Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Physica B 336 (2003) 27–38
PHYSICA B
www.elsevier.com/locate/physb

Phase sensitive reflectometry and the unambiguous determination of scattering length density profiles

C.F. Majkrzak*, N.F. Berk

NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-8562, USA

Received 6 February 2003; accepted 13 February 2003

Abstract

Exact methods for determining the complex neutron reflection amplitude for a thin film, which make use of multiple measurements of the specularly reflected intensities of composite systems, composed of the film adjacent to a reference layer and/or surrounding media, have been developed over the past several years. These techniques are valid even where the Born or distorted wave Born approximations break down. Thus, given both the modulus and phase of the specular reflection, a first-principles inversion can be performed which yields the scattering length density (SLD) depth profile of the film directly. Ideally, if the reflection amplitude is known for all wave vector transfers Q, the associated SLD profile is unique. Applying the aforementioned methods to a purely real SLD profile, which, effectively, is almost always that encountered in neutron reflection, at least two distinct reflectivity curves, corresponding to two different composite film systems, are required to determine the phase by direct algebraic computation, independently at each value of Q. Each of the composite systems consists of the common unknown part of the film plus a different reference layer segment and/or surrounding medium (e.g., the backing). Recently, investigations of certain classes of SLD profiles have been reported in the literature which examine whether a single X-ray reflectivity curve, given certain a priori knowledge about the system, i.e., about known parts of the film SLD and/or substrate, suffices to reconstruct the phase. Employing the exact formulation of phase sensitive reflectometry, we consider several illustrative and realistic cases in which a minimum of two reflectivity curves are required to distinguish the true SLD profile.

PACS: 61.12.−q; 68

Keywords: Neutrons; X-ray; Reflectivity; Thin film; Phase

1. Introduction

Specular neutron and X-ray reflectometry are potentially powerful probes of the chemical as well as magnetization depth profiles of layered thin film materials. Subnanometer spatial resolutions are currently achievable in many cases. Nonetheless, the loss of intrinsic phase information, common to all scattering techniques whereby only reflected intensities are measured, can lead to ambiguous scattering length density (SLD) profiles obtained by fitting reflectivity data to curves generated from

*Corresponding author.
E-mail address: charles.majkrzak@nist.gov (C.F. Majkrzak).

0921-4526/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0921-4526(03)00266-7

model profiles. It is well-known [1,2, and references therein] that the complex specular reflection amplitude, $r(Q) = |r(Q)|e^{i\phi(Q)}$, as a function of scattering wave vector Q, is both sufficient and necessary information for the unique solution of the inverse-scattering problem for retrieval of the SLD profile $\rho(z)$ as a function of the z-coordinate, perpendicular to the film; a unique solution, mathematically speaking, means $\rho(z) \leftrightarrow r(Q)$, i.e., that just as $\rho(z)$ implies $r(Q)$—the direct problem—$r(Q)$ also implies $\rho(z)$—the inverse problem[1]. There are thus two aspects to the phase-inversion problem: determining the complex reflection amplitude from measurements of reflection intensities, and then inverting the reflection amplitude to retrieve $\rho(z)$. In practice, these mathematically distinct elements often have been combined using the Born approximation (BA) or the distorted wave Born approximation (DWBA), which provide explicit but approximate functional relationships between $r(Q)$ and $\rho(z)$, thereby enabling schemes that attempt to infer $\rho(z)$ from the data without explicit determination of the phase.

Interference methods involving reference layers and substrates have been introduced over the years, within the BA and DWBA, which, in some cases, enable the retrieval or inference of sufficient phase information that ambiguities in the deduced SLD profiles are either significantly diminished [3] or possibly eliminated [4]. Along different lines, Clinton [5] and Zimmermann et al. [6] have studied whether the phase of the reflection amplitude, for particular classes of potentials, can be well-approximated under certain conditions (e.g., in the presence of a known segment of the film and/or underlying substrate) given only a single reflectivity data set. These latter methods extract the phase from reflectivity data "non-locally" by invoking a dispersion relation, which entails integration of the data over all Q. For general $\rho(z)$ functions, however, the phase of $r(Q)$ is not uniquely determined by $|r(Q)|^2$. Mirror symmetric SLD profiles define a broad class of exceptions [7], which appears to be unique in this regard [8]. Examples of a multiplicity of $\rho(z)$ obtainable from the same $|r(Q)|^2$ have been given in theoretical terms [8,9] and in the context of model-independent fitting [10].

Exact methods for phase determination using references have been derived recently for specular neutron reflectometry [11–13] and have been successfully applied in various experiments to retrieve the reflection amplitude (e.g., as reviewed in Ref. [14]). These are "local" methods, in which the phase at each Q is determined algebraically using only data at the given Q. Thus, a rigorous theoretical framework exists for answering questions concerning uniqueness of solutions, both in mathematical and in practical terms. We will consider several realistic examples within this formulation to illustrate the extent to which an effectively unique SLD profile for an "unknown" film can be obtained from measurements of the reflectivities of composite film systems.

2. Theory

In the absence of significant nonspecular scattering from in-plane variations of the SLD, neutron specular reflectometry is accurately described by a one-dimensional Schroedinger wave equation,

$$-\partial_z^2\psi(k_{0z}, z) + 4\pi\rho(z)\psi(k_{0z}, z) = k_{0z}^2\psi(k_{0z}, z), \qquad (1)$$

where $\psi(k_{0z}, z)$ is the neutron wavefunction, k_{0z} is the z-component of the incident neutron wave vector, $\mathbf{k}_0$, as measured in vacuum, and $\rho(z)$ is the SLD profile as a function of the coordinate z, normal to the film. Notice that in the dimensions of Eq. (1), the scattering potential is $4\pi\rho(z)$. In terms of the solution to Eq. (1), the amplitude $r(Q)$ of the reflected wave can be represented by the integral [15]

$$r(Q) = \frac{4\pi}{iQ}\int_0^L \psi(k_{0z}, z)\rho(z)e^{ik_{0z}z}\,dz, \qquad (2)$$

where $Q = 2k_{0z}$ and L is the width of the SLD profile, i.e., the thickness of the film. It is assumed for now that the sample is a free-film in vacuum.

[1] When $\rho(z)$ is such that the corresponding scattering potential, $4\pi\rho(z)$, has one or more bound states, then the phase of $r(Q)$ is not, in fact, uniquely determined by $\rho(z)$, but this is a fairly weak exception in practice.

When the neutron wavefunction within the film is negligibly distorted from its plane-wave form in free space, i.e., $\psi(k_{0z}, z) \approx \exp^{ik_{0z}z}$, then Eq. (2) becomes the BA result,

$$r_{BA}(Q) = \frac{4\pi}{iQ}\int_0^L \rho(z)e^{iQz}\,dz \equiv \frac{4\pi}{iQ}F(Q). \qquad (3)$$

When the film is backed by a (semi-infinite) substrate, the upper limit of integration in Eq. (3) is extended to $z = \infty$. In addition, if the finite film consists of a known reference layer and an unknown portion, then in the BA, the structure factor $F(Q)$ in Eq. (3) can be written as a sum of separate terms representing the known and unknown layers and a term for the substrate [16,14]. Thus, a measurement of the composite reflectivity $|r_{BA}(Q)|^2$ can be related to a series of terms which include an interference term involving the reflection amplitude for the unknown part of the film. Thus, if we measure the reflectivity for two composite films consisting of the same unknown layer and substrate but with two different reference layers and subtract the results, the common term depending only on the unknown layer cancels out. Then the unknown layer only appears linearly in the result, and its structure factor can be obtained by standard algebraic methods. However, the BA is only asymptotically correct as $Q \to \infty$ and the reflectivity diminishes to zero, justifying the plane-wave approximation to the true wave function in the sample. Often the BA provides a reasonable numerical approximation for smaller Q, depending on film thickness and the detailed behavior of $\rho(z)$; but as $Q \to 0$ it necessarily breaks down, both numerically and analytically, and ultimately the BA, and thus Eq. (3), ceases to provide a proper mathematical description of the reflectivity. Eq. (2) always applies, but as distortion of the wavefunction under the integral grows, the convenient cancellations that occur in the BA are compromised, making the solution for the unknown harder. Despite such difficulties, successful applications of reference layers and substrates using either the BA or DWBA have been made in certain cases [3,4]. A completely general and accessible solution method for Eq. (1) is available, however.

First, let us represent the combined neutron wavefunction in Eq. (1), $\psi(k_{0z}, z)$, and its first derivative with respect to z by the column vector

$$\chi(k_{0z}, z) = \begin{pmatrix} \psi(k_{0z}, z) \\ k_{0z}^{-1}\partial_z\psi(k_{0z}, z) \end{pmatrix}. \qquad (4)$$

Now also introduce the 2×2 matrix

$$\mathbf{M}(k_{0z}, z) = \begin{pmatrix} A(k_{0z}, z) & B(k_{0z}, z) \\ C(k_{0z}, z) & D(k_{0z}, z) \end{pmatrix}, \qquad (5)$$

and assert the property

$$\chi(k_{0z}, z) = \mathbf{M}(k_{0z}, z)\chi(k_{0z}, 0), \qquad (6)$$

for $0 \leqslant z \leqslant L$, with the boundary condition

$$\mathbf{M}(k_{0z}, 0) = \mathbf{1}, \qquad (7)$$

to make Eq. (6) consistent at $z = 0$. The matrix $\mathbf{M}(k_{0z}, z)$ thus "transfers" the exact wavefunction and its derivative from the front edge of the film, at $z = 0$, to an arbitrary interior point, z. An equation for the transfer matrix $\mathbf{M}(k_{0z}, z)$ can be obtained directly from the Schroedinger equation for $\psi(k_{0z}, z)$. Thus, after differentiating $\chi(k_{0z}, z)$, as defined in Eq. (4), and then using Eq. (1) to clear the resulting second derivative of $\psi(k_{0z}, z)$, one finds

$$\partial_z\chi(k_{0z}, z) = \Gamma(k_{0z}, z)\chi(k_{0z}, 0), \qquad (8)$$

where the new matrix,

$$\Gamma(k_{0z}, z) = \begin{pmatrix} 0 & k_{0z} \\ 4\pi\rho(z)/k_{0z} - k_{0z} & 0 \end{pmatrix}, \qquad (9)$$

is completely defined by the SLD profile $\rho(z)$. But we also have directly from Eq. (6) that

$$\partial_z\chi(k_{0z}, z) = \partial_z\mathbf{M}(k_{0z}, z)\chi(k_{0z}, 0). \qquad (10)$$

Thus substituting Eq. (8) into Eq. (10) and using Eq. (6) to eliminate $\chi(k_{0z}, z)$, we easily get the evolution equation for the transfer matrix,

$$\partial_z\mathbf{M}(k_{0z}, z) = \Gamma(k_{0z}, z)\mathbf{M}(k_{0z}, z). \qquad (11)$$

If we overlook the appearances of matrices for a moment, then Eq. (11) is simply a linear first-order equation, subject to the "initial" condition in Eq. (7), and thus it has a unique solution at each value of k_{0z}, completely determined by $\rho(z)$. When the matrix form is made explicit, using Eqs. (5)

and (9), Eq. (11) generates four coupled linear first-order equations for the transfer matrix elements, A, B, C, and D, subject to the initial conditions, $A = 1$, $B = C = 0$, and $D = 1$ at $z = 0$. Explicit solutions are difficult to achieve for arbitrary $\rho(z)$, but the essential point here is that they exist and are unique. Moreover, for real-valued $\rho(z)$, the resulting transfer matrix is real-valued, because $\Gamma(k_{0z}, z)$ then is real.

For the purposes of general analysis, explicit solutions for $\mathbf{M}(k_{0z}, z)$ are not required, however. Most importantly, because Eq. (11) is first-order, and because the boundary condition on $\mathbf{M}$ is an initial condition, the solution for $\mathbf{M}$ at any $z = z'$ depends on $\rho(z)$ only for $0 \leqslant z \leqslant z'$; the behavior of $\rho(z)$ for $z' < z$ is inconsequential. Thus, consider that the film between $0 \leqslant z \leqslant L$ is arbitrarily divided into two parts at some value of z, say $z = z_1$. Then Eq. (5) implies that, suppressing k_{0z}, $\chi(z) = M_1(z)\chi(0)$ for $0 \leqslant z \leqslant z_1$, where $M_1(z)$ corresponds to $\rho(z)$ in the first segment, i.e., for $0 \leqslant z \leqslant z_1$. Now Eq. (5) becomes $\chi(z) = \mathbf{M}(z - z_1)\chi(z_1)$ for any "initial" point $z_1 > 0$. Thus for $z_1 \leqslant z \leqslant L$ we can write $\chi(z) = M_2(z - z_1)\chi(z_1)$ for $0 \leqslant z \leqslant z_1$, where M_2 corresponds to $\rho(z)$ in the second segment. Therefore, for an arbitrary cut of $\rho(z)$ into two contiguous parts, say, at z_1, we have $\mathbf{M}(z) = M_2(z - z_1)M_1(0)$ for $z_1 \leqslant z \leqslant L$, and at $z = L$, in particular, $\chi(L) = \mathbf{M}(L)\chi(0)$, where

$$\mathbf{M}(L) = M_2(L - z_1)M_1(0). \tag{12}$$

In other words, the transfer matrix for the entire film is the product of transfer matrices for the two parts, regardless of where the cut occurs or the behavior of $\rho(z)$ in each of the two segments. More generally, by induction, this implies

$$\mathbf{M} = M_N M_{N-1} \cdots M_1 \tag{13}$$

for any partitioning of $\rho(z)$ into N segments at $z = z_1, \ldots, z_{N-1}$ where $0 \leqslant z_1 \leqslant z_2 \leqslant \cdots \leqslant z_{N-1}$. Since in any segment, $M_n(z_n - z_{n-1})$ depends implicitly on the segment length, $z_n - z_{n-1}$, we can suppress the spatial argument when the context is clear, as in Eq. (13). Such "matrification" of the solution of Eq. (1) is well-known for piecewise continuous, or slab-like, SLD profiles, where $\rho(z)$ is modeled as a histogram, i.e., a set of N "bins" in each of which $\rho(z)$ is constant. In classical derivations [17–19], the properties of the transfer matrix emerge from explicit solutions of the Schroedinger equation within each bin and the applications of boundary conditions at each slab interface. Subsequent generalization to continuous $\rho(z)$ then may be implied, casually, at least, by taking the limit, $N \to \infty$. In actuality, as we see, the transfer matrix representation of Eq. (1) is not tied in any way to a model description or computational rendering of $\rho(z)$. Various general properties of $\mathbf{M}$ can be derived from Eqs. (4)–(11) [20]. Two are required subsequently. First, for any $\rho(z)$, including complex valued functions, the transfer matrix is unimodular, i.e., it has unit determinant: AD − BC = 1. (For the more mathematically inclined, this very general property essentially expresses the linear independence of waves traveling to the left and to the right in the film.) Second, the only effect of mirror-reversing the film, i.e., taking $\rho(z) \to \rho(L - z)$, is to interchange the diagonal elements of $\mathbf{M}$: $A \leftrightarrow D$.

To obtain a formula for the reflection amplitude in terms of the transfer matrix, we use Eq. (4) and the known plane-wave solutions to Eq. (1) in the semi-infinite fronting ($z < 0$) and backing ($z > L$) components of the sample:

$$\psi_f(Q/2, z) = e^{if(Q)Qz/2} + r(Q)e^{-if(Q)Qz/2}, \tag{14a}$$

$$\psi_h(Q/2, z) = t(Q)e^{ih(Q)Qz/2}, \tag{14b}$$

respectively, where $r(Q)$, again, is the reflection amplitude and $t(Q)$ is the transmission amplitude, and where

$$n(Q) = \sqrt{1 - \frac{16\pi\rho_n}{Q^2}}, \tag{15}$$

for $n = f$ (fronting medium, in which $\rho(z) = \rho_f$, a constant) and $n = h$ (backing, or "behind," medium, in which $\rho(z) = \rho_h$, also a constant). In Eqs. (14) we have replaced k_{0z} by $Q/2$ to be consistent with the usual convention of giving notational primacy to the wave vector transfer rather than to the incident wave vector. By continuity, Eqs. (14) define $\psi(z)$ and $\partial_z\psi(z)$ at the leading and trailing edges of the film, i.e., at $z = 0$ and $z = L$, respectively. Thus $\chi(z)$ is known in terms of $r(Q)$ and $t(Q)$ at both $z = 0$ and $z = L$, and we get from Eq. (6) that

$$\begin{pmatrix} 1 \\ \mathrm{i}h \end{pmatrix} t\,\mathrm{e}^{\mathrm{i}hQL/2} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} 1+r \\ \mathrm{i}f(1-r) \end{pmatrix}, \tag{16}$$

where we have suppressed the implicit Q-dependence for easier reading. Eq. (16) constitutes a pair of equations for $r(Q)$ and $t(Q)$. Eliminating t leads to a representation of r as

$$r = \frac{fhB + C + \mathrm{i}(fD - hA)}{fhB - C + \mathrm{i}(fD + hA)}. \tag{17}$$

For the case of real-valued $\rho(z)$, appropriate for most applications to neutrons, the functions $A, \ldots, D$ are real, as mentioned above, and, with the aid of unimodularity, Eq. (17) then takes the rationalized form

$$r = \frac{(f^2h^2B^2 + f^2D^2) - (h^2A^2 + C^2) - 2\mathrm{i}(fh^2AB + fCD)}{(f^2h^2B^2 + f^2D^2) + (h^2A^2 + C^2) + 2fh}. \tag{18}$$

This looks complicated, written out in full, but in fact there are just three functions that comprise the formula. If we introduce $\alpha = f^{-1}hA^2 + (fh)^{-1}C^2$, $\beta = fhB^2 + fh^{-1}D^2$, and $\gamma = hAB + h^{-1}CD$—where $\gamma^2 = \alpha\beta - 1$ because of unimodularity—then Eq. (18) is easier to read as

$$r = \frac{\beta - \alpha - \mathrm{i}\gamma}{\alpha + \beta + 2}. \tag{19}$$

We see, in particular, that $Re\, r(Q)$ depends only on α and β. The reflectivity from the entire sample (film and "surround," i.e., including the fronting and backing media) is $R(Q) = |r(Q)|^2$. Using Eq. (18), $R(Q)$ can be related to the transfer matrix in terms of a new, defined quantity, $\Sigma(Q)$, as

$$\begin{aligned} \Sigma &\equiv 2fh\frac{1+R}{1-R} \\ &= (f^2h^2B^2 + f^2D^2) + (h^2A^2 + C^2) \\ &= fh(\alpha + \beta). \end{aligned} \tag{20}$$

We can see at once from Eq. (20) that, locally (i.e., at a given Q) $R(Q)$ contains less information than $r(Q)$, an alternative perspective of the phase problem.

To simplify a bit, while remaining realistic, let us consider the generalized schematic SLD profile shown in Fig. 1, where the beam is incident from the left in vacuum (meaning here that $f \equiv 1$), on a composite film consisting of an "unknown" segment of $\rho(z)$ on top of a reference segment. The composite film, in turn, is adjacent to a semi-infinite backing or substrate, the whole system comprising the sample. For this particular

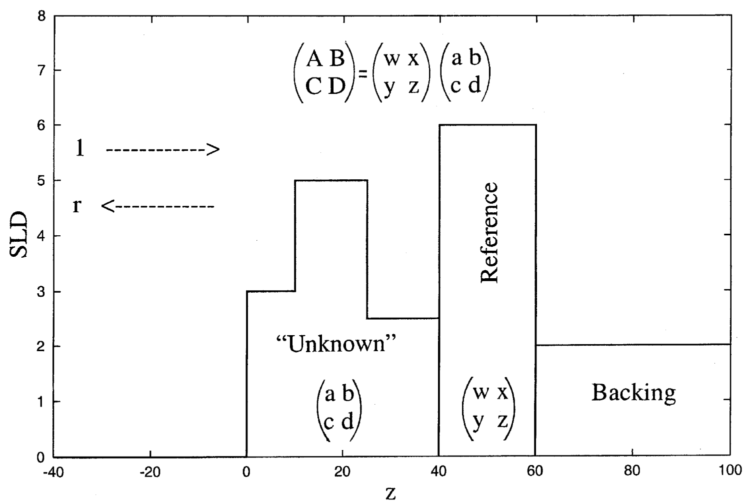

Fig. 1. General composite system SLD profile with "unkown" and reference film segments on semi-infinite backing or substrate. Dotted arrows are labeled by the normalized amplitudes of the incident (l) and reflected (r) beams.

geometry,

$$\Sigma = (h^2B^2 + D^2) + (h^2A^2 + C^2). \quad (21)$$

The figure also illustrates the formula in Eq. (12), showing the transfer matrix for the film expressed as the product of two transfer matrices, one for the unknown portion and one for the reference segment. The transfer matrix elements for the composite film ($A, \ldots, D$) then can be expanded in terms of the corresponding elements for the unknown ($a, \ldots, d$) and known ($x, \ldots, z$) parts to give

$$\Sigma = (h^2x^2 + z^2)(c^2 + d^2) + (h^2w^2 + y^2)(a^2 + b^2) + 2(h^2wx + yz)(ac + bd). \quad (22)$$

(This also can be written concisely in the α–β–γ notational style used above [14], but the explicit representation should be clear enough for the remainder of the discussion.) The three unknown functions, $a^2 + b^2$, $c^2 + d^2$, and $ac + bd$, appearing in Eq. (22) turn out to completely determine the reflection amplitude, $\tilde{r}_U(Q)$, for the *mirror-reversed* ($\tilde{\ }$) unknown (U) layer—i.e., the unknown layer with $a \leftrightarrow d$—viz.,

$$\tilde{r}_U = \frac{(a^2 + b^2) - (c^2 + d^2) - 2i(ac + bd)}{(a^2 + b^2) + (c^2 + d^2) + 2}. \quad (23)$$

The quantities pertaining to the reference layer and backing medium, viz., $x(Q), \ldots, z(Q)$, and $h(Q)$ are presumed to be exactly known, whereas $R(Q)$, and therefore $\Sigma(Q)$, are measured. Eqs. (22) and (23) thus provide a direct means of determining $\tilde{r}_U(Q)$, locally, i.e., independently, at each Q value. Namely, measure $R(Q)$ on each of three samples having the same unknown layer and backing but different reference layers. From Eq. (22) these produce three linear algebraic equations in the three variables, $a^2 + b^2$, $c^2 + d^2$, and $ac + bd$, and from the unique solution we construct the reflection coefficient, $\tilde{r}_U(Q)$, for the reversed unknown. This can be inverted to find $\tilde{\rho}_U(z) = \rho_U(L - z)$, and thus the desired $\rho_U(z)$.

In the Cartesian space of the three unknowns, $\tilde{\alpha}_U = c^2 + d^2$, $\tilde{\beta}_U = a^2 + b^2$, and $\tilde{\gamma}_U = ac + bd$, Eq. (22) defines a plane. Thus for a single measurement of $R(Q)$, i.e., of $\Sigma(Q)$, there are a multitude of solutions consistent with the data. The unimodularity of the transfer matrix imposes a constraint, however. For the case at hand this becomes $\tilde{\gamma}_U^2 = \tilde{\alpha}_U\tilde{\beta}_U - 1$, which, geometrically speaking, defines an hyperboloidal sheet, and this intersects the Σ-plane in a hyperbolic curve, thus greatly reducing the realm of allowable possibilities. However, this constraint is useful for finding a solution only when it is made explicit. A second measurement produces a plane which intersects the hyperbola in two points, one being the veridical or "physical" solution and the other, a spurious or "non-physical" solution, which, in principle, can be identified as such from other criteria [21,22]. Finally, a third measurement defines a third plane which contains only the physical solution (i.e., the unique point of intersection of the three Σ-planes). Reference layer experiments using three measurements [23] and using two measurements and the unimodular constraint [22] have been successfully performed.

An alternative reference methodology is provided by varying the media surrounding the film of interest, i.e., by varying the spatially constant SLD-value of either the semi-infinite fronting or backing. In this approach, a reference layer of finite thickness is not required. Indeed to see how this works, we need only shrink the thickness of the reference layer in Fig. 1 to zero; this has the effect of making $w = z = 1$ and $x = y = 0$ in Eq. (22), which then becomes (again, for the case of vacuum fronting, $f = 1$)

$$\Sigma = h^2(a^2 + b^2) + (c^2 + d^2). \quad (24)$$

We can see at once from this that two measurements of $R(Q)$ for a fixed film in contact with backings ρ_{h1} and ρ_{h2}, respectively, giving $h_1(Q)$ and $h_2(Q)$ in Eq. (24), provide two Σ-equations for the unknowns $c^2 + d^2$ and $a^2 + b^2$ (i.e., $\tilde{\alpha}_U$ and $\tilde{\beta}_U$) from which $Re\,\tilde{r}_U(Q)$ is obtained by Eq. (23). This "surround variation" method [13] has been implemented experimentally [24].

Whichever reference variation technique is used, once $r(Q)$ is determined, a first-principles inversion can be performed to obtain the SLD profile of the unknown film of interest directly [1,7]. Specific aspects of the inversion problem are described elsewhere [14]. We only remark here that, in fact, for most situations of interest, $Re\,\tilde{r}(Q)$ is sufficient information for exact inversion to find $\rho(z)$.

Some of the formulas discussed above require real-valued $\rho(z)$ and thus are not valid for cases characterized by strong absorption, which apply to most instances of X-ray reflectometry. However, using a different approach, phase-determination for absorptive scattering potentials has been described [25].

3. Illustrative examples

The question then is whether it is necessary to employ multiple references, either adjacent reference layers or a substrate with tunable SLD, to determine the phase for the film of interest; or can a single measurement of a reflectivity curve for the film having a known segment or backing medium suffice. Using the exact or "dynamical" theory outlined above, we now consider some specific examples of realistic SLD profiles that are potentially problematical insofar as their unambiguous determination is concerned.

3.1. Free-standing film

Fig. 2 shows the mathematically identical reflectivity curves that are calculated for the two distinct SLD profiles shown in the inset, one the mirror image of the other. It is clear that, lacking other information, it is impossible to determine the orientation of the free-standing film relative to the incident beam. Although perhaps an esoteric example, for the lack of mechanical support, it is not an entirely implausible one. In practice, such a situation can be approximately realized for neutron reflection in the case of a deuterated organic film floating on the surface of ordinary water (to increase the SLD of the film relative to the water, which is slightly less than zero). Fig. 3 presents a plot of $Q^2\,Re\,r(Q)$ vs Q for these two film orientations relative to the incident beam: it is remarkable the degree to which the phase information implicit in $Re\,r(Q)$ provides an unambiguous identification. Thus, in this circumstance, multiple (two) references are indispensable for phase determination. Now for a film with a symmetric SLD the original and mirror image are, of course, identical. Furthermore, as mentioned earlier, $r(Q)$, and thus $Re\,r(Q)$, can be extracted unambiguously from a single measurement of the reflectivity of the free standing film in this special case, albeit only with a non-local method [7].

3.2. Unknown film on known backing (substrate)

Consider next, in Fig. 4a, the SLD profile adjacent to a semi-infinite substrate (the SLD

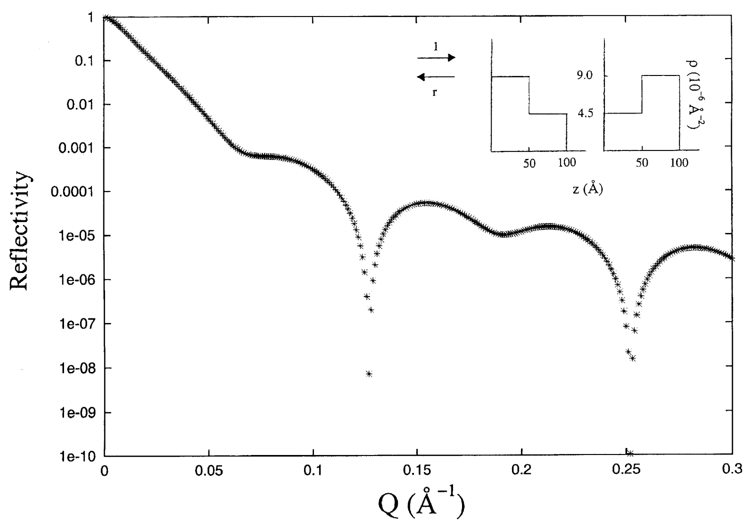

Fig. 2. Identical (neutron) reflectivity curves corresponding to mirror image SLD profiles shown in the inset. (After Fig. 1 of Ref. [14].)

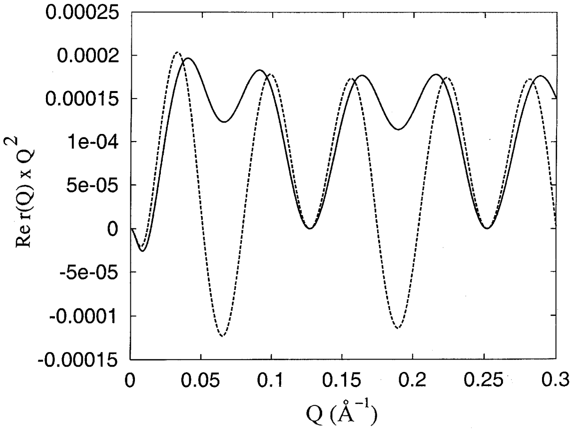

Fig. 3. Q^2 *Re* $r(Q)$ for the two SLD profiles in the inset of Fig. 2.

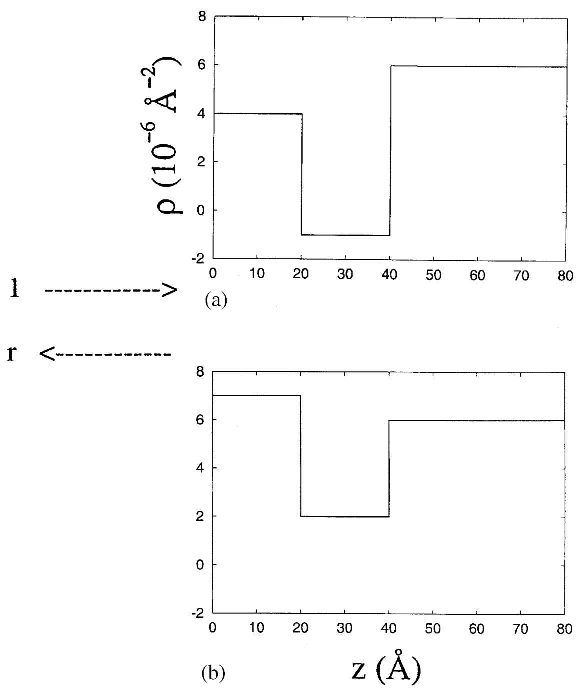

Fig. 4. Symmetry-related SLD film profiles (reflection about vertical axis through $z = 20$ Å, followed by reflection about horizontal axis through ρ-scale $= 3$) on fixed known backing, as discussed in the text.

value of which, in actuality, is close to both sapphire and heavy water). The mirror reversed and flipped SLD of Fig. 4a is shown in Fig. 4b. The calculated reflectivities for both of these composite systems, i.e., film plus backing, are plotted in Fig. 5. Even without including instrumental broadening, the two curves are practically indistinguishable from one another. (An actual film with an SLD profile similar to this model was encountered in a neutron reflectivity measurement performed on a titanium/titanium oxide film deposited on a Si substrate and adjacent to an aqueous reservoir [10].) It would seem unlikely, therefore, that a single reflectivity curve could be used to determine which of the two possible film orientations depicted in Fig. 4 was the veridical one, i.e., the one responsible for the data, despite the fact that a known substrate was behind the film. Yet, the *Re* $r(Q)$ curves for the two symmetry-related films, shown in Fig. 6, are markedly different. Therefore, if two different composite reflectivity curves were measured, one for the unknown film on a substrate with a SLD of 6.0×10^{-6} Å^{-2} (roughly the value for sapphire) and another for the same film but on a substrate with SLD value of, say, 2.0×10^{-6} Å^{-2} (approximately the value for silicon), *Re* $r(Q)$ for the common "unknown" film could be determined from the appropriate equations derived in the preceding section. Fig. 7 shows the composite reflectivities for the film of Fig. 4a on sapphire and silicon backings. Solving Eq. (24), using the two measured values of $\Sigma(Q)$ (independently, at each value of Q), the quantities $a^2 + b^2$ and $c^2 + d^2$ can be found, from which *Re* $r(Q)$ (for the reversed unknown film—*Re* $\tilde{r}_U(Q)$ in Section 2) can be subsequently computed from Eq. (23), as discussed above. Fig. 8 shows *Re* $r(Q)$ obtained by this procedure compared to that computed from the original (but *reversed*) SLD profile of Fig. 4a. The two curves are the same theoretically and, as expected, effectively coincide computationally. Once *Re* $r(Q)$ is thereby determined, the SLD of the unknown film can be obtained by direct inversion, without any adjustable parameters, as mentioned earlier.

3.3. Unknown film adjacent to reference layer on a substrate

As the final illustration, suppose now that not only is a film of interest deposited on a known

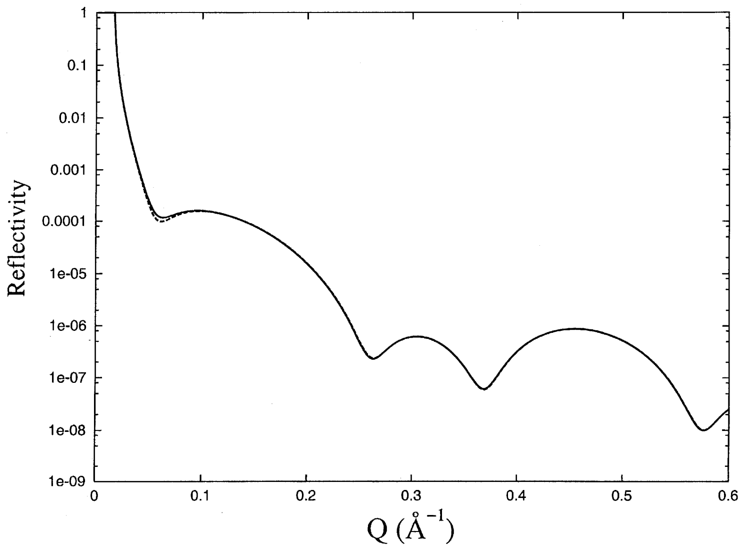

Fig. 5. Reflectivity (neutron) curves corresponding to the SLD profiles of Fig. 4.

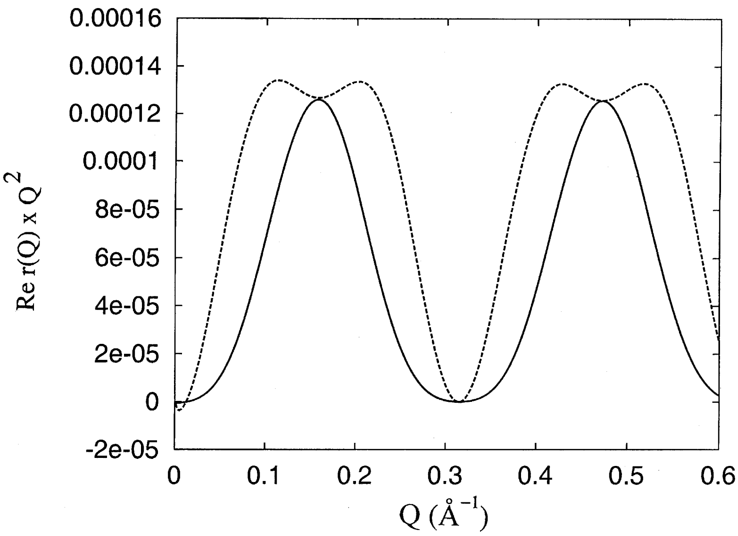

Fig. 6. Q^2 $Re\, r(Q)$ for the SLD profiles of Fig. 4 without backing.

substrate material, but that the film is either next to a reference layer or, what is essentially equivalent, contains a known segment of the SLD profile. Fig. 9a depicts such a case where the portion of the film between, for instance, $z =$ 20 and 60 Å is taken as completely known in both its SLD value and its position relative to the substrate. It happens, however, that the SLD profile of Fig. 9b, possessing an identical known reference layer section and substrate, produces very nearly the same calculated composite reflectivity curve as that generated by the SLD profile of Fig. 9a, as shown in Fig. 10 (again, without simulating instrumental resolution, which would

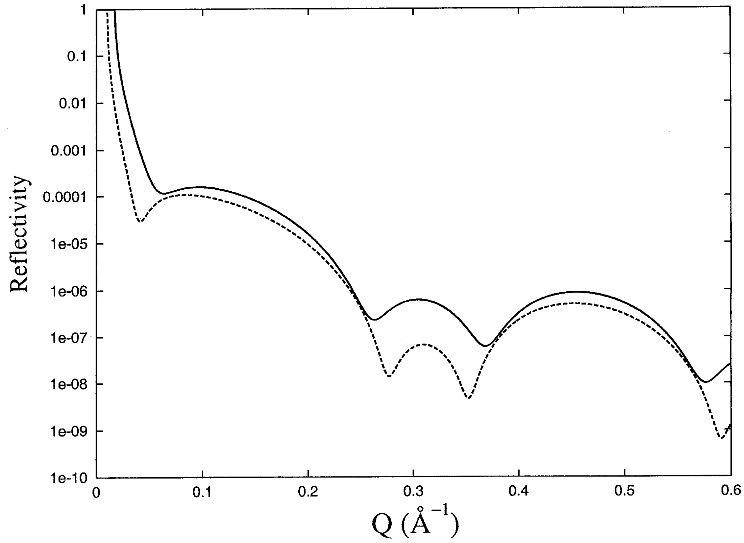

Fig. 7. Composite system neutron reflectivities $|r(Q)|^2$ for the SLD profile of Fig. 4a on backings of SLD equal to 6.0×10^{-6} Å^{-2} (approximately sapphire value) and 2.0×10^{-6}Å^{-2} (roughly that for silicon).

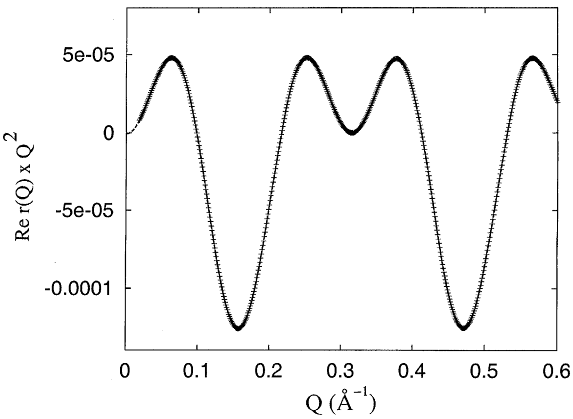

Fig. 8. Q^2 *Re* $r(Q)$, as determined algebraically by the exact methods described in the text, from the two reflectivity model "data" sets of Fig. 7 compared to that computed directly for the reversed SLD profile of Fig. 4a (free film only, i.e., no backing).

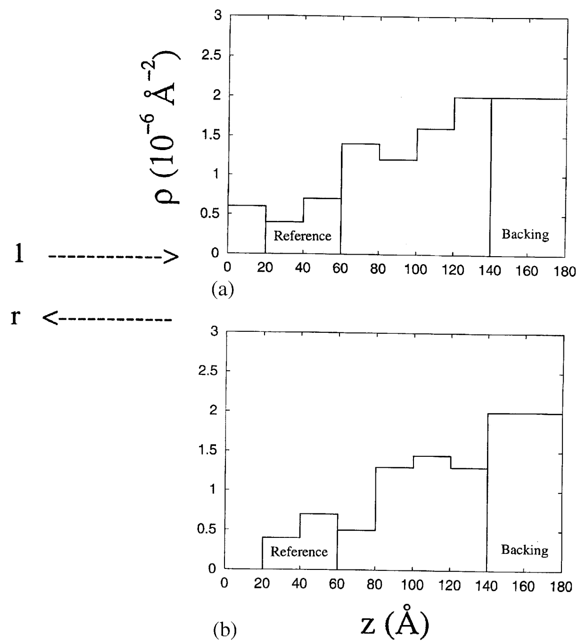

Fig. 9. Model SLD (neutron) profiles, (a) and (b), similar to two of the profiles considered by Zimmermann et al. in Fig. 3 of Ref. [6] for X-ray reflection. Note that not only are the backings the same, but both profiles share a common "reference" or known segment between $z = 20$ and 60 Å.

further diminish the already small differences that occur near a few of the minima). Thus, even "armed" with the prior knowledge of a portion of the film, it would seem unlikely that analysis of a single measurement of $R(Q)$ could distinguish between these two instances. These two model SLD profiles, in fact, are similar to two of the profiles considered in Fig. 3 of the work of

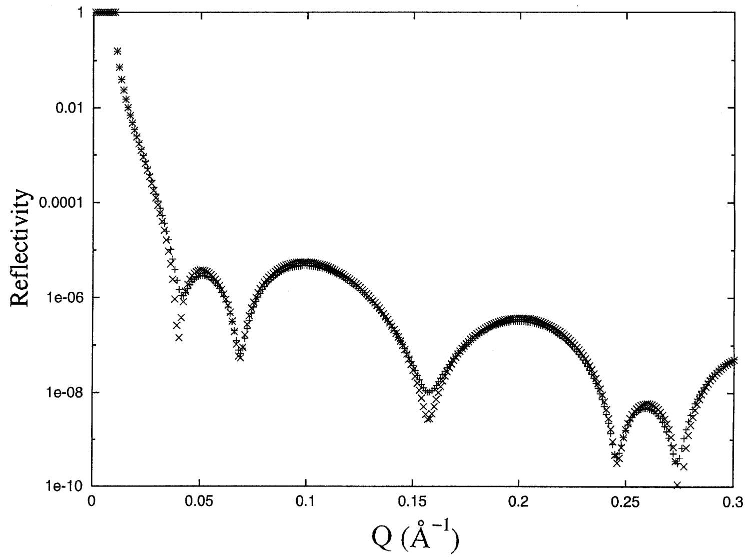

Fig. 10. Neutron reflectivities for the two composite film systems (including backing) of Figs. 9a and b. Convolution for instrumental resolution has not been applied. The two curves are practically indistinguishable from one another; slight differences primarily occur in the vicinity of some of the minima.

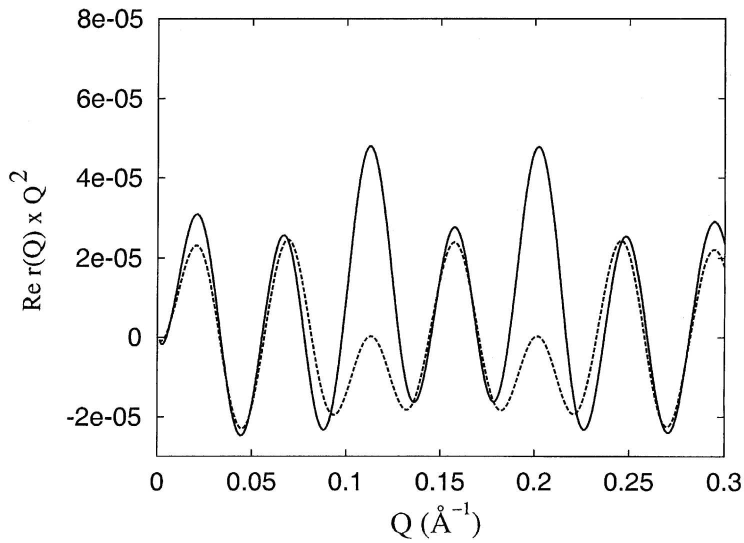

Fig. 11. Q^2 *Re r*(Q) for the (reversed) film structures of Fig. 9 (not including the backing but incorporating the known or reference sections of the films). These *Re r*(Q) correspond to what would be retrieved, for example, by phase-sensitive reflectivity experiments (for each of the two SLD profiles) in which the backing SLD density was varied according to the methods discussed in the text. In contrast to the situation illustrated in Fig. 10, these curves are markedly different over a wide range of Q.

Zimmermann et al. [6] for X-ray reflection. Within the BA, it was demonstrated that the X-ray reflectivity curves corresponding to three different SLD profiles (those depicted in Fig. 3 of Ref. [6]) were essentially indistinguishable from one another. As Zimmermann et al. concluded, although sets of SLD profiles exists for which, under the right conditions, the phase can be approximately reconstructed with enough accuracy that a single reflectivity curve suffices, this is not always so.

It is true that the two SLD profiles of Fig. 9 do not produce mathematically identical reflectivities, and thus there are some observable differences in the reflectivity curves plotted in Fig. 10. But from the standpoint of practical measurement, the two spectra are essentially equivalent, even without instrumental effects. On the other hand, the corresponding $Re\,r(Q)$ for the films, shown in Fig. 11, which can be retrieved by application of the reference methodologies discussed above, can significantly enhance the sensitivity for identifying the true SLD profile in practice.

4. Conclusions

The possibility of exactly determining the complex reflection amplitude for a film of interest, through the use of reference structures, enables a first-principles inversion that yields a unique SLD profile. These exact methods of phase determination are valid in general at all wave vector transfers, even where the BA and DWBA schemes break down; and they can be directly applied to determine what measurements are necessary in a given case to ensure that the SLD profile subsequently deduced will be unambiguous. Although it has been shown in the literature that certain potentials exist for which the measurement of a single reflectivity curve under the right conditions suffices to reconstruct a satisfactory approximation of the phase, such is not the case in general. Other, realistic, SLD profiles produce reflectivity curves close enough to a degree which cannot be experimentally distinguished by present instrumentation. For these latter cases, multiple reference methods are necessary to restore phase sensitivity.

References

[1] K. Chadan, P.C. Sabattier, Inverse Problems in Quantum Scattering Theory, Springer, New York, 1989.
[2] T. Aktosun, P.E. Sacks, Inverse Problems 16 (2000) 821.
[3] W. Leslauer, J.K. Blasie, Acta Crystallogr. A 27 (1971) 456.
[4] M.K. Sanyal, S.K. Sinha, A. Gibaud, K.G. Huang, B.L. Carvalho, M. Rafailovich, J. Sokolov, X. Zhao, W. Zhao, Europhysics Lett. 21 (1993) 691.
[5] W.L. Clinton, Phys. Rev. B 48 (1993) 1.
[6] K.-M. Zimmermann, M. Tolan, R. Weber, J. Stettner, A. K. Doerr, W. Press, Phys. Rev. B 62 (2000) 10377.
[7] N.F. Berk, C.F. Majkrzak, J. Phys. Soc. Jpn. 65 (Suppl. A) (1996) 107.
[8] P.E. Sacks, J. Math. Phys. 38 (1997) 3497.
[9] G. Reiss, R. Lipperheide, Phys. Rev. B 53 (1996) 8157.
[10] N.F. Berk, C.F. Majkrzak, Phys. Rev. B 51 (1995) 11296.
[11] C.F. Majkrzak, N.F. Berk, Phys. Rev. B 52 (1995) 10827.
[12] V.O. deHaan, A.A. Van Well, S. Adenwalla, G.P. Felcher, Phys. Rev. B 52 (1995) 10831.
[13] C.F. Majkrzak, N.F. Berk, Phys. Rev. B 58 (1998) 15416 (Erratum Phys. Rev. B 60 16211.).
[14] C.F. Majkrzak, N.F. Berk, Langmuir, in press.
[15] C.F. Majkrzak, N.F. Berk, Doon Gibbs, in: L.E. Bennett, R.E. Watson (Eds.), Magnetic Multilayers, World Scientific, Singapore, 1994, p. 299.
[16] C.F. Majkrzak, N.F. Berk, J.F. Ankner, S.K. Satija, T.P. Russell, in: C.F. Majkrzak, J.L. Wood (Eds.), SPIE Conference Proceedings, Vol. 1738, SPIE, Bellingham, WA, 1992, p. 282.
[17] M. Born, E. Wolf, Principles of Optics, Pergamon Press, Oxford, 1987, p. 51.
[18] P. Croce, B. Pardo, Nouv. Rev. Opt. Appl. 1 (1970) 229.
[19] S. Yamada, T. Ebisawa, N. Achiwa, T. Akiyoshi, S. Okamoto, Annu. Rep. Res. Reactor Inst. Kyoto Univ. 11 (1978) 8.
[20] N.F. Berk, C.F. Majkrzak, Langmuir, in press.
[21] T. Aktosun, P.E. Sacks, SIAM J. Appl. Math. 60 (2000) 1340.
[22] A. Schreyer, C.F. Majkrzak, N.F. Berk, H. Gruell, C. Han, J. Phys. Chem. Solids 60 (1999) 1045.
[23] C.F. Majkrzak, N.F. Berk, J.A. Dura, S.K. Satija, A. Karim, J. Pedulla, R.D. Deslattes, Physica B 248 (1998) 338.
[24] C.F. Majkrzak, N.F. Berk, V. Silin, C.W. Meuse, Physica B 283 (2000) 248.
[25] H. Leeb, H. Groetz, J. Kaspar, R. Lipperheide, Phys. Rev. B 63 (2001) 45414.