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Non-Gaussian Roughness of Interfaces: Cumulant Expansion in X-ray and Neutron Reflectivity

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Abstract

Within the Born approximation, a cumulant expansion is used for the formulation of X-ray or neutron reflectivity. Odd- (third-) order cumulants indicate asymmetric profiles; they may only be detected in layer systems *via* a Q_z dependence of the oscillation period of Kiessig fringes. Fourth-order cumulants are also visible in the larger Q_z regime for single interface systems. As an example of an asymmetric surface, a triangular height distribution function is discussed.

1. Introduction

When X-rays or neutrons are scattered from surfaces and interfaces, both a specular and a diffuse contribution are observed. In the past few years the scattering theory has been considerably advanced and now can deal with both contributions rather well. The major breakthrough for scattering in the small-angle regime came with the formulation of the scattering from rough surfaces within the distorted-wave Born approximation (Vineyard, 1982) and the use of a fractal description of interfaces (Sinha, Sirota, Garoff & Stanley, 1988). Recently, this approach has been generalized for layer systems (Pynn, 1992; Holý, Kuběna, Ohlídal, Lischka & Plotz, 1993; Holý & Baumbach, 1994). There are several applications which make use of this theory (Bahr, Press, Jebasinski & Mantl, 1993; Schlomka *et al.*, 1995; Schlomka *et al.*, 1996; Jenichen, Stepanov, Brar & Kroemer, 1996; Stettner *et al.*, 1996). In many cases, the best results are achieved and a more stable set of surface parameters is obtained when true specular and diffuse scattering are refined simultaneously. In this context, a problem has arisen: sometimes, but not always, a sizable difference between the r.m.s. roughness σ obtained from the true specular reflectivity and that from the simultaneous fit (the σ tends to be large) is found (Schlomka *et al.*, 1995; Lütt *et al.*, 1997). This may be related to a premise in the scattering theories mentioned above: they all rely on a Gaussian height distribution $p(z)$ of width σ of a rough interface. An analysis of reflectivity data alone need not follow this restriction.

There are several ways of generating density profiles from reflectivity data, more precisely from true specular reflectivities, where the diffuse scattering has been subtracted from the measured reflectivity. It is a matter of fact that, in general, there is no way to reconstruct a density profile from a single reflectivity measurement. The measurement of intensities introduces the well known phase problem and leads to ambiguities in the reconstruction of profiles. Several efforts have been made in the past to overcome this problem, both theoretically (Clinton, 1993; Lipperheide, Reiss, Fiedeldey, Sofianos & Leeb, 1993) and experimentally (Sivia, Hamilton, Smith, Rieker & Pynn, 1991; Felcher, Dozier, Huang & Zhou, 1992; Sanyal *et al.*, 1993; Majkrzak & Berk, 1995). Anomalous dispersion (X-rays) or the magnetic contribution from a reference layer (neutrons) are used to give two prominent methods.

We have looked into this problem again, with special emphasis on the description of interfaces beyond Gaussian height distributions and uniqueness of the determined profiles. A cumulant expansion of the amplitude of the field reflected from an interface with non-Gaussian roughness is used in kinematic calculations.

Simple model profiles which are non-Gaussian are studied within a Fresnel-type description (without approximations) using matrix methods (Abelés, 1950; Parratt, 1954; Lekner, 1987). For angles of reflection $\alpha_i > 3\alpha_c$ (with the critical angle α_c), these calculations agree with the kinematic approach. Several conclusions, pertaining both to surfaces and interfaces (we first restrict ourselves to a single layer), can be drawn. The loss of information when taking the modulus (squared) of Fourier-transformed distributions becomes quite obvious, particularly for a single interface.

2. Cumulant expansion for describing rough surfaces

Cumulant expansions (Kendall, 1994) are rather frequently used in crystallography. They describe the scattering from atoms and molecules performing large-

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amplitude motions, both translational and orientational (Willis & Pryor, 1975; Johnson, 1969). Accounts of this can be found in the *International Tables of Crystallography* (and references therein) and in a recent review (Kuhs, 1992).

Cumulant expansions can also be usefully applied to interfaces with non-Gaussian roughness. The reflection from interfaces is only sensitive to the corresponding projection of the height function $z(\mathbf{r})$ [$\mathbf{r} = (x, y)$ is a vector parallel to the surface] onto the interface normal z. Therefore, only a one-dimensional description is needed. The reflectivity within the kinematic theory can be written as (Als-Nielsen *et al.*, 1994)

$$R \simeq R_F \left| \frac{1}{\rho_{\rm av}} \int \frac{{\rm d}\rho(z)}{{\rm d}z} \exp(iQz)\,{\rm d}z \right|^2 . \quad (1)$$

Here, R_F is the Fresnel reflectivity ($\propto Q^{-4}$ for large Q), $\rho(z)$ is the density profile (with $\rho_{\rm av}$ the average density) and $p(z) \propto {\rm d}\rho(z)/{\rm d}z$ the height distribution function; $Q = Q_z$ is the momentum transfer perpendicular to the surface. Apparently, the change in the density profile at an interface determines the contrast. To be more exact, 'density profile' means the profile of the refractive index $n = 1 - \delta - i\beta$, where δ is the dispersion and β the absorption of the respective material. For X-rays, the dispersion is almost proportional to the electron density; for neutrons it is proportional to the scattering length density.

2.1. *Single surface*

Instead of modelling the interface profile in direct space, the Fourier-transformed quantity $\int[{\rm d}\rho(z)/{\rm d}z]\exp(iQz)\,{\rm d}z$ is expanded. We obtain

$$\frac{1}{\rho_{\rm av}} \int \frac{{\rm d}\rho(z)}{{\rm d}z} \exp(iQz)\,{\rm d}z \simeq e^{iQz}e^{-1/2Q^2\sigma^2}e^{-1/6iQ^3K^{(3)}}e^{1/24Q^4K^{(4)}}. \quad (2)$$

$K^{(l)}$ denotes the cumulant of order l. With restriction to terms of order $l \leqslant 2$ the usual (harmonic) Debye–Waller-like factor results. Higher-order terms ($l \geqslant 3$) describe anharmonic motions in crystallography. In our case, the term with $l = 3$ is related to the asymmetry of the height distribution $p(z)$ and $l = 4$ to symmetric deviations from the Gaussian shape [$K^{(4)} < 0$ 'flatter', $K^{(4)} > 0$ 'steeper' than a Gaussian]. A more quantitative formulation is provided by the relation to the moments $M^{(l)} = \int z^l p(z)\,{\rm d}z$ of the distribution $p(z)$. When taking $M^{(1)} = 0$ (then $z_0 = 0$ marks the mean interface position), one obtains

$$M^{(2)} = K^{(2)} = \sigma^2$$
$$M^{(3)} = K^{(3)} \quad (3)$$
$$M^{(4)} = K^{(4)} + 3K^{(2)2}$$

The relation between moments and cumulants up to the tenth order is given by Kendall (1994). Unfortunately, no unambiguous reconstruction of the distribution $p(z)$ from a finite number of cumulants is possible. Realistically, one may hope to determine the cumulants up to order $l = 4$ from a reflection experiment.

Calculating the reflectivity makes it obvious that the situation is even worse. From equations (1) and (2), it is clear that only cumulants of even order can be determined. As $|e^{i\alpha}| = 1$, odd-order terms do not affect the reflectivity R and, hence, the asymmetry of an interface (more precisely, the asymmetry of its height distribution function) cannot be determined from a simple reflection experiment. This is a demonstration of the phase problem already mentioned in the introduction.

The resultant ambiguities are demonstrated with a triangle as model height distribution (Fig. 1), which corresponds to a parabolic interface profile. In comparison to a Gaussian distribution function, which has only a nonzero second-order cumulant, the triangular dis-

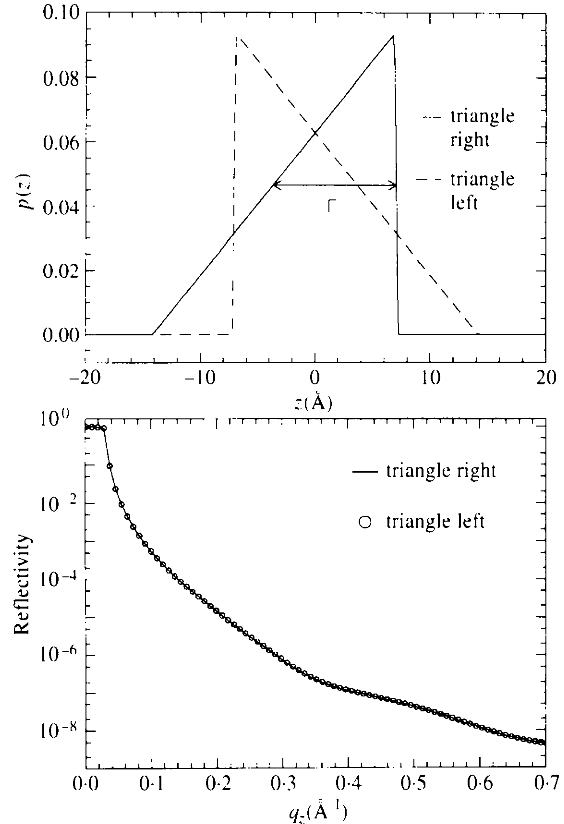

Fig. 1. The two triangular probability functions (top) result in the same reflectivity curve (bottom) in the case of a single interface. The third-order cumulant is negative for the 'triangle right' profile, positive in the other case. For the calculation of the reflectivity, a silicon substrate (refractive index $n = 1 - 7.56 \times 10^{-6} - i1.73 \times 10^{-7}$) with roughness $\sigma = 5$ Å and an X-ray wavelength of 1.54 Å (Cu $K\alpha$) was assumed.

tribution also has nonzero cumulants of higher order. The two distributions 'triangle left' and 'triangle right' shown in Fig. 1 differ in the sign of the odd-order cumulants. Independently of the sign, the same reflectivity results.

Since one obviously cannot determine asymmetric components, it may be advisable to adopt the symmetric solution $\tilde{p}(z) = 1/2[p(z) + p(-z)]$ in the single interface case.

To estimate roughly the effect of higher-order cumulants, we calculate the even-order cumulants for the profile in Fig. 1. [Γ is the full width at half-maximum (FWHM) of the distribution]

$$\begin{aligned} K^{(2)} &= 2/9\Gamma^2 \\ K^{(4)} &= -4/135\Gamma^4. \end{aligned} \tag{4}$$

One calculates from equation (2) that intensities $I(Q)$ have to be measured up to $Q \simeq 3/\Gamma \simeq 1.5/\sigma$ to obtain a 10% contribution from the fourth-order term. For a roughness $\sigma = 5$ Å, this requires a dynamic range of at least six orders of magnitude, which can be obtained with good laboratory sources.

2.2. *Two interfaces*

The reflectivity of a layer on a substrate (two interfaces) reads as follows (always within the Born approximation) (Als-Nielsen *et al.*, 1994)

$$\begin{aligned} R &\simeq R_F|F(Q)|^2 \\ &\propto R_F|\Delta\rho_1 \prod_m \exp[i^m Q^m K_1^{(m)}/m!] \\ &\quad + \Delta\rho_2 \prod a_l \exp[i^l Q^l K_2^{(l)}/l!)|^2. \end{aligned} \tag{5}$$

Here $\Delta\rho_j$ refers to the change in electron density (or neutron scattering length density) at the respective interface and $K_1^{(m)}, K_2^{(l)}$ are the cumulants of the two interface profiles. Differences of odd-order cumulants now appear in the interference terms, proportional to (neglecting cumulants of order >3)

$$\cos[Q(z_2 - z_1) - Q^3(K_2^{(3)} - K_1^{(3)})/6]. \tag{6}$$

The dominant contribution, at least at small Q, is the modulation of the intensity with a period $\Delta Q = 2\pi/d$, sometimes called Kiessig fringes, with the layer thickness $d = z_2 - z_1$. After introducing the difference $\Delta K^{(3)} = K_2^{(3)} - K_1^{(3)}$, one can redefine an effective periodicity $\Delta Q = 2\pi/d(Q)$ with $d(Q) = d - Q^2\Delta K^{(3)}/6$. Apparently, the modulation period becomes Q dependent in this case. An example is given in Fig. 2. The asymmetric triangular probability distributions (Fig. 1) now describe the surface of a 100 Å layer with half of the substrate electron density on top of a silicon substrate. The substrate/film interface has the usual hyperbolic tangent or error-function shape. The difference between an error-function-shaped and a hyperbolic tangent-shaped profile is very small. [See also Bahr, Press, Jebasinski & Mantl (1993).] In the calculations the latter is used. Because of the interference between the reflected waves from the two interfaces [equation (6)] a Q-dependent oscillation period occurs and then the two parabolic density profiles shown in Fig. 2 become distinguishable. For the 'triangle right' profile [$K^{(3)} < 0$], the period decreases with Q; for the 'triangle left' profile it increases.

None of the two Gaussian interface roughnesses should be too large, otherwise the contribution of one interface as well as that of the interference term decays rapidly and $\Delta K^{(3)}$ cannot be determined.

Here one may also note the following aspect. When dealing with wetting problems, it is customary first to characterize the dry substrate, in order to minimize the number of surface parameters in subsequent refinements. As only even-order cumulants can be determined in a measurement with a single surface, a problem may result. A possible asymmetry of the substrate surface,

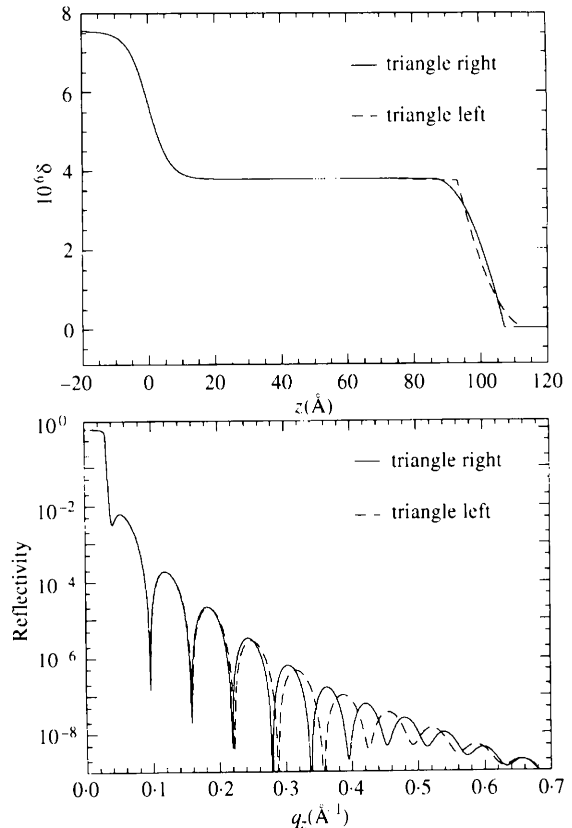

Fig. 2. The density profiles of a 100 Å film on a silicon substrate (top). The asymmetric probability distributions from Fig. 1 were used to model the film surface; the substrate/film interface is tanh-shaped. The asymmetry leads to an increasing or decreasing 'effective periodicity' (see text) for the calculated reflectivities (bottom). The film was assumed to have half of the electron density of the substrate; the roughness of each interface is $\sigma = 5$ Å.

which is invisible to the dry case, can indeed affect the measured reflectivity when the wetting film is present. This may result in a wrong interpretation of the data, *e.g.* by introducing an additional layer in the refinement which is in fact only a manifestation of the asymmetry of the substrate.

Using the cumulant expansion and non-Gaussian density profiles may help to limit the number of free parameters in the refinement procedure. For example, if one measures the reflectivity of Fig. 1, which cannot be refined using the model of a single Gaussian-shaped interface, the next assumption would be the presence of a thin surface layer. In fact, the 'data' can also be refined using a model of a single layer with tanh-shaped symmetric interfaces as shown in Fig. 3. (For a thin layer with roughnesses of the order of the film thickness the height distributions of the two interfaces overlap. The refinement routine used in this example adds the two contributions numerically, obtains the density profile by integration and calculates the reflectivity of that profile.)

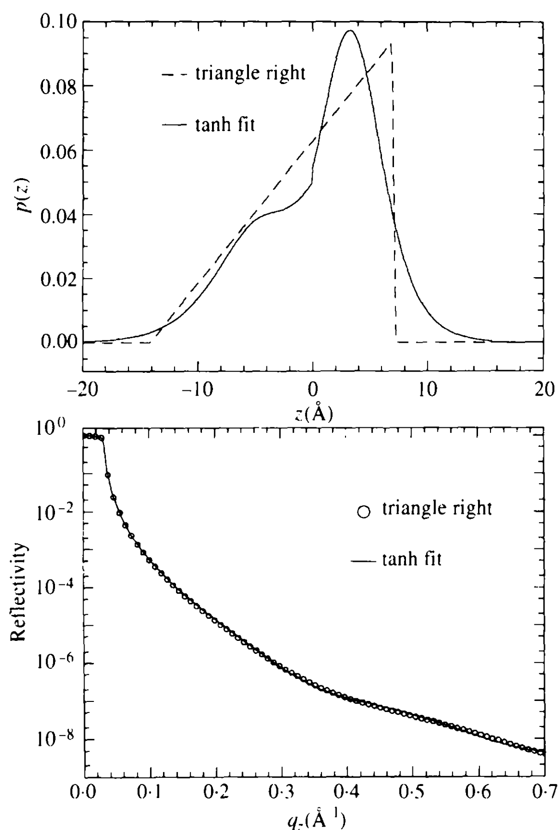

Fig. 3. The reflectivity from Fig. 1 was refined using a model of a single layer with two tanh-shaped interfaces. The resulting probability distribution (top) and the refined reflectivity are shown (bottom). The refined parameters of the film are: $\sigma_{\rm substrate} = 4.0$ Å, $\sigma_{\rm film} = 2.9$ Å, $n_{\rm film} = 1 - 5.0 \times 10^{-6} - i1.14 \times 10^{-7}$, film thickness = 8.0 Å. The model has four free parameters in comparison to only two for the triangular profile (width and asymmetry).

That system has four free parameters (thickness, electron density and roughness of the layer and substrate roughness) compared to only two parameters for the triangular profile [width (= roughness) and asymmetry].

3. Conclusions

At present, we cannot provide an experiment in which odd-order cumulants (note: change of modulation period of Kiessig fringes) apparently contribute. There are, however, examples where the fourth-order cumulant $K^{(4)}$ obviously plays a role. In these it is referred to as polymer interdiffusion in the near-surface regime, *e.g.* Kunz & Stamm (1994, 1996). For modelling the interface profile it became necessary to introduce two Gaussians of different widths. The underlying reptation model for polymer diffusion requires at least two different diffusion constants. In this case, the introduction of a cumulant $K^{(4)}$ would represent an alternative approach.

It would also be extremely interesting to calculate the diffuse scattering of non-Gaussian profiles. Dietrich & Haase (1995) give solutions for the diffuse scattering cross section of various profiles. Unfortunately, the given formulae require very time-consuming numeric calculations. Using the cumulant expansion may be a simple, alternative approach which could more easily be included into a χ^2-minimization algorithm.

Note added in proof. After acceptance of our manuscript we became aware of the fact that similar work has been published by Rieutord, Braslau, Simon, Lauter & Pasyuk (1996).

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