Neutron scattering by rough surfaces at grazing incidence

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There are a number of calculations in the literature of the effect of statistical surface roughness on the specular and diffuse scattering of neutrons and x rays which impinge on surfaces at grazing incidence. These calculations do not agree with one another and in some cases lack internal consistency. In this paper I show that these discrepancies can be resolved within the distorted-wave Born approximation. The result I obtain for the specular reflectivity is the widely used version of Nevot and Croce, while that for the diffuse scattering is the same as a recent calculation by Sinha, Sirota, Garoff, and Stanley. The approximations made by Nevot and Croce are clearly revealed by the distorted-wave Born approximation. A simple numerical algorithm is proposed for the calculation of diffuse scattering from a surface whose roughness is self-affine, and the form of the scattering is calculated for a range of parameters within this model. The calculation of diffusion scattering is extended in this paper to the case of films with rough surfaces. Correlation between roughness at the two film surfaces is considered and shown to be important for the description of neutron reflectivity data obtained with a thin film of titanium deposited on a sapphire substrate.

INTRODUCTION

The reflection of radiation by rough surfaces has been studied since the turn of the century in many different fields of physics. It is generally conceded that a smooth surface may be defined as one that reflects incident radiation in a single (specular) direction whereas a rough surface reflects in many directions, even though the specular direction may be privileged. With rough and smooth surfaces defined in this manner, a given surface may be experienced as rough or smooth depending on the wavelength of the scattered radiation and the angle of incidence. For example, "road glare" is a relatively common phenomenon for asphalt surfaces illuminated by the evening sun but does not occur at midday when the angle of incidence is larger. More mathematically, the Rayleigh criterion allows one to discriminate between a rough surface for which $q_z\sigma > 1$, and a smooth surface for which $q_z\sigma \ll 1$. Here q_z is the wave vector transfer of the radiation perpendicular to the surface and σ^2 is the variance of the height distribution of the (horizontal) surface.

In the past few years, x-ray and neutron reflectometry have been developed as techniques for probing the density of matter close to the solid and liquid surfaces or in thin films. These methods are extremely sensitive and provide unique information on phenomena as different as wetting and the penetration of magnetic fields in superconductors. However, the analysis of results of grazing incidence experiments of this kind requires a detailed understanding of the effect which surface roughness has on reflectivity. Without an appropriate formalism, density gradients close to surfaces cannot be determined properly nor can the nature of surface roughness be probed.

There is a large body of literature, summarized in a book by Beckmann and Spizzichino,[1] and inspired by problems such as the "sea clutter" observed in radar imaging of ships, which deals with the reflection of electromagnetic waves from rough surfaces. Almost all of this work is based on approximations in which the local radius of curvature of a rough surface is assumed to be much greater than the wavelength of the illuminating radiation. In this case, the surface may be considered to be composed of elemental flat surfaces, the slopes of which match the local gradients of the real surface. Each of the elemental surfaces is assumed to reflect specularly in a direction which is determined entirely by the local gradient of the surface. While such a model is probably quite reasonable for a description of the sparkling surface of the sea observed late in the day, it is not universally applicable. In particular, it is probably not appropriate for the problem of interest here, the reflection of neutrons or x rays by the surfaces of solids and liquids in conditions of grazing incidence. For many of the samples used in such experiments the radius of curvature of rough surface features is likely to be smaller than the radiation wavelength.

The theory of reflection of x rays or neutrons by rough surfaces has been discussed by several authors. For example, there is a large body of work, extending over almost two decades, by Nevot and Croce[2,3,4] and their coworkers who have used x rays to probe surfaces and thin films. These authors have produced a theory of reflection which is both elegant and original. Among other results, they assert that the specular reflection coefficient, R_r, of a surface with Gaussian roughness is related to that for an ideal smooth surface, R_i, by the relation

$$R_r = R_i \exp(-q_z q_z^t \sigma^2/2) \ . \tag{1}$$

Here q_z is the wave-vector transfer in air[5] while q_z^t is the wave-vector transfer in the reflecting medium. Since the

reflection coefficients, R_r and R_i, in Eq. (1) relate the amplitude of a reflected wave to that of an incident wave, the quantity actually measured in an experiment is $|R_r|^2$.

Sinha *et al.*[6] applied both the Born approximation and a form of the distorted-wave Born approximation (DWBA) to a calculation of the specular and diffuse scattering of neutrons from statistically rough surfaces. Within the Born approximation, they found that the q_z^t which appears in Eq. (1) is replaced by q_z, the wave-vector transfer in air. This result is, in fact, the same as that obtained in the approximation described above for radar waves in which small elements of the surface reflect specularly in different directions. Extension to the DWBA allowed Sinha *et al.* to obtain Eq. (1) as an approximate result, valid only for small values of q_z and q_z^t. For large values of q_z and q_z^t, the version of the DWBA used by Sinha *et al.* gave results which disagreed both with Eq. (1) and with the simple Born approximation. The latter result should be accurate for large q_z because the scattering is weak in this limit. It is worth noting that the Nevot-Croce result given in Eq. (1) is indistinguishable from the Born approximation for large values of q_z because q_z and q_z^t are almost identical in this limit.

In a 1972 paper, Steyerl[7] investigated the transmission of neutron guide tubes and approached the problem of reflection of neutrons from a rough surface using a Green's function formulation which, at first sight, ought to be equivalent to the DWBA. However, Steyerl found, instead of Eq. (1), that roughness causes the specular reflectivity to be reduced by an amount which is essentially independent of q_z.

These conflicting results leave experimentalists in a quandary: which theory should be used to deduce surface roughness from measurements of neutron or x-ray reflectivity? Most recent work with which I am familiar has used Eq. (1) which is, I believe, a good approximation. In this paper, I will demonstrate that Eq. (1) can be obtained from the DWBA provided a suitable approximation is used for the matrix elements involved in the calculation. Sinha *et al.*[6] evaluated these matrix elements between states which correspond to wave functions appropriate to the Fresnel solution of the "ideal surface" problem. This is an approximation to the DWBA. In fact, the matrix elements should be evaluated using the Fresnel state and the "exact" wave function for the rough surface. When this is done, the DWBA becomes equivalent to the expressions derived by Nevot and Croce,[2] and is valid providing the refractive index of the reflecting medium is close to unity and the amplitude of the surface roughness is not too large. Since the amplitude of surface roughness permitted by the calculation is unlikely to be exceeded in practical situations, Eq. (1) can be used with impunity in most cases.

I find that the result obtained by Steyerl[7] is not a useful approximation for the interpretation of neutron reflectivity data, especially when small values of the reflectivity are measured. Steyerl's formulation of the surface scattering problem is correct and equivalent to the DWBA used by Sinha *et al.*[6] However, Steyerl assumes that there is a coherent addition of waves scattered from the "peaks" and "troughs" of the rough surface and calculates the phases of all such waves as if they were reflected by an average surface. Steyerl's approximation for the diffuse (nonspecular) scattering is valid for $q_z\sigma \ll 1$, a case which is of little practical interest to those wishing to use reflectivity to investigate surface roughness. Steyerl's approximation is, however, useful in the area to which he applied it—reflection from neutron guide tubes at angles less than the critical angle. In that case, the approximation $q_z\sigma \ll 1$ is justified and one can calculate the effect of roughness on the specular reflectivity below the critical angle from a unitarity argument.

The same DWBA which gives Eq. (1) provides an expression for the diffuse scattering from a rough surface that is essentially the same as that obtained by Sinha *et al.*[6] The theory can be extended to permit evaluation of the diffuse scattering from a thin film with rough surfaces. It is worth noting that this paper, like its predecessors, ignores shadowing effects due to surface protrusions as well as contributions from multiple diffuse scattering.

THE GENERALIZED BORN APPROXIMATION

The generalized, or distorted-wave Born approximation is described in detail in textbooks on quantum mechanics such as that by Messiah.[8] Part of this description is repeated here in order to introduce appropriate notation. The Schrödinger equation for a neutron interacting with a rough surface involves a Hamiltonian H which is the sum of the free-particle Hamiltonian H_0 and an interaction potential $V_1(\mathbf{r})+V_2(\mathbf{r})$. Here $V_1(\mathbf{r})$ represents the interaction of neutrons with a reflecting medium with a smooth surface and $V_2(\mathbf{r})$ is the perturbation due to surface roughness. Let us suppose that the exact eigenstate of the Schrödinger equation for the smooth surface is denoted $\Psi_{1i}^{(+)}(\mathbf{r})$, where the notation is chosen to indicate that the wave function refers to neutrons (or x rays) of wave vector $\mathbf{k}_1$ incident on an ideal surface. According to the Fresnel formalism, $\Psi_{1i}^{(+)}(\mathbf{r})$ can be written as

$$\Psi_{1i}^{(+)}(\mathbf{r})=\begin{cases}\exp[i(k_{1x}x+k_{1y}y)][\exp(-ik_{1z}z)+R_i(k_{1z})\exp(ik_{1z}z)] & \text{for } z>0\ , \quad (2)\\ \exp[i(k_{1x}x+k_{1y}y)]T_i(k_{1z})\exp(-ik_{1z}^t z) & \text{for } z<0\ . \quad (3)\end{cases}$$

In Eqs. (2) and (3), k_{1z}^t is the z component of the wave vector of the transmitted beam. The positive z direction is taken to be away from the reflecting medium, while x and y are contained in the reflecting surface, defined by the condition $z=0$. R_i and T_i are the reflection and transmission coefficients for the "ideal," smooth surface given by

$$R_i=\frac{k_{1z}-k_{1z}^t}{k_{1z}+k_{1z}^t}\ , \quad (4)$$

$$T_i = 1 + R_i \ . \tag{5}$$

The transfer matrix for the reflection of a neutron from a state $\mathbf{k}_1$ to a state $\mathbf{k}_2$ by the smooth surface is given by the matrix element of V_1 evaluated between $\Psi_{1i}^{(+)}(\mathbf{r})$ and an eigenfunction of H_0, that is, a plane wave. Thus

$$t^i_{k_1 \to k_2} = \langle \exp(i\mathbf{k}_1 \cdot \mathbf{r}) | V_1 | \Psi_{1i}^{(+)} \rangle \ , \tag{6}$$

where the matrix element in Eq. (6) is defined by

$$\langle \exp(i\mathbf{k}_1 \cdot \mathbf{r}) | V_1 | \Psi_{1i}^{(+)} \rangle = \int \exp(-i\mathbf{k}_1 \cdot \mathbf{r}) \times V_1(\mathbf{r}) \Psi_{1i}^{(+)} d\mathbf{r} \ . \tag{7}$$

Note that Eq. (6) is *not* the Born approximation because the matrix element is not evaluated between two plane waves.

To include surface roughness we need to carry the calculation one step further and include the perturbation $V_2(\mathbf{r})$ within the generalized Born approximation. We first define an approximate time-reversed solution for the *rough* surface problem, which we denote $\Psi_{2r}^{(-)}(\mathbf{r})$, with the superscript denoting time reversal. This solution represents neutrons of wave vector $\mathbf{k}_2' = (k_{2x}, k_{2y}, k_{2z})$, specularly reflected with wave vector $\mathbf{k}_2 = (k_{2x}, k_{2y}, -k_{2z})$: $\mathbf{k}_2'$ is the wave vector of neutrons in the medium which come towards the surface and combine with neutrons of wave vector $\mathbf{k}_2'$ to produce neutrons of wave vector $\mathbf{k}_2$. At this level of approximation, the diffusely scattered waves which should be included in the exact wave function for the rough surface problem are omitted from $\Psi_{2r}^{(-)}(\mathbf{r})$ which is then defined by

$$\Psi_{2r}^{(-)}(\mathbf{r}) = \begin{cases} \exp[i(k_{2x}x + k_{2y}y)][\exp(ik_{2z}z) + R_r^*(k_{2z}')\exp(-ik_{2z}z)] & \text{for } z > 0 \ , \quad (8) \\ \exp[i(k_{2x}x + k_{2y}y)] T_r^*(k_{2z}') \exp(ik_{2z}'z) & \text{for } z < 0 \ , \quad (9) \end{cases}$$

where the star indicates complex conjugation and R_r and T_r are the reflection and transmission coefficients for the rough surface. In the generalized Born approximation the transfer matrix for the rough surface is given by

$$t^r_{k_1 \to k_2} = t^i_{k_1 \to k_2} + \langle \Psi_{2r}^{(-)} | V_2 | \Psi_{1i}^{(+)} \rangle \ , \tag{10}$$

where the first term in Eq. (10) comes from Eq. (6).

Equation (10) differs in one important respect from the DWBA used by Sinha *et al.*:[6] $\Psi_{2r}^{(-)}(\mathbf{r})$ is defined here in terms of reflection from a *rough* surface whereas Sinha *et al.* define it as a time-reversed eigenfunction of the smooth surface problem. There is no doubt that Eq. (10) is correct.[8] In many cases, of course, it makes little difference if the second term of Eq. (10) is evaluated between eigenfunctions of the "ideal" problem because these eigenfunctions are close to those for the "real" problem. For the scattering of neutrons by surface, however, reflection becomes weak as q_z increases and the Fresnel eigenfunctions for the "ideal" problem may no longer be good representations of the "real" eigenfunctions. For large enough values of q_z, the simple Born approximation evaluated between plane waves gives an adequate description of the scattering for precisely this reason.

For neutron reflection, the final term in Eq. (10) can be written explicitly as

$$\langle \Psi_{2r}^{(-)} | V_2 | \Psi_{1i}^{(+)} \rangle = (1 - n^2) \frac{h^2 k_1^2}{8\pi^2 m} \left[\int dx \int dy \int_{z>0} dz \, e^{-i\vec{\kappa}\cdot\vec{\rho}} [e^{-ik_{1z}z} + R_i(k_1) e^{ik_{1z}z}][e^{-ik_{2z}z} + R_r(k_2') e^{ik_{2z}z}] + \int dx \int dy \int_{z<0} dz \, e^{-i\vec{\kappa}\cdot\vec{\rho}} T_i(k_1) T_r(k_2') e^{-i(k_{1z}' + k_{2z}')z} \right] , \tag{11}$$

where $\vec{\kappa}$ is the component of the neutron scattering vector parallel to the surface and $\vec{\rho}$ is a vector that describes the position of a point in the surface, i.e.,

$$\vec{\kappa} \cdot \vec{\rho} = (k_{2x} - k_{1x})x + (k_{2y} - k_{1y})y \ .$$

The first integral in Eq. (11) is evaluated over those parts of the rough surface which are above the average surface, while the second integral refers to parts of the rough surface below the $z = 0$ plane. Equation (11) includes an explicit expression for the perturbation $V_2(\mathbf{r})$ which is zero above the actual rough surface and equal to $h^2 k_1^2 (1 - n^2)/8\pi^2 m = Nbh/(2\pi m)$ below (m is the neutron mass, n and Nb are, respectively, the refractive index and the coherent scattering length density of the reflecting medium). By changing the form used for $V_2(\mathbf{r})$, equation (11) may be applied to x ray reflection from surfaces.

THE NEVOT-CROCE RESULT

To evaluate Eq. (11) in a self-consistent manner and to make contact with the work of Nevot and Croce,[2] we note that the wave functions $\Psi_{1i}^{(+)}(\mathbf{r})$ and $\Psi_{2r}^{(-)}(\mathbf{r})$ and their derivatives are continuous across the average surface at $z = 0$. This means, for example, that it is a good approximation to replace the solution above the surface

given by Eq. (2) by an analytic continuation of Eq. (3) to positive values of z. The error made by this replacement, to lowest nonvanishing order in z, is $(k_{1z}z)^2[2R_i/(1+R_i)]$, a quantity which is largest close to the critical angle and which achieves a limiting value for large k_{1z} that is proportional to the difference between the refractive indices of the media separated by the reflecting surface. Thus the approximation of replacing Eq. (2) by an analytic continuation of Eq. (3) close to the surface will give the greatest error for values of q_z in the neighborhood of critical reflection. However, even in this case and for materials such as nickel which have large refractive indices for neutrons, the error in the amplitude of the wave function is less than 5% for values of z up to 25 Å.

When $\Psi_{2r}^{(-)}(z>0)$ from Eq. (8) is replaced by an analytic continuation of $\Psi_{2r}^{(-)}(z<0)$ from Eq. (9), the error introduced in the integrand of Eq. (11) is linear in z to leading order, tending to $iz(k_{1z}-k_{1z}^t)$ at large values of k_{1z}. The numerical value of the error is similar to that which pertains when $\Psi_{1i}^{(+)}(z>0)$ is replaced by $\Psi_{1i}^{(+)}(z<0)$, however. Thus, the approximation of replacing wave functions defined for $z>0$ by analytic continuations of functions defined with $z<0$ is a good one in most practical situations. This approximation is used implicitly by Nevot and Croce.[2]

With the approximations introduced in the previous paragraphs, Eq. (11) may be rewritten as

$$\langle \Psi_{2r}^{(-)}|V_2|\Psi_{1i}^{(+)}\rangle=(1-n^2)\frac{h^2k_1^2}{8\pi^2m}\left[\int dx\int dy\int dz\, e^{-i\vec{\kappa}\cdot\vec{\rho}}T_i(k_1)e^{-ik_{1z}^t z}[e^{-ik_{2z}z}+R_r(k_2')e^{ik_{2z}z}]\right], \tag{11a}$$

where the integral over z now extends both above and below the average surface. Combining Eqs. (10) and (11a) at the specular condition ($k_{1z}=k_{2z}$) one finds that

$$R_r(k_1)=R_i(k_1)-i(k_{1z}-k_{1z}^t)\int dz[e^{-ik_{1z}z}+R_r(k_1)e^{ik_{1z}z}]e^{-ik_{1z}^t z}. \tag{12}$$

Equation (12) is the neutron version of an equation derived by an entirely different method for electromagnetic radiation by Nevot and Croce.[2] From the derivation given here, the approximations inherent in the formalism of Nevot and Croce are clear. In particular, as these authors themselves state without explanation, their formalism is valid when the spatial roughness is of high frequency and when there is a small difference between the refractive indices of the media separated by the reflecting surface. The first condition guarantees that there are no perfectly reflecting surface elements such as those in the calculations described by Beckmann and Spizzichino[1] for radar waves. The second condition implies that only a small error is made when wave functions defined for $z<0$ are replaced by analytic continuation of functions defined for $z>0$ and *vice versa*. A further condition for the validity of the Nevot-Croce result is that the amplitude of the surface roughness be small enough to permit this replacement of wave functions. In practice, this condition restricts the validity of the Nevot-Croce result to roughness whose standard deviation is less than about $(10\sqrt{Nb})^{-1}$, where Nb is the scattering length density of the medium.

Not surprisingly, since Eq. (12) is the same as that given by Nevot and Croce, the result it gives for R_r is also the same. The advantage of this solution is that it calculates the quantity R_r introduced in Eqs. (8) and (9) in a self-consistent manner. Carrying out the integral in Eq. (12) and assuming that the height of the surface with respect to the plane $z=0$ is a Gaussian variable of variance σ^2, the specular reflection coefficient is found to be

$$R_r=R_i+R_i\{\exp[-\tfrac{1}{2}(k_{1z}+k_{1z}^t)^2\sigma^2]-1\}-R_r\{\exp[-\tfrac{1}{2}(k_{1z}-k_{1z}^t)^2\sigma^2]-1\}. \tag{13}$$

Simple manipulation of this equation yields the result given in Eq. (1).

There are other ways in which one could choose to replace wave functions in Eq. (11). To derive the Nevot-Croce result, the ideal-surface term in the first integral in Eq. (11) was replaced by an analytic continuation of the transmitted wave function for the ideal case, and the rough-surface wave function in the second integral was replaced by a continuation of the wave function for a beam reflected by a rough surface. These replacements, which give Eq. (11a), have the advantage that errors made in the two integrals in Eq. (11) tend to cancel. Nevertheless, one could equally well imagine, for example, replacing both of the wave functions in the first integral of Eq. (11) with continuations of transmitted wave functions. If this is done, the resulting expression for the reflection coefficients is not as compact as the Nevot-Croce result, nor does it approach the Born approximation in the limit of large q_z. On the other hand, the numerical values obtained are identical for reflection coefficients greater than about 10^{-5}. The advantage of Eq. (11a) is that it yields a result for R_r that approaches the correct Born limit at large wave-vector transfers, as well as being accurate close to the critical edge. It is for this reason that the Nevot-Croce result is to be preferred to any other form that can be derived from the DWBA.

In at least one case the Nevot-Croce result is remarkably accurate. When the probability of a particular surface height, z, is proportional to $\cosh^{-2}(z/2d)$, where d is a constant, the density distribution around the mean interface at $z=0$ yields a graded index of refraction for which the reflection coefficient can be calculated exactly.[10] This exact result differs from that obtained from Eq. (12) only by a phase factor. The phase is very small and

scales as the cube of the interface thickness, d, and as the difference in the scattering length densities of the media separated by the interface. Detailed numerical calculations[11] have shown that this phase will be very difficult to observe, even in carefully chosen thin films with large amplitude roughness. Obviously the phase cannot be observed by measuring reflection from a single rough surface because the quantity obtained experimentally is $|R|^2$.

One may ask why the Green's function method of Steyerl[7] fails to find any exponential damping of reflection due to surface roughness. Steyerl's expression for the diffuse scattering from a rough surface is essentially equivalent to Eq. (11) of this paper with R_r and T_r replaced by the corresponding quantities for a smooth surface. However, to evaluate this equation, Steyerl set all the phase factors in the integrand to unity (as they are at $z=0$) so that the integral given by Eq. (11) becomes linear in the distance between the actual surface and the smooth surface at $z=0$. Although this approximation is justified when $k_{1z}\sigma$ is sufficiently small, it is irrelevant for most reflectometry experiments.

DIFFUSE SCATTERING FROM A ROUGH SURFACE

For off-specular conditions, Eq. (11) is the t matrix which describes diffuse scattering from a rough surface. In terms of the t matrix, the cross section for diffuse scattering is given by[8]

$$\frac{d\sigma}{d\Omega}=\frac{(2\pi m)^2}{h^4}|t_{k_1\to k_2}|^2 . \tag{14}$$

Thus, evaluation of Eq. (11) in the off-specular condition gives directly the diffuse scattering cross section for a rough surface. To evaluate Eq. (11), we again make use of the continuity of $\Psi_{1i}^{(+)}(\mathbf{r})$ and $\Psi_{2r}^{(-)}(\mathbf{r})$ and their derivatives at the reflecting surface. This calculation differs from that of the specular reflectivity in that each of the possible transformations of Eq. (11) gives an expression for the diffuse scattering that approaches the Born approximation at large q_z, essentially because R tends to zero and T tends to unity in this limit. The most compact result is obtained by approximating each of the terms in the first integral of Eq. (11) by analytic continuations of the corresponding wave functions evaluated below the average surface. Straightforward algebraic manipulations then yield

$$\left[\frac{d\sigma}{d\Omega}\right]_{\text{diffuse}}=N^2b^2L_xL_y|T_i(k_1)|^2\,|T_r(k_2)|^2S(\kappa) , \tag{15}$$

where L_x and L_y are the dimensions of the surface, and Nb is the coherent scattering length density of the reflecting medium. The structure factor $S(\kappa)$ which appears in Eq. (15) is defined by

$$S(\kappa)=\frac{1}{|\alpha|^2}e^{-(\alpha^2+\alpha^{*2})\sigma^2/2}\int dx\int dy\, e^{i\vec{\kappa}\cdot\vec{\rho}}(e^{|\alpha|^2C(x,y)}-1) , \tag{16}$$

where α is given by

$$\alpha=k_{1z}^t+k_{2z}^t . \tag{17}$$

The wave vector of the incident neutrons is $\mathbf{k}_1$ while that of the diffusely scattered neutrons is $\mathbf{k}_2$. In this case, of course, $\mathbf{k}_1$ and $\mathbf{k}_2$ are not related by the specular condition. The height-height correlation function $C(x,y)$ which appears in Eq. (16) is the same as that introduced by Sinha *et al.*:[6]

$$C(x,y)=\langle z(x,y)z(0,0)\rangle , \tag{18}$$

where $\langle\cdots\rangle$ denotes a configurational average.

Equations (15) and (16) are almost identical to these obtained by Sinha *et al.*[6] The only difference is the appearance of the term $T_r(k_2)$ in Eq. (15) in place of the $T_i(k_2)$ found in Ref. 6. This can be traced directly to the wave functions used in evaluating the DWBA. Because of the form of the DWBA used here, Eq. (15) is not explicitly symmetric in k_1 and k_2 whereas the result of Sinha *et al.*[6] is symmetric. However, microscopic reversibility,[8] manifested by the equation

$$\langle\Psi_{2r}^{(-)}|V_2|\Psi_{1i}^{(+)}\rangle=\langle\Psi_{2i}^{(-)}|V_2|\Psi_{1r}^{(+)}\rangle \tag{19}$$

implies that interchange of k_1 and k_2 in Eq. (11) should not change the value of the matrix element. Thus, the diffuse scattering cross section *should* be symmetric in k_1 and k_2. Because $T=1+R$ and $R\to 0$ as q_z increases, the difference between T_i and T_r is very small except for wave vectors very close to the critical wave vector and for large-amplitude roughness. For this reason Eq. (16) usually gives results that are numerically indistinguishable from those given by the expression obtained by Sinha *et al.*[6] Nevertheless, it may be preferable to use the result given in Ref. 6 because it explicitly displays the correct symmetry with respect to interchange of k_1 and k_2.

Several authors[6,12] have pointed out that the roughness of some surfaces might be described by a self-affine correlation function, $C(\rho)$, of the form

$$\langle[z(x',y')-z(x,y)]^2\rangle=2[\sigma^2-C(\rho)]=g(\rho)=A\rho^{2h} , \tag{20}$$

where $\rho^2=(x-x')^2+(y-y')^2$, A is a constant, and the exponent h takes values between zero and one. For $h<0.5$, the changes in surface height that occur over neighboring increments of the surface are negatively correlated while for $h>0.5$ changes over neighboring increments are positively correlated. The boundary value, $h=0.5$, corresponds to an uncorrelated sequence of height changes, and is akin to Brownian motion.[13] Values of h that apply to many natural phenomena, from sunspot numbers to river discharges, have been calculated by Hurst:[14,15] a value of about 0.7 seems to be typical. The correlation function given in Eq. (20) cannot be used directly to evaluate diffuse scattering from a rough surface because it does not describe a surface which has a well-defined mean position when averaged over a large area. To overcome this problem, Sinha *et al.*[6] introduced a "cut-off" length, ζ, into the definitions of $C(\rho)$ and $g(\rho)$:

$$C(\rho)=\sigma^2e^{-(\rho/\zeta)^{2h}} , \tag{21a}$$

$$g(\rho)=2\sigma^2(1-e^{-(\rho/\zeta)^{2h}}) , \tag{21b}$$

In fact, the quantity ζ in the above equations plays the role of a length scale within the rough surface as well as providing a cutoff. Figure 1 compares the correlation functions given by Eqs. (20) and (21b) in terms of the scaled distance ρ/ζ between two points on a surface. As one moves away from a point in the surface, the height "escapes" more rapidly from its initial value for large values of h while small values of h correspond to surfaces whose heights remain within a small interval over large areas. Thus both h and the scale length, ζ, control how far a point wandering on the surface must move before it loses memory of the initial value of its z coordinate.

The scattering vector κ that appears in Eq. (16) has two components in the average ($z=0$) surface: q_x $[=(k_{1z}{}^2-k_{2z}{}^2)/2|k_1|]$ in the scattering plane defined by the wave vectors of the incident and scattered beams and q_y perpendicular to the scattering plane. In most reflectometry experiments, the spectrometer resolution in the q_y direction is relaxed, while that in the q_x direction is very good. This means that diffuse scattering is usually measured as a function of q_x and integrated over q_y. Since the quantity α in Eq. (16) does not depend on q_y, integration over the latter variable singles out the $y=0$ value of the integrand. Even so, evaluation of the diffuse scattering from a surface in terms of the self-affine correlation function is computationally costly unless some approximations are made. The Fourier transform in Eq. (16) takes the form

$$\int e^{iq_x x}[\exp(|\alpha|^2\sigma^2 e^{-(x/\zeta)^{2h}})-1]dx \ . \tag{22a}$$

To evaluate this equation by fast Fourier methods requires that calculations be done with α kept constant as q_x varies. While this can clearly be done, the values of k_{1z} and k_{2z} that result do not correspond necessarily to those that would be used in an experiment. For example, on the reflectometer SPEAR[18] at the Manuel Lujan Jr. Neutron Scattering Center, measurements of diffuse scattering are performed by varying the angle that the reflected neutron beam makes with the sample surface. An apparently worse computational problem arises if one attempts to evaluate the scattering at $q_y=0$ rather than integrating over q_y. In this case the term in square brackets in Eq. (22a) is replaced by an integral over the y coordinate of the surface to give

$$\int dx\, e^{iq_x x}\int dy[\exp(|\alpha|^2\sigma^2 e^{-(x^2+y^2)^h/\zeta^{2h}})-1] \ . \tag{22b}$$

Fortunately, however, one finds (cf. Fig. 2) for a large range of values of α, and for h greater than ~ 0.3, that the quantities to be Fourier transformed in Eqs. (22a) and (22b) may be approximated adequately by simple quadratic forms over the range of values of x that contributes significantly to the Fourier transform. Thus one may write

$$\ln[\exp(|\alpha|^2\sigma^2 e^{-(x/\zeta)^{2h}})-1]\cong c_0-c_1x-c_2x^2 \tag{23a}$$

or

$$\ln\left|\int dy[e^{|\alpha|^2\sigma^2 e^{-(\rho/\zeta)^{2h}}}-1]\right|\cong c_0-c_1x-c_2x^2 \tag{23b}$$

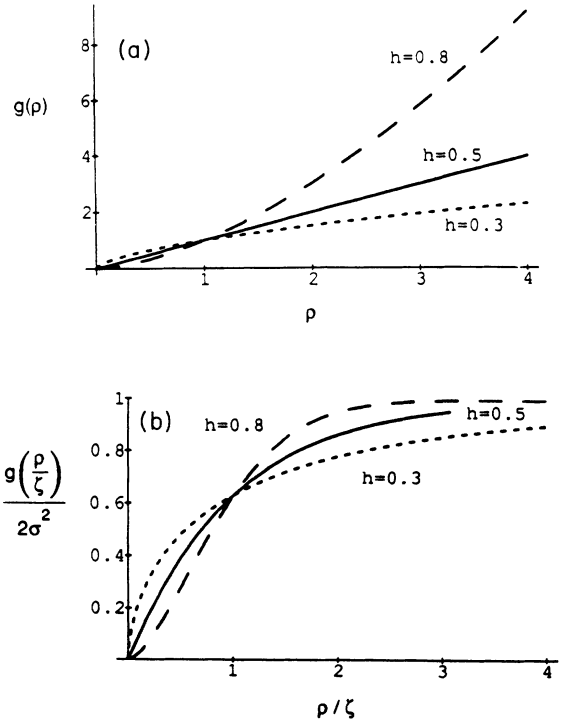

FIG. 1. (a) The correlation function $g(\rho)$ defined by Eq. (20) for a self-affine surface with the constant A set to unity. (b) The correlation function $g(\rho/\zeta)/2\sigma^2$ defined by Eq. (21b) as a function of ρ/ζ.

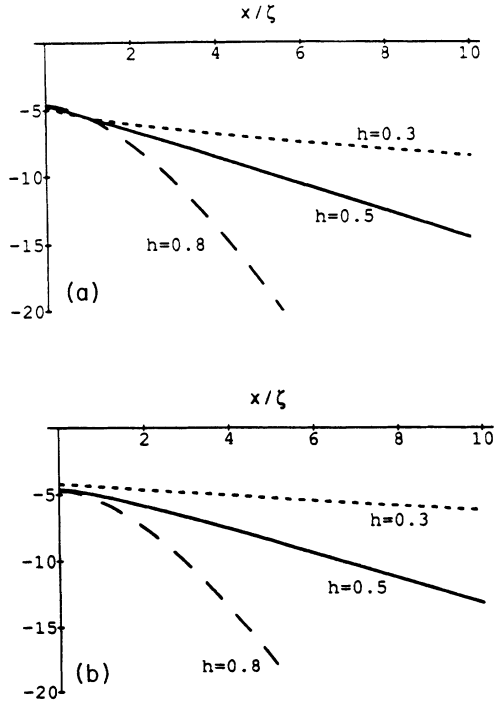

FIG. 2. (a) The left-hand side of Eq. (23a) plotted as a function of x/ζ. (b) The left-hand side of Eq. (23b) plotted as a function of x/ζ. $|\alpha|^2\sigma^2=0.1$ in both parts of the figure.

In both cases, the positive constants c_1, and c_2 depend only weakly on α but strongly on h, whereas c_0 depends weakly on h but strongly on α. Equation (23b) is a somewhat better approximation that Eq. (23a), especially at small values of x and h, but both are adequate. The parameters can be evaluated easily by using a computational program package such as *Mathematica*.[16]

Equations (23a) and (23b) imply that the entire expression in either Eq. (22a) or Eq. (22b) can be represented as a Voight function (the convolution of a Gaussian and a Lorentzian), for which simple numerical approximations exist.[17] Thus, the problem of evaluating the diffuse scattering from a surface is reduced to finding suitable values of the coefficients c_i and using these values to compute simple functions.

Figures 3, 4, and 5 show how the diffuse neutron scattering at $q_y=0$ from a rough nickel surface varies with different parameters in the problem. Several general features are clear. There is a maximum in the diffuse scattering when the incident and reflection angles are equal, that is, at the specular condition. The sharpness of this maximum depends on the value of the self-affine index, h: small values of h, corresponding to surfaces that subjectively appear more "jagged," give sharper peaks in the diffuse scattering. Larger values of ζ also tend to give sharper diffuse scattering: indeed the widths of both the Lorentzian and Gaussian contributions to the Voight profile of the scattering scale as $1/\zeta$.

The sharp cusp in the diffuse scattering that occurs for values of θ_2 less than 1.5° in each of the figures corresponds to the peak in the transmission function, $T(k_{2z})$, of the surface that arises when θ_2 is equal to the critical angle for nickel.[9] For a given material, the critical angle is proportional to neutron wavelength, as Fig. 4 shows.

DIFFUSE SCATTERING BY THIN FILMS

One of the motivations for this study was to explain data like that displayed in Fig. 6, taken with the neutron reflectometer SPEAR[18] at the Manual Lujan Jr. Neutron Scattering Center (LANSCE) using a sample composed of a thin titanium film on a sapphire substrate. Figure 6 is a grey-scale plot of scattered neutron intensity as a function of neutron wavelength, λ, and the grazing angle of reflection, θ_2. λ is the abscissa and θ_2 the ordinate. The bright modulated stripe running from right to left at $\theta_2 \approx 25$ units corresponds to the specular condition $\theta_2=\theta_1=1°$. Because the neutron source provides many more neutrons of short wavelength, the intensity of the specular reflection does not vary strongly with wavelength and several interference maxima are visible even though the grey scale does not have a particularly large dynamic range. The widths of the wavelength channels used in Fig. 6 are not constant across the figure. For wavelengths less than 1.6 Å (channel 50 in the figure), each channel has a constant width of ≈0.03 Å. At larger wavelengths, the width of each channel is 2% of the wavelength at the center of the channel. This binning algorithm, which is chosen for experimental convenience, means that the horizontal axis of Fig. 6 corresponds to $\ln(\lambda)$ for most of the interesting range of data. The interesting range, of course, corresponds to the diagonal fringes observed between wavelength channels 60 and 120. It is these fringes that we shall attempt to explain in the remainder of this paper.

The formalism developed here can be applied without great difficulty to calculating the diffuse scattering from a film deposited on a substrate. The simplest case to consider is that of a film with a rough film-air interface and a perfectly smooth film-substrate interface. When neutrons or x rays are scattering from such a film, the experiment is very similar to one first performed by Newton[19] when he reflected light from a dusty, silvered mirror. In that

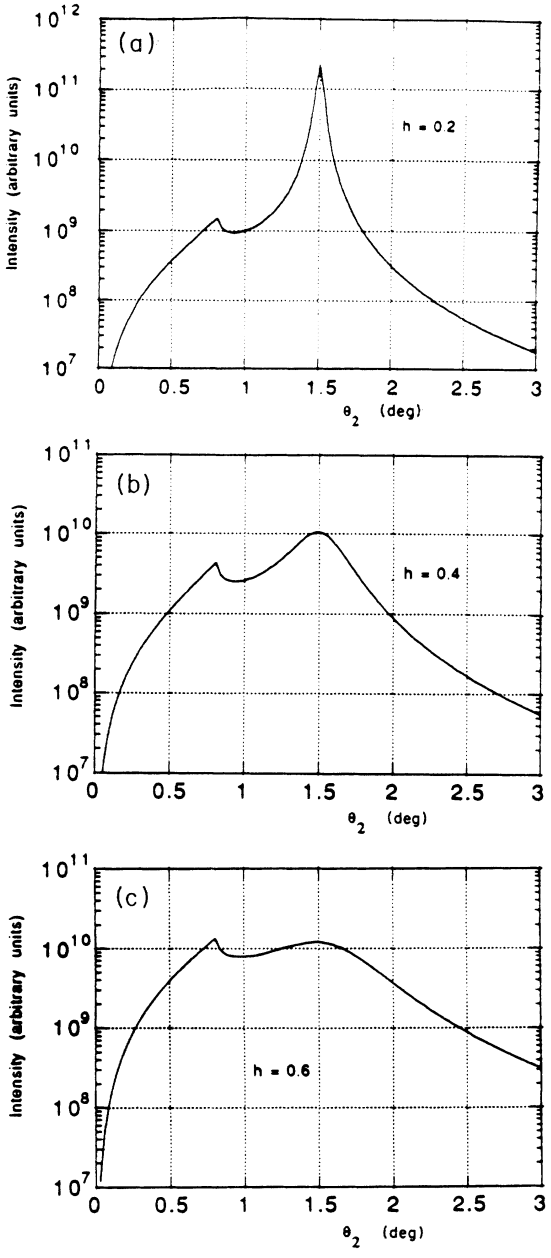

FIG. 3. Diffuse neutron scattering from a nickel surface with a roughness of standard deviation $\sigma=10$ Å, calculated for a neutron wavelength of 8 Å, a correlation range $\zeta=7000$ Å and an incident angle $\theta_1=1.5°$. The values of the self-affine index h are given in each part of the figure.

case, Newton observed a series of interference fringes that were later explained as the result of interference of two light rays scattered by each dust particle. One ray is reflected from the silvered surface and is then scattered by the dust particle, while the other is first scattered by the dust particle and then reflected by the silvered back of the mirror. In essence, light emanating from a dust particle and its image in the mirror interfere to produce the observed fringes.

To calculate the diffuse neutron scattering from a film with a rough air-film interface we again make use of Eq. (11), this time with the wave functions below the air-film interface replaced by analytic continuations of the wave functions above the surface. This gives

$$\langle \Psi_{2r}^{(-)}|V_2|\Psi_{1i}^{(+)}\rangle=(1-n^2)\frac{h^2k_1^2}{8\pi^2m}\int dx\int dy\int dz\, e^{-i\vec{\kappa}\cdot\vec{\rho}}[e^{-ik_{1z}z}+R_F(k_1)e^{ik_{1z}z}][e^{-ik_{2z}z}+R_F(k_2)e^{ik_{2z}z}]\,, \tag{24}$$

where R_F is the reflectivity of the film-substrate combination evaluated for a perfectly smooth air-film interface[20] and n is the refractive index of the film. Although the evaluation of the scattering cross section from Eq. (24) is somewhat tedious, it is straightforward. The result is

$$d\sigma/d\Omega = A\int dx\int dy\, e^{-i\vec{\kappa}\cdot\vec{\rho}} \times\sum_{n=1}^{n=6}\frac{(-1)^{n+1}}{f_n g_n}F_n e^{-(f_n^2+g_n^2)\sigma^2/2} \times\{\exp[(-1)^{n+1}f_n g_n C(\rho)]-1\}\,, \tag{25}$$

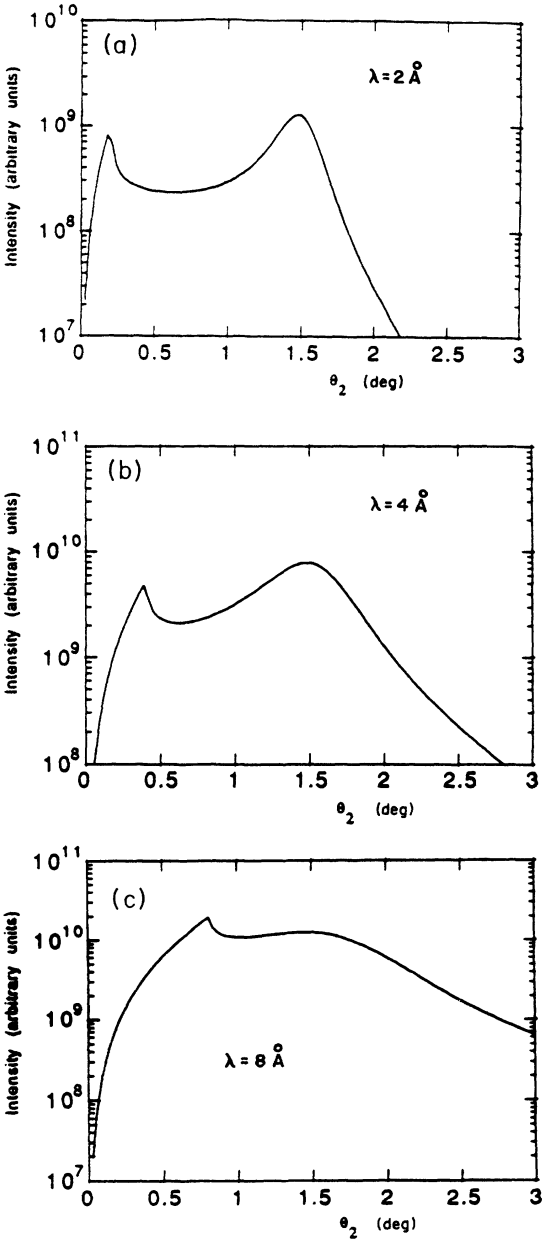

FIG. 4. Diffuse neutron scattering from a nickel surface with a self-affine index $h=0.8$, for various values of the neutron wavelength. The other parameters are the same as those used for Fig. 3.

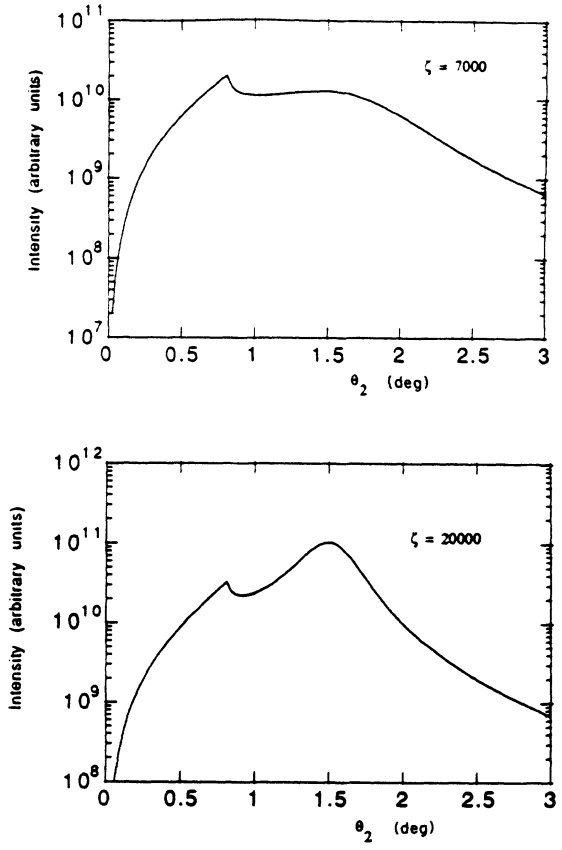

FIG. 5. The effect of the magnitude of the correlation range, ζ, on the diffuse neutron scattering from a rough nickel surface. The neutron wavelength is 8 Å and $h=0.8$. Other parameters have the same values as those used for Fig. 3.

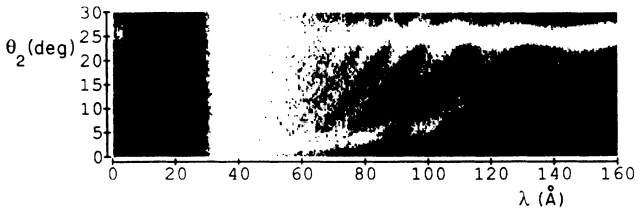

FIG. 6. Grey-scale representation of a result obtained with the neutron reflectometer SPEAR at the Manuel Lujan Jr. Neutron Scattering Center (LANSCE) using a sample composed of a 400-Å titanium film deposited on a sapphire substrate. Lighter shades represent greater intensity of scattered neutrons. The vertical axis represents angle of reflection from the surface while the horizontal axis is neutron wavelength binned in a nonlinear manner described in the text. The bright vertical stripe between wavelength channels ≈ 30 and ≈ 50 is background that is an artifact of the conditions under which the data were recorded. Both specular and diffuse scattering are included in this figure.

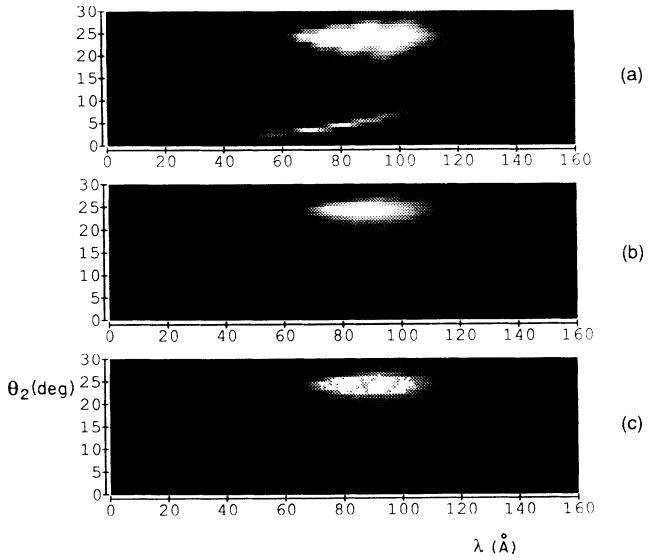

FIG. 7. Calculated diffuse scattering from a 400-Å titanium film on a sapphire substrate. The air-film interface is assumed to have a roughness described in terms of a self-affine correlation function [Eq. (21)] with $h=0.5$, $\sigma=20$ Å, and $\zeta=20{,}000$ Å. (a) smooth film-substrate interface: (b) film-substrate interface with a roughness amplitude $\sigma=20$ Å, with no correlation between the roughness of the two film surfaces: (c) perfect correlation between the roughness of the two film surfaces.

where
$A=(N_F b_F)^2 L_x L_y$ with $N_F b_F$ as the scattering length density of the film,

$$f_1=f_2=f_5=f_6=g_1=g_2=k_{1z}+k_{2z}\ , \tag{26a}$$

$$f_3=f_4=g_3=g_4=g_5=g_6=k_{1z}-k_{2z}\ , \tag{26b}$$

and

$$F_1=1+|R_F(k_{1z})|^2|R_F(k_{2z})|^2\ , \tag{27a}$$

$$F_2=2\,\mathrm{Re}[R_F(k_{1z})R_F(k_{2z})]\ , \tag{27b}$$

$$F_3=|R_F(k_{1z})|^2+|R_F(k_{2z})|^2\ , \tag{27c}$$

$$F_4=2\,\mathrm{Re}[R_F^*(k_{1z})R_F(k_{2z})]\ , \tag{27d}$$

$$F_5=2\,\mathrm{Re}[R_F^*(k_{2z})+R_F(k_{2z})|R_F(k_{1z})|^2]\ , \tag{27e}$$

$$F_6=2\,\mathrm{Re}[R_F^*(k_{1z})+R_F(k_{1z})|R_F(k_{2z})|^2]\ . \tag{27f}$$

In Eq. (27), Re indicates that the real part of an expression is to be taken. Figure 7(a) shows the result of evaluating Eqs. (25)–(27) for neutrons incident at a 1° grazing angle on a 400 Å film of titanium deposited on a sapphire substrate. The results have been multiplied by the wavelength-spectrum of neutrons used on SPEAR and are binned in the same way as the experimental data displayed in Fig. 6. To facilitate comparison with experimental data, the calculation includes an integration of the scattering over q_y. This does not change Fig. 7 qualitatively, however, because, for each neutron wavelength, the diffuse scattering takes the form of fringes parallel to q_y whose intensity decays with increasing values of $|q_y|$. Figure 7(a) clearly shows the interference fringes that one might have expected from the phenomenon first seen by Newton. Although the visibility of the fringes changes as σ, h, ζ, and the refractive index contrast of the film are varied, the spacing between the fringes depends only on the film thickness. The crescent-shaped feature rising from left to right at the bottom of the figure is the locus of critical angles for the sapphire substrate. Because titanium has a negative scattering length for neutrons, the critical angle for the film is imaginary and has no manifestation in Fig. 7(a). As a comparison of Fig. 6 and 7(a) makes clear, the shape of the calculated fringes is different from that observed in an actual experiment using SPEAR.

Since there is no reason to suppose that the titanium film used to obtain the results in Fig. 6 had only one rough surface, we consider next the effect of roughness at the film-substrate interface. To include this roughness in the calculation of diffuse scattering, one must include terms in Eq. (11) that represent this interface. The term that needs to be added to the matrix element is

$$\langle \Psi_{2r}^{(-)}|V_2|\Psi_{1i}^{(+)}\rangle=(1-n^2)\frac{h^2k_1^2}{8\pi^2 m}\int dx\int dy\int dz\, e^{-i\vec{\kappa}\cdot\vec{\rho}}T_F(k_1)T_F(k_2)e^{-i(k_{1z}^t+k_{2z}^t)z} \tag{28}$$

evaluated over the film-substrate interface. Here T_F is the transmission coefficient of the film-substrate combination[20] and n is the difference between the refractive indices of the substrate and the film. When both surfaces of the film are included, the squared t-matrix in Eq. (14) introduces contributions to the scattering that depend on the correlations between the roughness of the two film surfaces, as well as terms that involve each surface separately. The new terms that must be added to Eq. (25) are

$$\frac{d\sigma}{d\Omega}=\int dx \int dy\, e^{-i\vec{\kappa}\cdot\vec{\rho}} \times \left\{ \frac{A}{|\gamma|^2}|T_F(k_1)|^2|T_F(k_2)|^2 e^{-(\gamma^2+\gamma^{*2}\sigma_2^2}(e^{|\gamma|^2\langle\eta(\rho)\eta(0)\rangle}-1) + B\,\mathrm{Re}\sum_{n=1}^{n=4}\frac{(-1)^{n+1}}{f_n\gamma}G_n e^{-(f_n\sigma_1^2+\gamma\sigma_2^2)/2}(e^{(-1)^{n+1}f_n\gamma\langle\eta(\rho)\xi(0)\rangle}-1)e^{i\gamma t}\right\}, \quad (29)$$

where $A=(N_S b_S-N_F b_F)^2 L_x L_y$ and $B=(N_S b_S-N_F b_F)N_F b_F L_x L_y$. $(N_S b_S)$ is the scattering length density of the substrate, σ_1 and σ_2 are, respectively, the standard deviations of roughness at the air-film and film-substrate interfaces whose height coordinates are given by ξ and η, and t is the thickness of the film. The quantity γ is defined as

$$\gamma=k_{1z}^s+k_{2z}^s \quad (30)$$

in terms of wave vectors evaluated in the substrate material, and the G_n are given by

$$G_1=T_F(k_{1z})T_F(k_{2z}) , \quad (31a)$$

$$G_2=T_F(k_{1z})T_F(k_{2z})R_F^*(k_{1z})R_F^*(k_{2z}) , \quad (31b)$$

$$G_3=R_F^*(k_{2z})T_F(k_{1z})T_F(k_{2z}) , \quad (31c)$$

$$G_4=R_F^*(k_{1z})T_F(k_{1z})T_F(k_{2z}) . \quad (31d)$$

The term in Eq. (29) involving the constant A represents the contribution to the scattering from the roughness of the film-substrate interface and is the only term that needs to be added to Eq. (25) if there is no correlation between the roughnesses of the two film surfaces. One might guess the effect of this term from Newton's experiment described earlier: it corresponds to reducing the reflectivity of the silvering on the mirror and should therefore decrease the visibility of interference fringes. This result is confirmed by Fig. 7(b), which is calculated assuming roughness of equal amplitude at the two film surfaces and the same values for h and ζ at the two surfaces.

To include the effect of correlations between the two rough surfaces of the film, one must include the term involving the constant B in Eq. (29). When correlation between the two surfaces is perfect, that is when the surfaces are conformal, $\eta=\xi$, and Eq. (29) can be evaluated straightforwardly without introducing a further correlation function. In this case, the calculation [cf. Fig. 7(c)] shows that there is a qualitative change in the shape of the interference fringes which makes them look much more like the experimental results displayed in Fig. 6. The shape of the diffuse fringes thus appears to be a qualitative signature of a thin film with correlated rough surfaces. Although it is not obvious from Fig. 7, the overall intensity of the diffuse scattering in Figs. 7(b) and 7(c) is about a factor of 10 greater than in Fig. 7(a).

One might ask why the fringes in Fig. 7(a) and 7(c) have the same spacing. In the first case—analogous to Newton's experiment with the dusty mirror—the fringes result from interference between waves emitted in phase from two sources: the rough film-air interface and its image in the smooth film-substrate interface. The phase factor governing the spacing of the fringes is thus $\exp(2ik_z t)=\exp(iq_z t)$. When the two rough surfaces of the film are perfectly correlated, the fringes result from interference between waves scattered by two planes—the rough film surfaces—separated by a distance t. In this case the phase factor that determines the fringe separation is $\exp(iq_z t)$. Thus the interference fringes have the same separation in Figs. 7(a) and 7(c), even though the physics that produces them is somewhat different in the two cases.

It has been asserted[21] that, when the two rough surfaces of a film are perfectly correlated, the oscillations of the diffuse x-ray scattering at $q_x=0$ are in phase with oscillations in the specular reflectivity. This result is true provided the dominant oscillatory contribution arises from the final term in Eq. (29), that is, provided the contrast between the film and the substrate is large enough. In this case, the leading-order oscillatory contribution to the diffuse scattering involves G_1 [Eq. 31(a)], a function that tends to unity as q_z increases. The oscillatory behavior results from the $\exp(i\gamma t)$ phase factor in Eq. (29). For x-ray scattering this term has the same period and phase as the film reflectivity in the high-q_z limit. For neutrons, however, the situation *can* be different. If the material of the film has a negative scattering length density, the parameter B that appears in Eq. (29) may be negative so that the diffuse scattering from correlated roughness is exactly out of phase with the film reflectivity.[22] Thus neutrons may provide a very sensitive method of investigating correlations between the rough surfaces of a film if the film has a negative scattering length density. In practice, this situation can be achieved with many hydrogenated materials.

X-ray experiments to probe the effect of surface roughness on a wetting film have recently been published by Tidswell *et al.*[23] The equation used to fit the data obtained in these experiments was somewhat simpler than the full results presented here. Nevertheless, many of the important features of the complete results are captured in Ref. 23, at least to leading order in the surface roughness. For sufficiently small values of σ, the exponential terms involving $C(\rho)$ and Eqs. (25) and (29) may be expanded to leading order to give a linear approximation similar in spirit to that used by Tidswell *et al.* However, application of this expression to data taken over a range in which the maximum value of $q_z\sigma$ is much greater than ≈ 0.5 can only be justified phenomenologically. In Ref. 23 this form was used to represent data out of values of $q_z\sigma$ of about 2.

CONCLUSION

The theory presented in this paper resolves a number of inconsistencies in previously published studies of the effect of surface roughness on the reflection of neutrons and x rays at grazing incidence. Furthermore, it extends those studies to the case of thin films whose rough surfaces may be correlated. With the advent of powerful neutron and x-ray reflectometers, these theories can now be checked and used to obtain information about surface roughness in a number of interesting systems. In particular, it appears that diffuse neutron scattering from thin films may contain important clues about the correlations between roughness of the film's surfaces that could contribute to studies of the wetting of rough surfaces.[12] From the results presented here it is clear that a map of the diffuse scattering as a function of both q_z and q_x is required for a complete picture of correlations between the rough interfaces of a film. Simply recording the diffuse scattering for small values of q_x can be misleading. In this respect, reflectometers based at spallation neutron sources have an important advantage, because a complete map of diffuse scattering can easily be collected at the same time as measurements are made of the specular reflectivity.

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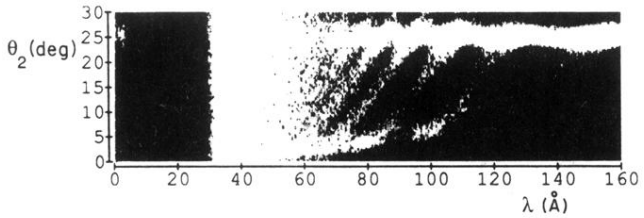
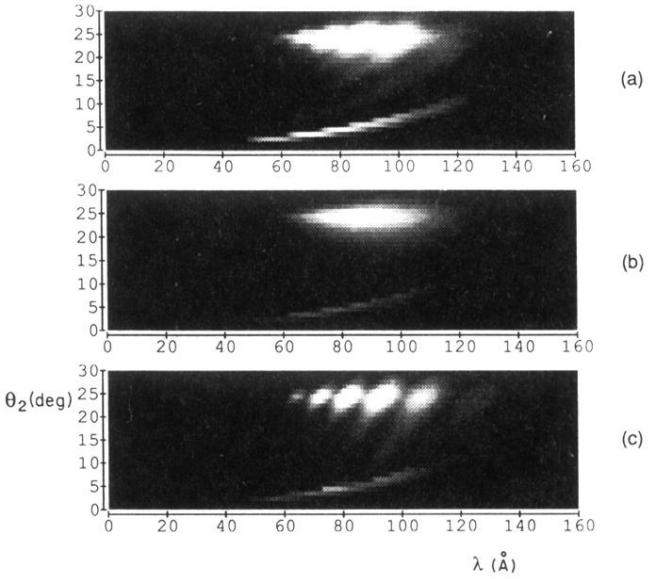


FIG. 6. Grey-scale representation of a result obtained with the neutron reflectometer SPEAR at the Manuel Lujan Jr. Neutron Scattering Center (LANSCE) using a sample composed of a 400-Å titanium film deposited on a sapphire substrate. Lighter shades represent greater intensity of scattered neutrons. The vertical axis represents angle of reflection from the surface while the horizontal axis is neutron wavelength binned in a nonlinear manner described in the text. The bright vertical stripe between wavelength channels ≈ 30 and ≈ 50 is background that is an artifact of the conditions under which the data were recorded. Both specular and diffuse scattering are included in this figure.



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