},$$

in which $F(\mathbf{q})$ is the structure factor of the Bragg peak. The measured intensity is the convolution of this scattering cross section with the resolution of the instrument. The convolution with the vertical dependence of the resolution function plays a key role in determining the real line shape of the measured intensity. In the present experimental arrangement the vertical resolution is completely relaxed while the horizontal resolution is extremely good, as described above. The resolution in q space can then be described to a good approximation by

$$R(\mathbf{q}) = \delta(q_x)\delta(q_z)r(q_y),$$

where δ stands for the Dirac distribution and $r(q_y)$ for the vertical resolution. Of course, the actual resolution functions in the x and z directions are not δ functions but are close enough if the measured intensity is broad. As a result the measured intensity is

$$I(\mathbf{q}) = S(\mathbf{q}) * r(q_y),$$

and since the resolution is completely relaxed in the vertical direction this means

$$I(\mathbf{q}) = \int_{-\infty}^{\infty} S(\mathbf{q})\, dq_y .$$

Similar proposals have already been made by Tidswell *et al.* [14] to describe the vertical resolution. These authors have suggested, more generally, that the measured intensity is the product of the result of the integration over q_y by the resolution in the incident plane. In the present case, the functional form of the intensity distribution for the transverse scan becomes

$$I(q_x, q_z) = \frac{2A\pi F^2(\mathbf{q})}{q_x^2 + (A/2)^2 q_z^4},$$

which is typically Lorentzian and for which the HWHM Δq_x will be given by

$$\Delta q_x = \frac{A}{2} q_z^2 .$$

Figure 4 gives a graph of the square root of the HWHM of the transverse scattering measured at the positions of the Bragg peaks, as a function of the longitudinal wave vector q_z and shows clearly the linear dependence expected on the basis of the discussion presented above. This leads to the value $A = 0.016 \pm 0.001$ Å showing that the fluctuations of the height within the interfaces are not very large relative to the scale of the multilayer structure. In addition, the measured and calculated HWHM's of the longitudinal resolution function are plotted, which shows that the approximation of this function by a δ function is acceptable. It is important to note that even when a surface is completely rough there is still no attenuation factor (such as a Debye-Waller factor) in the expression for the measured intensity. This means that Bragg peaks can be observed up to high values of the longitudinal scattering vector $q_z \approx 2$ Å^{-1} and that this observation is the signature that the rough layers exhibit a very high degree of conformation.

In conclusion, we have shown in this Letter that a Langmuir-Blodgett film can provide a beautiful example

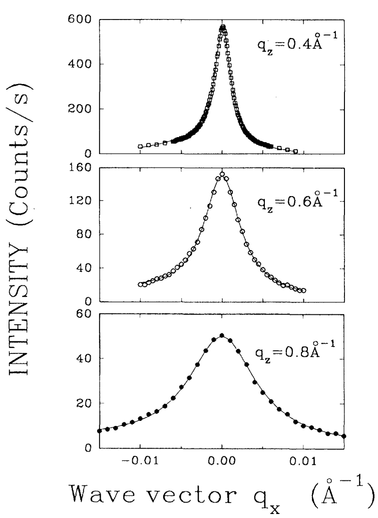

FIG. 3. Transverse scans through the Bragg peaks of the reflectivity profile are given showing their Lorentzian line shape (fitted by the full lines) and the increase of their HWHM for increased values of wave vector q_z.

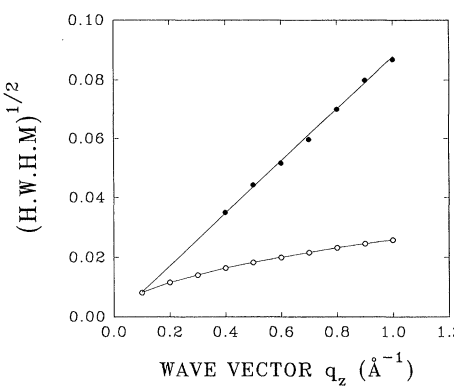

FIG. 4. The square root of the HWHM in Å$^{-1/2}$ (full circles) of the Lorentzian peaks obtained from fittings is plotted to illustrate the linear dependence with q_z. The variation of the measured (open circles) and calculated (full line) resolution function in the q_z direction is also given on the same graph.

of a system which exhibits rough interfaces with no cutoff length (at least on the scale of the coherence length of the x-ray beam, i.e., a few microns on the surface). We have observed that the off-specular reflectivity has a Lorentzian line shape and that the HWHM of these peaks varies according to the square of the longitudinal wave vector q_z. We have demonstrated, for the first time, by taking into account the resolution of the x-ray diffractometer, that such a variation is consistent with a model based on self-affine interfaces having an exponent h describing the roughness texture of $h = \frac{1}{2}$. It is very important to notice that any deviation of $h = 0.5$ will change the line shape of the transverse scans and that the evolution of the width together with the observation of the Lorentzian line shape are the signature of the model validity.

More generally, these results suggest that the growth process of this LB film must have been stochastic. Indeed the fact that h is strictly equal to 0.5 implies that the growth has a random walk nature. As discussed in the introduction, the scaling behavior for a self-affine surface is

$$g(R) = AR^{2h}$$

for $R \ll L$, where L is the lateral dimension of the film. All the models we have used to describe the value of h so far lead to $h = 0.5$ for the dimensionality $d = 2$ (for a detailed review, see [15]). The exponents which have been reported are the following: $h = (3 - d)/2$ for surface diffusion [15]; $h = 0.5$ for the Eden model [16]; and $h = 2/(d + 2)$ for the solid-on-solid model of Kim and Kosterlitz [17].

In addition, Kertesz and Wolf [18] have also conjectured that $h = 1/d$ on the basis of numerical evidence alone. These authors have computed the evolution of a multilayer structure under the assumptions of the Eden model (which is a stochastic model) which involves a random growth process of nonfractal clusters. Their calculations lead to a constructed object which presents a rough surface with a high degree of conformation, as is the case in our LB film.

Finally, it is important to notice that our results call for further stimulating experiments to test the influence of the surface pressure on the growth of LB films. This parameter can indeed play a key role during the growth, since, as recently reported, crumpled or collapsed conformations can be observed if the surface pressure is too large [19]. We have not yet been able to identify those physical characteristics of the LB film which are responsible for our current results, except through the general result above [19]. Our study is therefore presented, first, as a novel observation of a multilayer sample which shows self-affine roughness, and, second, to encourage the study of LB films as potential model systems in the area of surface roughening transitions.

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