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# Using polarized neutrons to determine the phase of reflection from thin film structures

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## Abstract

It is now known that the phase of neutron specular reflection from a flat film structure can be determined exactly using reference layers, even in the dynamical regime at small wavevector transfer where the Born approximation is not valid. By employing a single buried ferromagnetic layer and polarized beams, two complex reflection amplitudes for the unknown part of the film can be algebraically extracted, only one of which is physical. We describe here a means of identifying the physical branch for actual polymer film data which fits the true reflection amplitude and produces the film's scattering length density profile directly and unambiguously. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

As in crystal diffraction where only scattered intensities are measured, specular neutron reflectivity experiments, which probe the scattering length density (SLD) profile along the surface normal of a film, usually suffer from the loss of essential phase information. Consequently, widely disparate SLDs can produce nearly identical fits to reflectivity spectra [1]. One technique used in crystallography to inform structure determination with phase information is isomorphic substitution [2], in which one or more atoms of the unit cell of interest are replaced in a known manner. Spectra from the original and referenced crystals can then be subtracted to reveal the phase of diffraction, leading to a direct determination of the unknown structure. This approach is valid, however, only when the scattering is kinematical, requiring the assumption that the incident neutron or X-ray wave is negligibly distorted by its interaction with the crystal, which usually is the case in Bragg scattering. Then the Born approximation applies, thereby

relating the scattering amplitude of the unit cell to its SLD by a Fourier transform. In reflectometry, however, reflection at small wavevector transfers Q is often sufficiently strong, either due to the film itself or the substrate supporting it, that the Born approximation breaks down; a dynamical description of the scattering is necessary, which properly accounts for the distortion of the wave within the reflecting media. This is especially important since some of the most significant information about the typical film SLD is contained in the low-Q reflectivity. Thus phase determining concepts stemming from isomorphic substitution need to be generalized to be useful in reflectometry.

It is possible, in fact, to determine the complex neutron specular reflection amplitude r exactly at each Q—even in the dynamical scattering regime—using reference layers [3,4]. In contrast to isomorphic substitution, these recent methods use reference structures that are external but adjacent to the "unknown" part of the composite film. (They also require that the SLD be effectively real valued, a condition almost always met with neutrons.) The original scheme [3,4] uses three independent references and concomitant reflectivity spectra to extract the unique complex reflection amplitude for the unknown common part of the composite films. The technique has been verified experimentally using

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Fig. 1. Polarized neutron reflectivities ("+" spin state, squares; "-" spin state, circles) for the film system shown schematically in the lower inset. Solid curves are model independent fits (see text) corresponding to the SLDs in the upper inset ("+" spin state, solid line; "-" spin state, dashed line).

three different metallic strips as references [5]. A simpler design [3] uses a single, saturated ferromagnetic reference layer with a neutron beam polarized first in the "+" and then in the "-" spin state to provide two distinct reference SLDs from the sum and difference of the nuclear and magnetic potentials of the reference layer. A third reference SLD can be realized by demagnetizing the magnetic layer or by aligning its moments along the direction of Q—i.e. parallel to the surface normal-so that the magnetic potential is effectively zero. This reference system has the benefit of needing only one composite chemical thin film structure to measure. Unfortunately, creating the third reference condition is not always feasible, because of magnetic domain sizes or the large applied fields needed to align the moments out of the film plane. However, related reference layer methods have subsequently been presented which employ only two measurements [6-8]. The simplest algebraic reduction of two measurements-say, two polarized beam reflectivities-gives two possible reflection amplitudes at each Q for the unknown part of the SLD, only one of which is physical. For some systems, identification of the physical solution is straightforward; and once known—actually, the real or imaginary part alone is sufficient—it can be inverted to obtain the desired SLD profile, using the method of Gel'fand, Levitan, and Marchenko (GLM) [9], which has been implemented in experiments [10], or other techniques. For some film systems, however, selecting the physical branch from actual data is problematical (indeed, even from some simulated systems).

We describe here a means of identifying the physical branch of the reflection amplitude from two measurements via a phase fitting scheme which simultaneously produces the SLD directly and unambiguously. This approach is shown to be effective in dealing with data where the physical solution is not immediately evident.

We illustrate this procedure with an application to a study in progress of the temperature dependent behavior of polymer films consisting of binary mixtures of deuterated polybutadiene and polyisoprene. Typically in binary polymer blends a preferential adsorption of either component at any interface can occur. Since a priori neither the layer sequence nor the adsorption properties is known, a unique,







Fig. 3. Polarized neutron reflectivities for the composite film structure consisting of the "unknown" polymer film and the previously characterized reference layers (symbols as in Fig. 1). Solid curves are model independent fits (see text) corresponding to the SLDs in the inset.

model independent determination of the SLD profile is especially important to avoid ambiguous determinations of the film structure.

### 2. Experimental procedures

### 2.1. Reference layer preparation and characterization

An Fe film nominally 50 Å thick was deposited by sputtering on a single crystal silicon substrate disc 10 cm in diameter and approximately 0.5 cm thick. The Fe layer was then capped with a sputtered film of Si about 100 Å, thick. Polarized beam neutron reflectivity measurements were made on this reference structure with the Fe layer saturated in the plane of the film in an applied magnetic field of about 20 mT (200 G). The reflectometry experiments were carried out at the NIST Center for Neutron Research on the NG-1 reflectometer at a nominal wavelength of 4.75 A. By varying the incident beam slit apertures with glancing angle of reflection, the beam footprint on the sample and the instrumental resolution dQ/Q were kept constant at approximately 2.5 cm (vertical direction)( × 5.0 cm (in the scattering plane) and 0.025, respectively. Polarizing efficiencies were maintained to be 95% or better at all wavevector transfers. The neutron beam was incident

on the sample from air with the Si substrate serving as the backing medium. Fig. 1 shows the reflectivities obtained after subtracting background and normalizing to the incident beam intensities. The inset in the upper right corner of Fig. 1 plots the SLD profiles— $\rho(z)$ , where z is along the film normal-one for each of the two Fe potentials, obtained by fitting the individual reflectivity curves using the model independent parametric B spline (PBS) method [1]. Note that the SiO/Si layer structures thus retrieved are nearly identical, as should be expected. Although the fits are good, and correspond to what was known to have been deposited, there is no guarantee that they are unique. To confirm that these SLD profiles are physically meaningful, we performed the following test: Im r pertaining to the SiO/Si layer alone was extracted via the phase determination method detailed below by taking the Fe layer portion of the composite as the reference. The result is plotted in Fig. 2; the inset shows the SLD profile for the SiO/Si layer subsequently obtained by inverting this Im r via the GLM method. The two SiO/Si profiles of Figs. 1 and 2 are in good agreement, demonstrating the consistency of the process.

## 2.2. Polymer film deposition

An approximately 400 Å thick film of deuterated polybutadiene (dPB, molecular weight = 108 kg/mol;



Fig. 4. Imaginary part of the complex reflection amplitude and sine of its phase angle,  $\phi$ , as obtained from the reflectivity data of Fig. 3using the method described in the text (symbols distinguish the two occurring roots). The dotted line for Im *r* is the best fit, produced by the SLD of Fig. 5; the dashed line shows the resulting selection of the physical branch from the two roots generated by the data. The solid line for sin( $\phi$ ) was calculated from the same SLD.

polydispersity = 1.06) and polyisoprene (PI, molecular weight = 138 kg/mol; polydispersity = 1.08) with a composition of 0.5 wt.% dPB was spin-coated out of toluene onto the Si/Fe/Si reference layer substrate. Previously, the substrate had been cleaned by UV light irradiation. This polymer blend exhibits a lower-critical-solution-temperature type behavior with a bulk critical decomposition temperature of  $T_{c,bulk} = 55^{\circ}$ C. In the present paper, we will restrict ourselves to a detailed discussion of the unique analysis of the neutron reflectivity data taken at 25°C in the homogenous single phase region. The analysis of the neutron data as a function of temperature measured through  $T_{c,bulk}$  into the two phase region will be presented elsewhere.

# 2.3. Neutron reflectivity measurements

The neutron reflectivity experiments on the composite polymer/reference film system were performed at the same facility and under similar conditions to those described in Section 2.1. The sample was maintained in vacuum (the Si substrate again serving as the backing medium) and at 25°C. The substrate was not the same one used for the reference layer characterization but was similar in size and

had reference layer films of nearly identical thicknesses and densities (the reference coatings were deposited in the same apparatus under the same conditions).

## 3. Results and analysis

To compensate for possible differences between the original reference layer and the one on which the polymer film was deposited, the reference SLDs finally used in the phase determination of the polymer experiment were obtained by an additional refinement. First, the original reference SLDs were employed to obtain a polymer SLD using the phasefitting method described below. Then, with this putative polymer SLD and the original reference SLDs as initializations, the two composite polarized beam measurements were fit using the PBS method. The polymer portion of the composite SLD changed relatively little in these fits, and the slightly modified reference portions were taken as the new reference SLDs for the final analysis.

Fig. 3 shows the measured reflectivities for the two composite systems as well as the SLD profiles resulting from model independent fits, indicated by the solid curved



Fig. 5. The same composite polarized neutron reflectivity data shown in Fig. 3 but with curves determined by the phase fitting method described in the text, and as applied in Fig. 4. The inset shows that part of the composite treated as unknown: namely the polymer and SiO/Si films. The dashed line schematically shows the result of a fit to X-ray data indicating an excess of the hydrogenous PI (which has nearly zero SLD) at the interfaces. The existence of an abrupt sample surface, instead of a rounded one, as seen with neutrons, has been independently confirmed with atomic force microscopy.

lines, using the PBS algorithm. Comparison of the SLD profile contained in the inset of Fig. 3 with that of Fig. 1 reveals nearly identical SiO/Si and Fe layers. The sharp peaks appearing at the edges of the Fe layer profile for the minus neutron spin state arise from interdiffusion between Fe and Si atoms at the interfaces; this effectively diminishes the Fe magnetization, in turn resulting in a reduced difference of nuclear and magnetic potentials [11].

The simplest algebraic reduction of the two composite reflectivities involves the solution of a quadratic equation at each Q, thus providing two possible solutions which are consistent with the measurements and certain mathematical constraints [10]. Nonetheless only one root is physically acceptable, i.e. consistent with an SLD for the unknown film: it is easy to show that if one root is independent of the reference SLDs, the other cannot be. The required continuity of the derivative of the reflection amplitude as a function of Q is sufficient, in principle, to reduce the choice of rto two smooth functions of Q, only one of which has the correct behavior as Q approaches the origin. Indeed, depending on the interplay of interferences from references and unknowns, choosing the physical branch can reduce to easy visual inspection [10] or it can be difficult, as in the cases described here. The determination of crossing points of the quadratic roots can be complicated by noise and by the actual shapes of the upper and lower root spectra.

Fig. 4 shows the two possible root branches of Im r—as obtained algebraically [10]—for the polymer and SiO/Si portions of the composite film extracted from the data of Fig. 3, taking the Fe film to act as the reference. To some extent, the physical member of the two branches appearing in Fig. 4 at small Q is evident; for example, as Q approaches zero, the lower branch can be identified as the physical one on grounds that the net scattering length density of the entire SLD profile is known to be positive; were it negative, Im r would approach the origin through positive values. However, identification of the correct branch at higher Q is difficult, due in part to signal to noise problems stemming from the large differences in magnitudes of the two reflectivity curves of Fig. 3.

Therefore, a new approach for selecting the physical root of the reflection amplitude was developed which fits r, using the PBS scheme but with a new optimization objective function. In the modified PBS, the objective compares (at each Q) a trial r (actually, we use Im r)—generated by a trial SLD—with each of the roots derived from the two measurements and computes the smallest discrepancy over the entire spectrum. Since only the physical branch of rderives from a reference-independent SLD, attempting to minimize this objective tends to draw the trial SLD toward the one consistent with the physical branch over the measured O-range. The measured value of r at each O is identified as the root lying closer to the best trial r. A significant benefit of the scheme is that the SLD profile being sought is obtained in the process of selecting the physical branch of r, namely the best trial SLD. This eliminates having to perform a separate calculation to invert r for the SLD, which may not always be practical. The dotted line plotted in Fig. 4 represents the result of this fitting process and corresponds to the SLD profile shown in the inset of Fig. 5, along with the reflectivity curves generated by it (in conjunction with the Fe references) for comparison with the original composite reflectivity data. The agreement between calculated and measured reflectivities is good, and the fact that the "known" portion of the profile, namely that made up of the SiO/Si layers, is well reproduced speaks of the uniqueness of the solution obtained from real data with phase information. Some degree of ambiguity remains, namely at high Q values in Fig. 5 and around z = 0 in the insets of Figs. 1 and 5, because of statistical uncertainties, truncation of the Q-range, and possible inaccuracies in the knowledge of the reference SLDs.

For the polymer film being studied, we have established here that the SLD profile is rounded at both interfaces. Independent X-ray reflectivity measurements, on the contrary, which cannot distinguish between the two constituents of the polymer blend, yield an SLD with much more abrupt boundaries, shown schematically in the inset to Fig. 5 by the dashed line. The rounding of the neutron SLD profile clearly indicates an excess of PI, which has nearly zero SLD, at the film edges. This effect is a result of a preferential adsorption of PI at both interfaces [12].

## 4. Conclusions

We have determined the complex amplitude for specular

neutron reflection from two measurements with references using a phase-fitting procedure, simultaneously retrieving the SLD profile unambiguously. The determination of the phase in neutron reflectometry experiments is important in establishing the quality and uniqueness of the SLD profile derived from such measurements. The use of ferromagnetic reference layers with polarized beams is an effective and practical means of doing so. In the case at hand, we have proven a preferential adsorption of the hydrogenous component of the dPB/PI polymer blend at both film edges.

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