Exact determination of the phase in neutron reflectometry

C. F. Majkrzak and N. F. Berk
Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-0001
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We show that by using a known reference layer having three tunable values of scattering density, an exact determination of the complex amplitude $R = \mathrm{Re}R + i\,\mathrm{Im}R$ for neutron specular reflection can be made for any unknown real potential (i.e., no absorption). This straightforward yet remarkable general result is valid even in the dynamical regime (where the conventional Born approximation fails) and makes it feasible to consider direct inversion methods for obtaining the scattering-length-density profile normal to the reflecting surface.

By measuring the number of neutrons elastically and specularly reflected from a flat surface as a function of glancing angle of incidence, information about the profile of the in-plane average of the scattering length density ρ along a direction z normal to the surface can be deduced. Neutron and x-ray reflectivity studies of various materials have increased dramatically in recent years with the growing interest in physical and chemical phenomena occurring at surfaces and interfaces.[1–5] However, extracting the profile from measured reflectivity $|R|^2$ as a function of wave vector transfer Q is difficult,[6] and no direct inversion scheme is possible in the absence of the phase of the complex reflection amplitude $R = \mathrm{Re}R + i\,\mathrm{Im}R$. Because of the difficulties in fitting measured $|R|^2$ to obtain $\rho(z)$, a variety of mathematical and experimental techniques have been advanced to provide knowledge of the phase. For example, techniques using references, as in interferometry, have been employed in both x-ray[7,8] and neutron[9,10] reflectometry to utilize implicit phase information in the process of reconstructing $\rho(z)$, but always in the Born and distorted-wave Born approximations. X-ray references can be structured, e.g., known multilayer sequence, or tunable, i.e., using a tunable x-ray synchrotron source to change the imaginary part of the scattering length density of the substrate with x-ray wavelength. Neutron reference layers have been fabricated from ferromagnetic substances having different scattering lengths for spin-up and spin-down neutrons. Alternatively, schemes for obtaining the phase of R have been proposed using logarithmic dispersion relations (within the Born approximation)[11] and based on measurements of absorption rates or dwell time.[12] Here we demonstrate a powerful yet simple means of obtaining the phase of R exactly for neutrons over the entire range of wave-vector transfer, from the kinematical limit to the dynamic scattering regime. We take advantage of the fact that the scattering length of neutrons almost always can be taken as real valued; the imaginary part accounts for absorption, which is negligible for neutrons, and for incoherent scattering, which generally can be ignored for thin films, even when incoherent scatterers such as water are involved.[13] Given the accessibility of the phase, fundamentally different approaches to determining the scattering-length-density profile, still a formidable problem, can be advanced.

In specular reflection from a film, the incident, reflected, and transmitted beams are plane waves, and the solution of the Schrödinger equation reduces to a one-dimensional problem within the film. For a scattering-length-density profile modeled by a sequence of layers of constant ρ, the amplitudes R of the reflected wave and T of the transmitted wave (for unit amplitude of the incident wave) can be calculated exactly from the matrix formula:[14]

$$\begin{pmatrix} T \\ in_b T \end{pmatrix} = \prod_{j=N}^{1} \begin{pmatrix} \cos\theta_j & \frac{1}{n_j}\sin\theta_j \\ -n_j \sin\theta_j & \cos\theta_j \end{pmatrix} \begin{pmatrix} 1+R \\ in_f(1-R) \end{pmatrix} \qquad (1)$$

with $\theta_j = \frac{1}{2}Qn_jd_j$ and $n_j = \sqrt{1-16\pi\rho_j/Q^2}$; n_b and n_f correspond to the "backing" (transmission) and "fronting" (incident) media, respectively; $Q = 2k_{0z}$[k_{0z} is the wave vector normal to the surface in free space (transverse components of the wave vector are constants of the motion)] and d_j is the thickness of a layer over which the scattering density has the constant value ρ_j. The matrix product is ordered with the sense of increasing distance into the film running to the left. The d_j can be made as small as necessary to represent an arbitrary profile, resulting in a transfer matrix, relating R and T, that in this representation is a product of N transfer matrices each representing a single layer. This way $|R(Q)|^2$ can be calculated over a finite Q range to arbitrary accuracy for all realistic profiles. More importantly for us, the rectangular representation is rigorously correct in the continuum limit, where the d_j become infinitesimals. Indeed, the transfer matrix and its intrinsic properties—those not depending on particular scattering potentials—are derivable directly from the continuum Schrödinger equation without the artifice of a discrete representation,[15] which then may emerge only when needed as a computational device. Thus results derived from the transfer-matrix formulation of the problem, including those here, are valid in general.

We denote the transfer-matrix product appearing in Eq. (1) as

$$\mathbf{M}(Q) = \begin{pmatrix} A(Q) & B(Q) \\ C(Q) & D(Q) \end{pmatrix}, \tag{2}$$

where, from Eq. (1), the matrix elements are seen to be real quantities for all values of Q, so long as ρ is real, which henceforth we take to be the case. Since the layer transfer matrices in Eq. (1) are unimodular, i.e., have unit determinant, this is also true of the product: $\det \mathbf{M} = AD - BC = 1$ (the unimodularity of $\mathbf{M}$ is an intrinsic property that can be established without the discrete representation.[15]) As the last preliminary, we take $n_f = n_b = 1$, corresponding to vaccum fronting and backing media. This is a mild restriction, which we repair later. By solving Eq. (1) and making use of these properties, one now finds

$$R = \frac{B + C + i(D - A)}{B - C + i(D + A)} \tag{3}$$

for the reflection amplitude. The directly measurable reflectivity then can be expressed as

$$2\left[\frac{1 + |R|^2}{1 - |R|^2}\right] = A^2 + B^2 + C^2 + D^2 \equiv \Sigma . \tag{4}$$

This result requires real-valued $\mathbf{M}$. Since $0 \leq |R| \leq 1$, $\Sigma \geq 2$. We also note that $\Sigma = \text{tr}\ \mathbf{M}^T\mathbf{M}$. (Thus $\mathbf{M}$ is not unitary, in general; otherwise $|R| \equiv 0$.) From a cursory comparison of Eqs. (3) and (4), it seems evident why measurements of $|R(Q)|^2$, which determines only the sum of squares of transfer-matrix elements, do not provide enough information to determine the individual matrix elements, even though they are real-valued quantities. The unrationalized form of Eq. (3) may lead one to an overly pessimistic view of the situation, however. When rationalized, Eq. (3) can also be expressed as

$$R = \frac{(B^2 + D^2) - (A^2 + C^2) - 2i(AB + CD)}{2 + (B^2 + D^2) + (A^2 + C^2)}, \tag{5}$$

which indicates that the determination of R needs only the three real quantities,

$$\begin{aligned} \alpha &= A^2 + C^2 , \\ \beta &= B^2 + D^2 , \end{aligned} \tag{6}$$

and

$$\gamma = AB + CD ,$$

rather than A, B, C, and D. It remains true that measurements of $|R|^2$ only yield $A^2 + B^2 + C^2 + D^2 = \alpha + \beta$, but we now derive a simple means of extracting α, β, and γ from reflectivity measurements of compound films containing the one of interest as a common constituent. Then reconstruction of the complex-valued $R(Q)$ for the isolated constituent follows from Eq. (5).

Suppose that a given scattering density profile is separated into two distinct regions representing known and unknown parts, as depicted in Fig. 1. The total transfer matrix can be expressed as a product of corresponding transfer matrices:

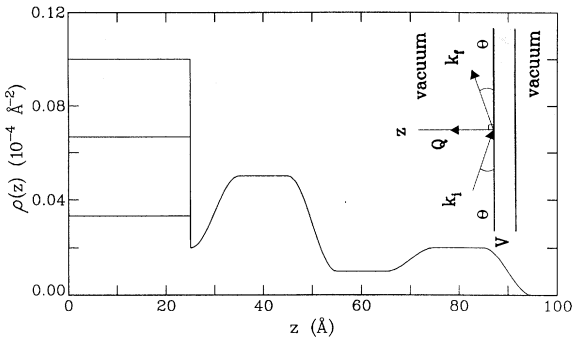

FIG. 1. Arbitrary scattering density profile separated into known reference layer (z = 0–25 Å) and "unknown" segment (z = 25–95 Å). The reference layer can take on three different values of ρ (3.33, 6.67, and 10.0×10^{-6} Å^{-2}) as described in the text. The inset in the upper right-hand corner of the figure indicates the scattering geometry.

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} w & x \\ y & z \end{pmatrix}, \tag{7}$$

where the matrix (a, b, c, d) describes the contribution from the unknown part of ρ and (w, x, y, z) gives the known part, which we call the reference. Now compose three films consisting of the unknown film and different reference films—we describe a practical means of carrying this out below—and make three corresponding measurements of the reflectivity, $|R(Q)|^2 = |R_1(Q)|^2$, $|R_2(Q)|^2$, and $|R_3(Q)|^2$. We thus measure three functions $\Sigma(Q) = \Sigma_1(Q)$, $\Sigma_2(Q)$, and $\Sigma_3(Q)$ as indicated in Eq. (4). However, using Eq. (7) we can write

$$\begin{aligned} A_i^2 &= a^2 w_i^2 + b^2 y_i^2 + 2ab w_i y_i , \\ C_i^2 &= c^2 w_i^2 + d^2 y_i^2 + 2cd w_i y_i , \\ B_i^2 &= a^2 x_i^2 + b^2 z_i^2 + 2ab x_i z_i , \\ D_i^2 &= c^2 x_i^2 + d^2 z_i^2 + 2cd x_i z_i \end{aligned} \tag{8}$$

for $i = 1, 2, 3$. Then from Eq. (4) [alternatively, write Eq. (7) as $\mathbf{M} = \mathbf{UK}$ and use $\Sigma = \text{tr}\ \mathbf{M}^T\mathbf{M} = \text{tr}\ (\mathbf{K}\mathbf{K}^T)(\mathbf{U}^T\mathbf{U})$], we have

$$\Sigma_i = (w_i^2 + x_i^2)\alpha + (y_i^2 + z_i^2)\beta + 2(w_i y_i + x_i z_i)\gamma \tag{9}$$

for each case, where α, β, and γ are defined as in Eq. (6)—but with A, B, C, and D replaced by a, b, c, and d—and are the same in each measurement. Because w_i, x_i, y_i, and z_i are known for each reference, Eq. (9) defines a system of three linear equations for the unknown part. The matrix of known coefficients generally is nonsingular for nondegenerate reference values, and Eq. (9) can be solved for $\alpha(Q)$, $\beta(Q)$, and $\gamma(Q)$ for $Q > 0$. Thus, from Eq. (5)—now using a, b, c, and d—we obtain the complex reflectivity amplitude, $R(Q)$, for the unknown film alone, translated to $z = 0$. We note that in Eq. (2), $A(-Q) = A(Q)$, $B(-Q) = -B(Q)$, $C(-Q) = -C(Q)$, and $D(-Q) = D(Q)$ (i.e., the diagonal elements of $\mathbf{M}$

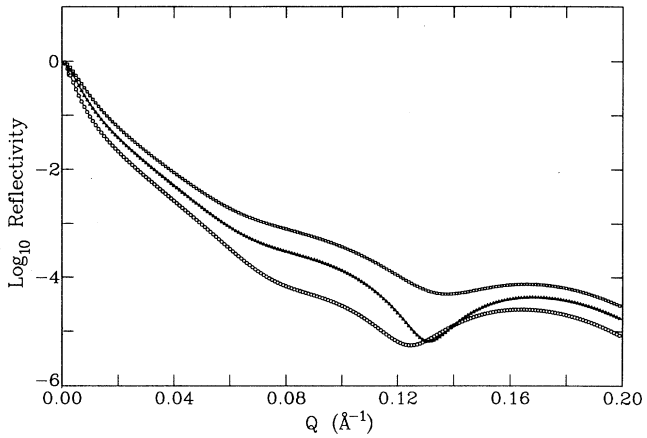

FIG. 2. Reflectivities corresponding to the scattering density profile of Fig. 1 for the three different reference layer densities ($\rho = 3.33 \times 10^{-6}$, 6.67×10^{-6}, and 10.0×10^{-6} Å^{-2}, indicated by circles, triangles, and squares, respectively).

are even in Q, while the off-diagonal elements are odd in Q). This also is an intrinsic property. Using it in Eq. (3) or (5), it follows that $R(-Q) = R(Q)^*$, so that $R(Q)$ is known over the entire Q domain if it is known for $Q \geq 0$.

In this method it is not required that the three reference portions have the same thicknesses or even that they be layers of constant ρ; it is only necessary that they be "known" in the sense of Eq. (9). In practice, however, the method likely will entail the use of simple reference layers of constant ρ values and common thickness, as illustrated in Fig. 1. As an example, Fig. 2 shows three reflectivity curves, corresponding to the three different reference ρ values for the model density profile shown in Fig. 1. In Fig. 3 are shown the real and imaginary parts of $R(Q)$ for the "unknown" part of the model, as obtained from the three sets of reflectivity plotted in Fig. 2 and Eqs. (9) and (5). Figure 3 also shows $R(Q)$ as directly calculated for the "unknown" part of the model—actually known to us, of course—using Eq. (1). Agreement is excellent—even near $Q = 0$, where Σ would diverge, and near points where the different reflectivities cross—and no incipient mathematical or computational instabilities are evident. The introductions of known nonvacuum fronting and backing media result in straightforward, if tedious, modifications of some of the formulas given above, but the only practical consequence is that with a material backing, the method is unusable below the critical edge, $|Q| < Q_c$, where $|R(Q)|^2 = 1$ and where $Q_c^2 = 16\pi\rho_b$. However, experiments can be arranged so that the beam is incident within a single-crystal medium such as Si, corresponding to real-valued $n_f(Q) > 1$. This fronting medium also acts as the mechanical substrate for the film with a backing medium that can be vacuum, $n_b = 1$. Thus the method described can be considered to be quite general. On the other hand, we see no easy relief for the restriction to real-valued ρ (real **M**).

We note in passing that the use of two known reference layers, one preceding and the other following the unknown region, make it possible—with nine, rather than three measurements—to determine the individual matrix elements (a, b, c, d) to within an overall sign, which is the best that can be done since, from Eq. (3), R itself is independent of the sign of M.

Finally, we describe a relatively easy way of realizing reference contrasts in actual experiments. With ferromagnetic Fe or Co as the reference layer, two scattering length densities can be obtained if the incident beam is polarized and the magnetic layer is saturated in the plane of the film. For spin-up and spin-down neutrons, the scattering densities of the reference layer are $\rho = \mathcal{N}(b \pm p)$, respectively, where b is the nuclear scattering length and p is the magnetic scattering length of the reference layer and $\mathcal{N}$ is the number density of scatterers. A third value, $\rho = \mathcal{N}b$, can be obtained from a demagnetized layer or with the magnetization perpendicular to the plane of the film. The use of magnetic reference layers has the advantage that the state of the layer can be changed without a chemical or structural effect on the sample. Of course, other contrast methods can be considered, including isotopic substitutions. Given such a relatively simple procedure to determine $R(Q) = \mathrm{Re}R(Q) + i\,\mathrm{Im}R(Q)$, direct inversion methods[16] can be revisited for practical application to neutron reflectometry.

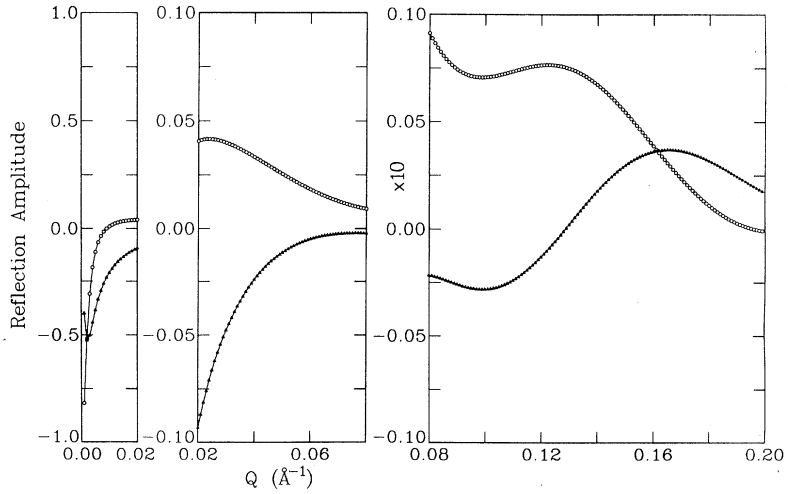

FIG. 3. Real (open circles) and imaginary (filled triangles) parts of the reflection amplitude $R = \mathrm{Re}R + i\,\mathrm{Im}R$ corresponding to the "unknown" segment of the scattering density profile of Fig. 1 as obtained from the three reflectivity curves of Fig. 2 via Eqs. (3)–(9). The solid curves through the symbols were generated directly (given the "unknown" part of the scattering density distribution) using Eq. (1). Note that the ranges of the vertical scale change by an order of magnitude from one region of Q to the next.

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