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Moments analysis of X-ray reflection profiles

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Abstract

We discuss an approach towards understanding the limitations of X-ray or neutron reflectivity methods for the determination of an interfacial density profile. A novel analysis is presented based on an expansion of the reflectivity function in terms of moments of the density profile.

0. Introduction

Neutron and X-ray reflectivity techniques have proven to be unique tools for the determination of interfacial profiles, i.e. the density profile across an interface. However, due to the limited range of wave-vector transfer accessible with these techniques, even using the most powerful new sources, and also due to the loss of the phase of the scattered amplitude, the determination of a profile is not unambiguous. We discuss here the pertinent parameters that can be extracted in a model-independent way from a reflection experiment in the case of simple interfacial profiles. The discussion is exemplified on the case of the helium liquid/vapour interface where the different possibilities are discussed.

1. X-ray and neutron reflection from surfaces

The reflection of X-rays or neutrons from surfaces can be used to study interfacial density profiles and roughnesses (in addition to thin-film thicknesses). The term "interfacial profile" may include very different contributions: it can be due to a true compositional gradient or to a projection on the surface normal of laterally structured surface. The lateral structure can be due to a wide range of physical phenomena ranging from capillary waves in the case of a liquid interface to steps, islands or surface defects in the case of solid surfaces. For a perfect diopter (step-like profile), the usual Descartes–Snell law of refraction applies, and there is very little penetration of the incident radiation for grazing angles of incidence inferior to the critical angle for total external reflection: $Q_{zc} = (4\pi/\lambda)\sqrt{2\delta(\lambda)}$, where $1 - \delta(\lambda)$ is the real part of the refractive index of the material. The specularly reflected intensity ideally follows the Fresnel law of optics which, for larger angles of incidence, falls off rather rapidly as $R_F(Q_z) \approx (Q_{zc}/2Q_z)^4$ $(Q_z \gg Q_{zc})$. Typically, from a measure of the reflectivity spectrum of a real interface, different models for the density profile $\rho(z)$ are tested. If the scattering is weak and one ignores the effects of multiple reflections, then the reflected intensity can be described in the equivalent of the first Born approximation by the square modulus of the Fourier transform of the profile gradient:

$$R(Q_z) \approx R_F(Q_z) \left| \int dz e^{iQ_z z} \frac{1}{\rho(-\infty)} \frac{\partial \rho(z)}{\partial z} \right|^2 \qquad (1)$$

(valid only at $Q_z \gg Q_c$). The Born approximation permits a fairly simple interpretation of the data and yields an analytic function for evaluation. Alternately, an exact calculation of the model reflectivity can be made using the optical matrix formalism, dividing the density profile into a succession of thin slabs of constant index [1]. This approach presents the advantage of remaining valid at small angles of incidence, notably near the critical angle, and for large density gradients. Except for the development of conceptional arguments, it is preferable to use the matrix approach for all analysis of

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reflectivity (which can be calculated easily using an iterative procedure).

2. Moments analysis of reflection data

2.1. Case of a single profile

Although, in principle, one can test different functional forms for the density profile through a measurement of X-ray or neutron reflectivity, experimental data are mostly sensitive to the lower moments of the density profile derivative. The zeroth and first moments are trivially the normalization (the bulk density: $\rho(-\infty)$) and the origin (z_0) of the profile. The first non-trivial contribution is due to the second moment of the derivative describing the interfacial width: $\sigma \equiv M_2^{1/2}$ with

$$M_i = \int_{-\infty}^{\infty} \mathrm{d}z\, z^i \frac{1}{\rho(-\infty)} \frac{\partial \rho(z - z_0)}{\partial z}. \tag{2}$$

The second moment of the distribution is very important in the case of a single interface since it defines the length scale of the problem. It is the first parameter (root-mean-squared roughness) that can easily be extracted in reflection studies of interfaces. Higher moments can be defined using this length scale such as the skewness or asymmetry: $r \equiv M_3/M_2^{3/2}$ or the kurtosis (curvature or "long-tailedness"): $K \equiv M_4/M_2^2 - 3$ [2]. In the case of the free-surface of helium, predictions show a non-trivial profile having a rather large asymmetry including a long-range tail extending into the bulk. For example, one recent density functional calculation [3] predicts the helium–vapor profile

$$\rho(z) = \frac{\rho(-\infty)}{[1 + \exp(z/a)]^{\nu}}, \tag{3}$$

where $a = 0.196\,\mathrm{nm}$ and $\nu = \frac{5}{2}$ for ^{4}He. For this profile, used here for illustration, one calculates: $\sigma = 0.286\,\mathrm{nm}$, $r = -0.695$ and $K = 1.474$.

We shall now see whether a measure of the reflectivity is sensitive to the profile asymmetry, for example. For that purpose, it is convenient to expand the profile derivative $\rho'(z)$ (after suitable normalization and scaling such that $M_0 = M_2 = 1$ and $M_1 = 0$) into a series involving successive derivatives of a Gaussian distribution [4]:

$$\rho'(z) = \sum_{n=0}^{\infty} c_n \phi^{(n)}(z) = \phi(z) \sum_{n=0}^{\infty} \left(\frac{-1}{\sqrt{2}}\right)^n c_n H_n(z/\sqrt{2}), \tag{4}$$

where $\phi(z) \equiv (1/\sqrt{2\pi})\exp(-z^2/2)$ and $H_n(z) = (-1)^n \mathrm{e}^{z^2} (\mathrm{d}^n/\mathrm{d}z^n)(\mathrm{e}^{-z^2})$ are the Hermite polynomials. The coefficients c_n are directly related to the moments M_i through orthogonality relations between H_n:

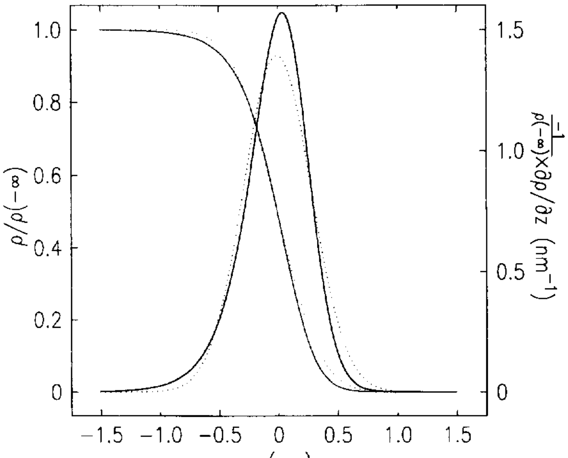

Fig. 1. Profiles of the helium liquid/vapour interface corresponding to Eq. (3) (solid line). The dotted line is the second moment (Gaussian) approximation. The derivatives are shown also (units = nm^{-1}).

$$\begin{aligned} c_0 &= 1, \\ c_1 &= c_2 = 0, \\ c_3 &= -r/6 = 0.116, \\ c_4 &= K/24 = 0.061, \\ c_5 &= (-M_5 + 10M_3)/5! = 0.031, \\ c_6 &= 1/6!(M_6 - 15M_4 + 30) = 0.024, \end{aligned} \tag{5}$$

where the numerical values given are those calculated for the profile presented above. Notice that the convergence of the series is rather slow for this particular profile. The profiles and their derivatives of expression (3) are shown in Fig. 1 together with the second-order (Gaussian) approximations.

The Fourier transform $\tilde{\rho}'(z)$ can be expressed as $\sum c_n(\mathrm{i}Q_z\sigma)^n\phi(Q_z\sigma)$ yielding an expression of the reflectivity:

$$\begin{aligned} \frac{R(Q_z)}{R_\mathrm{F}(Q_z)} &= \exp[-(Q_z\sigma)^2] \left|\sum_{n=0}^{\infty} (\mathrm{i}Q_z\sigma)^n c_n\right|^2 \\ &= \exp[-(Q_z\sigma)^2][1 + 2c_4(Q_z\sigma)^4 \\ &\quad + (c_3^2 - 2c_6)(Q_z\sigma)^6 + \cdots]. \end{aligned} \tag{6}$$

Expression (6) shows that the higher moments of the density profile will contribute to the reflection significantly only when $2c_4(Q_z\sigma)^4 + (c_3^2 - 2c_6)(Q_z\sigma)^6 \gg 0$, i.e. for $Q_z\sigma \gtrsim 1$. We illustrate this in Fig. 2 and compare the expansion of Eq. (6) for this particular model profile with its analytical

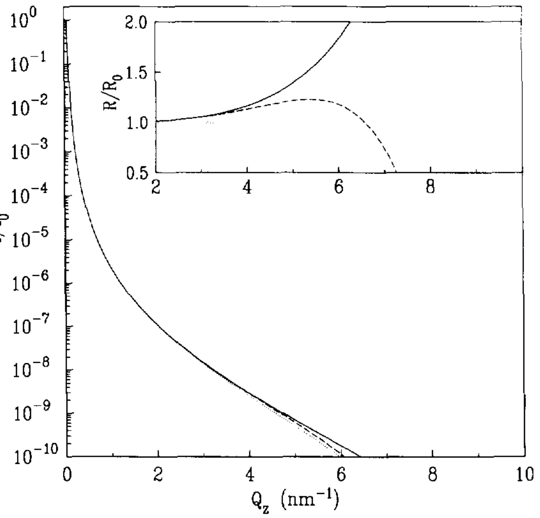

Fig. 2. Calculated specular reflectivity of the helium–vapor interface (free surface). The dotted line considers only the interfacial width (second moment of the helium–vapor density profile). The solid line is obtained by the Fourier transform of the full model density profile. The dashed line represents the expansion including higher moments of the density profile (Eq. (6)). Inset: reflectivity normalized to the Fresnel step-function reflectivity.

Fourier transform according to Eq. (1). One finds: $R/R_F = F(Q_z a)$, where

$$F(x) = \pi x[1 + (4/9)x^2][1 + 4x^2]/[\sinh(\pi x)\cosh(\pi x)]. \quad (7)$$

Since the specular reflectivity (ignoring the diffuse scattering in the specular direction) is already below 10^{-8} before any appreciable difference is indicated, it should be extremely difficult to measure any effect of the asymmetry. The higher moments of the profile contribute to the reflectivity even less.

2.2. Case of a system bounded by two profiles (a film)

Let us consider now the case of a thin helium film wetting a solid substrate [5]. One can perform a similar moment expansion for each interfacial profile. In addition to the contribution of each profile, the reflectivity will include an interference term:

$$\frac{R(Q_z)}{R_F(Q_z)} \approx \left|\tilde{\rho}'_1(Q_z\sigma_1) + \tilde{\rho}'_2(Q_z\sigma_2)e^{iQ_z d_{1,2}}\right|^2, \quad (8)$$

where $d_{1,2}$ is the distance between the two interfaces. Due to the interference product, odd-order terms of the moment expansion of each profile do not cancel out. Provided that one of the interfaces is very well known (i.e. including high-order terms in the moment expansion of its profile), the interference product will exhibit terms of the unknown profile in $c_3(Q_z\sigma)^3 \sin(Q_z d_{1,2})$ which may be significant for higher reflectivities than in the single-profile case. In this respect, the film geometry might be more favorable to extract information on the asymmetry, but detailed knowledge of the substrate–film interface is required. This, again, is hard to obtain from reflection data as the result will be strongly model-dependent. Also, if the interfacial width of the substrate–film interface is comparable to or larger than that of the film–vapor interface (which is almost always the case), the previous discussion indicates that effect of a profile asymmetry would also be unobtainable experimentally. Fig. 3 illustrates the simulated reflectivity of a 20 nm thick helium film adsorbed on a featureless silicon substrate. The effect of the profile asymmetry is an enhancement in the contrast of the interference fringes at large Q_z, but the reflectivity again falls below 10^{-8} before the difference becomes appreciable.

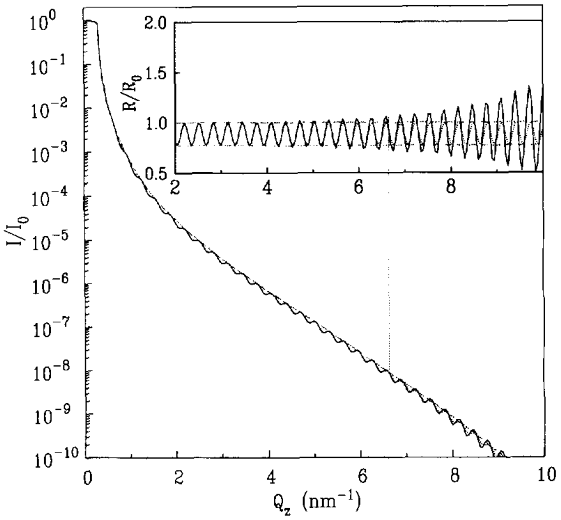

Fig. 3. Same as Fig. 2 but in the case of a 20 nm helium film adsorbed on a silicon substrate assuming a simple error-function helium–silicon density profile (ignoring the adsorption of solid helium, etc.). The reflection pattern is modulated by the interference with the substrate/film interface reflection.

3. Conclusion

Previous discussion has shown that getting information about asymmetry of an interfacial profile is a difficult task. Contrary to what could be thought at first, looking at a simple interface may be less favorable in this respect than considering a more complex arrangement. In this case, the second interface may act as a phase reference to the scattered amplitude of the unknown profile. The possibility for an interface to act as a phase reference to help to solve a structure has been suggested previously [6]. Moments analysis has also been used to derive model-independant data in the study of interdiffusion between layers of deuterated and protonated polystyrene [7]. In this study the authors were able to see evolution of the fourth moment during the interdiffusion process.

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