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The Use of Polarised Neutron Reflection for Unique Density Profile Determination in Thin Films

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Abstract

A recent paper by Sivia *et al*[1] has shown theoretically the use of polarised neutrons and a magnetised substrate to determine uniquely a density profile from neutron reflectometry data. Presented here are preliminary results of the technique applied to a polymer film on a magnetised nickel substrate.

Introduction

Although the application of neutrons to the study of density profiles as a function of depth is now well established, the information obtained is often subject to questions of uniqueness. The experimental data holds vital information about layer thicknesses as well as interfacial and surface structure, but the inability to directly invert this data to a density-depth profile can in some cases prevent the technique being fully exploited.

Recently however, theoretical developments have led to a potential method for overcoming some of these ambiguities. The method is based on a distorted-wave Born approximation, which Sanyal *et al*[2] have successfully applied to X-ray data. This method becomes very powerful if polarised neutrons are used in conjunction with a magnetised substrate. In this short communication preliminary results for a thin polymer film deposited onto a nickel substrate are presented.

Theory

The essential requirement of this technique is to be able to measure the unknown non-magnetic film on two different substrates whose scattering-length densities can denoted by a_1 and a_2. Using a magnetised substrate and polarised neutrons this condition is satisfied for the scattering-length densities of the parallel and anti-parallel spin components of the polarised neutrons. In this way two simultaneous experiments are being performed on the same film but effectively different substrates. The scattering-length densities of the nickel substrate will then be given by either the sum or difference of the nuclear and magnetic components. Under these conditions the difference in the reflectivities for the two neutron spin states is given by:

$$\frac{\left(R_1(Q)-R_2(Q)\right)}{R_f(Q)} = \left(a_1^2 - a_2^2\right) + 2\left(a_1 - a_2\right)\mathrm{Re}\left\{\int \frac{d\beta(z)}{dz} e^{iQ'z} dz\right\} \qquad ...(1)$$

Where z is the perpendicular distance to the surface, $R_i(Q)$ are the reflectivities as a function of the neutron wavevector transfer, Q, of the substrates ($i=1,2$) and Fresnel reflectivity ($i=f$) and Q' is the average wavevector transfer measured in the film. In the simplest approximation $R_f(Q)$ is given by $4\pi/Q^4$. The delta function, $\delta(0)$, arises from the interface between a substrate and the film deposited on it. If equation (1) is Fourier transformed, the derivative of the scattering length density, $d\beta(z)/dz$, of the film is obtained directly and unambiguously:

$$\frac{1}{2\pi}\int\left(\frac{\left(R_1(Q)-R_2(Q)\right)}{R_f(Q)}\right)e^{-iQ'z}dz=\left(a_1^2-a_2^2\right)\delta(0) \qquad \ldots(2)$$
$$+\left(a_1-a_2\right)\left[\frac{d\beta(z)}{dz}+\frac{d\beta(-z)}{dz}\right]$$

Experimental

A nickel film of the order of 1μm thickness was deposited onto a 50 mm diameter silicon optical flat (Semiconductor Processing Company, USA) by electron beam deposition. To a very good approximation such a thick nickel layer effectively becomes the substrate with respect to the neutrons which will not be influenced by the deeply buried Si-Ni interface. Before deposition the Si substrate was cleaned with Decon solution in an ultra-sound bath followed by $HF_{(aq)}$ treatment. The reflectivity of the sample was measured in the polarised mode of the CRISP reflectometer, with a magnetic field at the sample of 2.6 kG and an incident angle of 0.5°.The raw reflectivity data was normalised using corrections for the spin flipper efficiency. This correction removes the parallel spin contaminating component in the anti-parallel spin data. A thin polymer film was spun coated onto the nickel coated substrate from an 1% solution of deuterated polystyrene (dPS) in dry toluene. After air drying overnight the sample was remeasured in the polarised mode of CRISP at magnetic fields of 2.6 kG and also 5.9 kG, both at 0.5° incident angle and the data was reduced as before.

Results and Discussion

The reflectivity data for the nickel 'substrate' in the polarised mode with a field of 2.6 kG is shown in Figure (1). The difference in the two reflectivities for the spin states are clearly evident having critical edges at λ = 5.03Å (Q = 0.0193Å^{-1})and λ = 5.66Å (Q = 0.0218Å^{-1}) for the spins parallel and anti-parallel to the applied field. Both of the reflectivities are typical of a Fresnel reflectivity for a single interface between two bulk media. Fits to the data using standard matrix model calculations are superimposed on the data of Figure (1). The fitting parameters are given below in Table 1, where a is the scattering-length density and zb is the interfacial roughness. The values of a for R_1 and R_2 give an average moment per atom for the

nickel of $\overline{\mu}$ = 0.475/μB, which is 0.78 that of the saturation value, clearly indicating that the substrate is not fully saturated by the field.

The reflectivities of the two spin states of the sample coated with dPS is shown in Figure 2 with the nickel sample Fresnel behaviour superimposed for comparison. The two reflectivities were fitted simultaneously using a refinement fitting program which gave the fits to the data as shown in Figure 3 *a* and *b*. The resulting scattering-length density profiles are shown in Figure 3*c*. The two scattering-length densities for the substrate in the two different spin states are consistent with the theoretical values, as given in Table 1. However, although the values for the scattering-length density for the dPS layer for the two substrate spin states are consistent these are drastically smaller than the theoretical value of 0.62×10^{-5} Å. The value produced suggests one of two possibilities: either a very low density film or a substantial amount of hydrogenated polystyrene. It is unclear at this point which of these two possibilities is correct, and will require further investigation.

Using this normal fitting routine the dPS layer thickness of 270 Å with a air-dPS roughness of 20Å and a nickel-dPS interfacial roughness of 30Å. The nickel-dPS roughness is smaller than the value expected from the fits to the bare nickel sample, but with the polymer present the fitting procedure is relatively insensitive to this interface. This nickel-dPS interface roughness is a little too large for the distorted-wave Born approximation to work effectively, since a very sharp interface is required. However, it is now possible to compare the conventional fitting procedure against the results obtained by the distorted-wave Born approximation.

Table 1: *A comparison of the fitting parameters to the experimental data of the nickel substrate and theoretical calculations assuming bulk nickel densities and complete saturation by the magnetic field.*

	Experimental Data		**Theory**	
	Parallel	**Anti-parallel**	**Parallel**	**Anti-parallel**
a ($\times10^5$ Å^{-2})	0.99	0.76	1.09	0.79
zb (Å)	60	63	/	/

The normalised difference in the reflectivities is shown in Figure 4*a*, where the Q range has been restricted to avoid the total reflection data which are not in the kinematic regime. It is quite clear that the quality of the data is not good but this is mainly due to poor statistics. However, if Equation (2) is applied to this normalised data the ACF produced is shown in Figure 4*b*. A clear peak in the ACF is evident at about 250Å. This corresponds to the position of a maxima in $d\beta\ (z)/dz$ and is approximately consistent with the thickness of the dPS layer obtained by the conventional fitting procedure of 275Å. The peak at approximately 500Å is most probably an echo of the peak at 250Å. In using Equation (2) an assumption about the average scattering-length density of the dPS layer is made in order to calculate Q'. The effect of an incorrect choice of Q' is evidenced by the two minima either side of main peak at 250Å. The situation can be visually improved by applying maximum entropy reconstruction to the ACF data which removes the ringing associated with direct Fourier transformation, the result is shown in Figure 4*c*.

Conclusions

The distorted-wave Born approximation has been applied to the reflectivity data collected from a dPS film on a nickel magnetised substrate using polarised neutrons. By collecting the reflectivities from the two spin states of the neutrons the thickness of the polymer layer has been obtained unambiguously. The values obtained by this approximation are comparable to the thickness obtained by more conventional fitting procedures. These preliminary measurements show that the technique proposed by Sivia and Pynn[1] is viable provided high quality samples with sharp interfaces are prepared, and a sufficient Q range is measured.

Acknowledgements

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References

(1) D.S. Sivia and R. Pynn SPIE Conference proceedings *"Neutron Optical Devices and Applications"* vol. 1738 (1992)

(2) M.K. Sanyal, S.K. Sinha, A. Gibaud, K.C. Huang, B.L. Carvalho, M. Rafailovich, J. Sokolov, X. Zhao and W. Zhao *Europhys. Lett.* **21** (1993) 691

Figure Captions

Figure 1: Reflectivity profiles for the two neutron spin states of the bare nickel substrate in a magnetic field of 2.6 kG at an incident angle of 0.5°, the solid line through the data points are the fits to the data assuming the parameters given in Table 1. (● parallel spin, O anti-parallel spin.)

Figure 2: Comparison of the polarised neutron reflectivities for the bare nickel substrate (O) at 2.6 kG field and after spin coating with dPS (●) at 5.9 kG field strength.

Figure 3: Fits to the dPS on nickel reflectivity data (solid lines) of the polarised neutrons with spins (a) parallel and (b) anti-parallel to the magnet field. The field strength at the sample is 5.9 kG. The scattering-length density-depth profiles used in these fitting models are shown in part (c).

Figure 4: (a) Normalised difference in the reflectivity curves for the dPS film shown in Figures 3a and b restricted to the outside the region of total reflection. After applying Equation (2) to the difference data of part (a) the auto-correlation data is obtained (b). If the direct Fourier transformed data is reconstructed using a maximum entropy procedure the ringing observed is reduced, (c).

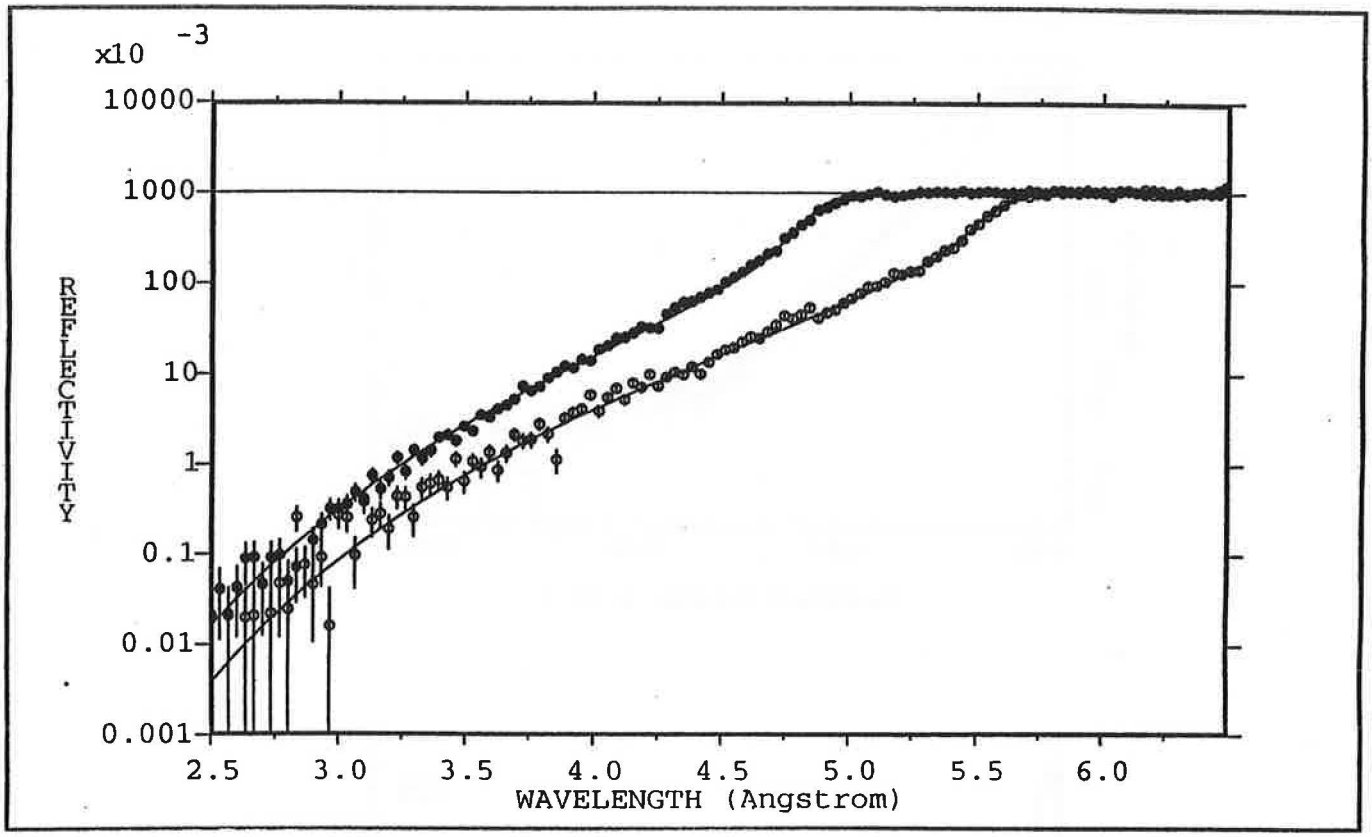


Figure 1

Figure 2

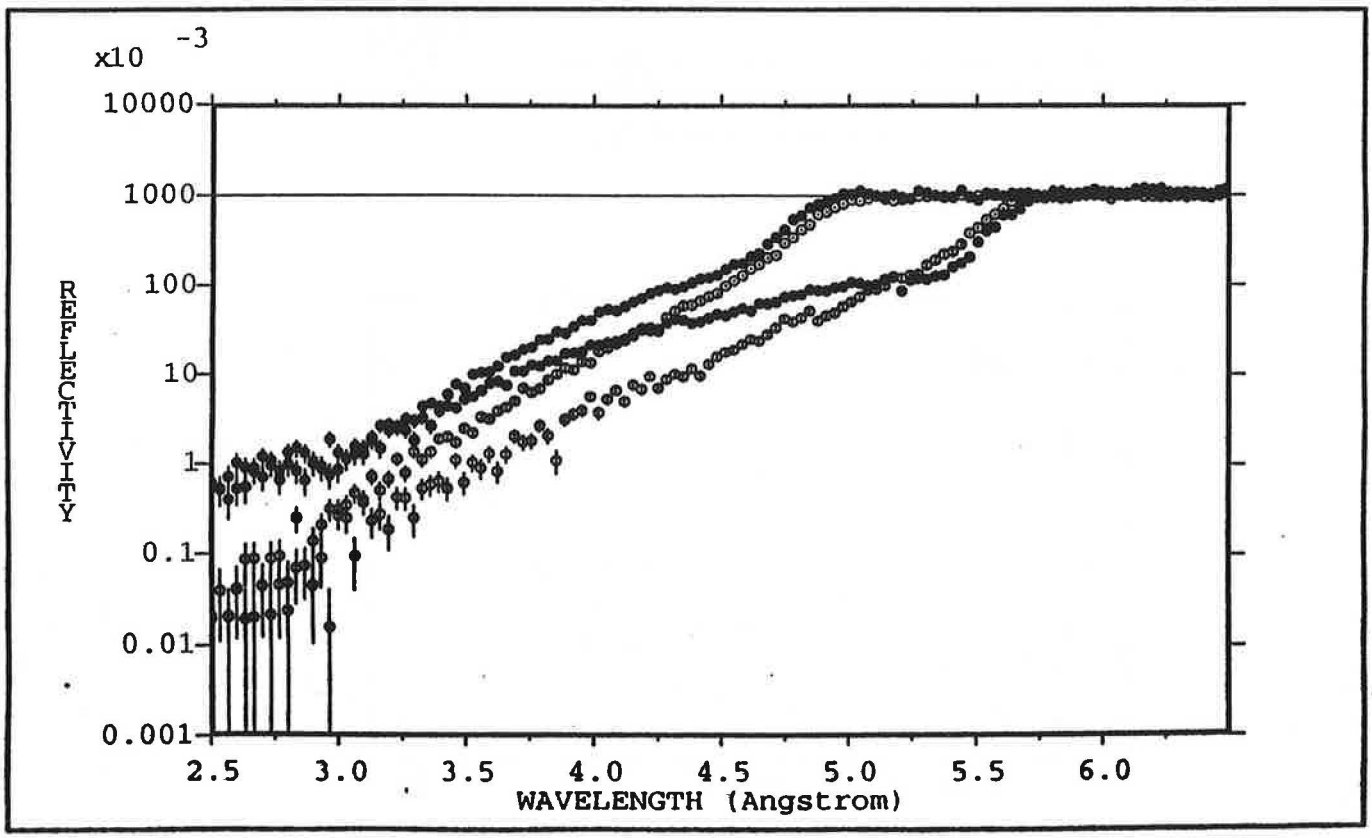
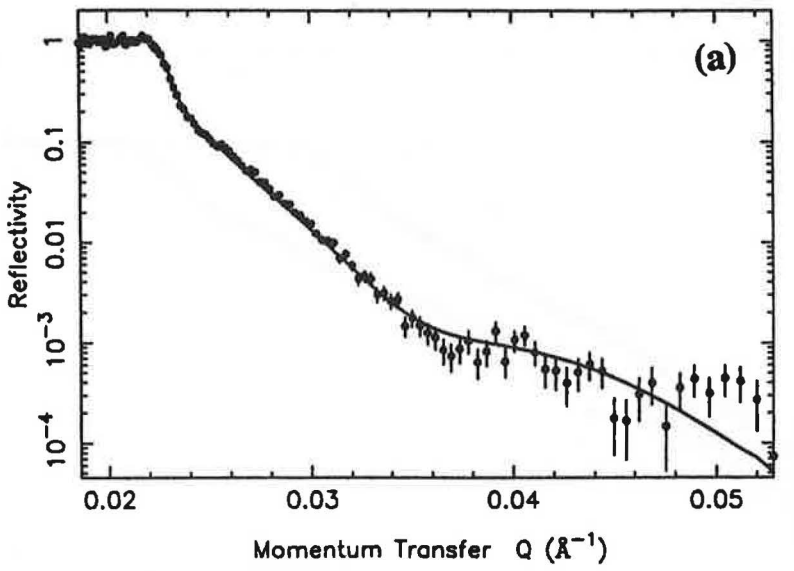
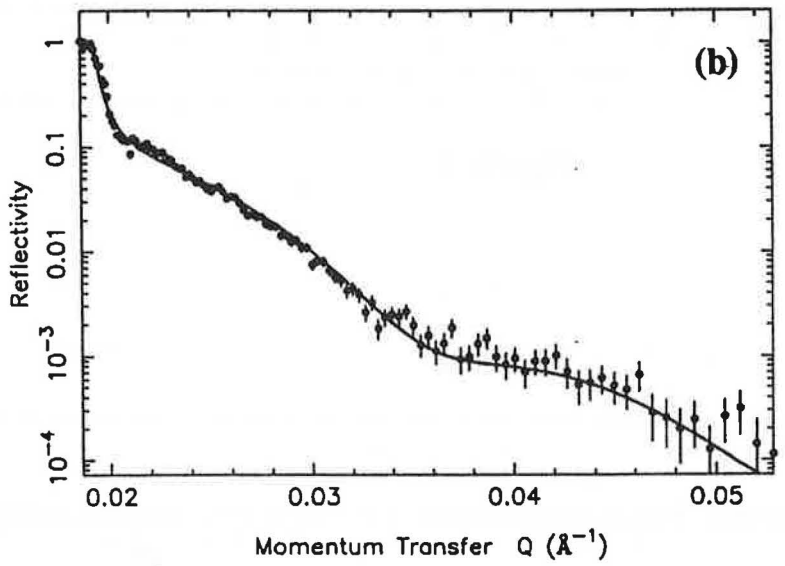


Figure 3


(a)
Reflectivity
1
0.1
0.01
10^{-3}
10^{-4}
0.02
0.03
0.04
0.05
Momentum Transfer Q ($Å^{-1}$)


(b)
Reflectivity
1
0.1
0.01
10^{-3}
10^{-4}
0.02
0.03
0.04
0.05
Momentum Transfer Q ($Å^{-1}$)

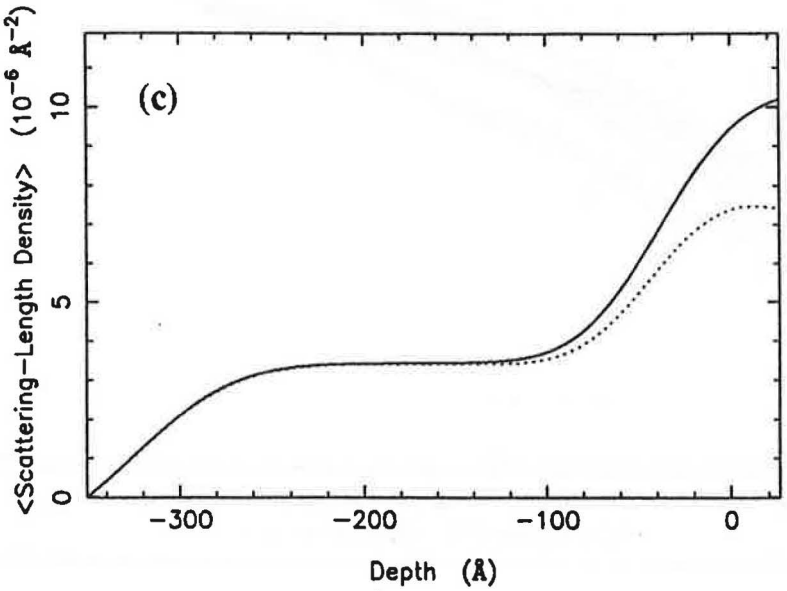
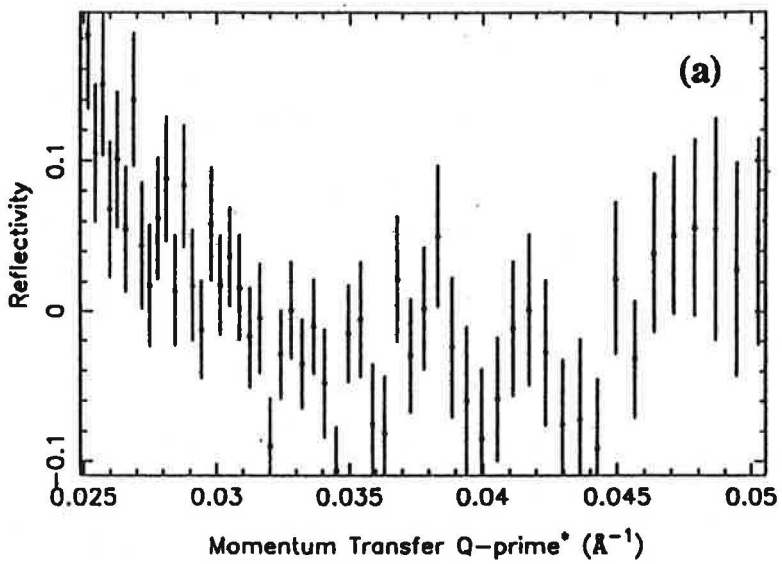
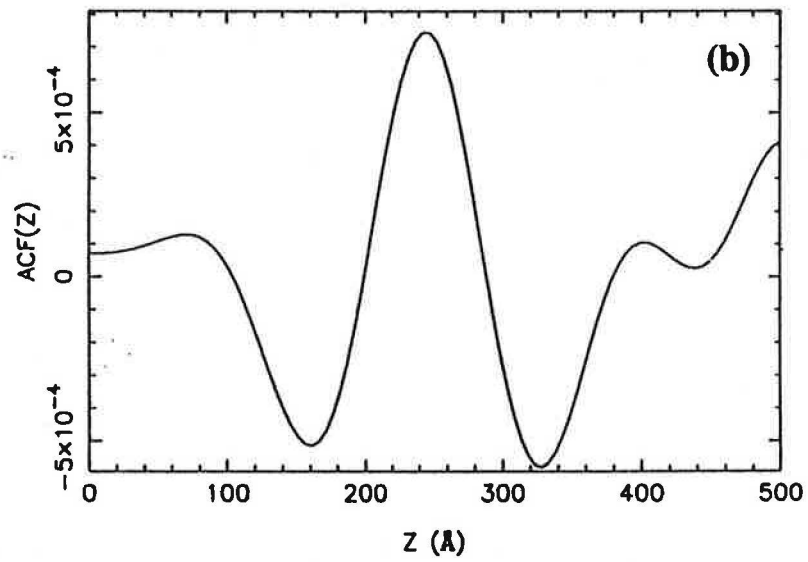
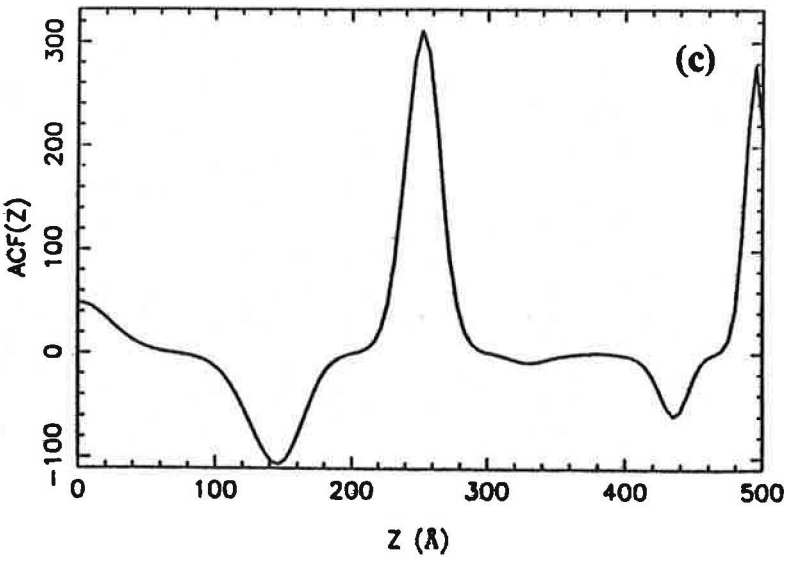

(c)
<Scattering-Length Density> (10^{-6} $Å^{-2}$)
0
5
10
−300
−200
−100
0
Depth (Å)

Figure 4


(a)
Reflectivity
0.1
0
−0.1
0.025
0.03
0.035
0.04
0.045
0.05
Momentum Transfer Q−prime* (Å^{-1})


(b)
ACF(Z)
5x10^{-4}
0
−5x10^{-4}
0
100
200
300
400
500
Z (Å)


(c)
ACF(Z)
300
200
100
0
−100
0
100
200
300
400
500
Z (Å)