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# SURFACE ROUGHNESS BY X-RAY AND NEUTRON SCATTERING METHODS

## S.K. SINHA

Experimental Facilities Division, Argonne National Laboratory Argonne, IL 60439, USA

We discuss how the roughness and morphology of surfaces and interfaces can be characterized by the nondestructive techniques of X-ray and neutron scattering. We first discuss the mathematical description of rough surfaces in terms of correlation functions and then discuss the various kinds of rough surfaces which exist. These fall into the category of self-affine (Gaussian) surfaces, surfaces with capillary wave fluctuations, stepped surfaces, and surfaces with islands or pits. We then discuss how the scattering from such surfaces may be described and which types of information are available from specular reflectivity, off-specular (diffuse) scattering, and grazing incidence reflection experiments, including a comparison with results obtained by other surface techniques. We then discuss multiple rough interfaces and the scattering from thin films and multilayers. Finally, we shall discuss scattering of neutrons by magnetically rough surfaces and multilayers.

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## 1. Introduction

Over the last several years, there has been an increasing amount of interest in methods for characterizing both theoretically and experimentally, the morphology of surfaces and thin films. The performance of many thin-film devices, whether they are semiconductors, superconductors or magnetic materials, depends sensitively on the roughness and morphology of the interfaces.

Nevertheless, the manner in which this morphology depends on film growth methods and the manner in which the roughness affects the magnetic or transport properties of thin films is still poorly understood. X-rays and neutrons have proved to be powerful, non-destructive and in some cases, *in situ* probes for the study of the roughness and morphology of interfaces. While not yielding direct imaging information, as obtained from the complementary techniques of scanning probe microscopes, e.g., scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc., scattering experiments are capable of yielding *global* statistical information about interfaces over an enormous range of length scales (angstroms to microns). In addition, buried interfaces can be probed with ease. Consequently, the use of such techniques is becoming increasingly popular, particularly with the advent of high-brightness synchrotron sources of X-ray radiation.

## 2. Roughness at a single interface

As is well known, no surface is perfect in general, but almost always possesses some roughness. At the atomic level, crystal surfaces may have steps or clusters of atoms forming islands or plateaus. Amorphous surfaces may have random clusters of atoms, as may non-equilibrated sputtered films. Liquid surfaces will in general have capillary wave fluctuations on them. The problem in general then is (a) how to characterize the roughness and its morphology mathematically, (b) how to relate it to the scattering of radiation and (c) how to extract quantitative information about the surface roughness from scattering experiments.



Fig. 1. Schematic for X-ray surface scattering,  $k_0$ ,  $k_1$  are the incident and scattered wave vectors, respectively, making grazing angles  $\alpha$ ,  $\beta$ , respectively, with the average surface.  $q = k_1 - k_0$ .

Let us consider a surface centered on the plane z = 0, but with fluctuations  $\delta z(x, y)$  as a function of the lateral coordinates (x, y). Such fluctuations may often have a statistical distribution which is Gaussian, which we shall assume to be the case here. (The case of non-Gaussian roughness will be discussed later.) An important quantity is the mean-square height-deviation function  $g(\mathbf{R})$  ( $\mathbf{R} \equiv x, y$ ), defined by

$$g(\mathbf{R}) \equiv \langle [\delta z(\mathbf{r}) - \delta z(\mathbf{r} + \mathbf{R})]^2 \rangle \tag{2.1}$$

representing a statistical average over position r on the surface (see Fig. 1). A surface which is *self-affine* has the property that

$$g(R) \propto R^{2h},\tag{2.2}$$

where h (known as the roughness exponent) has a value between 0 and 1. The morphology of the roughness depends sensitively on h. For small h, the surface is sharp and jagged, while as h approaches 1, the surface becomes more gently rounded. h = 1/2 corresponds to the case of random-walk fluctuations. In order to be realistic at large values of R, we may introduce a cut-off length for the roughness  $\xi$  which makes g(R) saturate as  $R \to \infty$ , i.e., we write [1]

$$g(R) = 2\sigma^2 \left\{ 1 - \exp[-(R/\xi)^{2h}] \right\}.$$
(2.3)

Since  $\langle [\delta z(r)]^2 \rangle = \sigma^2$ , Eqs. (2.1) and (2.3) imply that

$$C(\mathbf{R}) \equiv \langle \delta z(\mathbf{r}) \delta z(\mathbf{r} + \mathbf{R}) \rangle = \sigma^2 \exp[-(R/\xi)^{2h}].$$
(2.4)

 $C(\mathbf{R})$  is referred to as the height-height correlation function. The justification of Eqs. (2.3) and (2.4) may to some extent be found in the equations which govern the growth of deposited films, such as the Kardar-Parisi-Zhang (KPZ) theory [2]. For such surfaces, the height function H(r,t) as a function of r and time is governed by an equation of the form

$$\frac{\partial H}{\partial t} = \gamma \nabla^2 H + \frac{\lambda}{2} (\nabla H)^2 + \eta(r, t), \qquad (2.5)$$

where  $\gamma, \lambda$  are constants and  $\eta(\mathbf{r}, t)$  is a white-noise random function. An analysis of the solutions of this equation, either numerically or using renormalization group methods, reveals that the corresponding width function (given by Eq. (2.1) with  $\delta z(\mathbf{r}, t) \to H(\mathbf{r}, t), g(\mathbf{R}, t)$  obeys the following scaling form:

$$g(\mathbf{R},t) = R^{2h}G(t/R^z),$$
 (2.6)

where G(x) is a scaling function, and h, z are scaling exponents. The scaling function G(x) must have the properties that

$$G(x) \rightarrow \text{constant} \quad \text{for} \quad x \gg 1,$$

$$G \to x^{2\beta} \quad \text{for} \quad x \ll 1.$$
 (2.7)

A function which satisfies these conditions is

$$G(x) = C_1 x^{2\beta} \left\{ 1 - \exp\left[ -\left(\frac{1}{2}\right)^{2\beta} \right] \right\}, \qquad (2.8)$$

where  $C_1$  is a constant. Substituting Eq. (2.8) into Eq. (2.6), it may be verified that we recover the form of Eq. (2.3) if

$$\sigma^2 = \left(\frac{1}{2}C_1\right)t^{2\beta} \tag{2.9}$$

 $\mathbf{and}$ 

 $\xi = t^{\frac{1}{2}},\tag{2.10}$ 

where  $\beta$ , h, and z satisfy the relation

$$z = h/\beta. \tag{2.11}$$

Thus, we conclude that a self-affine surface with a finite cut-off length for the roughness is consistent with growth models if we assume that it corresponds to the surface which results after *finite* growth time. Equations (2.9) and (2.10) are specific predictions for such growth models, and we shall discuss experimental tests for such models later. Regardless of the validity of growth models for surfaces, Eq. (2.4) seems to work remarkably well in describing a wide variety of rough surfaces encountered in nature, as deduced from both scattering experiments and direct imaging probes used to profile the surface [3]. Its convenience is that it characterizes the surface roughness mathematically in terms of three parameters, the root-mean-square roughness ( $\sigma$ ), the roughness exponent (h) and the roughness cut-off length ( $\xi$ ). Other forms have been proposed for the height-height correlation function (see for instance Palasantzas and Krim in Ref. [4]), but most of them do not show any preferred advantages. One slightly modified form which does have certain advantages was first proposed by Church [5] and later discussed by Palasantzas [6] and DeBoer [7] is

$$C(\mathbf{r}) = \frac{2h\sigma^2}{\Gamma(1+h)} \left(\frac{r\sqrt{2h}}{2\xi}\right) K_h\left(\frac{r\sqrt{2h}}{\xi}\right), \qquad (2.12)$$

where  $\Gamma(x)$  is the gamma function, and  $K_h(x)$  is the modified Bessel function of non-integral order. This has the advantage that it does yield an analytic expression for the Fourier transform of  $C(\mathbf{R})$  which is simply the noise spectral function  $(|\delta z(q)|^2)$ , i.e., it yields

$$\langle |\delta z(q)|^2 \rangle = \frac{A}{(2\pi)^5} \frac{\sigma^2 \xi^2}{(1+uq^2 \xi^2)^{1+h}},$$
(2.13)

where A, u are constants, and q is a two-dimensional wave vector in the x-y plane. Equations (2.12) and (2.13) also have the advantage that they show that  $C(R) \propto \ln R$  as  $h \to 0$ , making this a special case of the general form. (A logarithmic height-height correlation function is characteristic of liquid surfaces having capillary wave fluctuations [8], or a surface undergoing a roughening transition [9].)

## 3. Scattering by a single interface

Let us assume, for the moment, that the surface represents an interface between two media with uniform scattering length densities  $\rho_1$  and  $\rho_2$ . Let  $\Delta \rho = \rho_1 - \rho_2$ . (For X-ray scattering,  $\rho_1$  is simply the Compton scattering length  $(e^2/mc^2)$  times the electron number density, while for neutrons it is a weighted average of the coherent nuclear scattering length times the nuclear number density, averaged over all types of nuclei.) For scattering experiments (see Fig. 1), where the magnitude of the wave vector transfer q (defined as  $k_1 - k_0$ , where  $k_0$ ,  $k_1$  are the incident and scattered wave vectors of the radiation, making grazing angles  $\alpha, \beta$ , respectively, with the average surface) is small compared to the inverse of the interatomic distances, we may neglect the crystallinity of each medium, a topic to which we shall return. For experiments at small grazing angles, we may also neglect polarization effects in the X-ray scattering and consider for simplicity the case of X-rays polarized normal to the plane of scattering (TE polarization), so that we may use a scalar wave equation. Then the Born approximation for scattering yields

$$S(q) = (\Delta \rho)^2 \int \int d\mathbf{r} d\mathbf{r}' \exp[iq \cdot (\mathbf{r} - \mathbf{r}')], \qquad (3.1)$$

where the integral is over the volume on one side of the surface. (We may use periodic boundary conditions and a small absorption in the lower medium to ignore all surfaces except the one shown in Fig. 1, such as the surface at  $z \to \infty$ , etc.)

The integration over the z-coordinates may then be carried out in the above integral, yielding

$$S(q) = \frac{(\Delta \rho)^2}{q_z^2} \int \int \int \int dx dy dx' dy' \exp\{i\left[q_z(\delta z(x, y) - \delta z(x', y'))\right]\}$$
$$\times \exp\{i\left[q_x(x - x') + q_y(y - y')\right]\}.$$
(3.2)

Since  $\delta z(x, y)$  is a Gaussian random variable, carrying out a statistical average yields an integrand which depends only on the *relative* separation (X, Y) of the coordinates (x, y), (x', y'), and we obtain

$$S(q) = A \frac{(\Delta \rho)^2}{q_z^2} \int \int dX dY \exp\left[-\frac{1}{2}q_z^2 g(R)\right] \exp\left[-i(q_x X + q_y Y)\right], \quad (3.3)$$

where g(R) is defined by Eq. (2.1), and A is the surface area. Equation (3.3) may also be rewritten by using the relation between g(R) and the height-height correlation function as

$$S(q) = \frac{(\Delta \rho)^2}{q_z^2} A \exp(-q_z^2 \sigma^2) \int \int dX dY \exp[q_z^2 C(R)]$$
  
  $\times \exp\left[-i(q_x X + q_y Y)\right].$  (3.4)

Since  $C(R) \to 0$  as  $R \to \infty$  the integral in Eq. (3.4) contains a delta function which yields the specular reflectivity and we may write

$$S(q) = S_{\rm sp}(q) + S_{\rm diff}(q), \tag{3.5}$$

where

$$S_{\rm sp}(q) = 16\pi^2 A \frac{(\Delta\rho)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \delta(q_x) \delta(q_y)$$
(3.6)

and

$$S_{\text{diff}}(q) = A \frac{(\Delta \rho)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \int \int dX dY$$
  
 
$$\times \left\{ \exp[q_z^2 C(R)] - 1 \right\} \exp[-\mathrm{i}(q_x X + q_y Y)].$$
(3.7)

The specular part may be converted into an expression for the specular *reflectivity* by integrating over the detector solid angle and dividing by the incident beam intensity (see Ref. [1] for details) to yield

$$R(q_z) = R_{\rm F}(q_z) \exp(-q_z^2 \sigma^2), \qquad (3.8)$$

where  $R_{\rm F}(q_z)$  is identical to the limiting case of the Fresnel reflectivity from a smooth surface at large  $q_z$ ,

$$R_{\rm F}(q_z) = 16\pi^2 (\Delta \rho)^2 / q_z^4 \tag{3.9}$$

and Eq. (3.8) modifies it with a Debye-Waller-like factor due to the roughness "smearing" of the average surface. Equation (3.7) yields the off-specular or diffuse scattering in this approximation, which can only be written down as an analytical function of q for special cases [1], but may be calculated quite generally if the height-height correlation function is known. If sufficiently accurate data can be taken over a wide enough range of  $q_x$ ,  $q_y$  (e.g. with a linear or 2D position-sensitive detector) it may be possible to Fourier transform S(q) and thus invert Eq. (3.7) to yield g(R) directly. Such experiments have been done recently [10] and the g(R) obtained is consistent with the self-affine form given in Eq. (2.3). In other cases, forms such as given by Eqs. (2.3) or (2.4) have been used to fit scattering data, and compared into the corresponding statistical quantities derived by digitizing STM or AFM data taken on the same surfaces. These methods are now yielding consistent results [3].

## 4. Specular reflectivity

The case of specular reflectivity (where  $a = \beta$  and q is always exactly normal to the surface) has been widely discussed in the literature (see Ref. [11] and references therein, or Ref. [12]), and we now discuss it in slightly greater generality here. Let us for the moment ignore lateral fluctuations of the interface and replace the interface with an *arbitrary* graded density profile  $\rho(z)$  (averaged over the x-yplane). Then the generalization of Eq. (3.8) is [13]

$$R(q_z) = R_{\rm F}(q_z) \left| \frac{1}{\rho_0} \int \mathrm{d}z \frac{\mathrm{d}}{\mathrm{d}z} \rho(z) \exp(-\mathrm{i}q_z z) \right|^2, \tag{4.1}$$

where  $\rho_0$  is the asymptotic value of  $\rho(z)$  well inside the medium. This basically is the Born approximation result and is not accurate in the vicinity of and below the critical angle for that reflection. In such cases, there are well-known methods, used in optics (cf. Refs. [14], [15]) to solve for  $R(q_z)$  as accurately as we please by dividing  $\rho(z)$  into a set of histogram slices of constant  $\rho_i$  (i = 1, ..., N) and obtaining an iterative solution by matching boundary conditions at each interface. The method is basically numerical but quite accurate for large enough N. Using



Fig. 2. Specular reflectivity data for liquid alkanes with carbon members n = 18, 20 and 24, respectively at  $T_m + 4^{\circ}$ C (monotonically decreasing curves) and  $T_m + 3^{\circ}$ C (oscillating curves), where  $T_m$  is the freezing temperature for each. The inset shows a fit of the electron density at the interface (z = 0) for  $T_m + 3^{\circ}$ C.

this method or Eq. (4.1), one may attempt to obtain  $\rho(z)$  from the measured reflectivity function. In general, a unique solution cannot be obtained because of the lack of phase information in  $R(q_z)$  as is evident from Eq. (4.1) but reasonable density profiles can often be obtained by fitting and other methods. Gaussian roughness corresponds to  $d\rho/dz$  being a Gaussian function of z and yields exactly Eq. (3.8) again. Another special case is a uniform thin film on a substrate of different density. Neglecting roughness, this yields two delta functions in  $d\rho/dz$ separated in z by  $\Delta$ , the film thickness, and from Eq. (4.1) this leads to modulations in  $R(q_z)$  with successive maxima separated by  $\Delta q_z = 2\pi/\Delta$ . This may be thought of as interference fringes from scattering by the top and bottom surfaces of the film and are known as *Kiessig fringes*.

An example of the use of such techniques is the use of specular reflectivity from a liquid surface to study surface crystallization. Figure 2 shows the reflectivity from the surface of three liquid alkanes (with carbon numbers C<sub>18</sub>, C<sub>20</sub> and C<sub>24</sub>, respectively) at  $T_m + 4^{\circ}C$  and  $T_m + 3^{\circ}C$ , where  $T_m$  is the bulk crystallization temperature. At the higher temperature, the reflectivity corresponds to that of a bulk liquid, with a root-mean-square roughness  $\sigma = 4.1-4.7$  Å, arising from surface capillary waves (see next section). However, the development of modulations at the lower temperature clearly shows the existence of a denser molecular layer at the liquid surface. By fitting the data, the thickness of the layer (see inset to Fig. 2) was found to be very close to the length of the alkene molecule, and the electron density of the layer to correspond closely to that of the bulk "rotator" phase of the alkane [16]. These results, combined with further investigations of the in-plane structure using grazing incidence diffraction, and with surface tension measurements, revealed that liquid alkanes actually first crystallize in a surface layer a few degrees above the bulk freezing transition (for carbon numbers greater than C12). The same behavior has been found in long chain alcohols [17] and liquid alkane mixtures [18]. Similar behavior was seen earlier in liquid crystals [19].

#### 5. Diffuse scattering from a rough surface

The Born approximation results are only valid if the scattering is weak, which will be the case when  $\alpha$  or  $\beta$  (Fig. 1) are small or close to the critical angle for total reflection. A slightly better approximation in this case is to use the so-called distorted wave Born approximation (DWBA). In this case, instead of using plane waves to calculate the matrix elements of the scattering as in the Born approximation, one uses the actual wave functions which closely approximate the actual system, i.e. one may use the true wave functions for reflection and transmission at the corresponding smooth surface. In this case, the main effect on  $S_{\text{diff}}(q)$  as given by Eq. (3.7) is to modify it to

$$S_{\text{diff}}(q) = |T(\alpha)|^2 |T(\beta)|^2 A \frac{(\Delta \rho)^2}{|\bar{q}_z|^2} \exp\left[-\frac{1}{2}(\bar{q}_z^2 + \bar{q}_z^{*2})\sigma^2\right] \\ \times \int \int dX dY \left\{\exp[|\bar{q}_z^2|C(R)] - 1\right\} \exp\left[-i(q_x X + q_y Y)\right],$$
(5.1)

where  $T(\alpha)$  is the Fresnel transmission coefficient of the *average* interface for grazing angle of incidence  $\alpha$ , and  $\bar{q}_z$  is the z-component of the wave vector transfer



Fig. 3. Typical transverse diffuse scan for Ag deposited on Si, showing the specular peak, diffuse scattering and Yoneda wings referred to in the text.

in the medium under the surface (which may be complex or even purely imaginary for evanescent waves in the case of total external reflection). The main effect of this is to produce side-peaks in the transverse diffuse scans (rocking curves) when  $\alpha$  or  $\beta$  is equal to the critical angle, since at that point  $T(\alpha)$  reaches a maximum value of 2, the incident, and specularly reflected waves being in phase so that the field at the surface is at a maximum. Such side-peaks are known as "Yoneda wings" [20] (see Fig. 3). For large  $\alpha$ ,  $\beta$  and hence large  $q_z$ , Eq. (3.7) is a good approximation, and we may neglect the difference between  $q_z$  and  $\bar{q}_z$ . For large  $q_z$ but with  $q_x = q_y \approx 0$ , it may be shown that  $S_{\text{diff}}$  has the asymptotic form [1]

$$S_{\rm diff}(q) \approx q_{\star}^{-(2+2/h)},\tag{5.2}$$

so that the exponent h may be found from such asymptotic power laws. For many experiments, the instrumental resolution in the direction of q out of the scattering plane is kept rather loose, i.e.  $q_y$  is effectively integrated over (if the plane of scattering is defined as the x-z plane). Then Eq. (3.7) shows that what is measured is

$$I(q_x, q_z) = 2\pi A \frac{(\Delta \rho)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \int dX$$
  
 
$$\times \left\{ \exp[q_z^2 C(X)] - 1 \right\} \exp(-iq_x X),$$
(5.3)

i.e. a one-dimensional, rather than a two-dimensional Fourier transform. For isotropic rough surfaces, this yields the same information, but may be misleading if the surface is *anisotropic* (e.g. miscut single crystal surfaces with steps). The asymptotic form in this case which corresponds to Eq. (5.2) is

$$I(q_x \approx 0, q_z) \approx q_z^{-(2+1/h)}.$$
 (5.4)

The specular reflectivity is also modified in the DWBA from the simple expression Eq. (3.8), and is replaced by the form

$$R(q_z) = R_{\rm F}(q_z) \exp(-q_z \bar{q}_z \sigma^2) \tag{5.5}$$

which was first derived by Nevot and Croce [21]. However, DeBoer has recently considered going to *second order* in the DWBA [7] and finds that if the roughness cut-off length is small then Eq. (3.8) (known as the "Rayleigh expression" for the reflectivity) is actually a better approximation than the Nevot-Croce expression.

In the case of liquid surfaces, surface roughness is due to capillary wave fluctuations. There are some problems in connection with a truly first-principle calculation of such fluctuations (for a recent discussion, see Ref. [22]), but one may write down at least a phenomenological expression for the surface free energy of the liquid and derive from it the spectral function for surface height fluctuations in the form

$$\langle |\delta z(q)|^2 \rangle = \frac{kT}{\gamma(q^2 + \kappa^2)},\tag{5.6}$$

where  $\gamma$  is the surface (or interface) tension, and  $\kappa$  is the inverse of the capillary length defined by  $\kappa^{-1} = (\Delta \rho_0)g/\gamma$ ,  $\Delta \rho_0$  being the mass-density difference between the fluids on either side of the interface.  $\kappa$  is typically of the order of 10 cm<sup>-1</sup>. Fourier transformation of Eq. (5.6) leads to a form for the height-height correlation function

$$C(r) = -\frac{1}{2}BK_0(\kappa r), \qquad (5.7)$$

where

$$B = kT/\pi\gamma \tag{5.8}$$

and  $K_0(x)$  is the modified Bessel function. At length scales  $\ll \kappa^{-1}$  (which are in practice those relevant for scattering experiments) the Bessel function may be replaced by a logarithm and to prevent short (molecular) length scale problems we may also introduce a lower length scale cut-off [23]. Thus, we finally write

$$C(r) = -B \ln \left[ \kappa (r^2 + r_0^2)^{\frac{1}{2}} \right],$$
(5.9)

where  $r_0$  is defined to give the correct lateral surface roughness, given by the integral of Eq. (5.6).

Substituting this in Eq. (5.1) we may calculate the scattering in the DWBA, after folding with the resolution function. As shown by Sanyal et al. [24], the logarithmic form yields asymptotic power laws for S(q) as a function of transverse q at fixed  $q_z$ , as in the case of a 2D crystal with algebraic correlations. These are smeared out at small transverse q due to instrumental resolution effects [24]. The exponent of the power law  $\eta$  is equal to  $(1/2)Bq_z^2$  which can be calculated knowing the surface tension. Good agreement was obtained with the observed scattering from ethanol at room temperature. Braslau et al. [25] had earlier studied the specular and diffuse scattering from water and shown that the mean square roughness  $\sigma^2$  obtained from specular reflectivity experiments is decreased by an amount  $(\frac{1}{2}B \ln \frac{q_{\max}}{q_{\min}})$ , where  $q_{\max}$  is the short-wavelength cut-off ( $\approx r_0^{-1}$ ) and  $q_{\min}$  is the instrumental resolution cut-off, which pre-empties the capillary length cut-off  $\kappa$ ,

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since it is in general much larger. Thus we have in principle to correct for the instrumental resolution when we measure the roughness of a liquid surface using specular X-ray reflectivity. The dependence of the cut-off  $q_{\max}$  on molecular dimension has been checked by Ocko et al. [26].

## 6. Scattering by multiple interfaces

When one has a thin film on a substrate or a multilayer, the roughness at the various interfaces may be correlated. This is indicated in Fig. 4, which shows clearly in a sectioned TEM micrograph of a multilayer how interface fluctuations propagate from the substrate to each deposited interface. The roughness is said to



Fig. 4. Micrograph of a Nb/Si multilayer (after sectioning) showing the conformal roughness (plus independent random fluctuations) of the interfaces (from E.B. Fullerton, J. Pearson, C.H. Sowers, S.D. Bader, X.Z. Wu, S.K. Sinha, *Phys. Rev. B* 48, 17432 (1993)).

be "conformal" in such cases. We may discuss the scattering from such interfaces in terms of the height-height correlation function between different interfaces, i.e. we generalize Eq. (2.4) to define

$$C_{ij}(R) = \langle \delta z_i(r) \delta z_j(r+R) \rangle, \tag{6.1}$$

 $z_i(r)$ ,  $z_j(r+R)$  are now height fluctuations of the *i*-th and *j*-th interfaces. The generalization of Eq. (3.7) for the diffuse scattering in the Born approximation is [27-31]

$$S_{\text{diff}}(q) = (A/q_z^2) \sum_{i,j=1}^{N} \exp\left\{-\frac{1}{2}q_z^2[\sigma_i^2 + \sigma_j^2 + \delta^2(i-j)]\right\} \\ \times \Delta \rho_i \Delta \rho_j \exp[iq_z(z_i - z_j)]E_{ij}(q),$$
(6.2)

where

$$E_{ij}(q) = \int \int dX dY \left\{ \exp[q_z^2 C_{ij}(R)] - 1 \right\} \exp[-i(q_x X + q_y Y)]$$
(6.3)

and  $\sigma_i$  is the root-mean-square roughness of the *i*-th interface,  $\Delta \rho_i$  is the scattering length density contrast across it,  $z_i$  is its average height, and  $\delta$  is the

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Fig. 5. (a) Specular reflectivity and longitudinal diffuse scattering from a wetting film of water on a glass substrate, showing conformal roughness as evidenced by Kiessig fringes in the diffuse which mirrored those in the specular. (b) Longitudinal diffuse scattering from a GaAs/AlAs multilayer showing conformal roughness, as evidenced by the "quasi-Bragg" peaks. The solid line is a fit to the data assuming perfect conformal roughness (from Ref. [29]).

root-mean-square deposition error in the layer spacing, which is cumulative from layer to layer. If there is no correlation between the interfaces,  $C_{ij}(R) = 0$  for  $i \neq j$  and Eq. (6.2) reduces to the sum of the diffuse scattering from the individual

interfaces. However, in general  $C_{ij}(R) \neq 0$ , and the phase factors  $\exp[iq_z(z_i - z_j)]$ in Eq. (6.2) will cause the diffuse scattering to peak in ridges of constant  $q_z$  at the  $q_z$  values corresponding to the maxima in the specular reflectivity, i.e. at the Kiessig fringe maxima in the case of a thin film on a substrate, or at the positions of the multilayer Bragg peaks in the case of multilayers [27-31]. This is illustrated in Figs. 5a and 5b for a single thin film of water wetting a glass substrate [32], and for a multilayer film, respectively [29]. The fringes and peaks due to conformal roughness between the interfaces is quite evident. In the case of the multilayer, an excellent fit was obtained to the data using the expression in Eq. (6.2) and assuming perfect conformality between all the interfaces, i.e.  $C_{ij}(R)$  independent of i, j [29]. Most thin films, unless extremely rough, show a degree of conformality with the substrate over often surprisingly large thicknesses. For multilayers, Stearns et al. [33] have developed a theoretical model for the propagation of conformal height fluctuations through a multilayer. They approach it from the noise spectral function, or the Fourier transform of C(R), since the conformality is obviously a function of the lateral Fourier component of the fluctuations, i.e. large q (rapid) fluctuations will be more likely to be uncorrelated than small q (long wavelength) fluctuations. For the case of liquid films wetting a rough substrate, Andelman et al. [34] have calculated theoretically the amplitude of the fluctuations of the upper surface of the liquid film in terms of those of the substrate and shown that the coefficient of proportionality depends on the lateral wave vector q of the fluctuation, the liquid/vapor surface tension, and the interaction between the liquid and the substrate. Recent X-ray scattering experiments on thin liquid [35] and polymer [36] films have been used to check the predictions of these types of theories, with on the whole satisfactory results.

For multiple interfaces, going beyond the Born approximation becomes very complicated [30, 37]. We cannot go into the details here, but simply point out that, in the vicinity of both the critical angles for total reflection and the angles for multilayer Bragg reflections, the use of the DWBA, or the "dynamical theory" (where one uses the true eigenfunctions) [38] yields an additional sharp structure in the diffuse scattering due to multiple wave interfaces. These are the generalizations of the "Yoneda wings" seen for single interfaces and discussed in Sec. 3.

## 7. Scattering by non-Gaussian surface fluctuations

Many kinds of surfaces have specific surface features that cannot be discussed within the random Gaussian self-affine model of roughness discussed in Sec. 2. Examples are surfaces with islands of fixed or variable heights above the reference surface, surfaces with pits (as in the case of corrosion), surfaces with steps, etc. In order to discuss the scattering from such surfaces in the Born approximation, we must go back to the basic formula for S(q) given in Eq. (3.2). Let us for the moment imagine that the height function z(x, y) for the interface has a bimodal distribution, being 0 with probability  $P_1(x, y)$  and  $\Delta$  with probability  $P_2(x, y) =$  $1 - P_1(x, y)$ . (This corresponds to islands of fixed height  $\Delta$  across the interface.) Then Eq. (3.2) may be written as

$$S(q) = \frac{A(\Delta \rho)^2}{q_z^2} \int \int dX dY \left\{ [P_1(0,0)P_1(X,Y) + P_2(0,0)P_2(X,Y)] \right\}$$

$$+P_{1}(0,0)P_{2}(X,Y)\exp(-iq_{z}\Delta) + P_{2}(0,0)P_{1}(X,Y)\exp(iq_{z}\Delta)\}$$

$$\times \exp[-i(q_{x}X + q_{y}Y)].$$
(7.1)

Writing  $\phi$  for the fractional coverage of islands, we may express the above in terms of the two-dimensional analogue  $\gamma_0(x, y)$  of the Debye correlation function related to the probability of crossing over from no island to an island within a relative separation of (x, y), and obtain

$$S(q) = S_{\text{spec}}(q) + S_{\text{diff}}(q), \tag{7.2}$$

where

$$S_{\rm spec}(q) = \frac{A4\pi^2 (\Delta \rho)^2}{q_z^2} \delta(q_x) \delta(q_y) \left[ 1 - 4\phi(1-\phi) \sin^2(q_z^2 \Delta/2) \right]$$
(7.3)

and

$$S_{\text{diff}}(q) = \frac{A(\Delta\rho)^2}{q_z^2} (1-\phi) \sin^2(q_z^2 \Delta/2) \int \int \mathrm{d}x \mathrm{d}y \\ \times \gamma_0(x,y) \exp[-\mathrm{i}(q_x X + q_y Y)].$$
(7.4)

Note that the longitudinal diffuse scattering  $(q_x, q_y \approx 0)$  has a modulation along  $q_z$  with period  $(2\pi/\Delta)$  which is exactly out of phase with a similar modulation in the specular reflectivity. This is in contrast to the case of conformal roughness, where the Kiessig fringes in the specular and the diffuse are in phase. The above theory can be easily generalized to the case of a film with islands deposited on a substrate, and to include roughness fluctuations as well. The expression for the specular reflectivity may be written as

$$R(q_z) = \frac{16\pi^2}{q_z^4} \Big\{ \rho_1^2 \exp(-q_z^2 \sigma_1^2) \left[ 1 - 4\phi(1 - \phi) \sin^2(q_z \Delta/2) \right] \\ + (\rho_2 - \rho_1)^2 \exp(-q_z^2 \sigma_2^2) + 2\rho_1(\rho_1 - \rho_2) \exp\left[ -\frac{1}{2} q_z^2(\sigma_1^2 + \sigma_2^2) \right] \\ \times \left[ \phi \cos(q_z(t + \Delta)) + (1 - \phi) \cos(q_z t) \right] \Big\},$$
(7.5)

where t is the total film thickness,  $\rho_1$  is the film electron density,  $\rho_2$  — that of the substrate and  $\sigma_1$ ,  $\sigma_2$  are the roughness values at the film/air and film/substrate interfaces, respectively. This reflectivity expression yields both the rapid Kiessig fringes, as well as modulations due to the islands on the surface. Figure 6 shows the specular reflectivity and longitudinal diffuse scattering from a polymer film decorated with such islands, where both the Kiessig fringes (which appear in phase in the specular and the diffuse scattering due to conformal roughness of the film and substrate) and the "island modulations" (which are out of phase in the specular and in the diffuse) are observed [39]. Figure 7 shows transverse diffuse scats (rocking curves) obtained for another system studied, namely a copper film in contact with an electrolyte in an electrochemical cell to which a negative (oxidizing) voltage is applied, as a function of the time for the applied voltage [40]. It may be seen that side peaks grow in the diffuse scattering on either side of the specular reflection. This is a consequence of the pit correlations, which are reflected in a peak in the Fourier transform of the  $\gamma_0(x, y)$  function.

Steps on a surface can result from a miscut of a single crystal surface relative to high symmetry crystallographic planes, of facets, and such steps lead to

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Fig. 6. Specular and longitudinal diffuse scattering as a function of  $q_z$  for a polystyrene/PMMA film decorated with islands on the surface. The fitted curves are not shown for clarity as they are indistinguishable from the experimental curves (from Ref. [39]).



Fig. 7. Transverse diffuse scans for a copper film on silicon in contact with an electrolytic solution at a voltage of +0.5 V for various times of application of the voltage (from Ref. [40]).

roughness which is very anisotropic. The steps can be quasi-periodic and of uniform height, resulting in satellite peaks about the specular position [41], or they can meander in a disordered way and give rise to a characteristic diffuse scattering which has been discussed elsewhere [31]. At the so-called "roughening transition" [9], the height-height correlation function between the steps becomes logarithmic, as for a liquid surface with capillary wave fluctuations, and results in power-law tails in the transverse diffuse scans.

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