Grazing incidence surface scattering of X-rays

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A comprehensive presentation of new developments in the theory of diffuse (off-specular) surface scattering of X-rays is given and illustrated with experimental results on different kinds of films and surfaces. This technique allows the determination of surface and interface morphology through height-height correlation spectra over a wide in-plane wave-vector range (10^5–10^10 m^-1). A general method for the determination of the tensorial Green function relevant to the problem is indicated. The Born approximation and the more accurate distorted-wave Born approximation are evaluated. The need for even better approximations is stated and possible methods are indicated. The theoretical results are compared with the results of experiments and non-trivial effects are evidenced. Finally, different methods for the measurements of liquid fluctuation spectra with synchrotron radiation are discussed, demonstrating the ability of this technique to provide more insight into the statistical physics of liquid interfaces down to molecular scales.

The diffuse (off-specular) surface scattering of X-rays has recently emerged as a powerful tool for the investigation of the morphology and fluctuations of interfaces. A field of particular interest is that of liquid surfaces where there are few other available techniques.1–3 Whereas in the micrometre range, liquid interfaces can be studied using light scattering, their investigation at a more local scale requires the use of a radiation of shorter wavelength, i.e. X-rays or neutrons. The related techniques of grazing incidence X-ray diffraction and X-ray reflectivity allow the determination of in-plane and normal structures at the molecular scale. The diffuse scattering of X-rays allows the investigation of the statistical mechanics of off-plane fluctuations of liquid surfaces and liquid/liquid interfaces, or of phase separation at such interfaces. Of particular interest, and still unresolved, are the problems of the shape of an intrinsic profile, the physics of short-range out-of-plane fluctuations, the role of long-range forces.4 Interfaces with adsorbed films of amphiphilic molecules (i.e. composed of a hydrophobic hydrocarbon chain and a hydrophilic headgroup) are also of interest. Such a film adsorbed at a liquid/gas or liquid/liquid interface will modify the fluctuations of the bulk liquid surface by changing its surface tension and, more importantly, by altering its surface elastic properties and therefore its fluctuation spectrum. In particular, a key parameter controlling the stability and topology of many molecular supramolecular structures of considerable practical importance formed of films (such as microemulsions, lamellar phases, vesicles etc.) is the bending rigidity modulus.5

The reflection of light when it is incident on a perfectly flat interface can be determined by the Descartes and Fresnel laws (see for example ref. 6). The reflected and transmitted waves will be in the plane formed by the incident light and the normal to the surface (plane of incidence), with the angle of reflection equal to the angle of incidence, \( \theta_i \). As no real surface can be perfectly flat, particularly at the nanometre scale, the incident wave will, in fact, not be entirely specularly reflected, but there will be a part which will be scattered non-specularly i.e. with in-plane angles other than \( \theta_i \), or out of plane. This non-specularly reflected light can give us information on the degree of roughness of the interface, characterised in particular by the r.m.s. roughness \( \langle z^2 \rangle \) and the height-height correlation function \( \langle z(x)z(0) \rangle \). For example, the fluctuation spectrum of a liquid surface with bending rigidity, obtained by Fourier transforming the free energy and applying the equipartition theorem, is expected to be:

\[
\langle z(x)z(0) \rangle = \frac{k_B T}{\Delta P_g + \gamma q^2 + K q^4}
\]

where the first term in the denominator describes the limitation of out-of-plane fluctuations by gravity, \( \gamma \) is the surface tension and \( K \) the bending rigidity modulus. Another Fourier transformation yields the correlation function:

\[
\langle z(0,0)z(x, y) \rangle = k_B T/2\pi \gamma \times \left[ K_0(r_{xy}/(\gamma K)) - K_0(r_{xy}/(\gamma K)) \right]
\]

where \( r_{xy} = \sqrt{(x^2 + y^2)} \) and \( K_0 \) is the modified Bessel function of second type of order 0. Another widely used correlation function which gives account of many solid surfaces is the self-affine correlation function:

\[
\langle z(0,0)z(x, y) \rangle = \sigma^2 \exp - [r_{xy}/\xi]^2
\]

where \( \sigma \) is an indication of the amplitude of the roughness, \( \xi \) is a cut-off in the roughness spectrum and \( \nu \) is the roughness exponent. The smaller \( \nu \), the wider the spectrum, i.e. it includes roughnesses at all scales. This is the case for example for a silicon surface roughened by hydrofluoric acid treatment (see Fig. 7 below where the scattering by this surface and the water surface are compared). The consistency of diffuse-scattering correlation function determination with atomic force microscopy measurements (for solid surfaces) has been verified in a particular case in ref. 8.

A similar situation occurs for inhomogeneities in an interfacial film even in the ideal case where it is not rough. The quantity of interest is in that case the density correlation function \( \langle n(\theta)\rho(\theta) \rangle \) (Fig. 1). Except for some early developments,9–14 the surface scattering of X-rays and neutrons has become extensively used only recently.15–17 The principle of a typical experiment is illustrated in Fig. 1: for measurements in the plane of incidence, the in-plane \( q_x \) and normal \( q_z \) wave-vector transfers are:

\[
q_x = \frac{2\pi}{\lambda} \left[ \cos(\theta_{\text{out}}) - \cos(\theta_{\text{in}}) \right]
\]

\[
q_z = \frac{2\pi}{\lambda} \left[ \sin(\theta_{\text{out}}) + \sin(\theta_{\text{in}}) \right]
\]

Scattering cross-section for X-rays

As we have already stated, we consider the case where the interface between two media is rough and/or where a film contains density fluctuations (Fig. 1). From Maxwell's equations:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

(5)

$$\nabla \times \mathbf{H} = \mu_0 \frac{\partial \mathbf{D}}{\partial t}$$

(6)

we obtain the equation for electric field propagation:

$$\nabla \nabla \cdot \mathbf{E} - \frac{n^2 \omega^2}{c^2} \mathbf{E} = \nabla \nabla \cdot \mathbf{H} - \frac{\omega^2}{c^2} \left( \frac{\mathbf{P}}{\varepsilon_0} \right)$$

$$\nabla^2 \mathbf{E} + \frac{n^2 \omega^2}{c^2} \mathbf{E} = 0$$

(7)

for waves whose time dependence is given by \(\exp(i\omega t)\). \(n\) is the refractive index, \(\varepsilon = n^2\) is the dielectric permittivity and \(k = \omega n / c\) is the wave vector, which is \(k_0 = 2\pi / \lambda\) in vacuum, where \(\lambda\) is the wavelength of the incident light. For X-rays of frequency much higher than atomic frequencies, \(\omega\), the index is proportional to the local electron density \(\rho_e\):

$$n = 1 - \frac{\lambda^2}{2\pi} r_s \rho_e$$

(8)

where \(r_s = 2.8 \times 10^{-10}\) m is the classical electron radius. For the materials considered in this paper \(n \approx 1 - 10^{-5}\), and in general an imaginary part \(\alpha\) is included in order to take account of absorption. Because the index is less than 1, total external reflection occurs for angles of incidence below a critical angle \(\theta_c = \sqrt{2[1 - (1 - n)]} = \sqrt{k_0^2 r_s / n}\) and this has important consequences that will be extensively used in the following. When neutron scattering (and not X-ray scattering) is being considered, it is necessary to solve the Schrödinger equation which is found to be of the same form, viz.

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + \frac{2m \hbar^2}{m} \sum_{\alpha} b_{\alpha} \rho_{\alpha} \right) \psi(r) = E \psi(r)$$

(9)

where \(b_{\alpha}\) is the scattering length for nuclei of type \(\alpha\), whose density is \(\rho_\alpha\). We write

$$n^2 = n^2 + \delta n^2$$

(10)

In the simple classical DWBA approximation, \(n^2\) will correspond to a distribution of matter with perfectly, arbitrarily located interfaces instead of the real rough ones. \(\delta n^2\) will be the perturbation of this "ideal" arbitrary distribution of matter restoring the real rough one. \(n^2\) gives the specular reflection and \(\delta n^2\) gives the non-specular (or diffuse) reflections. In a more sophisticated approach giving better account of the field structure, \(n^2 + \delta n^2\) will be the refractive index averaged over the \((x, y)\) coordinates so that it varies only in the direction perpendicular to the interface. Eqn. (7) can be written as:

$$\nabla \nabla \cdot \mathbf{E} - n^2 k_\perp^2 \mathbf{E} = \delta n^2 k_\perp^2 \mathbf{E}$$

(11)

A point in the system is located at \(r'\) with respect to the origin, the origin being a distance \(R\) from the detector and \(r = |r + r'|\). Since the Maxwell equations are linear it can be seen from eqn. (7) that the electric field at any point \(r\) above the interface can be given by superimposing fictitious sources \(\delta \mathbf{P} = \varepsilon_0 \delta n^2 \mathbf{E}(r')\) at \(r'\), where the refractive index is given by \(n^2(r')\), on the electric field related to the ideal case (i.e. \(n^2\) case). From eqn. (7) and (11) we obtain:

$$\nabla \nabla \cdot [\mathbf{E} + \delta \mathbf{E}] - n^2 k_\perp^2 [\mathbf{E} + \delta \mathbf{E}] = \delta n^2 k_\perp^2 [\mathbf{E} + \delta \mathbf{E}]$$

(12)
where $\mathbf{E}$ is the field when the refractive index is $n^2$, obeying:

$$\nabla \times \nabla \times \mathbf{E} - n^2 \epsilon_0 \mathbf{E} = 0$$  \hspace{1cm} \text{(13)}$$

and where we have

$$\mathbf{E}(r) = \mathbf{E}(r) + \delta \mathbf{E}(r)$$  \hspace{1cm} \text{(14)}$$

The electric field caused by the fictitious sources can be obtained by use of the reciprocity theorem, which tells us that if we have two systems $A$ and $B$ with sources $P_A$, and $P_B$ and fields $E_A$ and $E_B$ respectively, then

$$\int d^3r E_A \cdot P_B = \int d^3r E_B \cdot P_A$$  \hspace{1cm} \text{(15)}$$

The proof of this can be given by integrating $\nabla \cdot (E_A \wedge H_B - E_B \wedge H_A) = E_B \cdot P_A - E_A \cdot P_B$ on a surface infinitely remote, where the fields are given by plane waves. The two following systems can be considered:

(i) The fictitious sources give a polarisation vector of $\mathbf{E} = \epsilon_0 \delta n^2 \mathbf{E}(r')$ which causes the $\delta \mathbf{E}(r)$ field in the non-ideal rough or inhomogeneous situation.

(ii) A unit dipole at $r'$ at the detector position $R$ in the ideal case. The field is thus $\mathbf{E}(r, r')$ in $r'$.

We then have:

$$\int d^3r' \delta n^2 \mathbf{E}(r') \cdot \mathbf{E}(r, r') = \delta \mathbf{E}(r') \cdot \mathbf{u}$$  \hspace{1cm} \text{(16)}$$

By writing this equation for the three cases where $\mathbf{u}$ is along $x$, $y$ or $z$, and summing we arrive at:

$$\delta \mathbf{E}(R) = \epsilon_0 \int d^3r' n^2 \mathbf{G}_0(r, r') \cdot \mathbf{E}(r')$$  \hspace{1cm} \text{(17)}$$

$\mathbf{G}_0$ is the relevant tensorial Green function.

From eqn. (14)

$$\mathbf{E}(R) = \mathbf{E}(r) + \epsilon_0 \int d^3r' n^2 \mathbf{G}_0(r, r') \cdot \mathbf{E}(r')$$  \hspace{1cm} \text{(18)}$$

Eqn. (18) is an exact relationship from which various approximations can be achieved. In particular, it has been shown in ref. 17 that the specular reflection from a perfectly flat film could be obtained as a perturbation of propagation in vacuum from eqn. (18). The asymptotic of the Green function (i.e. the one relevant to the detector position) can be obtained from the asymptotic form of a dipole field, viz.

$$E = k_0^2 (\mathbf{n} \wedge \mathbf{p}) \times \frac{\exp(ikr)}{r}$$  \hspace{1cm} \text{(19)}$$

in vacuum

and

$$\mathbf{G}_0(r, r') = \frac{k_0^2}{4\pi\epsilon_0} \frac{\exp(ik_0 r) + \exp(-ik_0 r)}{4\pi^2} \times U(r')$$  \hspace{1cm} \text{(20)}$$

for a stratified system. $U(r')$ is the field at $r'$ when the interface is illuminated by a plane wave coming from the detector in the ideal case (see Fig. 1). This can be calculated by iterative methods.

**First Born approximation**

This approximation which neglects multiple scattering of the incident light is not valid in the region of the critical angle where the scattering cross-sections are large. It has the advantage of showing clearly the structure of the non-specular (i.e. scattered) intensity and will be presented with this in mind. This approximation corresponds to the case where both the Green function and the electric field [eqn. (17)] are evaluated in vacuum.

$$\mathbf{G}_0(R, r') = \frac{k_0^2}{4\pi\epsilon_0^2} \frac{\exp(\mathbf{i}k_0 R) + \exp(-\mathbf{i}k_0 R)}{4\pi R} \times \frac{\exp(\mathbf{i}k_0 r')}{\mathbf{E}(r') = \mathbf{E}_0 \exp(\mathbf{i}k_0 r') \times \int d^3r \delta n^2 \exp(\mathbf{i}q \cdot r)}$$  \hspace{1cm} \text{(21)}$$

where the wave vector $k_0$ orientated from the detector to the surface gives us the dipole field equation [eqn. (16)]. From eqn. (18), we have,

$$E = \mathbf{E}_0 \exp(-\mathbf{i}k_0 r') + \frac{k_0^2}{4\pi R} \int d^3r \delta n^2 \exp(\mathbf{i}q \cdot r)$$  \hspace{1cm} \text{(22)}$$

wave-vector transfer:

$$q = k_0^2 - k_0 (24)$$

For such a field the differential scattering cross-section (power radiated per unit solid angle per unit incident flux) can be written as :

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4}{16\pi^2} \times \left| \int d^3r \delta n^2 \exp(\mathbf{i}q \cdot r) \right|^2$$  \hspace{1cm} \text{(25)}$$

This equation can be applied in a variety of limiting cases. We briefly discuss two of these cases below.

**Rough interfaces in the case of a stratified medium**

The numbering scheme for a multilayered system is given in Fig. 2. Then,

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4}{16\pi^2} \times \sum_{i=0}^{N} \int \int \int \int \exp(\mathbf{i}q \cdot z) \exp(\mathbf{i}q \cdot y)$$  \hspace{1cm} \text{(26)}$$

by integrating over $z$:

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4}{16\pi^2} \times \sum_{i=0}^{N} \int \int \int \int \exp(\mathbf{i}q \cdot z) \exp(\mathbf{i}q \cdot y)$$  \hspace{1cm} \text{(27)}$$

which can be reorganised in the following manner:

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4}{16\pi^2} \times \sum_{i=0}^{N} \int \int \int \int \exp(\mathbf{i}q \cdot z) \exp(\mathbf{i}q \cdot y)$$  \hspace{1cm} \text{(28)}$$

We assume that:

$$z_i = z_i + z_i(x, y)$$  \hspace{1cm} \text{(29)}$$

Eqn. (28) then becomes:

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4}{16\pi^2} \times \sum_{i=0}^{N} \sum_{j=0}^{N-1} \int \int \int \int \exp(\mathbf{i}q \cdot z) \exp(\mathbf{i}q \cdot y)$$  \hspace{1cm} \text{(30)}$$

A point to note is that eqn. (36) has exactly the same form as the reflection coefficient, each term being simply weighted by a 'transverse' coefficient:

$$\frac{1}{4\pi^2} \int dx dy [\exp(q_y z(x, y)z(0, 0)) - 1] \times \exp[-i(q_x x + q_y y)] \quad (37)$$

Eqn. (36) shows that the integration of the scattered intensity over the normal wave-vector transfer $q_z$ yields the average value of the self correlation $\langle z(0, 0)z(x, y) \rangle$ of the different interfaces. The cross-correlation between two interfaces $i$ and $j$ $\langle z(x, y)z(0, 0)) \rangle$ can, in principle, be determined from the analysis of the $z$ profile: for instance in the case of a single film of thickness $h$ (medium 1) between a substrate 2 and a medium 0:

$$\frac{d\sigma}{d\Omega} = (n_z^2 - n_0^2)^2 \Sigma (q_x, q_y, z_i, z_j)$$

$$+ 2(n_z^2 - n_0^2) \Sigma (q_x, q_y, z_i, z_0)$$

$$+ (n_i^2 - n_0^2) \Sigma (q_x, q_y, z_0, z_j)$$

(38)

where

$$\Sigma (q_A, q_B, z_i, z_j) \approx \frac{k_0^4}{16\pi^2} \int dX dY \exp[q_x z_A(z_A(X, Y)z_B(0)) - 1] \times \exp[iq_xX + iq_yY] \quad (39)$$

and we see that the coefficient of the interference term depends on the cross-correlation.

If we develop the $\Sigma$ function for small $q_z$:

$$\Sigma_x(q_A, q_B, z_i, z_j) \approx \frac{k_0^4}{16\pi^2} \exp[-\frac{1}{4}q_x^2(z_i^2 - z_j^2)] \times \exp[\int dx dy \exp[q_y z(x, y)z(0, 0))] \times \exp[-i(q_x x + q_y y)]$$

(40)

In that case, the cross-correlation spectrum is therefore directly determined from the interference term. This method has been used to measure the interaction between the surfaces limiting a soap film in ref. 34.

**Inhomogeneities in a multilayered system**

Another limiting case is that of inhomogeneities in a system where all of the interfaces are perfectly flat. The non-specularly reflected intensity is then simply:

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4}{16\pi^2} \sum_{i=0}^{n_i} \sum_{j=0}^{n_j} \exp[-i(q_x x + q_y y)]$$

$$\times \int dx dy [\exp[q_y z(x, y)z(0, 0)) - 1] \times \exp[-i(q_x x + q_y y)] \times \exp[-i(q_x x + q_y y)]$$

(41)

Here, again, we have both specularly and non-specularly reflected components.

**DWBA**

**Calculation of the scattering cross-section**

In this approximation (which has a higher order of accuracy than the preceding), the field used in eqn. (17) is approximated by the field reflected and transmitted in the perfectly flat system. This calculation can be performed iteratively. This approximation which gives better results in the region around the critical angle than those predicted by the first Born
approximation, generally used in the examination of experimental data.

The main modifications to the Born approximation are as follows:

(i) Because refraction is taken into account, the normal components of the wavevectors depend on the local parameters:

\[ k_{nz} = k_0 \sqrt{(\sin^2 \theta - \sin^2 \theta_0)} \]

where \( \theta_0 = \sqrt{(2 - n_i)} \) is the critical angle for medium \( i \) in the sample.

(ii) The reflections at each of the various interfaces are taken into account so that the combinations \( q_i = k_0 \) and \( q'_i = k_0^2 + k_0^2 \) of all the wave vectors appear in the formulae.

(iii) If we wish to examine only a single (rough) interface between medium 1 and medium 2 [with \( s \) polarisation, which is generally a valid approximation at grazing values of the incident angle, see below]:

\[ \mathcal{G}_R(R, r') = \frac{k_0^2 \exp(i_0 R)}{4 \pi \alpha R^2} \mathcal{T}(\theta_{in}) \exp(-i_0 \cdot r') \]

\[ \mathcal{E}(r') = E_0 \mathcal{T}(\theta_{in}) \exp(-i_0 \cdot r') \]

where \( t(\theta_{in}) \) is the Fresnel s-polarisation coefficient as a function of the scattering angle. These expressions are valid up to third order in the angles.\(^{17}\)

An important characteristic of these formulae is that they are symmetric as regards the positions of the source and detector.

At the critical angle the transmission coefficients in eqn. (45), which are the main improvement on the Born approximation, reach their maximum value of 2. This maximum is produced because the incident and reflected waves are in-phase. This yields a peak in the transmitted signal, referred to as Yoneda's peak;\(^{35}\) see Fig. 3 and 4.

For the case of a film of medium 1 placed between media 0 and 2:\(^{17}\)

\[ \frac{d\sigma}{d\Omega} = (n_1^2 - n_2^2)^2 (1 + |r_1|^2 |t_2|^2) \]

\[ \times \sum_i (q_0, q_0, z_0, z_1) + 2Re(r_{in}t_{out}^*) \sum_i (q_0, q_0, z_0, z_1) \]

\[ + |r_{in}t_{out}^*|^2 \sum_i (q_0, q_0, z_0, z_1) \]

\[ + 2Re(r_{in}t_{out}^*) \sum_i (q_0, q_0, z_0, z_1) \]

\[ + 2Re(r_{in}t_{out}^*) \sum_i (q_0, q_0, z_0, z_1) \]

\[ + 2(n_1^2 - n_2^2)^2 |r_{in}|^2 |t_{out}|^2 \sum_i (q_0, q_0, z_0, z_1) \]

\[ \times [r_{in}t_{out}^*] \sum_i (q_0, q_0, z_0, z_1) \]

\[ + r_{in}t_{out}^* \sum_i (q_0, q_0, z_0, z_1) \]

\[ + r_{in}t_{out}^* \sum_i (q_0, q_0, z_0, z_1) \]

\[ + (n_1^2 - n_2^2)^2 |r_{in}t_{out}^*|^2 \sum_i (q_0, q_0, z_0, z_1) \]

\[ \text{Fig. 3} \text{ Scattered intensity as a function of } q_x \text{ and } q_y \text{ for a 2 nm thick rough film. The dependence on } q_x \text{ gives the structure normal to the film. The dependence on } q_y \text{ gives the roughness spectrum (the Fourier transform of the height–height correlation function).} \]

\[ \text{Fig. 4} \text{ 'Rocking curve' } \mathcal{U}(q_x) \text{ for a polymer film (polystyrene–poly(methyl methacrylate) symmetric diblock copolymer) on a silica substrate, the thickness of the film being 18.9 nm. The correlation function used was } \langle \zeta(0) \rangle = \sigma^2 \exp \left\{ - [x/\xi]^2 \right\} \text{ with } \sigma = 0.2 \text{ nm, } \nu = 0.3, \text{ and } \xi = 20 \text{ Å. Yoneda's peak can be seen at } 0.75 \times 10^{-4} \text{ m}^{-1} \text{ and its profile is associated with interferences in the film (kink and fringe on the right of the Yoneda peak in the inset).} \]
fig. 5 Symmetry of the reflected field for parallel polarization, i is incident, r reflected.

The field is then given by:

\[ E = E_0 + \frac{k_0^2 \exp(i k_0 R)}{4\pi \varepsilon_0} \sum_{j} \int_{-\infty}^{\infty} \frac{r_{\text{out}}}{J_j^2} \, dx_0 (n_j^2 - n_{j-1}^2) U_j^{\text{in}} U_j^{\text{out}} \]

Eqn. (49) and (50) then lead us to:

\[ \frac{d\sigma}{d\Omega} = \sum_{j} \sum_{k} \sum_{l} \sum_{m} \sum_{n} \left( \frac{n_j^2 - n_{j-1}^2}{k_0^2} \right) \times \sum_{l} \left( q_{l,1}^2 + q_{l,2}^2 \right) \]

\[ \times \sum_{m} \left( q_{m,1}^2 + q_{m,2}^2 \right) \times \sum_{n} \left( q_{n,1}^2 + q_{n,2}^2 \right) \]

which can be calculated numerically.

Polarisation effects

For the degree of accuracy currently being considered we must now study the effects due to polarisation. From the Fresnel equations, the relationship between the perpendicular and parallel reflection coefficients of a single interface is given by:

\[ \frac{r_{\text{perp}}}{r_{\text{par}}} \approx 1 \pm 2i \theta_1 \theta_2 \]  

where \( \theta_1 \) and \( \theta_2 \) are the angles made by the incident and transmitted beams. In general, when at least one of these two angles is small, the difference between \( r_{\text{perp}} \) and \( r_{\text{par}} \) is also small. This does not, however, imply that the polarisation effects are always negligible.

Subtle effects can be produced by conditions analogous to those which produce Yoneda’s peaks described above. In the proximity of the critical angle it is possible to cancel the field at the air-film interface, by choosing the incidence angle such that \( \theta_{\text{film}} = -1 \) (standing waves). In this case \( E_i \) and \( E_{\text{film}} \) also disappear. (However, it can be seen from Fig. 5 that it is impossible for \( E_i \) and \( E_{\text{film}} \) to disappear simultaneously.) Scattering effects become dominated by the parallel component, unlike what is given by a simple average of the polarisations, which predicts the same result for both s- and p-polarisation in the plane of incidence.24

Further approximations

Despite the fact that the DWBA, as presented above, is a great improvement on the first Born approximation, it does not give sufficiently accurate predictions in the vicinity of the critical angle for some applications.26 It is highly desirable to have a theory which is valid for such grazing angles because, for angles of incidence below the critical angle for total external reflection, penetration of the incident beam into the bulk liquid is minimal, and therefore bulk scattering background intensity is also minimal. Two possible paths can be seen to derive more accurate approximations than the classical DWBA. Currently only the first method has been fully explored.

This consists of taking an average interface profile in eqn. (17). At the moment this approach can only be followed analytically in the case of a hyperbolic tangential profile.27 Note that the treatment in ref. 36 is not correct because boundary conditions are not satisfied.

One objective would be to find some way to take the multiple scattering caused by the surface roughness into account. Then it would be possible to iterate eqn. (17). This is equivalent to the equation24, 27

\[ G = G_0 + C_0 \tilde{G} \]

which is a generalisation of eqn. (18). \( \tilde{G}_0 \) is the Green function for a perfectly flat interface; the potential \( V = \Delta n^2 \) can be seen as an index of the difference between the real interface being studied and the ideal (perfectly flat) interface and \( \tilde{G} \) is the Green function for the real system. This generalisation is obvious for a scalar field since Maxwell’s equations are then equivalent to Schrödinger’s equation.38 Note that the treatment in ref. 36 is not correct because boundary conditions are not satisfied.

Finally, the statistical average of eqn. (53) must be calculated,27 yielding Dyson’s equation:

\[ \langle \tilde{G} \rangle = \tilde{G}_0 + \tilde{G}_0 \langle \tilde{M} \rangle \langle \tilde{G} \rangle \]

where \( \tilde{M} \) is the self-energy operator. Following the lines of ref. 27, the roughness can be seen to lowest order as equivalent to an additional absorption factor (Fig. 6) giving a qualitative account of the experimental data of ref. 25, i.e. a less pronounced Yoneda peak.

Scattered intensity

Unlike the case of reflectivity, where the specular condition \( \delta(q_{\text{sc}}) \) yields a simple convolution, scattered intensity is proportional to the resolution volume. (Measurements taken during experiments, and all calculations, should always be in absolute intensities.) The differential scattering cross-section must then be integrated over the detector solid angle \( \Omega_4 \) and the dispersion of the incident beam, \( \Delta \theta_i \). If we suppose that the incident beam has a Gaussian form, then the measured intensity, \( I_0 \), will be:

\[ I_0 = \frac{1}{l_x \times l_y} \int \frac{d\theta_i}{2\pi \Delta \theta_i} \int \frac{d\Omega_4}{2\pi \Delta \theta_4} \times \exp \left( \frac{-\Delta \theta_i^2}{2\Delta \theta_i^2} - \frac{\Delta \theta_4^2}{2\Delta \theta_4^2} \right) \frac{d\sigma}{d\Omega_4} \]

The normalization factor, $1/(l_x \times l_y)$, is due to the fact that the scattering cross-section is defined for unit incidence flux whereas the non-specular intensity is defined for the total flux. This equation can be better written with the integration performed over the wave vectors than over the angles, since the scattering cross-section can also be written in terms of the wave vectors. The wave-vector density in Fourier space is

$$2\pi \rho_4 \delta(\mathbf{q}_4)$$

(scattering cross-section is defined for unit incidence flux)

The normalization factor,

$$D \equiv \frac{1}{l_x \times l_y \sqrt{2\pi} \Delta \theta_n \Delta \theta_n} \int \frac{2\Delta \theta_n \, d\sigma}{k_0^2 \rho_4 \Delta \theta_n \, d\Omega} \times (q_x + \delta q_x) dq_x \, \delta (\delta q_x)$$

(56)

(for most experiments $\Delta \theta_{\text{spec}} > \Delta \theta_n$). To solve this we need to evaluate integrals of the form:

$$\mathcal{J}(\mathbf{q}_4) = \frac{\pm k_0^2}{8\pi^2 q_x \sin \theta_k k_0} \int dX dY \left[ \exp \left( -\frac{1}{2} q_x^2 \langle z^2 \rangle - \frac{1}{2} q_y^2 \langle z^2 \rangle \right) \right]$$

$$\times \left[ \exp (i q_x X + i q_y Y) \mathcal{A}(X, Y) \right]$$

(57)

where integration over $\delta q_x$ has been replaced by the factor $\sqrt{2\pi} \Delta \theta_n = \sqrt{2\pi} k_0 \Delta \theta_n$. Integration over $\delta q_x$, $\delta q_y$, gives $\mathcal{A}$, the Fourier transform of $\mathcal{A}$:

$$\mathcal{A}(X, Y) = 2\pi q_x \Delta q_x \Delta q_y \exp \left[ -\frac{1}{2} \Delta q_x^2 \langle X^2 \rangle + \langle q_x^2 \rangle \langle X \rangle \right]$$

(58)

where $\Delta q_x$, $\Delta q_y$ (2 log 2) and $\Delta q_x \sqrt{2} \Delta q_y$ (2 log 2) are the half-widths, at half-height of the resolution function $\mathcal{A}$. This gives us:

$$\mathcal{J}(\mathbf{q}_4) = \frac{\pm k_0^2}{8\pi^2 q_x \sin \theta_k k_0} \int dX dY \left[ \exp \left( -\frac{1}{2} q_x^2 \langle z^2 \rangle - \frac{1}{2} q_y^2 \langle z^2 \rangle \right) \right]$$

$$\times \left[ \exp (i q_x X + i q_y Y) \mathcal{A}(X, Y) \right]$$

(59)

To calculate an intensity instead of a cross-section, it is necessary to replace $\Sigma_+ \mathcal{J}$ by $\Sigma_+ \mathcal{J}$ in eqn. (45), (47) and (51). In the limit of small $q_z$, we have:

$$I_D \propto \Delta q_z \langle \rho_z \rangle \approx \frac{1}{l_x} \int dX \langle z(X) \rho_z(X) \rangle \exp \left( i q_z X \right) \exp \left( -\frac{1}{2} \rho_z^2 X^2 \right)$$

In a wave-vector representation, we therefore obtain the convolution:

$$I_D \approx \langle q_z \rangle \mathcal{J}(q_z) \mathcal{A}(q_z)$$

Implications for reflectivity measurements

The scattered intensity often (but not always) has a pronounced maximum in the specular direction. This is the case for water in Fig. 7, but not for the solid surface with a very wide roughness spectrum. When the diffuse scattering intensity is peaked is the specular direction, it cannot easily be separated from the specular intensity. This is a real problem because the analysis of the, now widely used, reflectivity curves requires, in principle, to resolve the signal received into specular and non-specular components as the variable $q_z$ is altered. Moreover, the diffuse intensity $\propto q_z^{-2}$ becomes large as compared with the specularly reflected intensity $\propto q_z^{-4}$ at relatively large wave vectors. Since the separation into specular and non-specular is in general not possible, both contributions must be included when analysing reflectivity curves. In particular, roughness is generally taken into account by including the Debye-Waller factor $\exp [-q_z^2 \langle z^2 \rangle]$ in the expression for the specular intensity. This method does not, in general, enable the true profile due to both specular and non-specular contributions to be obtained. This is the position in Fig. 8 where we have a thin film of octadecyltrichlorosilane on a water subphase. The roughness spectrum (in this case from capillary waves) is obtained by a Fourier decomposition of the free energy.\cite{39}

$$\langle \xi^2 \rangle = k_B T \times (\Delta \rho q + \rho q^2 + K q^{4\gamma})^{-1}$$

(60)

where $\Delta \rho q$ is the gravity term, $\gamma$ the surface tension and $K$ the bending rigidity modulus. The correlation function can be acquired by Fourier transforming:

$$\langle z(0)z(X) \rangle = k_B T / 2\pi |K_0| [\sqrt{\Delta \rho q / \gamma} - K_0 / K]$$

(61)

where $K_0$ is the modified Bessel function of second type of order 0. In this case eqn. (46) becomes $|\Sigma (q_z = 0, q_x)|$:

$$\Sigma(q_z = 0, q_x) = \pi^{-1/2} \Gamma \left[ \frac{1}{2} - \frac{1}{2} k_B T q_z^2 \frac{3}{4} \Delta \rho q \Delta q_z \sqrt{\langle z^2 \rangle} K \right]$$

$$\times \exp \left\{ q_z^2 k_B T \frac{2}{2\gamma} \ln \left[ \frac{\exp(q_z \sqrt{\gamma} / K)}{\Delta q_z / \Delta q_x} \right] \right\}$$

(62)

where $\Gamma$ is the incomplete Gamma function and $\gamma_0$ is Euler's constant.

Fig. 7 Non-specular scattering by water (calculated) and by a silicon wafer treated with hydrofluoric acid having a wide roughness spectrum: calculated and experimental values for a height-height correlation function $\langle z(0)z(x) \rangle = \sigma^2 \exp [-x/2^{\nu}]$ with a roughness $\sigma = 1.4$, $\gamma = 30$ nm and a roughness exponent $\nu = 0.3$.

Fig. 8 Reflection from a film of octadecyltrichlorosilane. The dotted line is the specular signal, which is dominated for wave vectors greater than 2 nm$^{-1}$ by the diffuse scattered signal (thick solid line). The thin solid line is the best fit obtained with a 'box model' (with one box for chains and one for headgroups) and Debye-Waller factors, without taking diffuse scattering into account.
For wave vectors larger than 2 nm\(^{-1}\), the signal is dominated by diffuse scattering. It is not possible to get reasonable physical parameters if the correlation function [eqn. (61)] is not taken into account (Fig. 8). In conclusion, it must be stressed that reflectivity measurements generally include a diffuse scattering contribution for relatively small values of \(q_z\), and that this contribution must be taken into account in the analysis.

**Measurement of liquid surface fluctuation spectra with synchrotron radiation**

The thermal fluctuations of the free surface of liquids (r.m.s. roughness of ca. 0.4 nm for water) yields only a very weak scattering of X-rays at large in-plane wave vectors (\(10^{-12} \times I_0\) for \(q_z \approx 1\) nm\(^{-1}\)). Very brilliant sources i.e. synchrotron radiation are therefore required. We discuss in this section the different ways of measuring fluctuation spectra with synchrotron radiation. The experiments were carried out at the D32 beamline of the European Synchrotron Radiation Facility in Grenoble (CEA-CNRS Collaborative Research Group ‘Interfaces’).

A first point is that measurements in the \((x, z)\) plane of incidence should, in principle, be preferred to measurements in the plane of the surface \((x, y)\) because the resolution is then better. From eqn. (4):

\[
\Delta q_z = \frac{2\pi}{\lambda} [\sin \theta_{in} \Delta \theta_{in} + \sin \theta_{out} \Delta \theta_{out}]
\]

At grazing incidences, the sine functions yield an enhancement of the resolution, which cannot be achieved in the \((x, y)\) plane, and pure \(q_z\) scans at constant \(q_z\), should therefore be preferred. Pure \(q_z\) scans at constant \(q_z\), which yield an intensity directly proportional to the spectrum require a continuous variation of the incident angle (Fig. 1). Such scans amount indeed to rocking the sample around its position (which is of course impossible for a liquid sample, and therefore requires both \(\theta_{in}\) and \(\theta_{out}\) to be varied). In our experiment, the beam was bent towards the surface by using a deflector whose principle is given in Fig. 9. A thin silicon crystal in Laue geometry is rotated around the incident beam. The diffracted beam then describes a cone of angle \(4\theta_B\) where \(\theta_B\) is the Bragg angle, therefore possibly varying the incidence on the sample (the diffractometer, on which the sample is mounted, must be translated in order to keep the point where the beam impinges on the sample constant). Finally, the deflecting crystal is bent in order to accommodate all the horizontal divergent incident beam. An intensity ca. 10% of the primary beam \(I_0\) is then obtained. However, as shown in Fig. 10, the scattered intensity cannot be measured efficiently using this method because of a background ca. \(10^{-8} I_0\). The origin of this background is explained in Fig. 11: above the critical angle for total external reflection \(\theta_c\), the beam penetrates in the bulk, and the resulting scattering is high as compared to that due to the surface thermal fluctuations. This scattering even becomes dominant for wave vectors of ca. \(10^8\) m\(^{-1}\), which demonstrates that it is only possible to measure the scattering at high wave-vectors in total external reflection conditions.

A second series of measurements was therefore attempted in the plane of the sample \((x, y)\) using a germanium (111) crystal analyser to compensate for the broader resolution. However, the deconvolution of the apparatus resolution is difficult owing to the analysing crystal. Whereas spectra consistent with theoretical expectations were obtained, the reliability of the method appeared quite low due to the deconvolution procedure and a third possibility was considered.

This consists in simply performing detector \(\theta_{out}\) scans in the plane of incidence for a grazing angle of incidence \(\theta_{in}\) below the critical angle for total external reflection. Bulk scattering background is therefore completely avoided. With this method however, both \(q_x\) and \(q_y\), are varied during a scan, making the interpretation of data less direct. The advantage in the case of an adsorbed film is, nevertheless, that the interference due to the normal structure, which are a signature of surface scattering, are immediately visible. Moreover, the normal structure can be determined through independent complementary X-ray reflectivity experiments in order to limit the number of parameters. The intensity scattered by thermal fluctuations of the bare water surface in this geometry are given in Fig. 12. They can be analysed with a spectrum \(\left< a(-q_x) a(q_x) \right> = \kappa^2 T(\Delta p_g + yg^2)^{-1}\) without any adjustable parameters, which were consistent with the theoretical expectations.

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**Fig. 9** Principle of the deflector: By rotating the crystal around the incident beam the diffracted beam described a cone of angle \(4\theta_B\) where \(\theta_B\) is the Bragg angle.

**Fig. 10** Diffuse scattering by out-of-plane thermal surface fluctuations. Pure \(q_z\) scans at constant \(q_z = 2.5\) nm\(^{-1}\) for water (■) and a monolayer with more contrast (●). The line is calculated for water.

**Fig. 11** Diffuse scattering by a monolayer projected on the \(q_z\) axis for detector scans in the incidence plane with grazing angles of incidence \(2\) mrad (-----) below the critical angle for total reflection \(\theta_c = 2.4\) mrad. Similar plots for 3 mrad (----) and 10 mrad (-----) above \(\theta_c\). The bump near \(q_z = 10^8\) m\(^{-1}\) is due to the interference between beams scattered at the film/air and film/water interfaces. Note that the background is an order of magnitude more intense at \(10^6\) m\(^{-1}\) above \(\theta_c\) than below \(\theta_c\).
parameter up to wave vectors of ca. $10^{9}$ m$^{-1}$. This is more than one order of magnitude larger than the best previous measurements$^{40}$ and demonstrates the ability of this method to provide more insight into the statistical physics of liquid surfaces down to molecular scales.

Concluding remarks

Our understanding of the grazing incidence surface scattering of X-rays is now such that the related experimental procedures (including the very important resolution effect) are sufficiently well defined for quantitative results to be obtained for the morphology or fluctuations of interfaces.

For instance, we can now observe and explain non-trivial effects only predicted by the DWBA. We also demonstrated that the very brilliant synchrotron sources which are now available, like the ESRF, enable the extension of the method to determine fluctuations down to the molecular scale.

More and more precise experiments will probably call for more accurate theory, particularly under total external reflection conditions for which the methods indicated in this paper need to be explored in more detail.

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