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WHAT CAN WE LEARN FROM OFF-SPECULAR NEUTRON REFLECTION?

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ABSTRACT

Specular reflection of neutrons or x rays has been developed recently as a tool to probe density variations in the neighborhood of flat interfaces. The techniques have been applied to a variety of materials problems ranging from polymer adsorption to hydrogenation of carbon films and the structure of magnetic multilayers. In addition to the specular scattering, diffuse scattering is often observed, sometimes in strikingly beautiful patterns. This scattering is caused by imperfections such as interfacial roughness or density fluctuations within a layer. As a general rule, the diffuse, off-specular scattering measures the density-density correlation function within and between the interfaces responsible for the specular scattering. Interpretation of diffuse x-ray and neutron scattering from surfaces and interfaces is in its infancy using theoretical schemes that are still being developed. In this talk I will show examples of diffuse scattering patterns and offer some guidelines for their interpretation.

INTRODUCTION

Let us consider the simple reflectometry experiment depicted in Figure 1. Incident neutrons of wavevector $\mathbf{k}_1$ are specularly reflected to wavevector $\mathbf{k}_2$. In this case, the grazing angle of incidence, θ_1, is equal to the grazing angle of reflection, θ_2. Provided $k_1 \sin \theta_1$ is large enough (i.e. greater than the critical wavevector for the reflecting material), some of the beam is transmitted with wavevector $\mathbf{k}^t_1$. Because the surface is rough, however, there is diffuse (i.e. off-specular) scattering both above and below the horizon (i.e. for $\theta_2 > 0$ and $\theta_2 < 0$) in addition to the specularly reflected and transmitted beams.

THE DISTORTED-WAVE BORN APPROXIMATION

The traditional way of calculating the scattering of neutrons in diffraction experiments is to use the Born approximation in conjunction with the Fermi pseudopotential, parametrised by the atomic scattering length. In this approximation, one imagines a plane wave incident on a weak scatterer and uses simple perturbation theory — Fermi's golden rule — to calculate the scattered intensity. The method gives very accurate answers when it is applied to neutron diffraction or small angle scattering, but we might imagine that it would not work well for reflection geometry, especially close to the critical wavevector. In the latter case, most of the incident beam is specularly reflected and only a small fraction transmitted — in contrast to situations in which the Born approximation is adequate, where *most* of the neutrons are not deviated by the scattering potential.

A better way of doing perturbation theory for a reflecting surface is to use as a basis the wavefunctions for a perfectly smooth surface, under the assumption that surface roughness will only cause small corrections to specular scattering. The wave functions in question are the incident and specularly reflected plane waves above the reflecting surface (for $z > 0$) and the transmitted plane wave below the surface. To calculate the diffuse scattering due to surface roughness, we do a perturbation calculation using these wavefunctions and a scattering potential that corresponds to the difference between a sample with an ideal flat surface and one with a rough surface. The extent of this scattering potential is indicated by the shaded region in Figure 1. The scattering potential in

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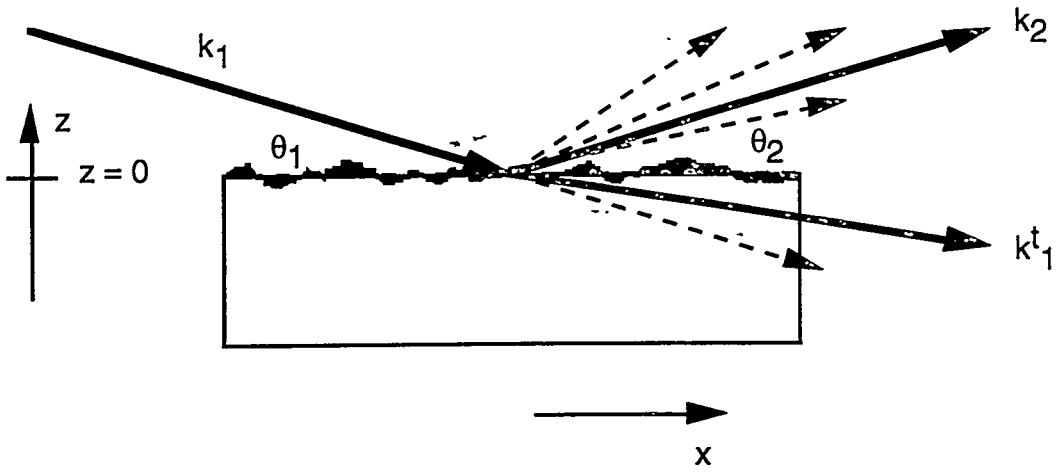

Figure 1: A neutron reflection experiment with a rough sample. The bold arrows represent the incident, specularly reflected and transmitted neutrons. The dashed arrows show diffuse scattering from the rough surface. The region between the rough surface and an average, smooth surface (referred to as the ideal surface) is shaded.

question is just $(h^2 N b) / (2 \pi m)$, where Nb is the scattering length density of the medium, h is Plank's constant and m the neutron mass. Scattering by this potential is added when the rough surface is above the smooth one and subtracted when it is below.

A fairly straightforward calculation based on this so-called Distorted Wave Born Approximation (DWBA) [1,2] yields an expression for the diffuse scattering cross section that can be written as:

$$\left(\frac{d\sigma}{d\Omega}\right)_{diffuse} = N^2 b^2 L_x L_y |T_i(k_1)|^2 |T_i(k_2)|^2 S(q_x,q_y,q_z^t) \qquad (1)$$

where $T_i(k_1)$ and $T_i(k_2)$ are the usual Fresnel transmission functions and

$$S(q_x,q_y,q_z^t) = \frac{1}{|q_z^t|^2} e^{-(q_{1z}^{t\,2} + q_{2z}^{t\,*2})\sigma^2/2} \int dx\, dy\, e^{i(q_x x + q_y y)} \left(e^{|q_z^t|^2 C(x,y)} - 1\right) \qquad (2)$$

$$q_z^t = k_{1z}^t - k_{2z}^t \qquad (3)$$

$$k_{1z}^t = \left(k_{1z}^2 - k_c^2\right)^{1/2} = \left(k_{1z}^2 - 4\pi Nb\right)^{1/2} \qquad (4)$$

$$C(x,y) = \langle z(x,y)\, z(0,0) \rangle \qquad (5)$$

C(x,y) in eqn (5) is just the height-height correlation function for the surface, whose roughness is assumed to be Gaussian with a standard deviation σ. Thus, the qualitative conclusion of the DWBA calculation is that the diffuse scattering provides a measure of C(x,y), the height-height correlation function within the rough surface.

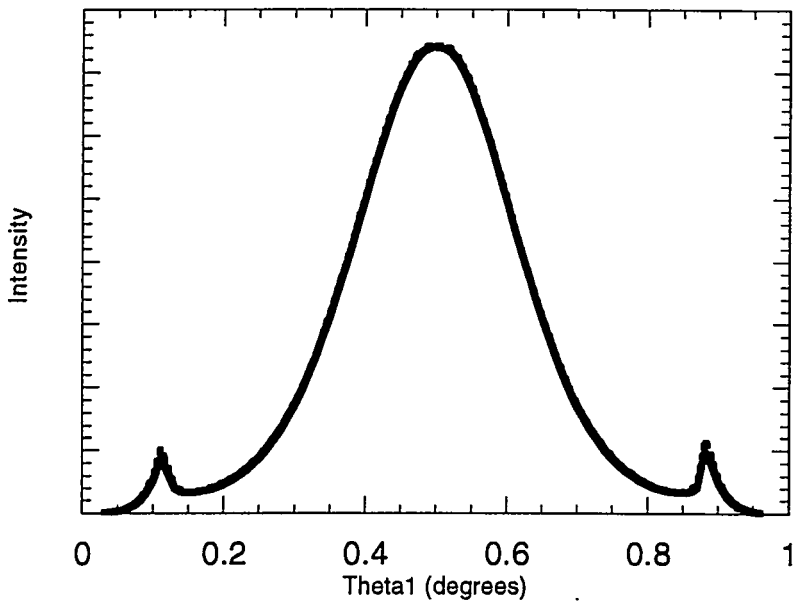

Figure 2a: Diffuse scattering for a rough sapphire surface with $\sigma = 50$ Å at a scattering angle $(\theta_1 + \theta_2)$ of 1°. The solid and dashed lines, which are essentially indistinguishable, are obtained when the transmission functions in eqn (1) are for smooth and rough surfaces respectively. The model for C(x,y) used is that for a self-affine surface proposed by Sinha et al [1] with h = 0.4 and $\xi = 3000$ Å. Specular reflection would appear as a delta function at $\theta_1 = 0.5°$.

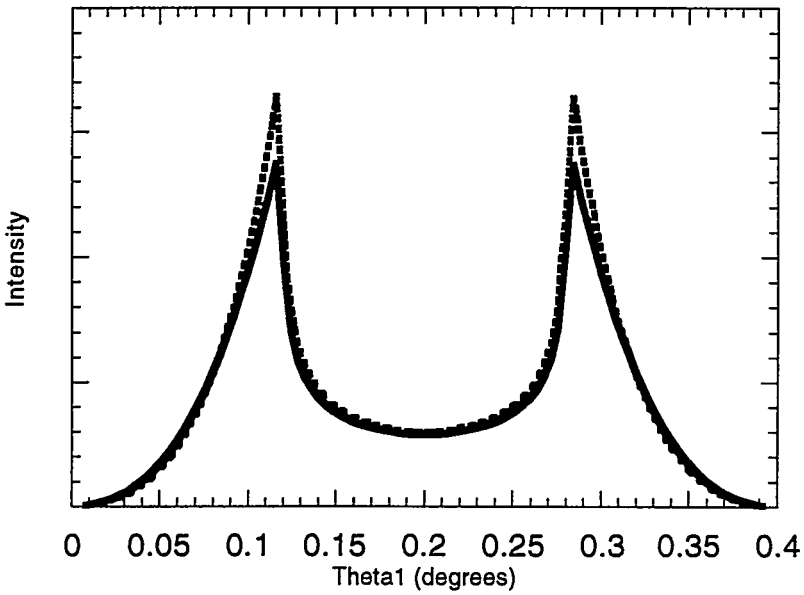

Figure 2b: Same as Figure 2a except that the scattering angle is 0.4°. In this Figure the difference between results obtained with transmission functions for rough (dashed line) and smooth surfaces (solid line) is much clearer.

Of course, we would have reached a similar conclusion from a calculation within the Born approximation. The most striking qualitative effect of using the distorted wave Born approximation is the appearance of the Fresnel transmission functions, $T_i(k)$, in eqn (1). These functions — which rise from a value of zero at k = 0, to a peak value of 2 at the critical wavevector, and then decrease to an asymptotic value of unity at large values of k — impose significant structure on the diffuse scattering, as shown in Figure 2. The sharp peaks in Figures 2a and 2b result from the singularity in the Fresnel functions at the critical wavevector for the reflecting medium. The peaks are often referred to as Yoneda scattering or angels' wings.

Although one can think of a variety of different expressions to describe the height-height correlation function, C(x,y), of a rough surface, all of them have the property of falling off with distance (x or y) in the reflecting plane in a fairly monotonic fashion. This means that the structure factor, $S(\mathbf{q})$, is a bell-shaped curve in both q_x and q_y. In most reflectometry experiments, an integral of the diffuse scattering over q_y (the coordinate into the plane of the paper in Figure 1) is performed automatically by the detector system and one only records the variation of the scattering as a function of q_x and q_z.

LIMITATIONS OF THE DWBA

Although the DWBA gives a reasonable qualitative description of diffuse neutron reflection from a rough surface, it is clear that if we are to extract meaningful results for the height-height correlations from experimental data we need to be sure that eqn (1) is accurate. Unfortunately, we are not as sure as we would like to be. Depending on the version of the DWBA that is used [2,3,4], the Fresnel transmission functions in eqn (1) may be evaluated either for a smooth (ideal) surface or for the rough (perturbed) surface. As the dashed curves in Figure 2b shows, these two approaches can give significantly different results even when the same form for $S(\mathbf{q})$ is used. Detlef Bahr [4] has fitted several of the suggested forms of the cross section to x-ray data obtained by Weber and Lengeler [3] and has reached the conclusion that transmission functions evaluated for a smooth surface give the best result. However, it is still somewhat disquieting that extraction of quantitative values of $S(\mathbf{q})$ from diffuse scattering data has such an uncertain theoretical basis.

There are several situations in which one might expect the DWBA to give incorrect results. Since the calculation is based on second order perturbation theory, it will be inadequate when the perturbative term becomes so large that the third order term needs to be considered. De Boer [5] has considered this situation and finds that the DWBA will break down when

$$\frac{\xi k_{1z}^2}{|\mathbf{k}_1|} >> 1 \qquad (6)$$

where ξ is the characteristic distance over which C(x,y) decays in the x-y plane. Since θ_1 is typically abut 1°, eqn (6) implies that the DWBA will break down when ξ is much greater than about 500 times the neutron wavelength used for an experiment. This means that the x or y dimension of a "typical" rough feature will have to be a micron or more for the DWBA to break down because second-order perturbation theory becomes inadequate. Of course, there may well be rough features that are smaller, but such a large value of ξ can only be obtained if large features are present over the entire surface. Figure 3 illustrates what we have in mind. Even though the surface is rough on the Ångstrøm scale, height correlations exist over micron distances because the surface seems to be composed of a series of rough facets whose smooth counterparts are the dashed lines in Figure 3.

Figure 3: Sketch of a rough faceted surface. In addition to the high-frequency roughness, much larger facets, represented by the dashed lines, are also visible. The DWBA may fail for such surfaces.

If the facets sketched in figure 3 are large enough they can reflect specularly and produce a fringe in the diffuse scattering whose locus is defined by $q_z = q_c = 2\ k_{zc}$ where k_{zc} is the critical incident (or scattered) wavevector for the reflecting material [6]. In this case, the DWBA applied to a rough "average" surface will not describe the pattern that is observed.

In addition to the inherent limitation of the DWBA as a perturbation theory, the method also involves approximations that limit the roughness of a surface to which it can be applied [2]. In practice, this limitation implies that the standard deviation of the roughness, σ, should be less than about $1/(10\sqrt{Nb})$, where Nb is the scattering length density of the reflecting medium. For most materials, this means that σ must be less than about 50 Å for the DWBA to work.

DISPLAYING DIFFUSE SCATTERING DATA

A straightforward way to measure neutron reflectivity, including the diffuse scattering, is to use the time-of-flight method with a linear position-sensitive detector. This method keeps the sample geometry constant and accumulates data for the entire reflection curve at the same time — low-q_z reflectivity is measured with long wavelength neutrons while high-q_z reflectivity is measured with short wavelengths. Because the decrease of reflectivity at high values of q_z is compensated to some extent by the increase of incident neutron intensity at short wavelengths, the entire reflectivity curve is measured with comparable statistical accuracy. The natural way to present the data from such TOF reflectometers is as a plot spanned by the scattering angle θ_2 and the neutron wavelength, λ. Such a plot is shown in Figure 4a. Many of my colleagues oppose the use of (λ,θ_2) plots, pointing out, quite correctly, that information about $S(\mathbf{q})$ is more naturally displayed in the (q_x,q_z) coordinate system. However, this argument ignores the fact that in eqn (1) the Fresnel transmission functions depend either on k_{1z} or k_{2z} and that structure related to these functions appears as straight fringes in a (λ,θ_2) plot (because $k_{2z} = 2\ \pi \sin\theta_2 / \lambda \approx 2\pi\theta_2/\lambda$). Of course, (λ,θ_2) plots are easily transformed to (q_x,q_z) plots, as Figure 4b shows, but the two types of plot often highlight different physics.

DIFFUSE SCATTERING FROM FILMS AND MULTILAYERS

It is straightforward to extend the DWBA calculation outlined above to describe the diffuse scattering from one or more layers of material deposited on a substrate. Holy et al [7] were the first to publish a detailed calculation of diffuse scattering by a multilayer system with an arbitrary number of layers, although both Sinha and the author [8] had derived and used similar expressions several years earlier. These calculations show two new qualitative effects that are not present in diffuse scattering patterns obtained with single surface.

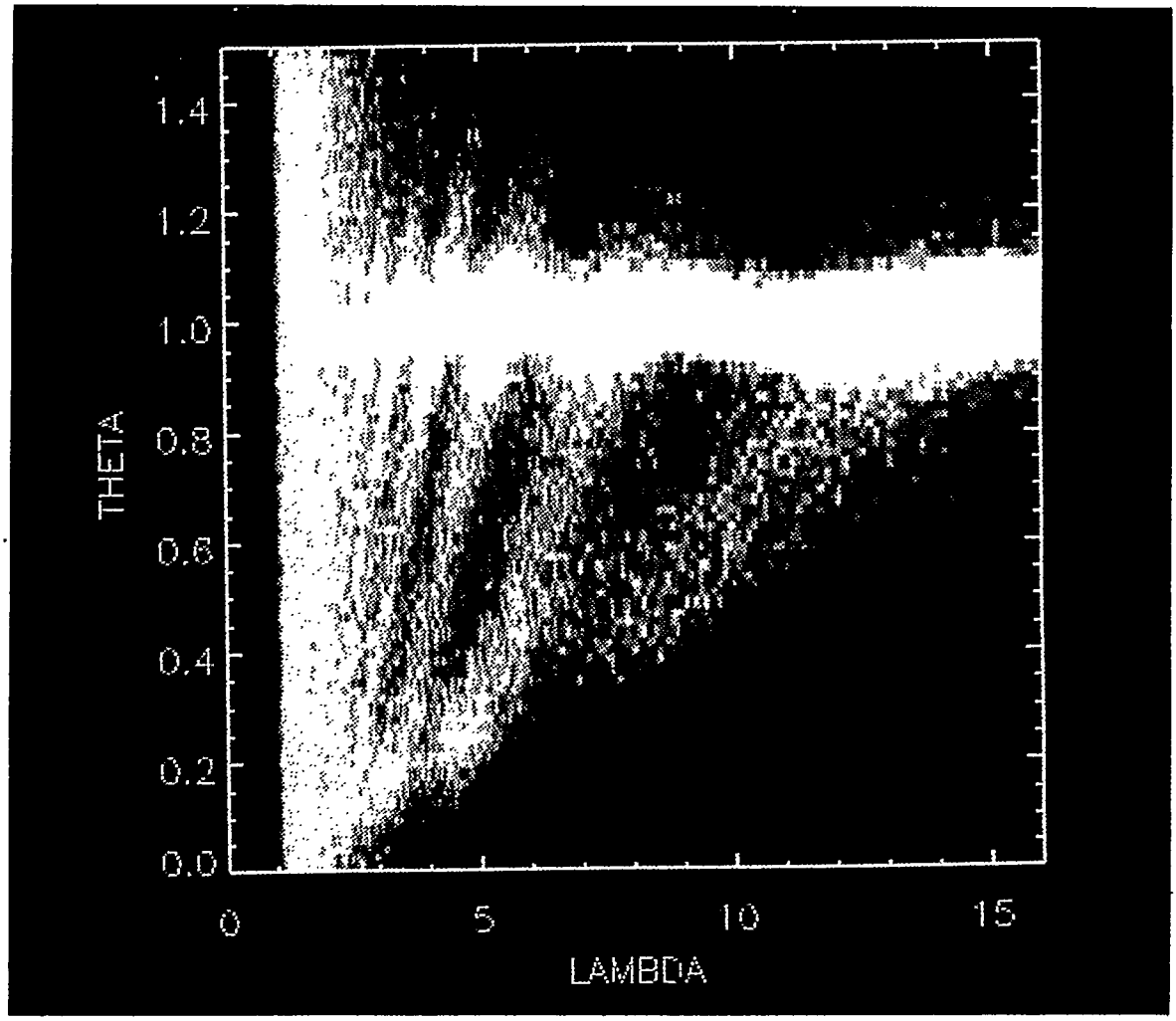

Figure 4a: Total scattering from a thin layer of titanium on sapphire plotted in a coordinate system spanned by λ (abscissa) and θ_2 (ordinate). These data were recorded with the SPEAR reflectometer at LANSCE.

The first such effect is illustrated in Figure 4, which displays data taken with a single film of titanium on sapphire. In addition to the Yoneda scattering, which appears as a fringe that extrapolates to the origin of Figure 4a, there are other fringes which extrapolate to $\theta_2 = -\theta_1$ at $\lambda = 0$ in Figure 4a and appear as constant-q_z fringes in Figure 4b. These fringes arise because the roughness at the titanium/sapphire interface is correlated with that at the air/titanium interface [2] — that is, mountains at the titanium/air interface occur above mountains in the sapphire/titanium interface and valleys occur above valleys. The correlation does not have to be perfect — i.e. the two interfaces do not need to be conformal — to generate such constant-q_z fringes, but some degree of correlation must exist for these fringes to appear.

Another effect which is seen in the diffuse scattering from multilayer systems [9] is the appearance of sharp structure (fringes) at constant values of k_{1z} or k_{2z} when one of these wavevectors coincides with a maximum in the specular reflectivity. These fringes occur because the neutron wavefunctions within the multilayer are strongly modulated by interference effects. The easiest way to understand the effect is to think about a periodic multilayer system in the Bragg condition. In this case, the wavefunctions of the incident and scattered beams have the same phase at each of the interlayer interfaces, ensuring that specular reflection from each interface adds coherently to produce a Bragg peak. When these wavefunctions are used in a perturbation calculation of the diffuse scattering from the interfacial roughness, their special phase relation at the interfaces

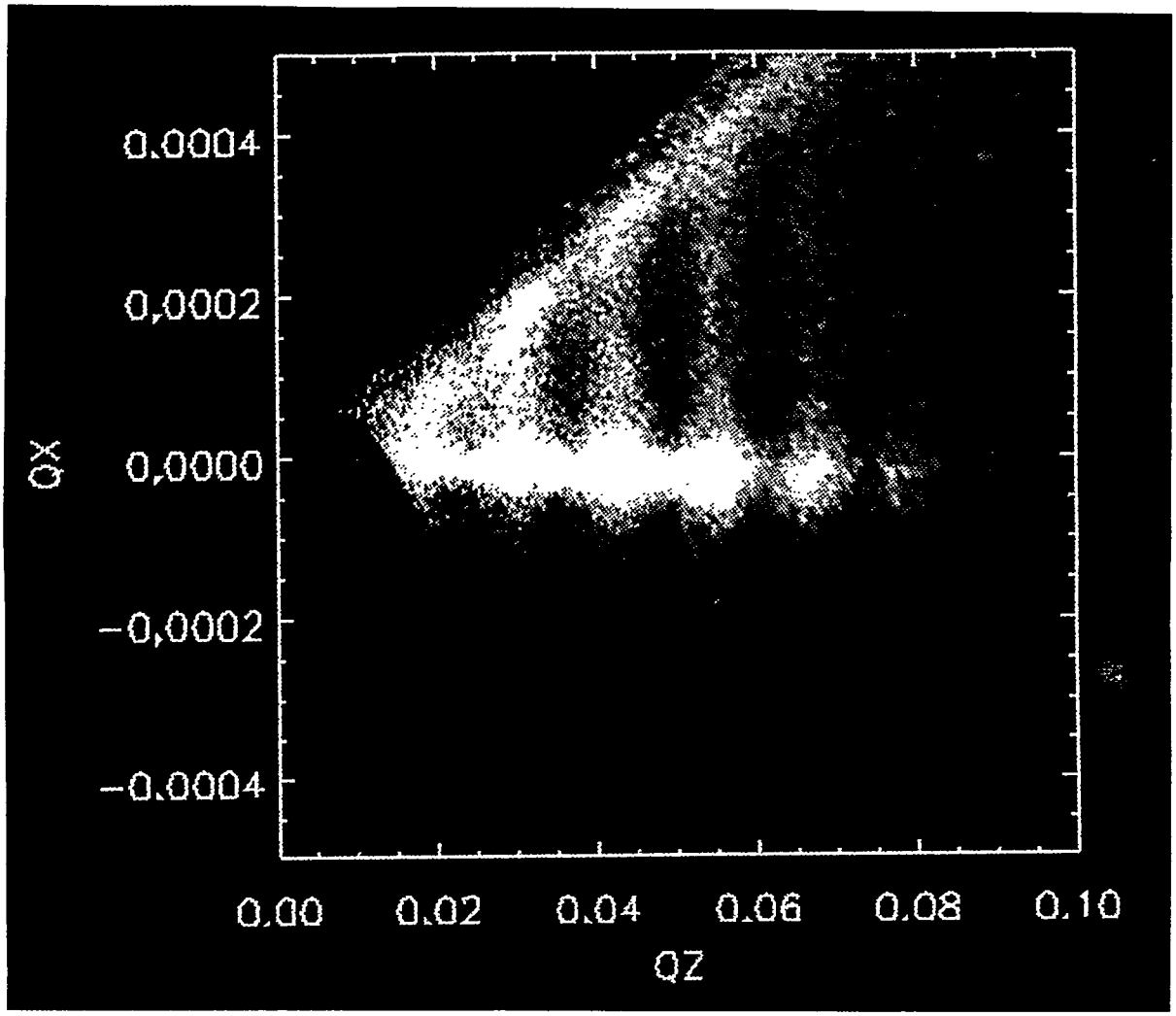

Figure 4b: The same data as Figure 4a transformed into the q_x - q_z coordinate system. In part (a) specular scattering occurs along a horizontal line at $\theta_1 = \theta_2 \approx 1°$ while in part (b) specular scattering corresponds to $q_x = 0$.

ensures coherent addition of diffuse scattering from each interface, giving rise to a fringe in the diffuse scattering. These fringes occur whenever either the incident or the scattered wavefunction is set to the Bragg condition because the relevant wavefunction has the phase behaviour described above. This argument applies to any multilayer that produces modulated specular reflection, not only to those that give Bragg reflections, because the intensity modulation is a direct manifestation of a coherent phase relationship between wavefunctions at the interlayer interfaces.

Recent experiments by Schlomka et al [10] have verified that the DWBA provides a good description of diffuse x-ray scattering from Si/Ge multilayers with various numbers of layers. In future, one can expect the theory to allow roughness spectra for individual interlayer interfaces as well as the nature of correlations between rough interfaces to be extracted from diffuse scattering data obtained with multilayer samples.

LENGTH SCALES PROBED BY SURFACE DIFFUSE SCATTERING

It is instructive to think about the length scales within a reflecting surface that are probed by diffuse scattering. q_x is given by

$$q_x = \frac{2\pi}{\lambda}(\cos\theta_1 - \cos\theta_2) \approx \frac{\pi}{\lambda}(\theta_1^2 - \theta_2^2) \qquad (7)$$

For reasonable parameter values (e.g. $\theta_1 = 0.02$, $\lambda = 4$ Å and $\theta_1 - \theta_2 = 0.001$), this means that q_x can be as small as 10^{-5} Å^{-1}, corresponding to a length scale in the x-y plane of 10 μm or more. This, of course, is a length scale that can easily be probed by optical microscopy. Thus, diffuse reflection from surfaces is one of the rare cases in which neutrons "see" the same length scales as light.

An example of the *range* of surface length scales that can be probed by diffuse neutron reflection is shown in Figure 5 which depicts the intensity profile along a constant-q_z fringe that passes through the lowest angle Bragg peak obtained with a thick multi-bilayer of dimyristoyl phosphatidylcholine (DMPC) spun on to a silicon substrate and maintained in a humid D_2O atmosphere at room temperature.

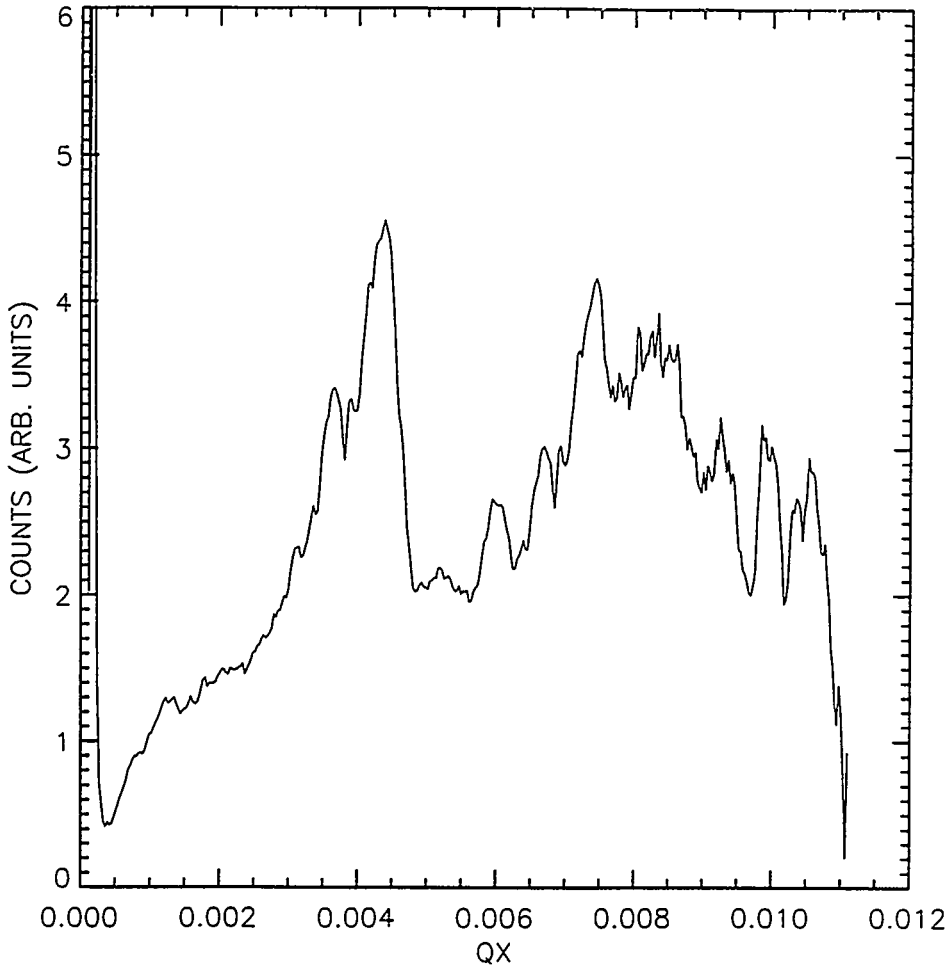

Figure 5: q_x-profile along a constant-q_z fringe of diffuse scattering obtained with a multibilayer of DMPC.

A remarkable feature of the data in Figure 5 is the range of q_x probed — from about 0.0002 $Å^{-1}$ to about 0.014 $Å^{-1}$ — corresponding to length scales ranging from less than 500 Å to over 3 μm. Figure 5 is also quite different from the usual bell-shaped form of S(**q**) (c.f. Figure 2) that peaks at $q_x = 0$. A detailed analysis of this profile and its implications for the structure of lipid layers is still in progress [11].

CONCLUSION

In this paper, I have given a brief introduction to the current state of knowledge about the effect of surface and interface roughness on neutron reflectivity experiments. In some cases, notably where the roughness has a high spatial frequency and is of small amplitude, a detailed theoretical description of the diffuse scattering and the effect of roughness on specular scattering can be obtained from the distorted wave Born approximation. In these cases, experimental data can be analysed to provide a quantitative description of the fluctuation spectrum of surface roughness.

ACKNOWLEDGEMENTS

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