National School on Neutron and X-ray Scattering
August 15-29, 2004
Argonne National Laboratory

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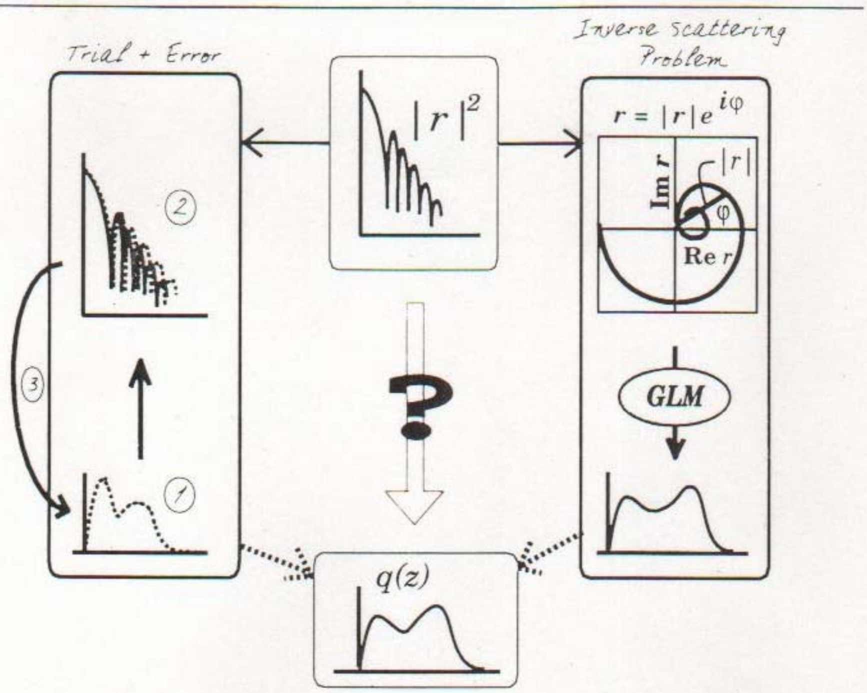
Interpretation of Reflectivity Data and the Phase Problem

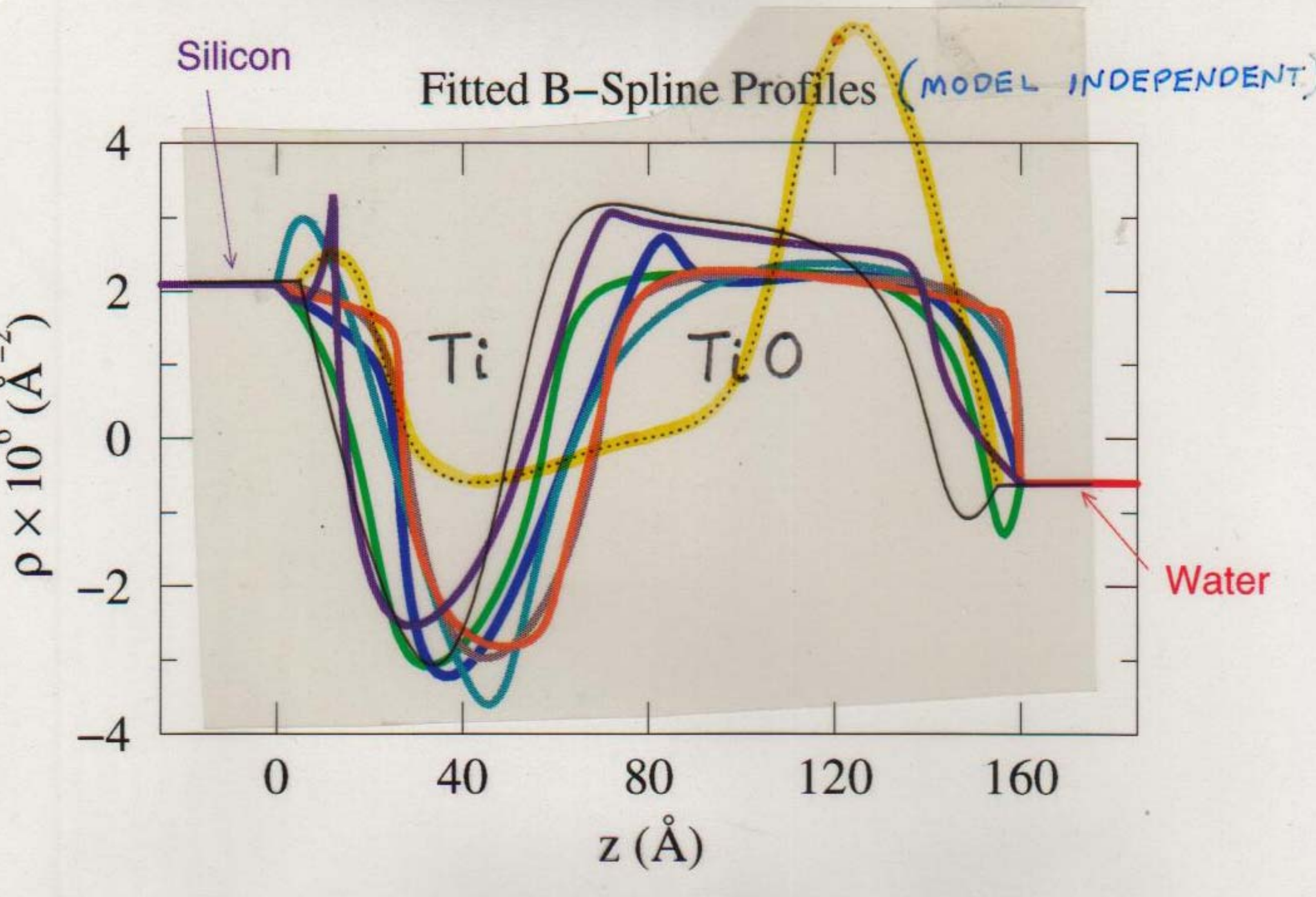


(After N.F.Berk et al.)

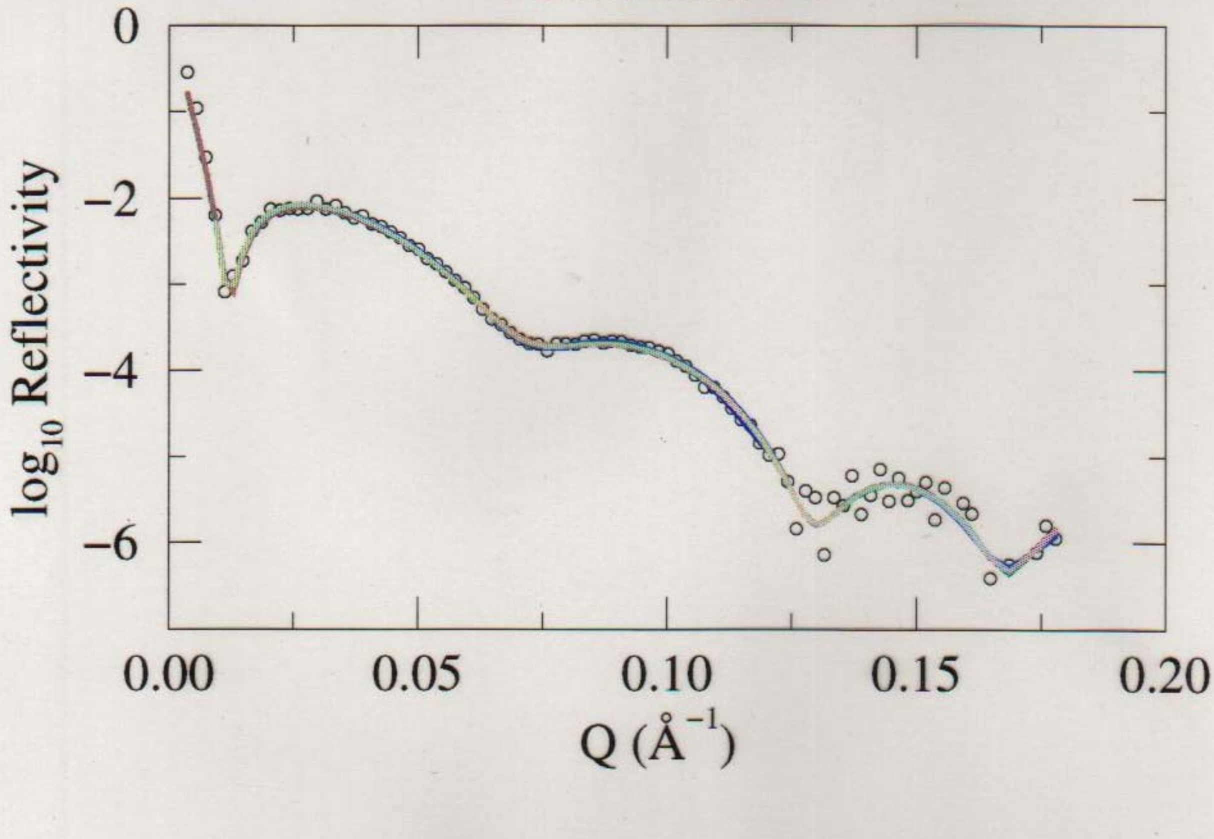
C.F.Majkrzak

National Institute of Standards and Technology

Fitted B−Spline Profiles (MODEL INDEPENDENT)



Fitted Reflectivities



- SINCE ONLY $|\Psi|^2$ IS A MEASURABLE QUANTITY, CANNOT <u>DIRECTLY</u> OBTAIN REFLECTION AMPLITUDE r, BUT ONLY THE <u>REFLECTIVITY</u> $|r|^2$: $r = |r| e^{i\phi}$: $|r|^2 = |r| e^{-i\phi} |r| e^{+i\phi}$

$$\boxed{|r|^2 = \frac{\text{REFLECTED } \underline{\text{INTENSITY}}}{\text{INCIDENT } \underline{\text{INTENSITY}}}}$$

⇨ HENCE, TO OBTAIN $\rho(z)$ FROM $|r(Q)|^2$ REQUIRES A CURVE FITTING ANALYSIS

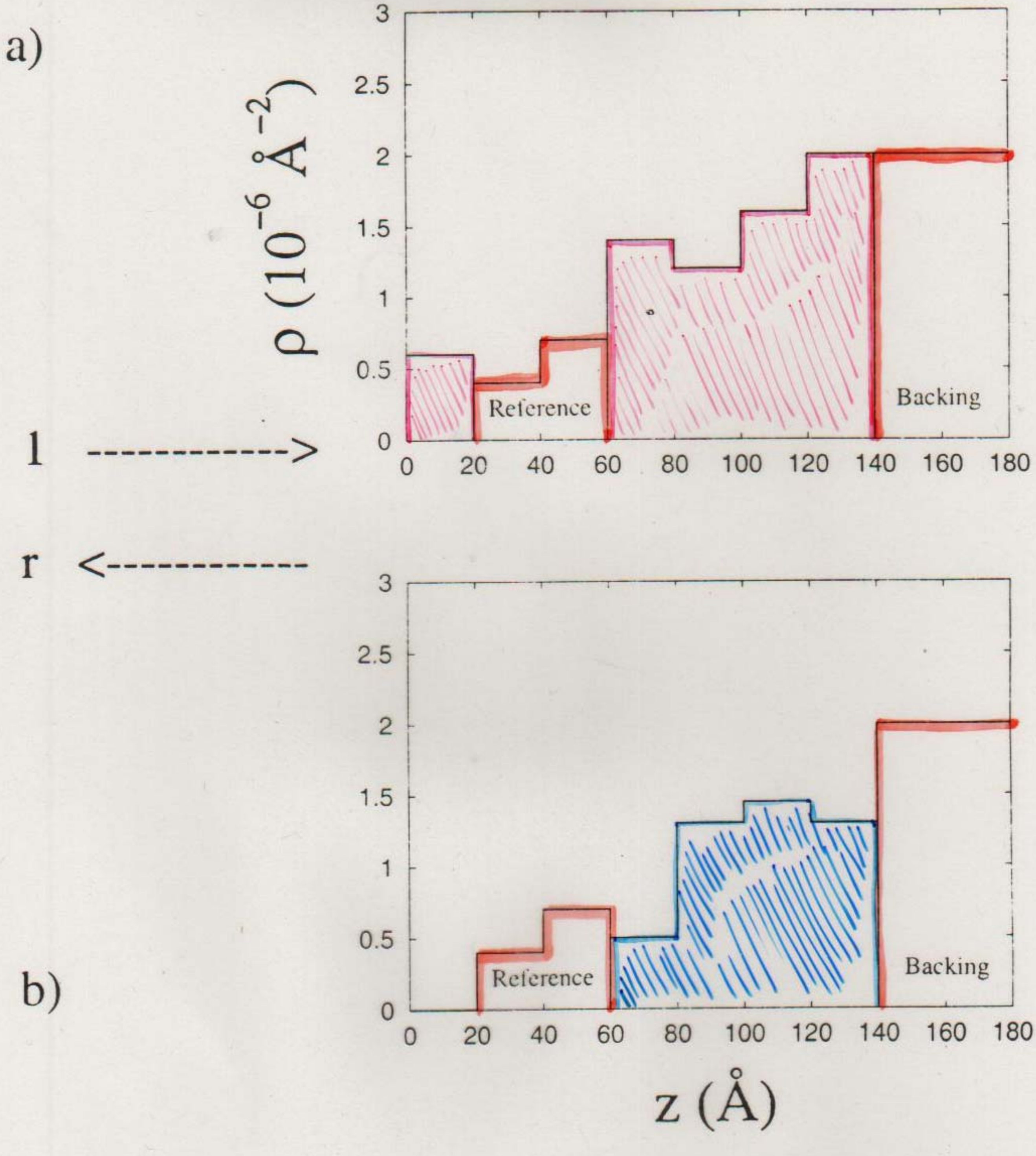
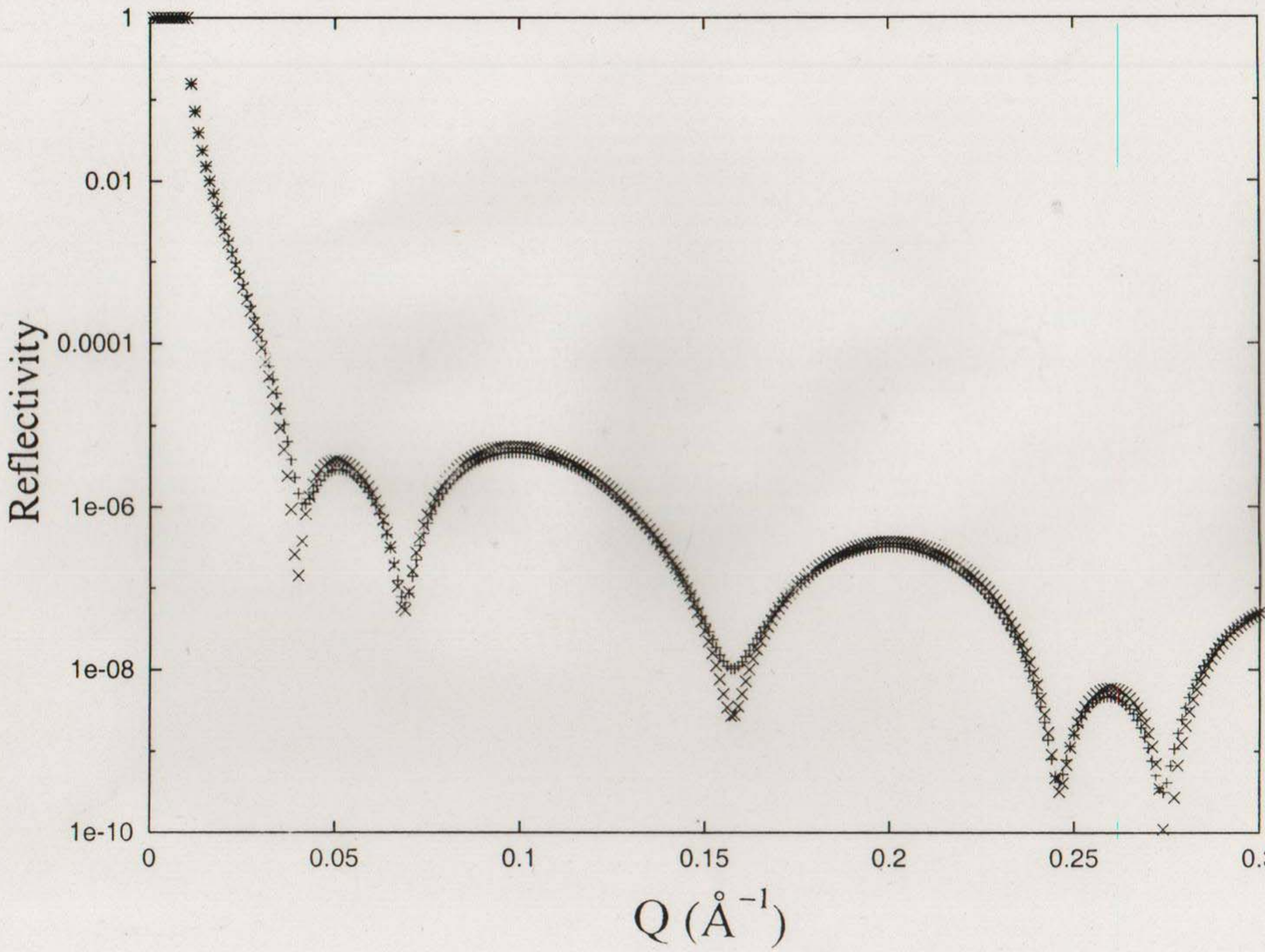


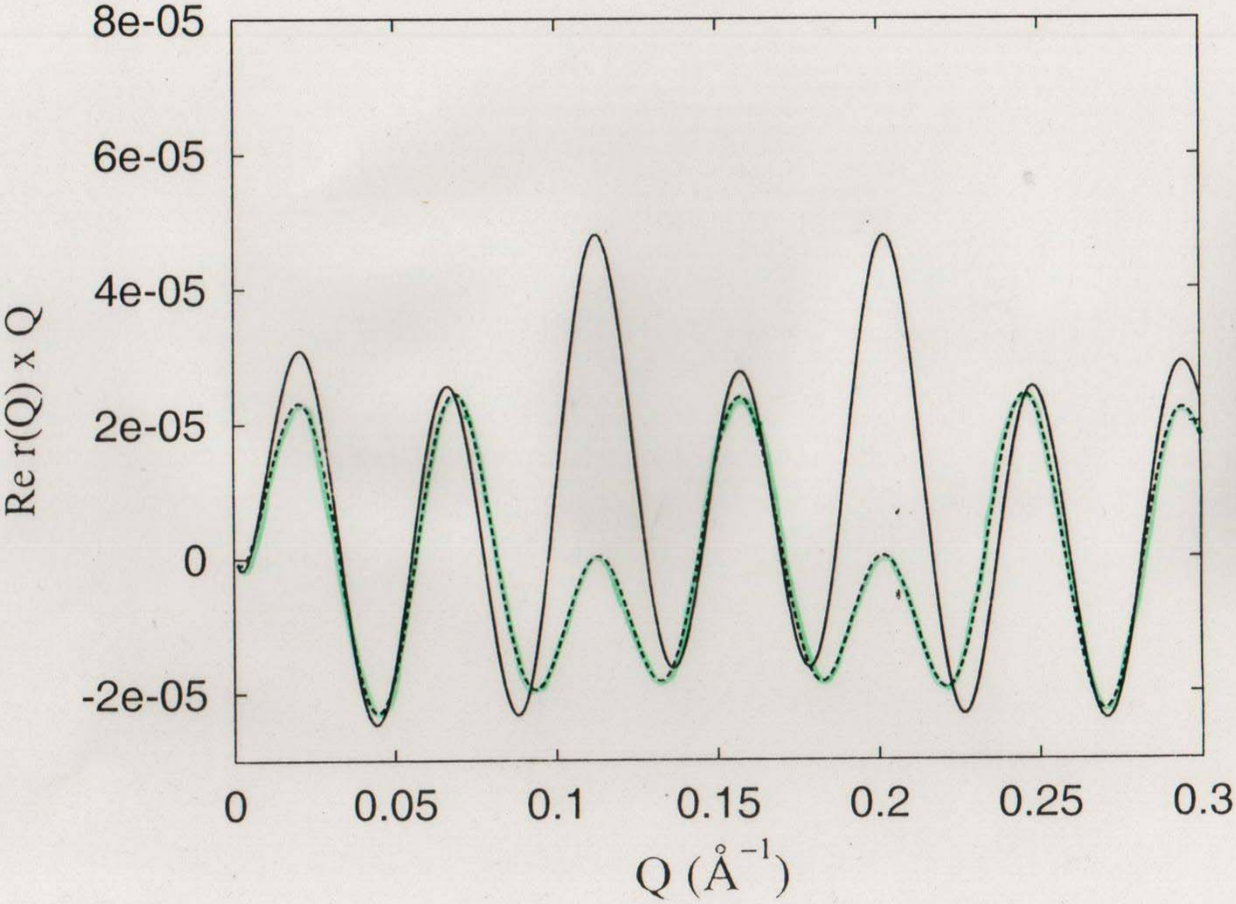
Figure 9.

Figure 10.

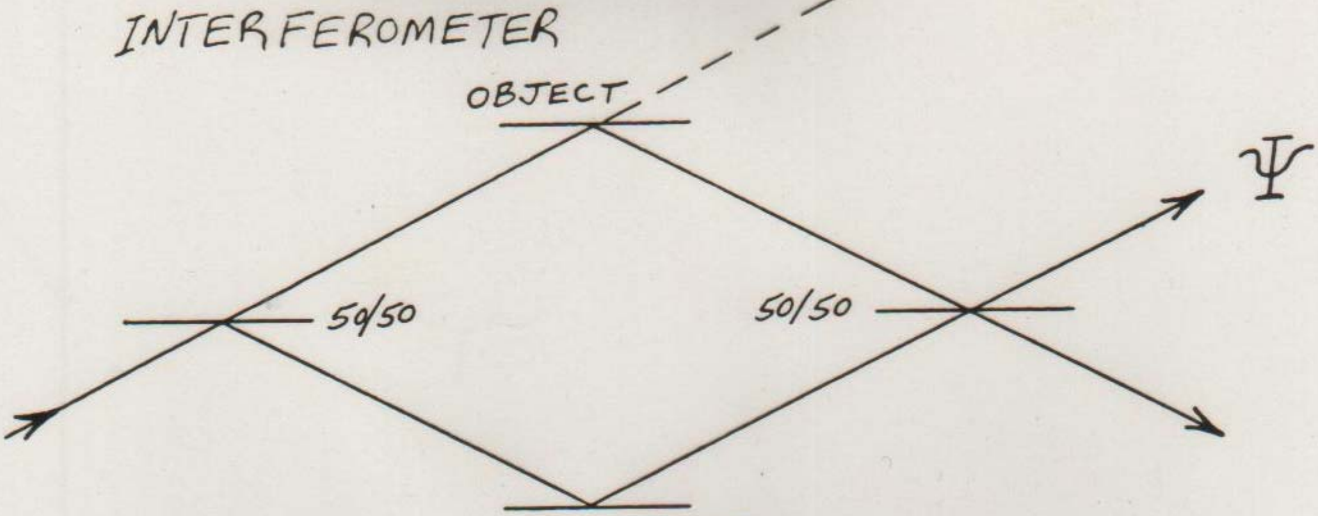


1
0.01
0.0001
1e-06
1e-08
1e-10
Reflectivity
0
0.05
0.1
0.15
0.2
0.25
0.3
Q (Å^{-1})

Figure 11.



INTERFEROMETER



(ASSUME EXACTLY SYMMETRIC PATHS) ← !

$$|\Psi|^2 = |\Psi_R + \Psi_0|^2 = |\Psi_R|^2 + |\Psi_0|^2$$
$$+ \Psi_R^* \Psi_0 + \Psi_R \Psi_0^*$$

IF $\Psi_R = |R_R| e^{i\phi_R}$

AND $\Psi_0 = |R_0| e^{i\phi_0}$

$$|\Psi|^2 = |R_R|^2 + |R_0|^2 + 2|R_R||R_0|\cos(\phi_0 - \phi_R)$$

PHASE ANGLE INFORMATION IS ENCODED AS INTENSITY WHICH CAN BE MEASURED

AMPLITUDE

$$R = \frac{4\pi}{iQ}\int_{-\infty}^{+\infty} \underbrace{\psi_F(x)}_{\left[A(x)e^{+ik_x x}+B(x)e^{-ik_x x}\right]}\ \underbrace{\rho(x)}_{Nb}\ \underbrace{\psi_I(x)}_{e^{ik_{0x}x}}\,dx$$

$$(k_x = m_x k_{0x})$$

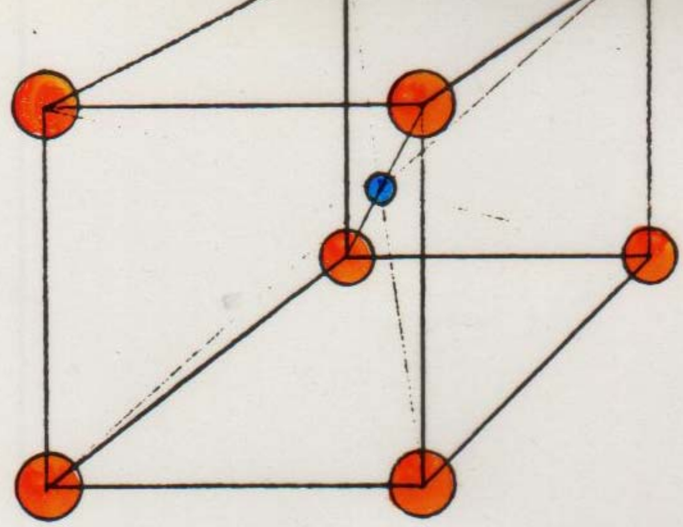
BORN APPROXIMATION

$$\psi_F(x) = e^{ik_x x} \quad \text{SET} \simeq e^{ik_{0x}x}$$

$$R_{BORN} = \frac{4\pi}{iQ}\int_{-\infty}^{+\infty} \rho(x)\, e^{iQx}\, dx$$

$$(Q = 2k_{0x})$$

$$|R_{BORN}|^2 = \Big|\underbrace{\frac{4\pi}{iQ}\int_{-\infty}^{+\infty}\rho(x)e^{iQx}dx}_{F}\Big|^2$$



ISOMORPHIC SUBSTITUTION IN CRYSTALLOGRAPHY

$$F \propto \sum_{j=1}^{N} f_j \, e^{i\vec{Q}\cdot\vec{r}}$$

$$\left.\begin{aligned} I_A &\propto |F_{SA} + F_R|^2 \\ &= |F_{SA}|^2 + |F_R|^2 + 2F_{SA}F_R \\ I_B &\propto |F_{SB}|^2 + |F_R|^2 + 2F_{SB}F_R \end{aligned}\right\} \text{CENTRO-SYMMETRIC CASE}$$

$$\underbrace{\frac{I_A - I_B}{C}}_{\text{MEASURE}} = |F_{SA}|^2 - |F_{SB}|^2 + 2(F_{SA} - F_{SB})\,F_R$$

SOLVE FOR MAGNITUDE & SIGN

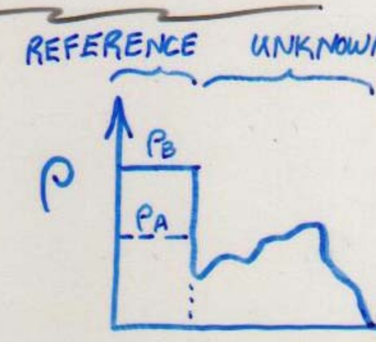
$(F_{SA}, F_{SB}$ KNOWN$)$

$$|R|^2 = \left(\frac{4\pi}{Q}\right)^2 \left| \int_{-\infty} \rho(z)\, e^{iQz}\, dz \right|^2$$

$$= \left(\frac{4\pi}{Q}\right)^2 \left| F(Q) \right|^2$$

USE REFERENCE LAYERS :

$$F_{A,B} = F + F_{REF.\,A,B}$$



$$|R_A|^2 - |R_B|^2 = \left(\frac{4\pi}{Q}\right)^2 \left[|F_A|^2 - |F_B|^2 \right]$$

$$= \left(\frac{4\pi}{Q}\right)^2 \left\{ |F_{REF\,A}|^2 - |F_{REF\,B}|^2 + 2\,\mathrm{Re}\left[F^* \left[F_{REF\,A} - F_{REF\,B} \right] \right] \right\}$$

X-RAY AND NEUTRON REFLECTOMETRY
(APPROXIMATION METHODS)

- W. LESSLAUER AND J.K. BLASIE, ACTA CRYST. <u>A27</u>, 456 (1971).

  (X-RAYS, THIN FILMS & MULTILAYERS, BORN APPROXIMATION)

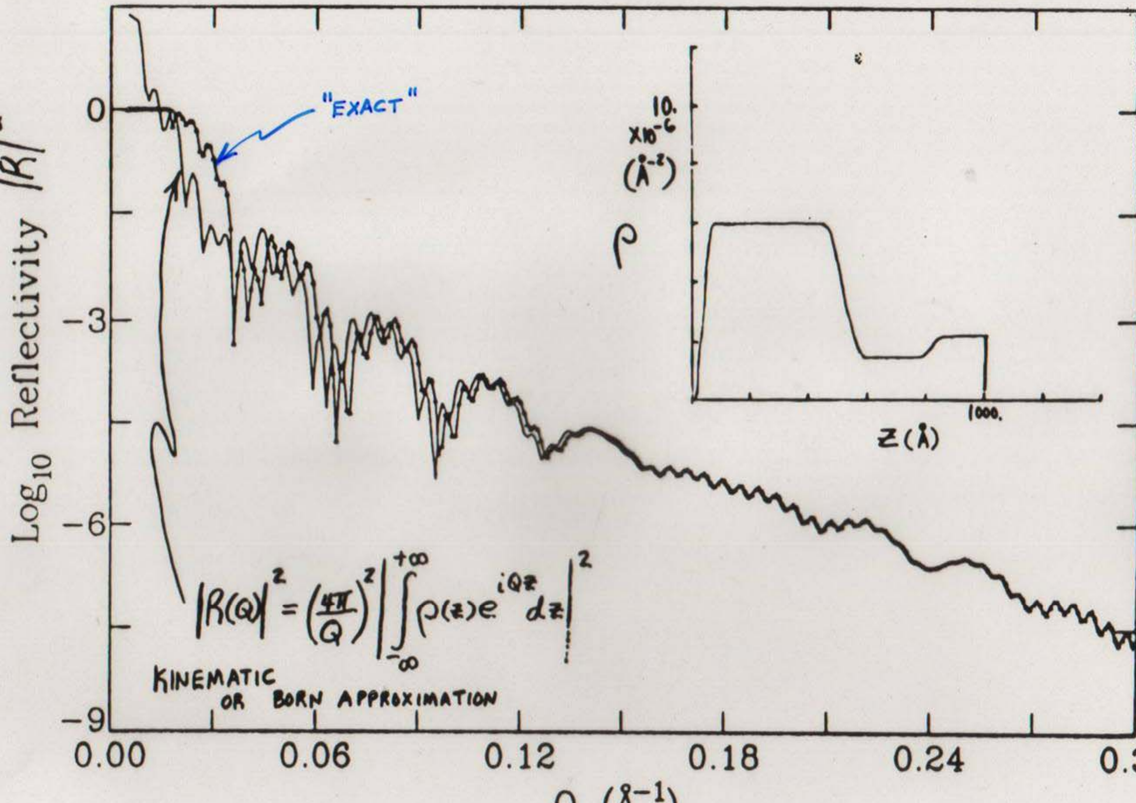
- S.K. SINHA, M.K. SANYAL, K.G. HUANG, A. GIBAU M. RAFAILOVICH, J. SOKOLOV, X. ZHAO, AND W. ZHAO, IN <u>SURFACE X-RAY AND NEUTRON SCATTERING</u>, EDS. H. ZABEL AND I.K. ROBINSON, (SPRINGER-VERLAG, BERLIN, 1992) p. 85.

  (X-RAYS, THIN FILMS, TUNING THROUG ABSORPTION EDGE OF SUBSTRATE, DWB

- C.F. MAJKRZAK, N.F. BERK, J.F. ANKNER, S.K. SATIJA, AND T.P. RUSSELL, IN SPIE PROC. VOL. 1738, EDS. C.F. MAJKR AND J. WOOD, (SPIE, BELLINGHAM, WA, 1992) p.

  (NEUTRONS, THIN FILMS, POLARIZED BEAM WITH MAGNETIC REFERENCE LAYER, BORN & DWBA)

PROBLEM: BORN APPROXIMATION FAILS AT SUFFICIENTLY SMALL Q — MUST THEN USE EXACT THEORY



Comparison between kinematic (line) and dynamic (triangle + line) plus-state reflectivities for a density profile similar to that of Fig.2 as described in the text.

FOURIER TRANSFORM OF THE COMPLEX REFLECTION AMPLITUDE

$$\mathcal{R}(z) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty r(k_z)\, e^{i k_z z}\, dk_z$$

GEL FAND LEVITAN MARCHENKO INTEGRAL EQUATION

$$K(z,y) + \mathcal{R}(z+y) + \int_{-z}^{+z} K(z,x)\,\mathcal{R}(x+y)\,dx =$$

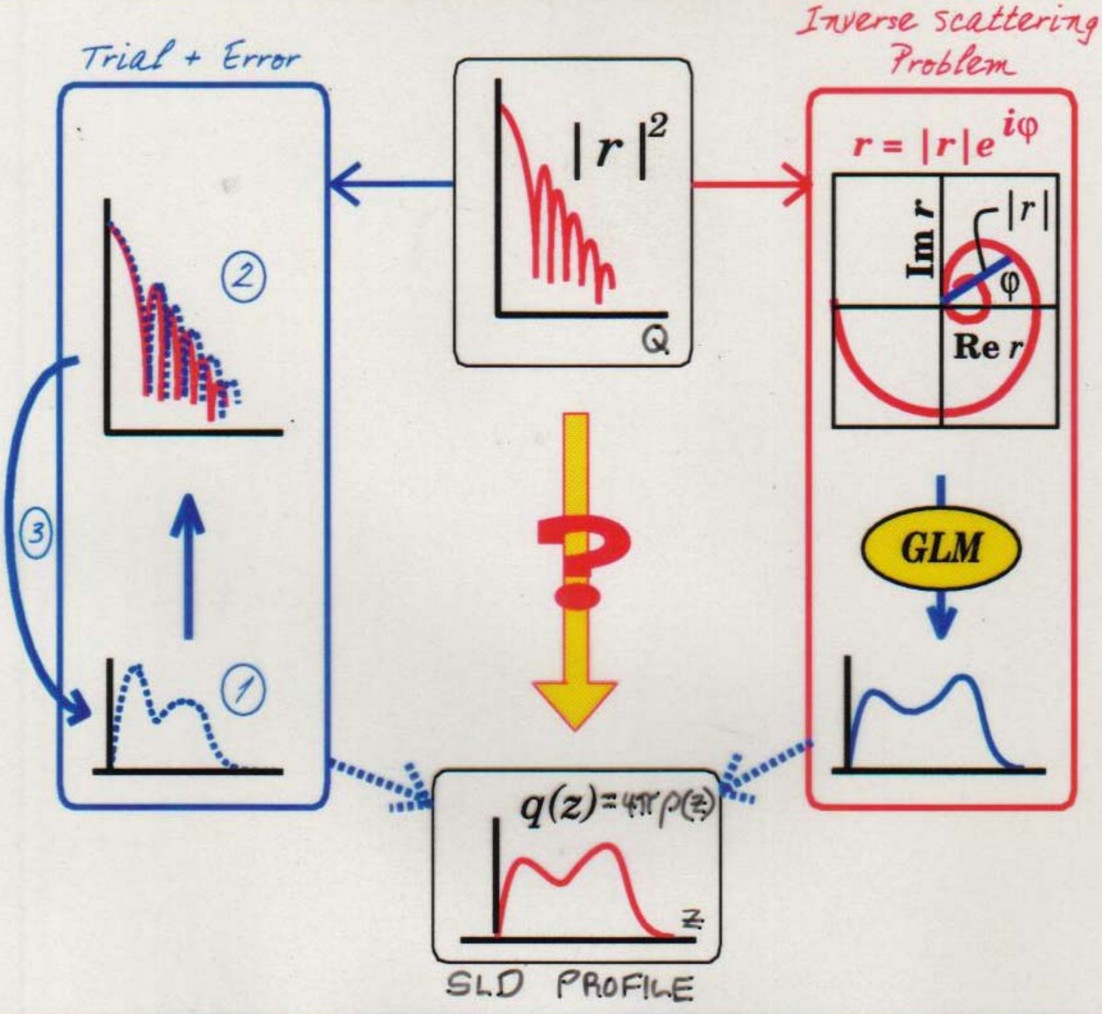
SCATTERING LENGTH DENSITY

$$\rho(z) = 2\,\frac{d\,K(z,z)}{dz}$$

GIVEN THE COMPLEX REFLECTION AMPLITUDE, THE SCATTERING LENGTH DENSITY ρ CAN BE OBTAINED FROM AN EXACT, FIRST PRINCIPLE INVERSION FOR A REAL POTENTIAL OF FINITE EXTENT — AND THE SOLUTION IS UNIQUE!

NO FITTING, NO ADJUSTABLE PARAMETERS

Inverting reflectivity



Phase determination

C.F. Majkrzak and N.F. Berk, Phys. Rev. B **52**, 10827 (1995).
V.–O. de Haan, et al., Phys. Rev. B **52**, 10830 (1995).
A.A. van Well, S. Adenwalla, & G.P. Felcher
H. Leeb, H.R. Lipperheide and G. Reiss, this conference.

Logarithmic dispersion

W.L. Clinton, Phys. Rev. B **48**, 1 (1993).

Tunneling times

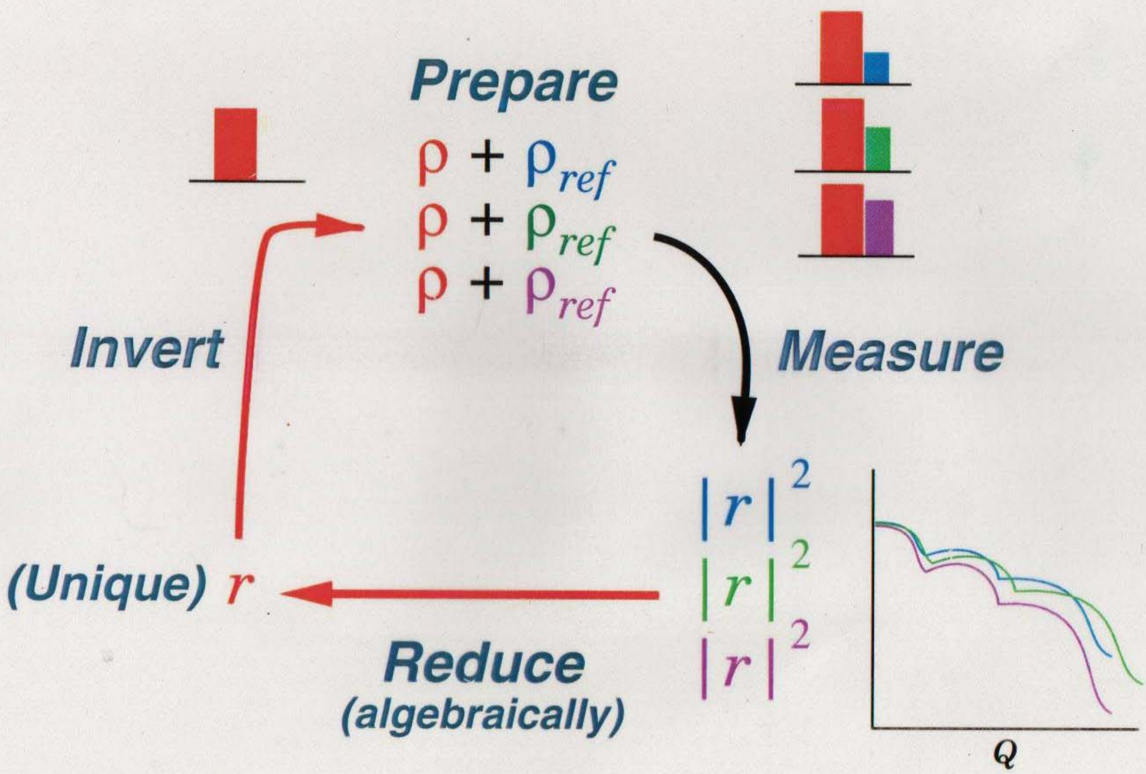
H. Fiedeldey, H.R. Lipperheide, et al., Phys. Lett. A **170**, 347 (1992).

Pseudo–inversion

S.K. Sinha, et al., *Surface X–Ray and Neutron Scattering*, 85 (Springer, 1992).
C.F. Majkrzak, N.F. Berk, et al., SPIE Proc. **1738**, 282 (1992).

NIST

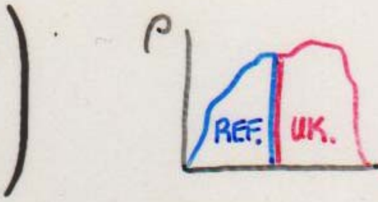
Phase Determination with 3 References



Majkrzak & Berk, 1995
de Haan, et al., 1995

POTENTIAL ...

$$\underbrace{\begin{pmatrix} A & B \\ C & D \end{pmatrix}}_{\substack{\text{COMPOSITE} \\ (1,2,3)}} = \underbrace{\begin{pmatrix} a & b \\ c & d \end{pmatrix}}_{\text{UNKNOWN}} \underbrace{\begin{pmatrix} w & x \\ y & z \end{pmatrix}}_{\text{REFERENCE } (1,2,3)}$$



$$|R(Q)|^2 = |R_1(Q)|^2, \ |R_2(Q)|^2, \text{ and } |R_3(Q)|^2$$

$$\Sigma_i \equiv 2\left[\frac{1+|R_i|^2}{1-|R_i|^2}\right] = A_i^2 + B_i^2 + C_i^2 + D_i^2$$

$$A_i^2 = a^2 w_i^2 + b^2 y_i^2 + 2ab w_i y_i$$

$$C_i^2 = c^2 w_i^2 + d^2 y_i^2 + 2cd w_i y_i$$

$$B_i^2 = a^2 x_i^2 + b^2 z_i^2 + 2ab x_i z_i$$

$$D_i^2 = c^2 x_i^2 + d^2 z_i^2 + 2cd x_i z_i$$

(INDEPEN
AT EACH

$$\Sigma_i = \overbrace{(w_i^2 + x_i^2)}^{\text{REF.}}\underline{\alpha} + \overbrace{(y_i^2 + z_i^2)}^{\text{REF.}}\underline{\beta} + 2\overbrace{(w_i y_i + x_i z_i)}^{\text{REF.}}\underline{\gamma}$$

SOLVE FOR UNKNOW
α, β, AND γ TO G

$\alpha = a^2 + c^2$

$\beta = b^2 + d^2$

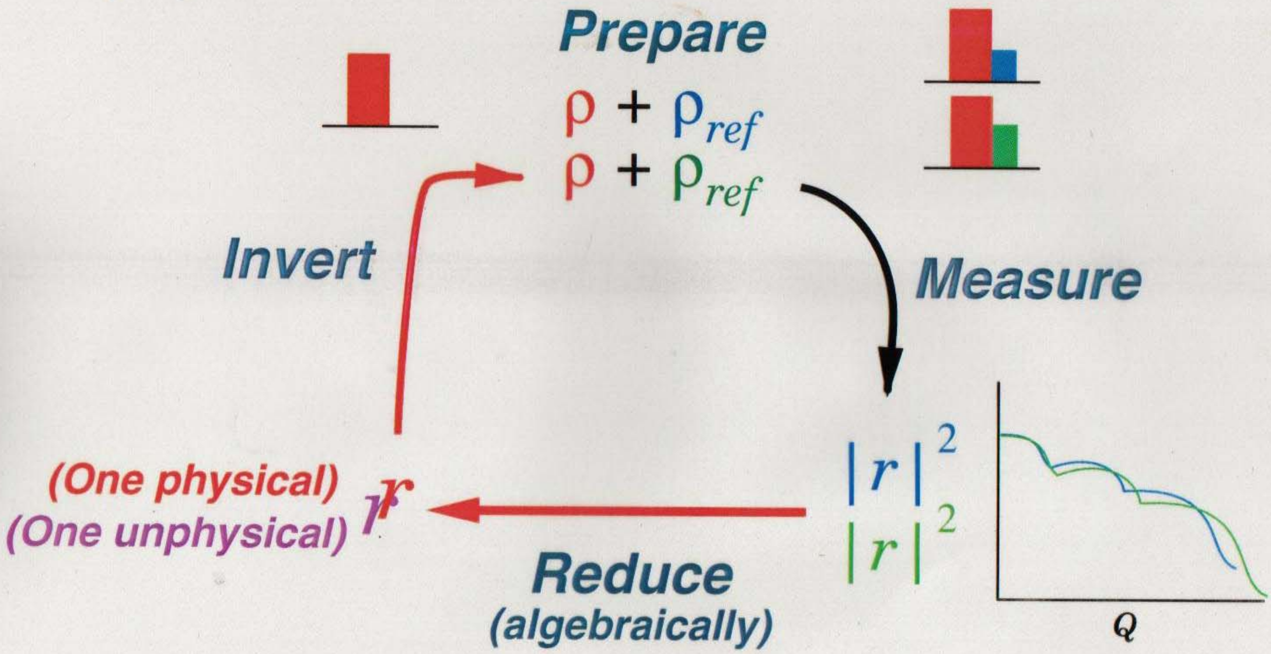
$\gamma = ab + cd$

$i = 1, 2, 3$

$$R_{\text{UNKNOWN}} = \frac{(\beta - \alpha) - 2i\gamma}{2 + \beta + \alpha}$$

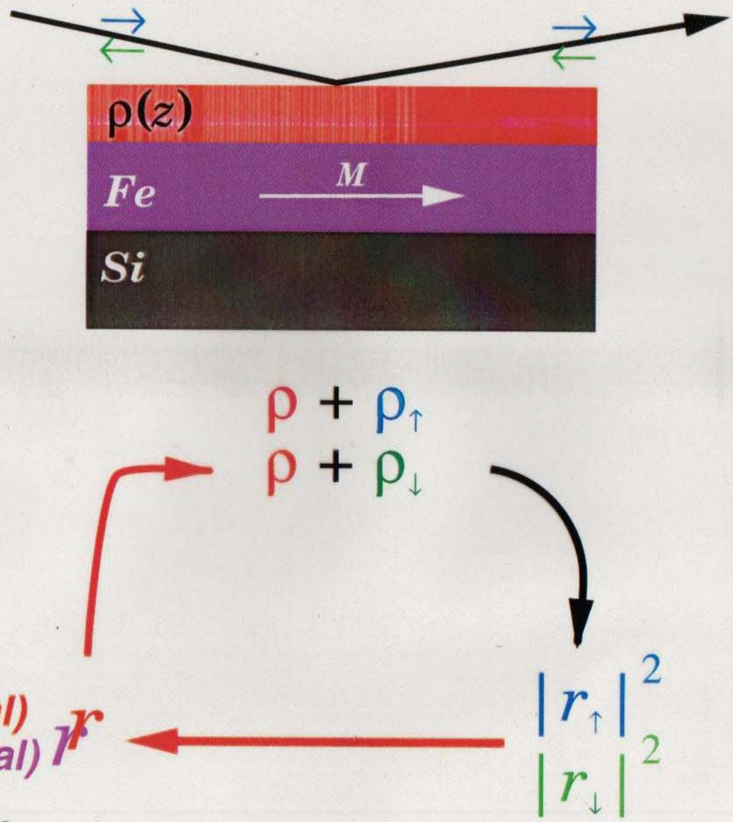
Phase Determination with 2 References

$\longrightarrow \gamma^2 = \alpha\beta - 1$



Majkrzak & Berk, 1998
Actosun & Sacks, 1998

Phase Determination with Polarized Neutrons



Majkrzak & Berk, 1998
Kasper et al., 1998

EXPERIMENTAL RESULTS USING REFERENCE LAYER OF FINITE THICKNESS:

- C.F. MAJKRZAK, N.F. BERK, J. DURA, S.K. SATIJA, A. KARIM, J. PEDULLA, & R.D. DESLATTES, PHYSICA B 241-243 (1998) 1101
- A. SCHREYER, C.F. MAJKRZAK, N.F. BERK, H. GRÜLL, & C.C. HAN, J. PHYS. & CHEM. OF SOLIDS 60 (1999) 1045.
- C.F. MAJKRZAK & N.F. BERK, PHYSICA B 267-268 (1999) 168

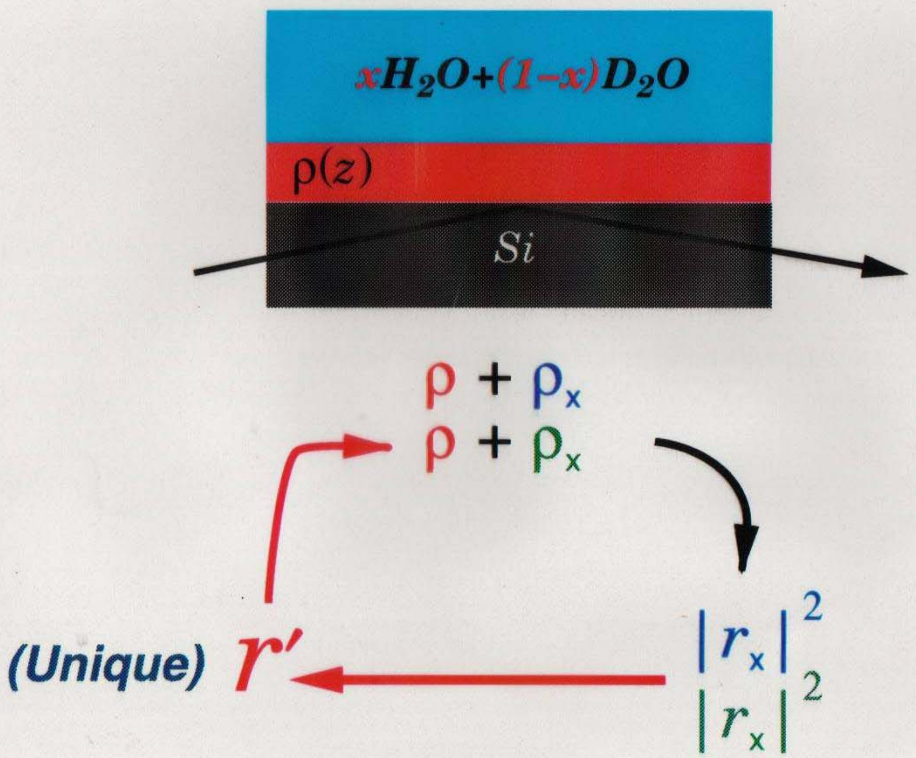
DISADVANTAGES OF FINITE THICKNESS REFERENCE LAYERS:

- FOR TWO* REFERENCE LAYERS, TWO SOLUTIONS FOR Im r ARE OBTAINED AND IDENTIFICATION OF THE ONE PHYSICAL RESULT CAN, IN CERTAIN CASES, BE PROBLEMATIC

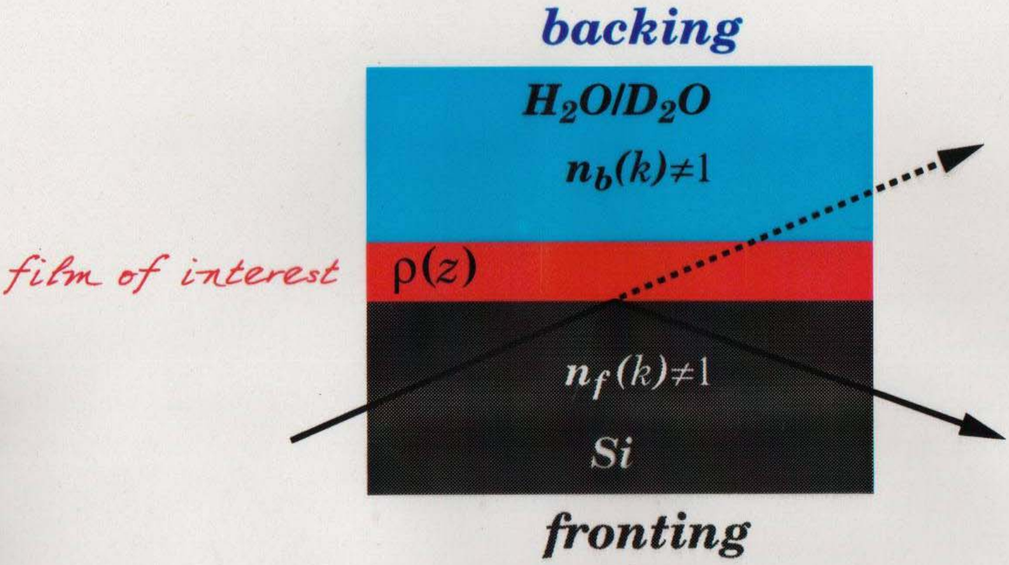
- THE ENTIRE SCATTERING LENGTH DENSITY (SL PROFILE OF EACH REFERENCE LAYER MUST BE KNOWN WITH SUFFICIENT ACCURACY TO AVOID THE INTRODUCTION OF SPURIOUS FEATURES IN THE SLD PROFILE OF THE UNKNOWN PART OF THE FILM UPON INVERSION OF Im r_{UK}

*(BUT NOT FOR 3)

Phase Determination with Surround Variation



Majkrzak & Berk, 1998, *Phys. Rev.* B58, p. 15416



$$\boxed{r = \frac{n_f n_b B + C + \mathrm{i}(n_f D - n_b A)}{n_f n_b B - C + \mathrm{i}(n_f D + n_b A)}}$$

$$R = |r|^2 = \frac{\Sigma - 2}{\Sigma + 2}, \quad \Sigma = \frac{n_b}{n_f} A^2 + n_b n_f B^2 + \frac{1}{n_b n_f} C^2 + \frac{n_f}{n_b} D^2$$

$$\begin{pmatrix} 1 \\ i \end{pmatrix} t e^{ikL} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} 1+r \\ i(1-r) \end{pmatrix}$$

$$r = \frac{(B^2+D^2)-(A^2+C^2)-2i(AB+CD)}{(B^2+D^2)+(A^2+C^2)+2}$$

$$2\frac{1+|r|^2}{1-|r|^2} = (B^2+D^2)+(A^2+C^2)$$

GENERAL FRONTING & BACKING

$$r = \frac{(f^2b^2B^2+f^2D^2)-(b^2A^2+C^2)-2i(fb^2AB+fCD)}{(f^2b^2B^2+f^2D^2)+(b^2A^2+C^2)+2fb}$$

$$\Sigma \equiv 2fb\frac{1+|r|^2}{1-|r|^2} = (f^2b^2B^2+f^2D^2)+(b^2A^2+C^2)$$

$$n^2(Q) = 1-16\pi\rho_n/Q^2$$ $(n = f \text{ or } b)$

VACUUM FRONTING, VARIABLE BACKING

$$\Sigma = b^2(A^2+B^2)+(C^2+D^2)$$

$$2b_1\left[\frac{1+|r_{comp_1}|^2}{1-|r_{comp_1}|^2}\right] = b_1^2\alpha+\beta$$

$$2b_2\left[\frac{1+|r_{comp_2}|^2}{1-|r_{comp_2}|^2}\right] = b_2^2\alpha+\beta$$

SOLVE F
α AND (
AT EACH
Q : THEN

$$\operatorname{Re} \underset{(REV.)}{r_{UK}} = \frac{\alpha-\beta}{\alpha+\beta+2}$$

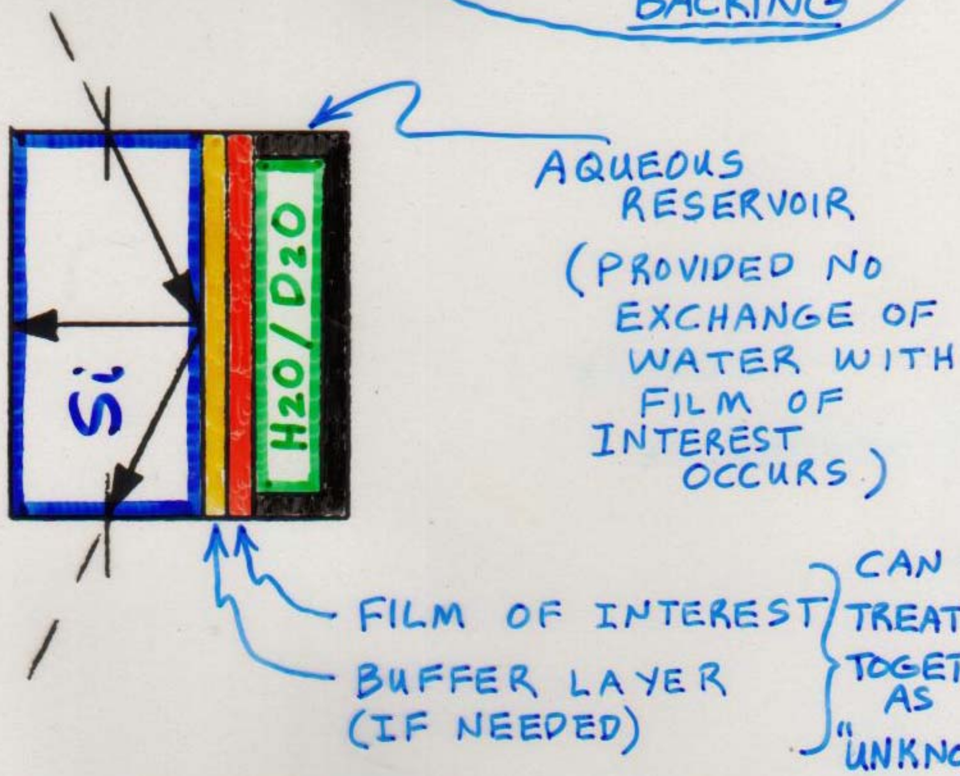
NONVACUUM FRONTING, VARIABLE BACKING

$$\Sigma = \frac{b^2}{f^2}[(fA)^2+(f^2B)^2]+[C^2+(fD)^2]$$

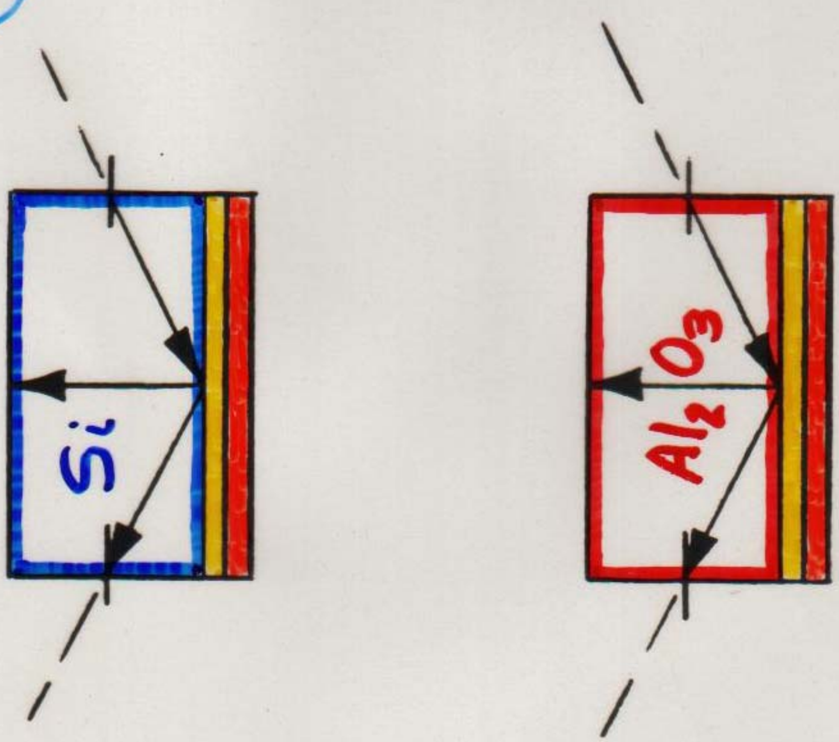
$$= \frac{b^2}{f^2}(\mathcal{A}^2+\mathcal{B}^2)+(\mathcal{C}^2+\mathcal{D}^2)$$

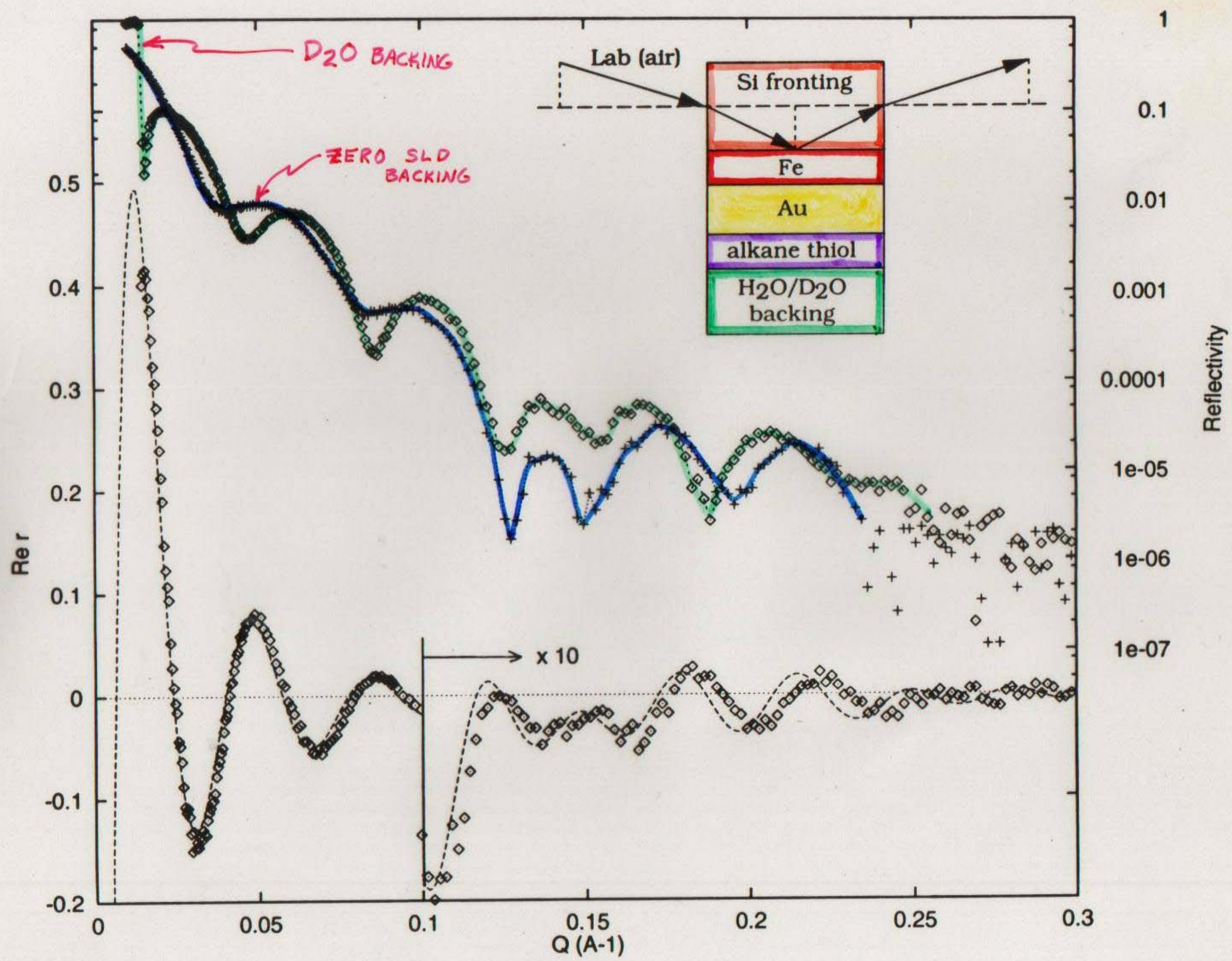
$$\rho_{\text{equiv}}(z) = \rho(z)-\rho_f$$

VARIABLE BACKING

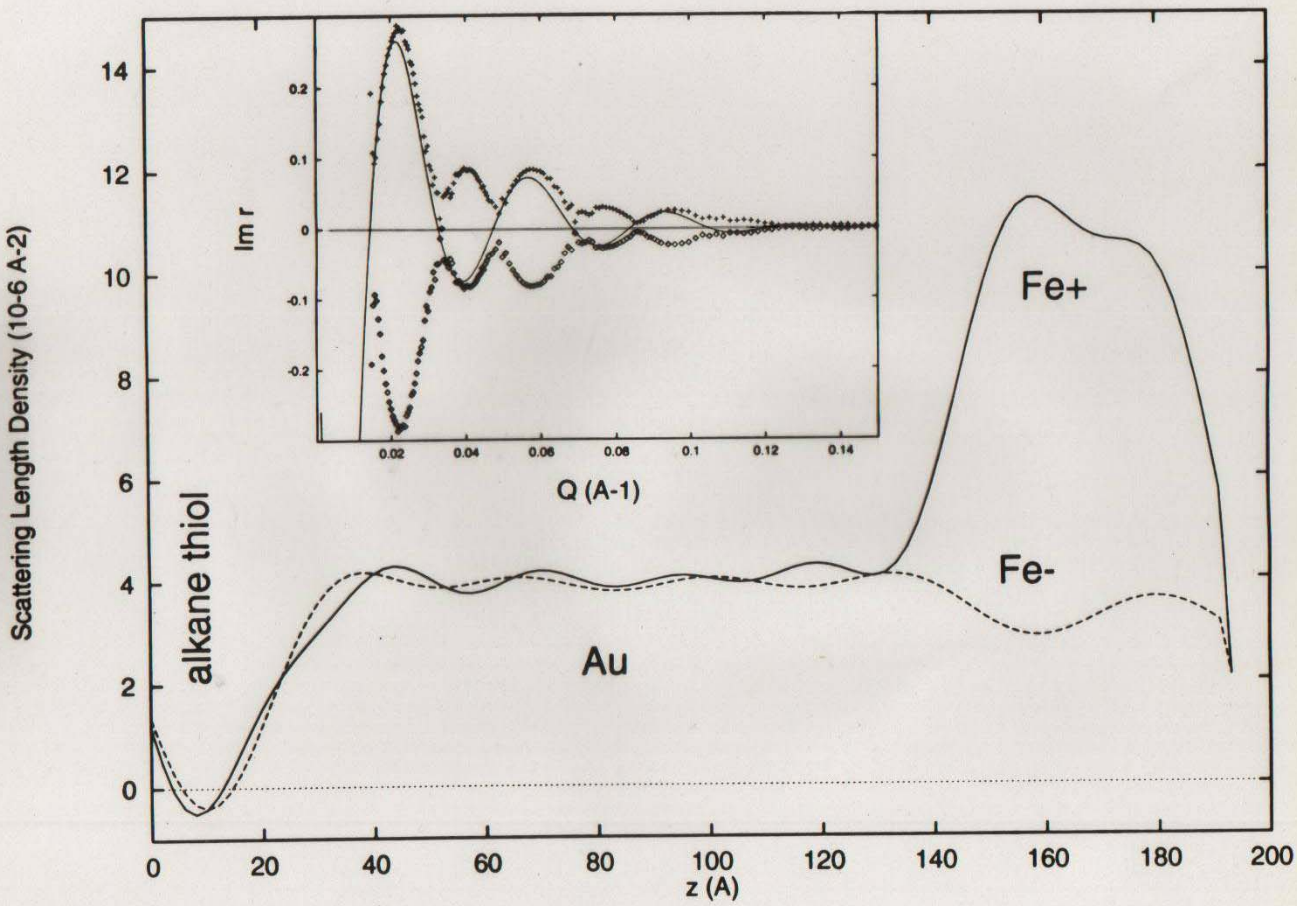


VARIABLE FRONTING





D2O BACKING
ZERO SLD BACKING
Lab (air)
Si fronting
Fe
Au
alkane thiol
H2O/D2O backing
x 10
Re r
Reflectivity
Q (A-1)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
0.05
0.15
0.25
0.3
1
0.1
0.01
0.001
0.0001
1e-05
1e-06
1e-07



Scattering Length Density (10-6 A-2)
z (A)
alkane thiol
Au
Fe+
Fe-
Im r
Q (A-1)

UNIQUE DETERMINATION OF BIOMIMETIC MEMBRANE PROFILES BY NEUTRON REFLECTIVITY

New biomimetic membrane materials, of fundamental importance in understanding such key biological processes as molecular recognition, conformational changes, and molecular self-assembly, can be characterized using neutron reflectometry. In particular, scattering length density (SLD) depth profiles along the normal to the surface of a model biological bilayer, which mimics the structure and function of a genuine cell membrane, can be deduced from specular neutron reflectivity data collected as a function of wavevector transfer Q. Specifically, this depth profile can be obtained by numerically fitting a computed to a measured reflectivity. The profile generating the best fitting reflectivity curve can then be compared to cross-sectional slices of the film's chemical composition predicted, for example, by molecular dynamics simulations [1]. However, the uniqueness of a profile obtained by conventional analysis of the film's reflectivity alone cannot be established definitively without additional information. In practice, significantly different SLD profiles have been shown to yield calculated reflectivity curves with essentially equivalent goodness-of-fit to measured data [2], as illustrated in Fig. 1.

The existence of multiple solutions, only one of which can be physical, is especially problematic in cases where a key additional piece of structural or compositional information is lacking as can happen in the investigation of these biological membrane systems.

Why this inherent uncertainty? The neutron specular reflection amplitude for a model SLD can be computed exactly from first principles; the square of its modulus gives the measurable reflectivity. It is firmly established, however, that the complex amplitude is necessary and sufficient for a unique solution of the inverse problem, that of recovering the SLD from reflection measurements. Unambiguous inversion requires both the magnitude and phase of reflection. Once these are known, practical methods [3] exist for extracting the desired SLD.

In fact, considerable efforts were made about a quarter century ago to solve the analogous "phase problem" in X-ray crystallography using known constraints on the scattering electron density [4] and by the technique of isomorphic substitution [5]. Variations of the latter approach have been applied to reflectivity, using a known reference layer in a composite film in place of atomic substitutions. These

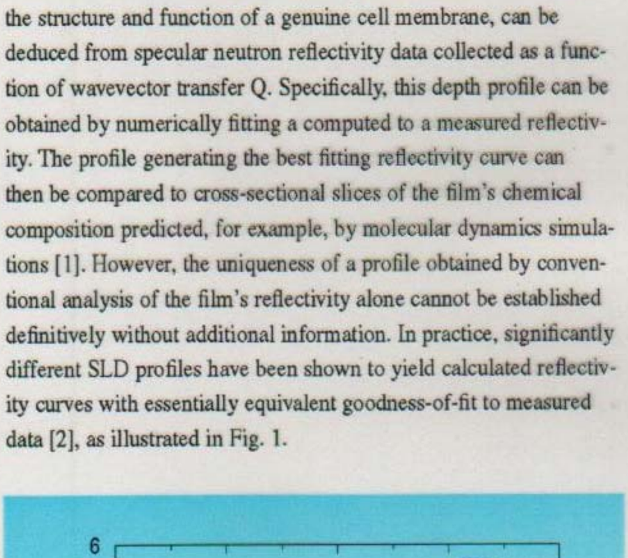


FIGURE 1. Family of scattering length density profiles obtained by model-independent fitting of the reflectivity data in the inset. The profile represented by the blue dashed line is unphysical for this Ti/TiO film system yet generates a reflectivity curve that fits the data with essentially equivalent goodness-of-fit (all the reflectivity curves corresponding to the SLD's shown are plotted in the inset but are practically indistinguishable from one another).

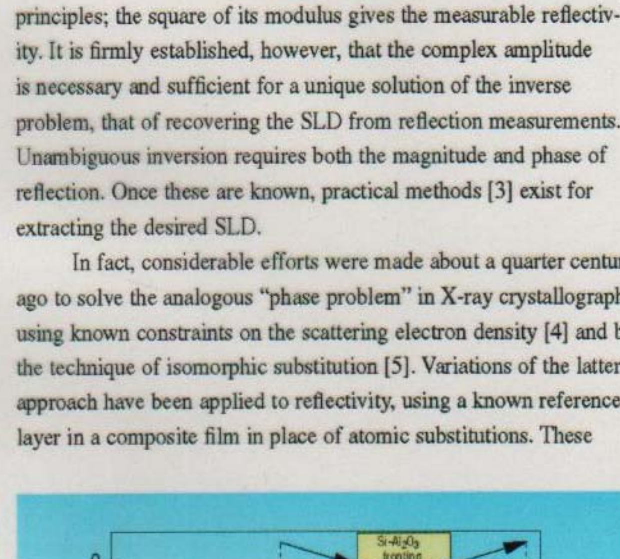


FIGURE 2. Reflectivity curves for the thin film system depicted schematically in the inset, one for a Si fronting (red triangles), the other for Al_2O_3 (black circles). The curve in the lower part of the figure (blue squares) is the real part of the complex reflection amplitude for the films obtained from the reflectivity curves by the method described in the text.

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solution methods, however, were tied to the Born approximation, which generally is valid in crystal structure determination but which fails catastrophically at low Q (low glancing angles) in reflection from slab-shaped samples such as thin films. Exact inversion requires accurate knowledge of the reflection amplitude over the entire Q-range, especially at low Q.

In this decade the reflection phase problem has been exactly solved using a protocol of three reflectivity measurements on composite films consisting of the film of interest in intimate contact with each of three known reference layers [6, 7]. Subsequently, variations using only two measurements have been shown to partially solve the phase problem, an additional procedure being required to choose between two solution branches, only one of which is physical [8, 9]. In the past year [10], an exact solution has been found for a two measurement strategy in which the film surround, either the fronting (incident) or backing (transmitting) medium, is varied. This new approach is simpler to apply than reference layer methods and is adaptable to many experiments. Surround variation neutron

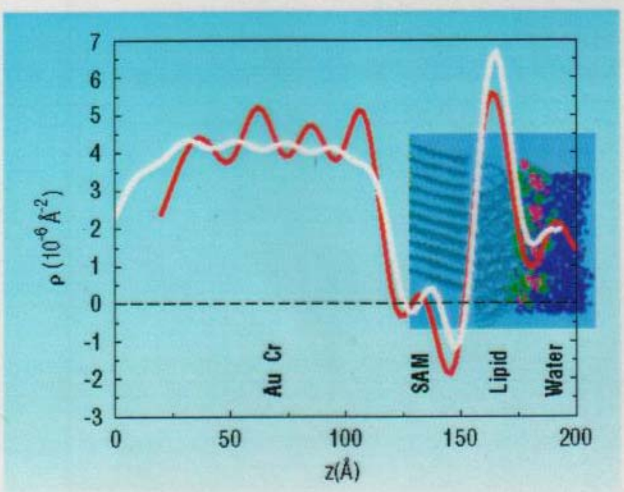

FIGURE 3. SLD profile (red line) resulting from a direct inversion of the Re r of Fig. 2 compared with that predicted by a molecular dynamics simulation (white line) as discussed in the text. The headgroup for the Self-Assembled-Monolayer (SAM) at the Au surface in the actual experiment was ethylene oxide and was not included in the simulation but, rather, modelled separately as part of the Au. Also, the Cr-Au layer used in the model happened to be 20 Å thicker than that actually measured in the experiment.

reflectometry has been successfully applied to the challenging type of biological membrane depth profiling described earlier.

In Fig. 2 are plotted a pair of neutron reflectivity curves measured for the layered film structure schematically depicted in the upper right inset, one with Si and the other with Al_2O_3 as the fronting medium. The lower part of Fig. 2 shows the real part of the complex reflection amplitude for the multilayer as extracted from the reflectivity data, according to the method described above, and which was subsequently used to perform the inversion to obtain the SLD shown in Fig. 3. For comparison, the SLD predicted by a molecular dynamics simulation is also shown in Fig. 3, in a slightly distorted version, corresponding to a truncated reflectivity data set, which indicates the spatial resolution of an SLD obtainable in practice. This latter SLD was obtained by inversion of the reflection amplitude computed for the exact model SLD, but using values only up to the same maximum Q value ($0.3\ Å^{-1}$) over which the actual reflectivity data sets were collected. Overall, agreement between the experimentally determined profile and the theoretical prediction is remarkable, essentially limited only by the Q-range of the measurement. Surround variation neutron reflectivity thus makes it possible to measure complicated thin film structures without the ambiguity associated with curve fitting. The veridical SLD profile is obtained directly by a first principles inversion.

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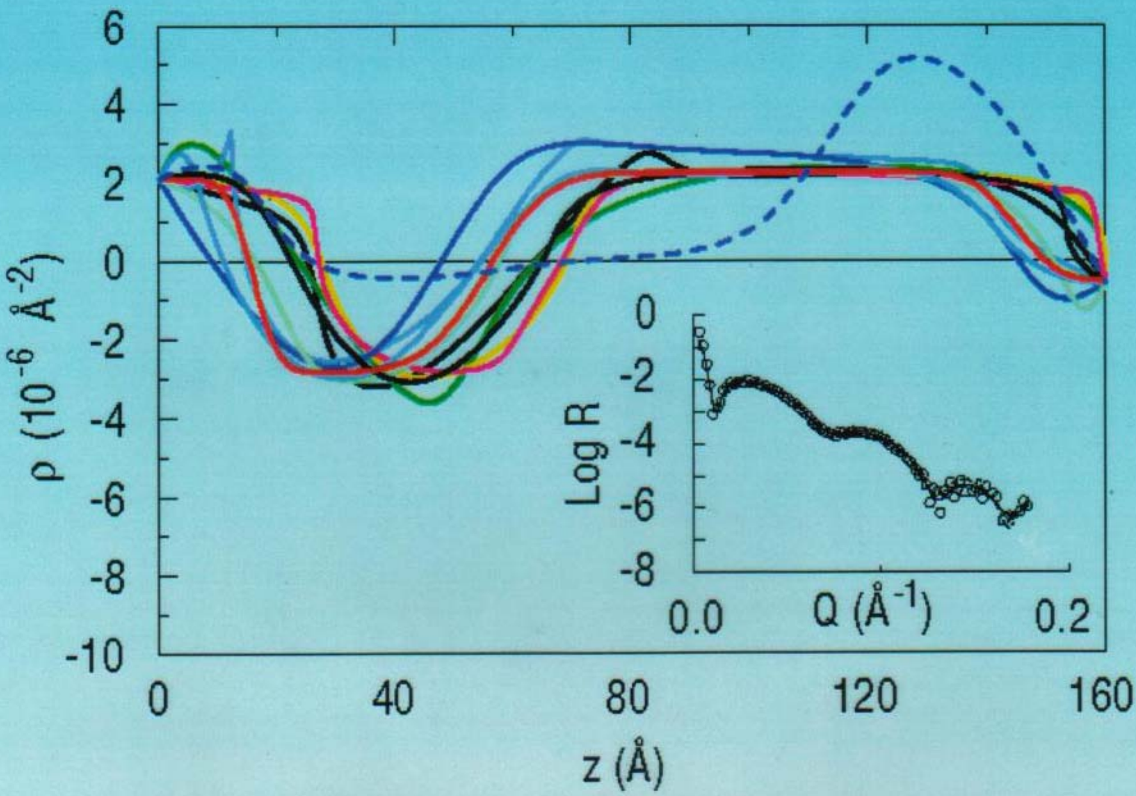


FIGURE 1. Family of scattering length density profiles obtained by model-independent fitting of the reflectivity data in the inset. The profile represented by the blue dashed line is unphysical for this Ti/TiO film system yet generates a reflectivity curve that fits the data with essentially equivalent goodness-of-fit (all the reflectivity curves corresponding to the SLD's shown are plotted in the inset but are practically indistinguishable from one another).

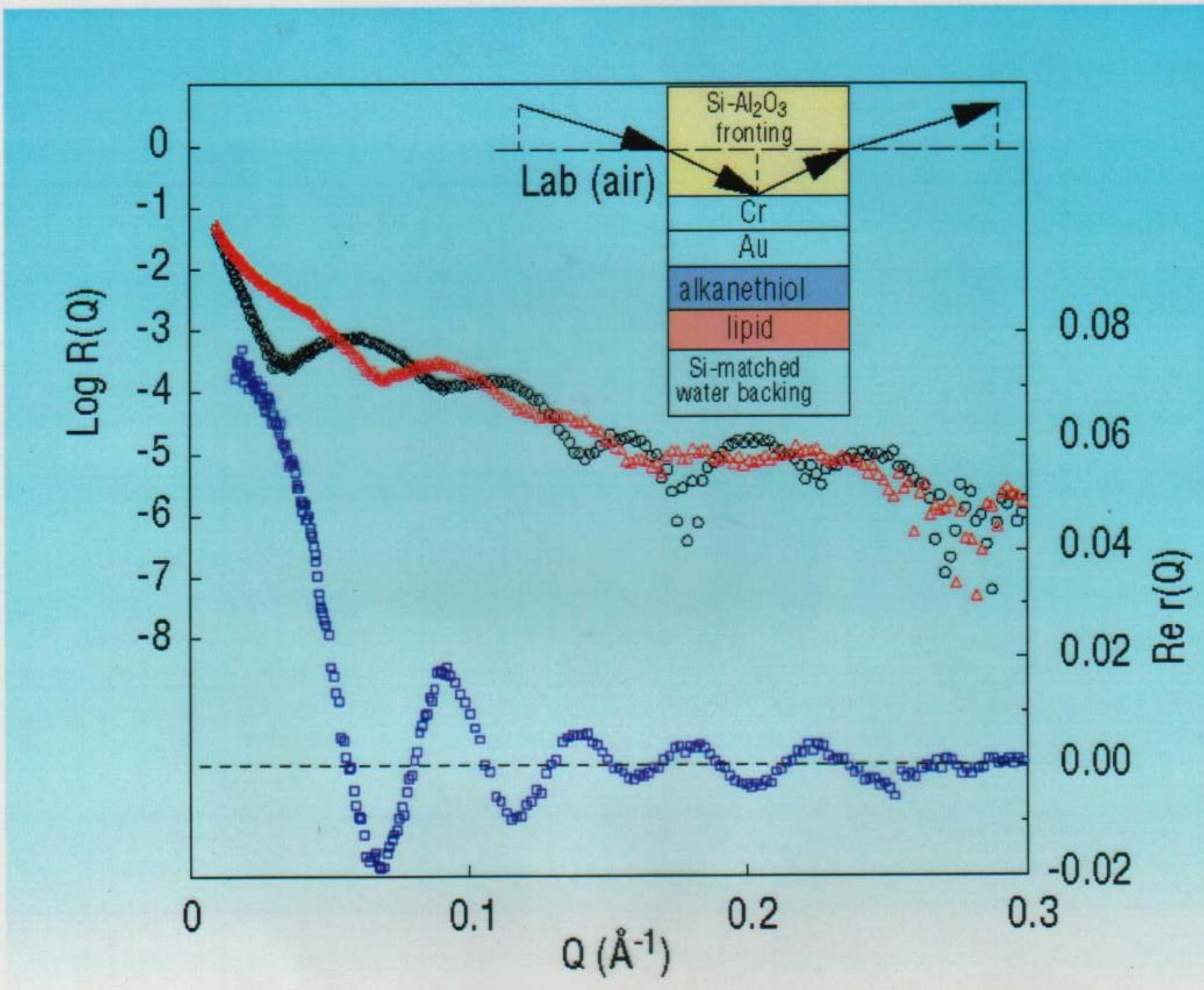


FIGURE 2. Reflectivity curves for the thin film system depicted schematically in the inset, one for a Si fronting (red triangles), the other for Al_2O_3 (black circles). The curve in the lower part of the figure (blue squares) is the real part of the complex reflection amplitude for the films obtained from the reflectivity curves by the method described in the text.

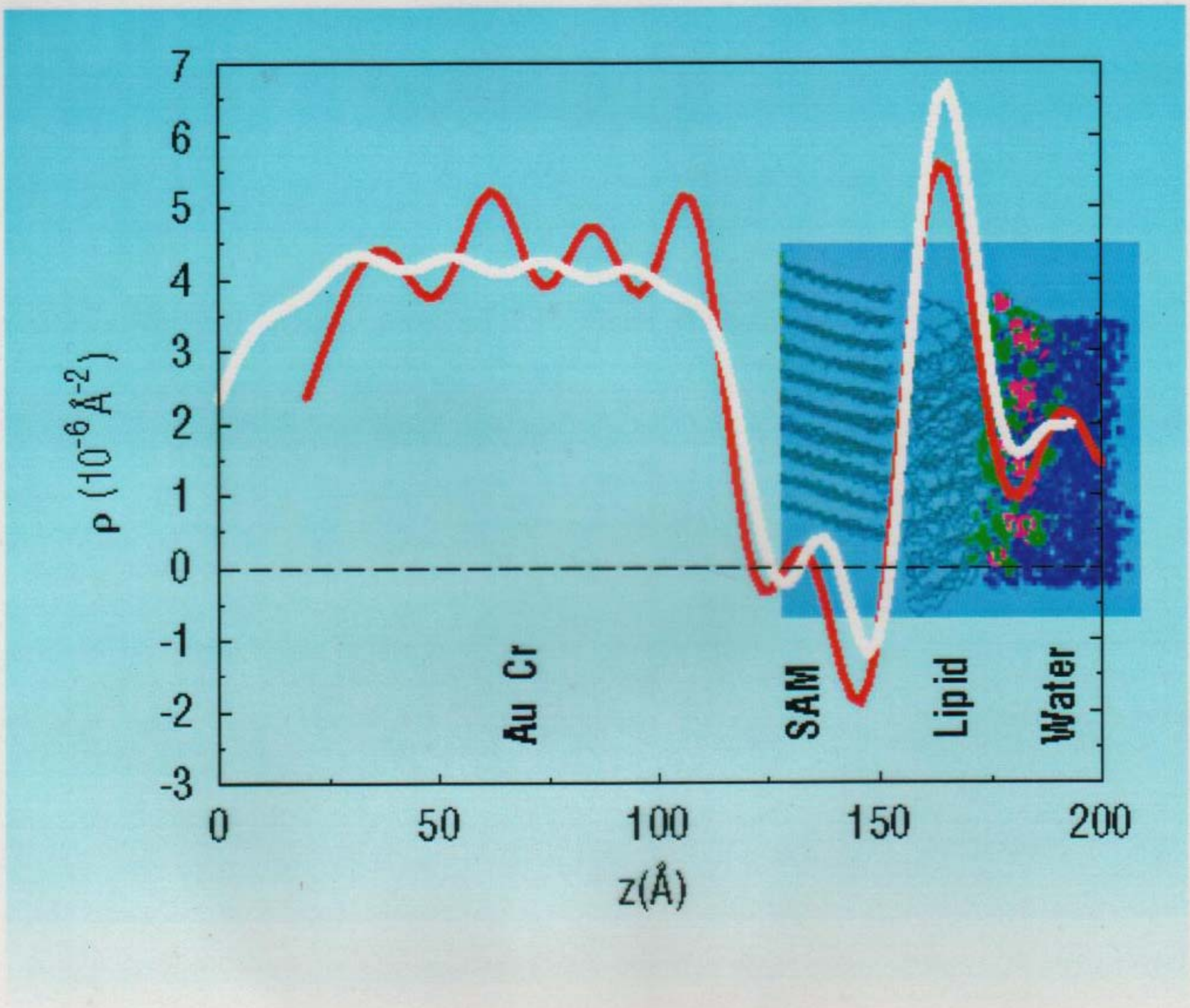
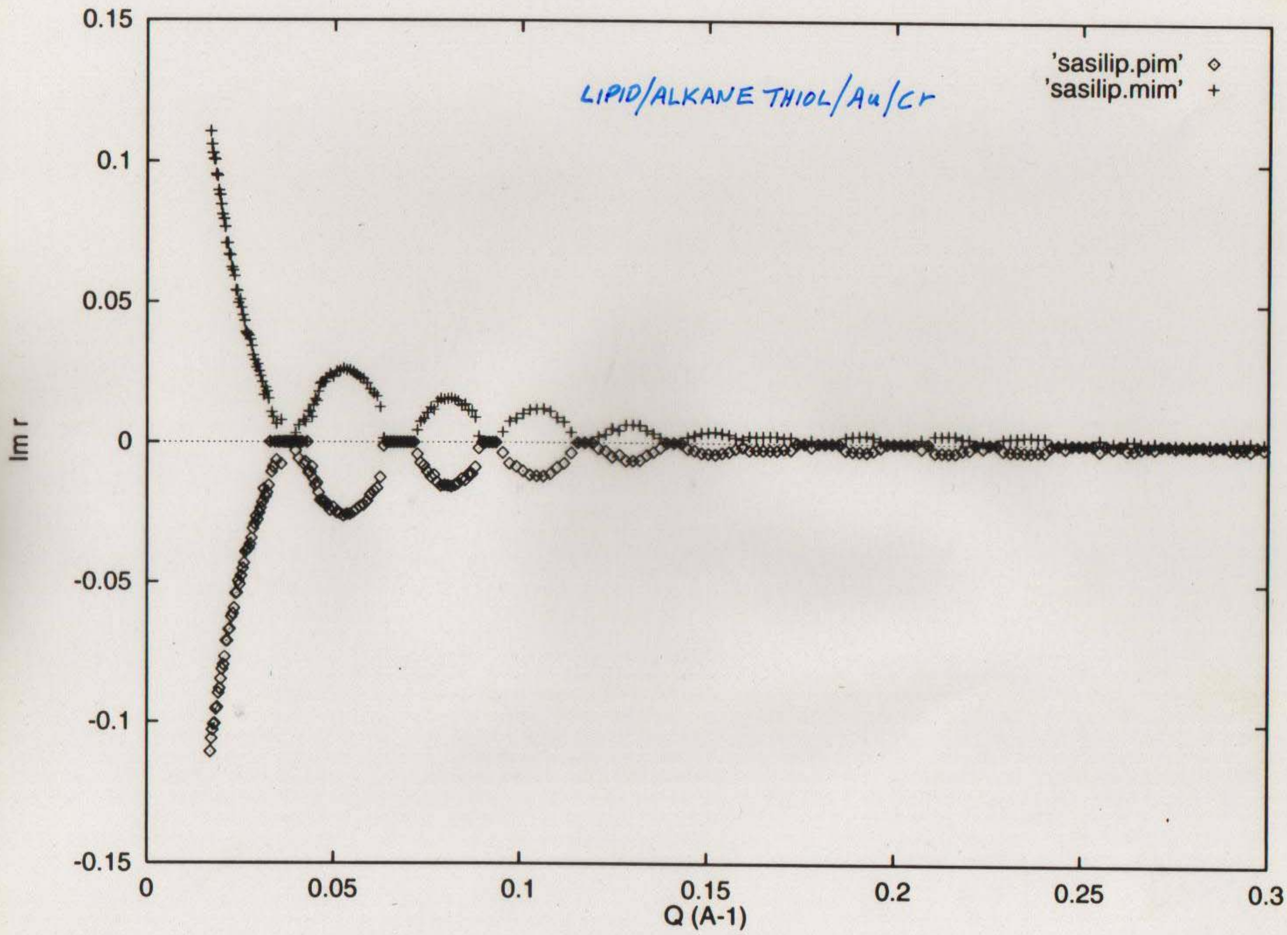
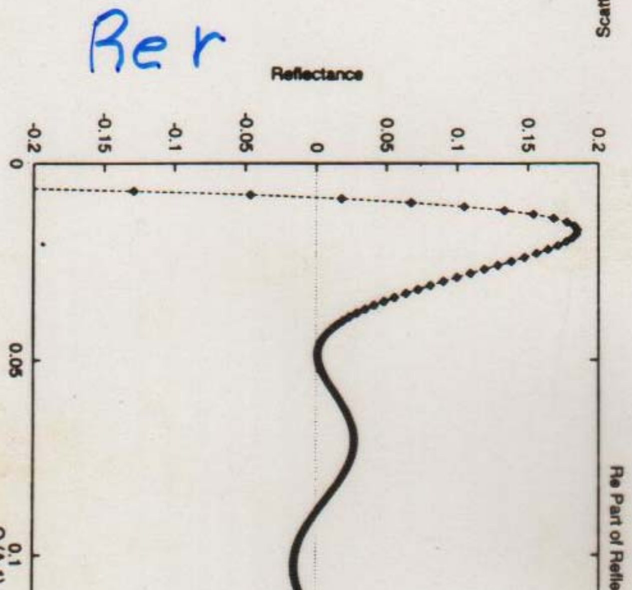
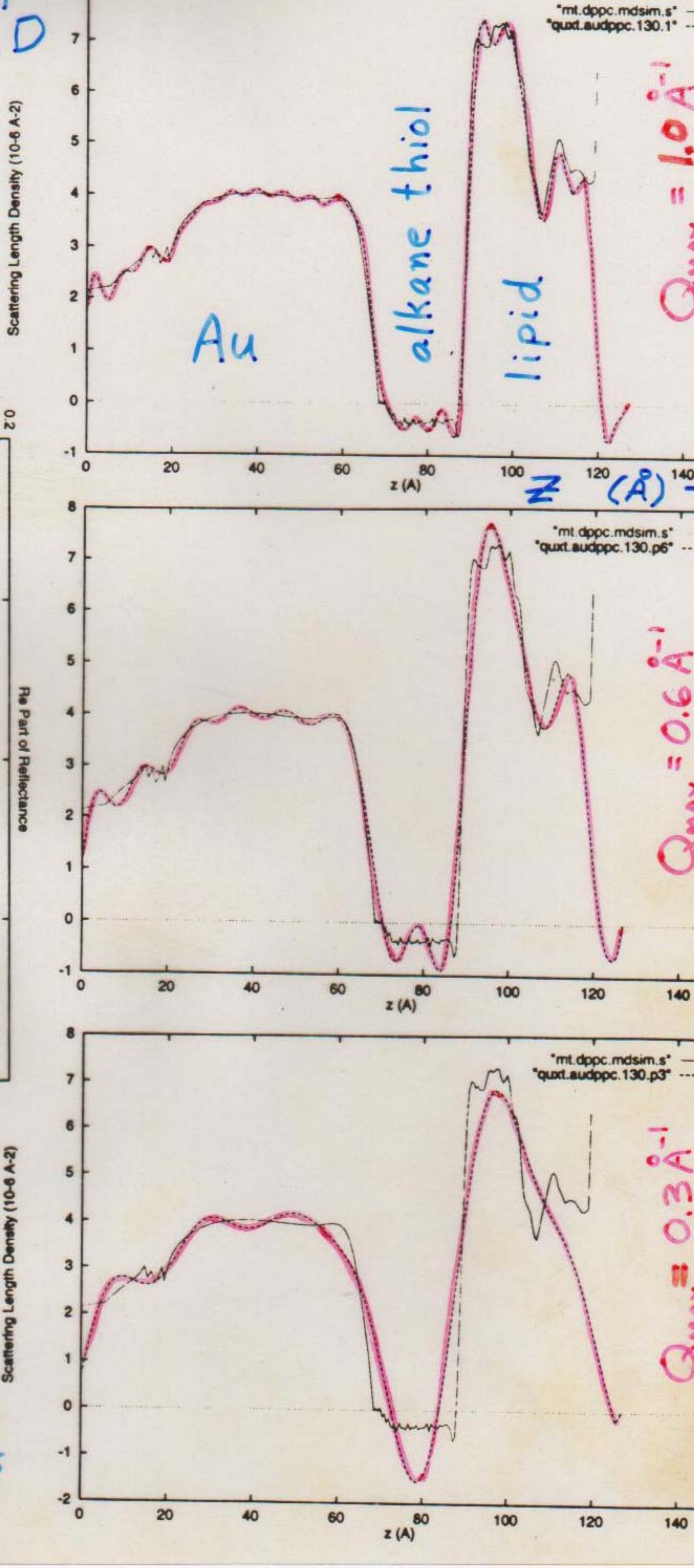


FIGURE 3. SLD profile (red line) resulting from a direct inversion of the Re r of Fig. 2 compared with that predicted by a molecular dynamics simulation (white line) as discussed in the text. The headgroup for the Self-Assembled-Monolayer (SAM) at the Au surface in the actual experiment was ethylene oxide and was not included in the simulation but, rather, modelled separately as part of the Au. Also, the Cr-Au layer used in the model happened to be 20 Å thicker than that actually measured in the experiment.

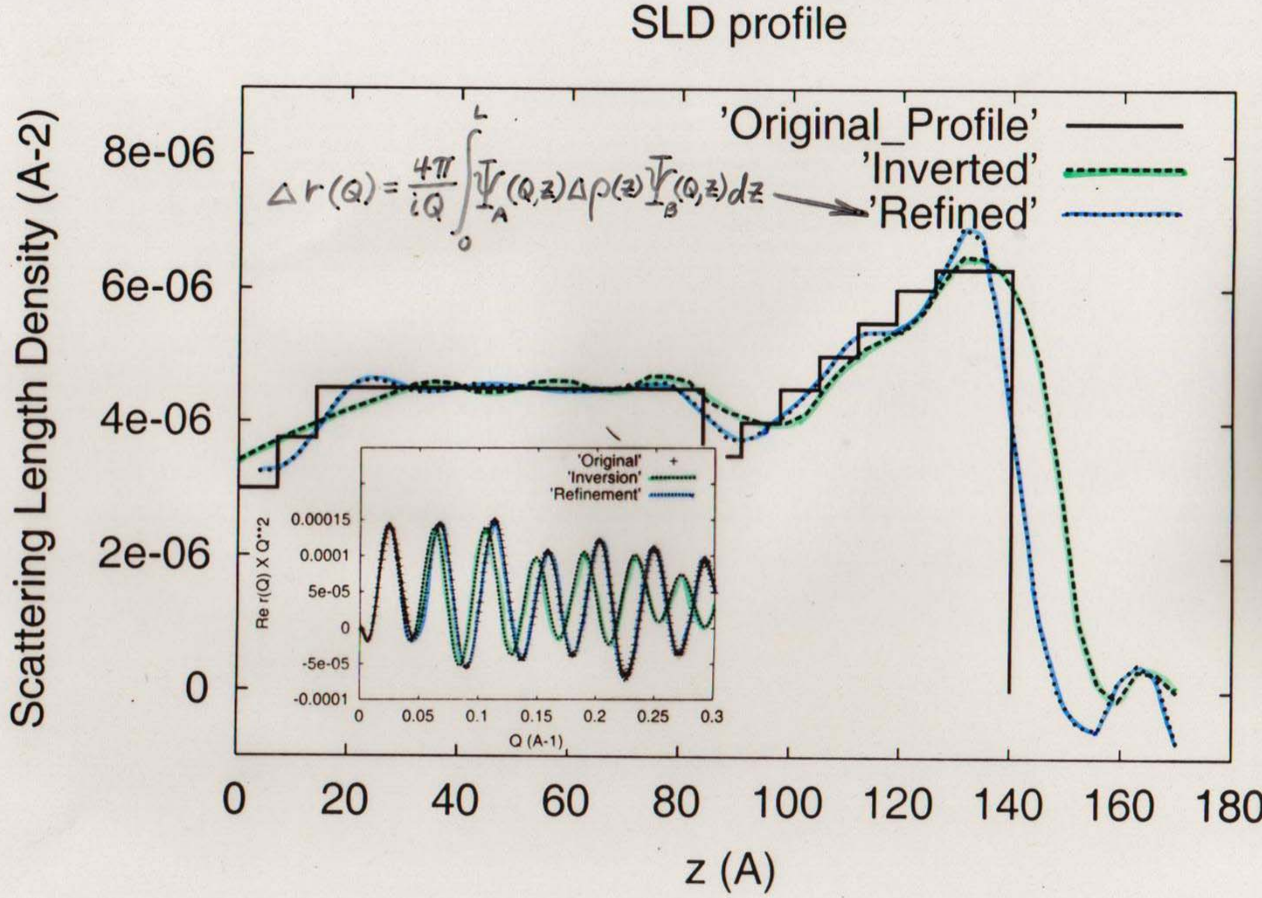


0.15
0.1
0.05
0
-0.05
-0.1
-0.15
Im r
0
0.05
0.1
0.15
0.2
0.25
0.3
Q (A-1)
'sasilip.pim'
'sasilip.mim'
LIPID/ALKANE THIOL/Au/Cr



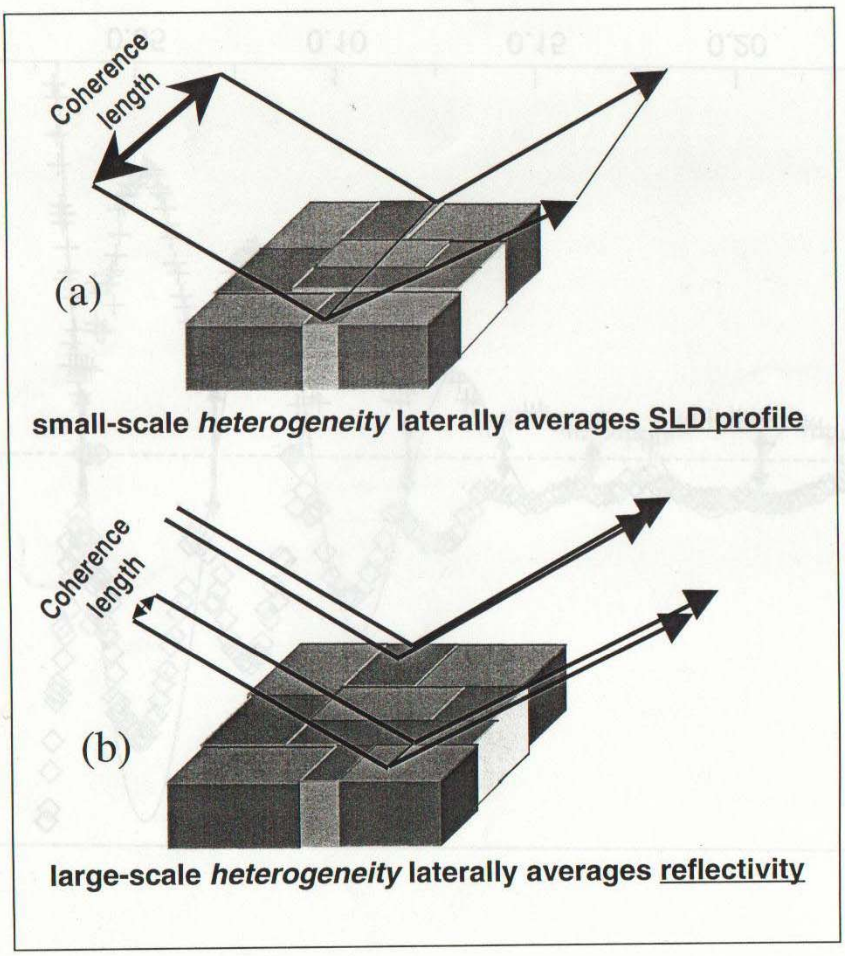


OMPARISON OF SLD
ROFILES OBTAINED BY
NVERSION OF Re r
ATA" SETS TRUNCATED
T DIFFERENT Q_{MAX}
ITH THAT PREDICTED
Y A MOLECULAR DYNAMICS
MULATION (SOLID LINE)

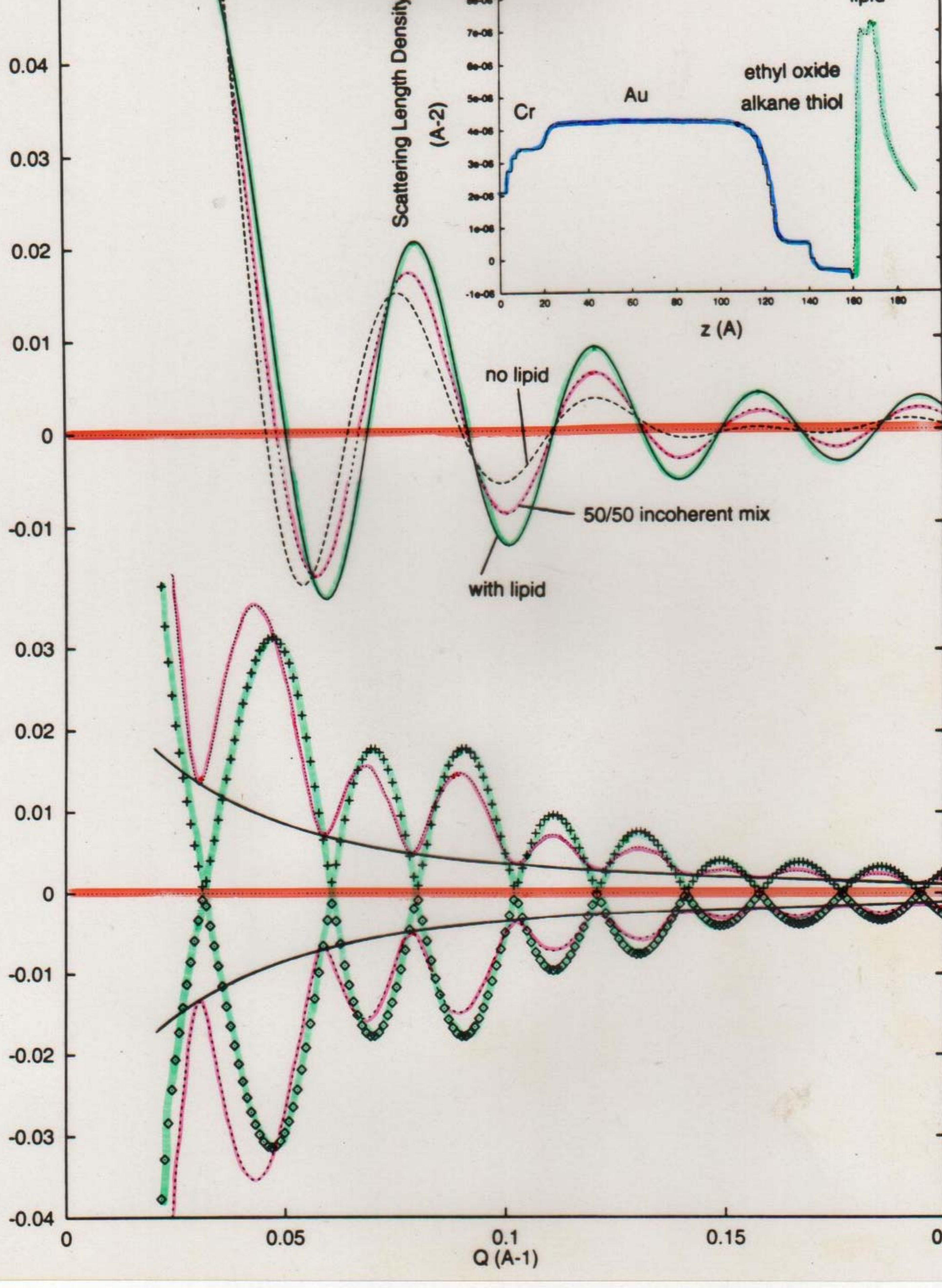


Majkrzak & Berk — Fig. 1

Figure 7.

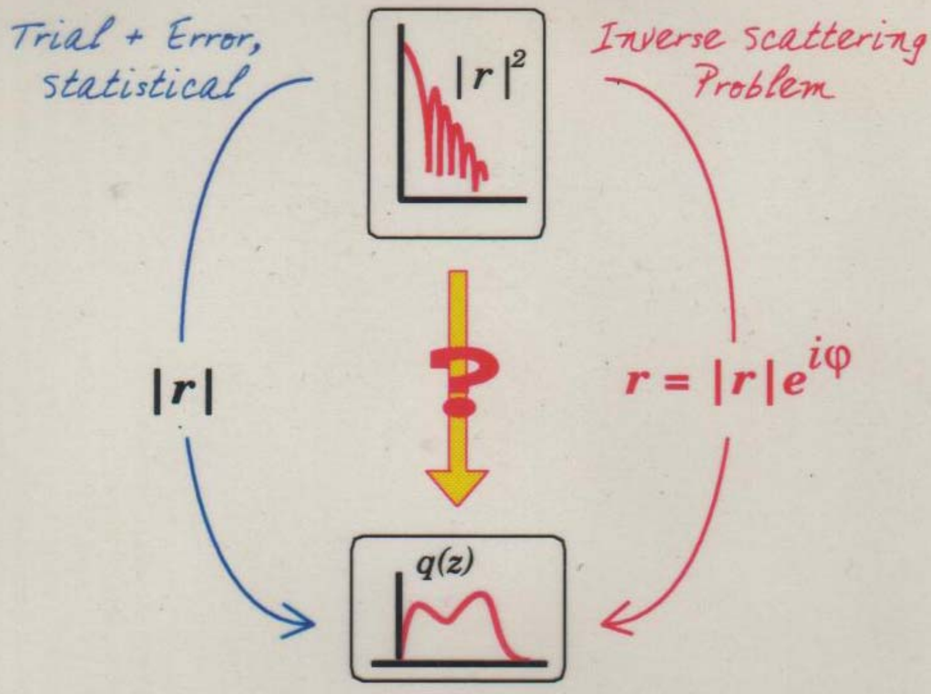


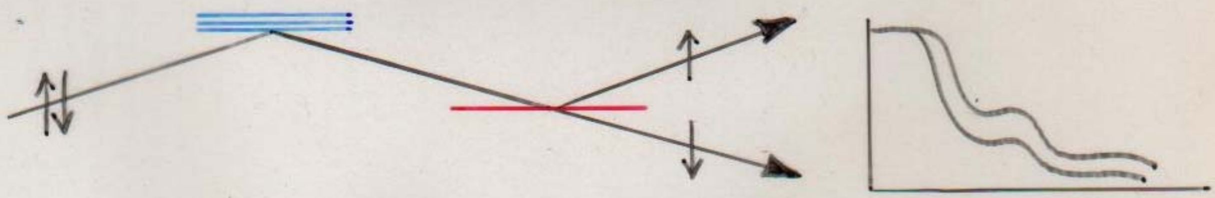
Coherence length
(a)
small-scale heterogeneity laterally averages SLD profile
Coherence length
(b)
large-scale heterogeneity laterally averages reflectivity



Scattering Length Density (A-2)
z (A)
Cr
Au
ethyl oxide
alkane thiol
no lipid
50/50 incoherent mix
with lipid
Q (A-1)

Inverting reflectivity: Summary





$$r(k_z) = |r|e^{i\varphi} \longrightarrow R(z)$$

$$K(z,y) + R(z+y) + \int_{-z}^{z} K(z,x)R(x+y)\,dx = 0$$

$$q(z) = 2\frac{dK(z,z)}{dz}$$