PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 48, NUMBER 1 1 JULY 1993-I

Phase determination in x-ray and neutron reflectivity using logarithmic dispersion relations

William L. Clinton
Department of Physics, Georgetown University, Washington, D.C. 20057
(Received 23 November 1992)

Logarithmic dispersion relations are shown to be applicable to the determination of the phase of the structure factor of surface layers probed by neutron and x-ray reflectivity. For certain profiles it is shown that the phase $\Phi(q)$ of the structure factor $F(q)$ is determined *entirely* by the observed reflectivity $R(q)$ through the modified Hilbert transform $\Phi(q)=2q/\pi\int_0^\infty \ln[|F(q')|/|F(q)|]/(q^2-q'^2)dq'$, where q is the momentum transfer, and $F(q)$ is related to $R(q)$ and the Fresnel reflectivity via $R(q)=R_F(q)|F(q)|^2$.

The use of logarithmic dispersion relations (LDR) in phase determination in scattering problems has been around for some time.[1] A number of applications have been made to scattering amplitudes in high-energy physics[2] as well as various problems in optics.[3] The theory of dispersion relations in general has a long and rich history,[4] and in particular LDR theory has been delineated in a detailed study by Burge *et al.*[3]

In this paper we show how the LDR can be applied to reflectivity measurements involving either neutrons or x rays. This is a completely new area of applicability. Its importance cannot be overemphasized as evidenced in recent applications to a variety of thin-film and surface layer structures.[5–10] It is also one in which a physically realizable scattering amplitude (structure factor) can be completely determined from the measured reflectivity alone. The reason for this is that the reflection amplitude for certain systems, when continued into the complex momentum-transfer plane can be shown to have no complex zeros, avoiding a serious complication that has plagued previous attempts to apply the LDR.

The basic theorem upon which dispersion relations are based is due to Titchmarsh. It insures that if a function $f(x)$ is zero on some domain, say $f(x)=0$ for $x<0$, then its Fourier transform is

$$g(q)=\int_0^\infty f(x)e^{iqx}dx \tag{1}$$

and is said to be a causal transform and is analytic in the upper half complex q plane.[4] It immediately follows from the Cauchy principal value theorem that $\mathrm{Re}g(q)$ and $\mathrm{Im}g(q)$ are Hilbert transforms. It is from this mathematics that all of the rich results of dispersion relations follow. A more complete statement of the Titchmarsh theorem along with a very lucid and thought provoking discussion of LDR can be found in Burge *et al.*[3]

The reflectivity function of neutron or x-ray scattering is given, in the Born approximation (BA), by[6]

$$R(q)=R_F(q)|F(q)|^2 , \tag{2a}$$

where $R_F(q)$ is the Fresnel reflectivity and the structure factor $F(q)$ is just the Fourier transform of the derivative of the scattering density profile, i.e.,

$$F(q)=\int_{-\infty}^{+\infty} dz e^{iqz}\rho'(z) \tag{2b}$$

and $\rho(z)$ is the depth profile with, for example, $\rho'(z)=0$ for $z<0$. This condition can always be arranged, of course, since in any real scattering problem the position $z=0$ denotes the demarcation between sample and nonscattering medium (target and vacuum, for example). This seemingly innocent condition is important in the present context because, as stated in the introduction, given such a condition we can show that $F(q)$ is analytic in the upper half q plane (UHP). This in turn implies that $\mathrm{Re}F(q)$ and $\mathrm{Im}F(q)$ are Hilbert transforms, which are dispersion relations. Titchmarsh has shown that $\ln F(\mathbf{q})$ is also analytic except where $F(\mathbf{q})=0$. From this can be derived the logarithmic dispersion relations (LDR), which are more pertinent in our case. They relate the phase of $F(\mathbf{q})=|F(\mathbf{q})|\exp[i\Phi(\mathbf{q})]$ to $\ln|F(q)|$ via a once-subtracted LDR:

$$\Phi(q)=-\frac{q}{\pi}\int_{-\infty}^{+\infty}\frac{\ln[|F(q')|/|F(q)|]}{q'(q'-q)}dq' , \tag{3}$$

provided $F(\mathbf{q})$ has no zeros in the UHP or on the real axis.

We next want to eliminate the $(-q)$ part of the integral determining $\Phi(q)$. Since $\ln|F(-q)|=\ln|F(q)|$, then

$$\Phi(q)=2\frac{q}{\pi}\int_0^\infty\frac{\ln[|F(q')|/|F(q)|]}{q^2-q'^2}dq' . \tag{4}$$

We have performed many tests of Eq. (4) using simulated as well as real reflectivity data. In the following discussion we derive conditions under which Eq. (4) is the sole contribution to the phase.

If a sample has N interfaces we write

$$\rho'(z)=\sum_{n=1}^{N}\Delta\rho_n f_n(z-z_n) , \quad (5)$$

where $f_n(z-z_n)$ represents the nth interface derivative function. We next calculate $F(q)$:

$$F(q)=\sum_{n=1}^{N}\Delta\rho_n\int_{-\infty}^{+\infty}dze^{iqz}f_n(z-z_n) , \quad (6)$$

which also can be written

$$F(q)=\sum_{n=1}^{N}\Delta\rho_n e^{iqz_n}\int_{-\infty}^{+\infty}dze^{iq(z-z_n)}f_n(z-z_n)$$
$$\equiv\sum_{n=1}^{N}\Delta\rho_n e^{iqz_n}g_n(q) , \quad (7)$$

where $g_n(q)\equiv\int_{-\infty}^{+\infty}dze^{iqz}f_n(z)$ is the interface form factor or Fourier transform of the interface density derivative. We have calculated $g(q)$ using various models such as the sharp interface,

$$\rho=\sum_n\Delta\rho_n\Theta(z-z_n) , \quad \rho'=\sum_n\Delta\rho_n\delta(z-z_n) , \quad (8a)$$

and a typical gradual interface,

$$\rho=\sum_n\Delta\rho_n\tanh\left[\frac{(z-z_n)}{a_n}\right] ,$$
$$\rho'=\sum_n\frac{\Delta\rho_n}{a_n}\mathrm{sech}^2\left[\frac{(z-z_n)}{a_n}\right] . \quad (8b)$$

The exact phase of $F(q)$ using the simulated profile is

$$\phi(q)=\tan^{-1}\frac{\mathrm{Im}F(q)}{\mathrm{Re}F(q)} . \quad (9)$$

In what follows we will calculate the Hilbert phase [Eq. (4)] and compare it to the exact model phase in Eq. (9). In the case where the profile structure factor $F(q)$ has no zeros in the UHP these should agree. The conditions for no zeros in these $F(q)$ models are determined next.

Let $\mathbf{q}=q+i\kappa$, then for real $\Delta\rho_n$ and $g_n(q)=1$, i.e., the sharp interface, we have

$$F(q)=\sum_n\Delta\rho_n e^{iqz_n}e^{-\kappa z_n} . \quad (10)$$

In this simplest case

$$\mathrm{Re}F(q)=\sum_n\Delta\rho_n\cos(qz_n)e^{-\kappa z_n} ,$$
$$\mathrm{Im}F(q)=\sum_n\Delta\rho_n\sin(qz_n)e^{-\kappa z_n} , \quad (11)$$

and for $F(\mathbf{q})$ to have a zero, both the real and imaginary parts must be zero. First consider two interfaces (one layer) with one at $z_1=0$ and the other at $z_2=d$. From Eq. (11)

$$\mathrm{Re}F(q)=\Delta\rho_1+\Delta\rho_2\cos(qd)e^{-\kappa d} ,$$
$$\mathrm{Im}F(q)=\Delta\rho_2\sin(qd)e^{-\kappa d} . \quad (12)$$

$\mathrm{Im}F(\mathbf{q})$ can only be zero if $qd=n\pi$ and then for $\mathrm{Re}F(\mathbf{q})$ to be zero also, we must have

$$\Delta\rho_1+(\pm1)^n\Delta\rho_2 e^{-\kappa d}=0 , \quad (13)$$

which, of course, is only true if $|\Delta\rho_1/\Delta\rho_2|=e^{-\kappa d}$. In this simplest case we see that for $\Delta\rho_1>\Delta\rho_2$ there are no zeros in the UHP since $\kappa>0$ and $\Delta\rho_1/\Delta\rho_2$ *cannot* satisfy Eq. (13).

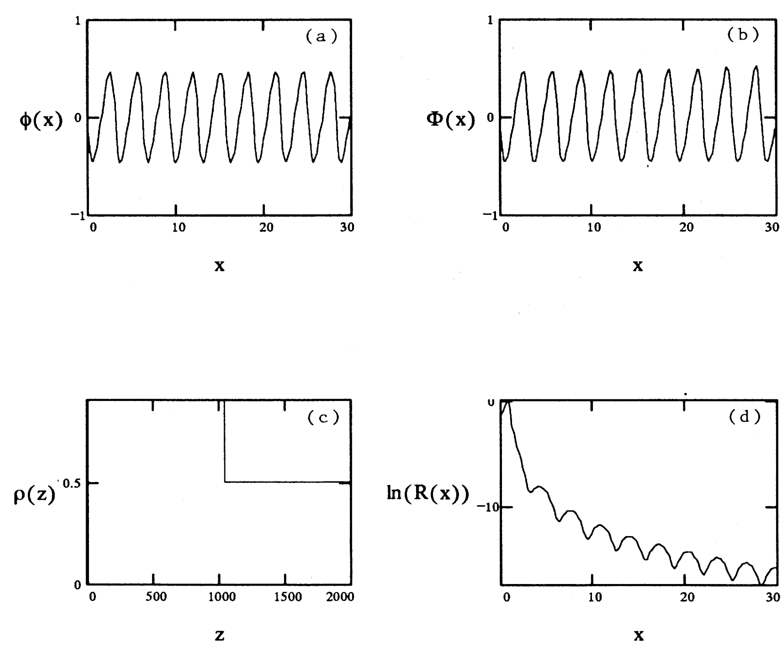

FIG. 1. Born approximation for the structure factor defined in Eq. (2). (a) Exact phase defined in Eq. (9). (b) Hilbert phase defined in Eq. (4). (c) Profile $\rho(z)$ depicts scattering density of layer thickness a. (d) log of the reflectivity defined in Eq. (2a).

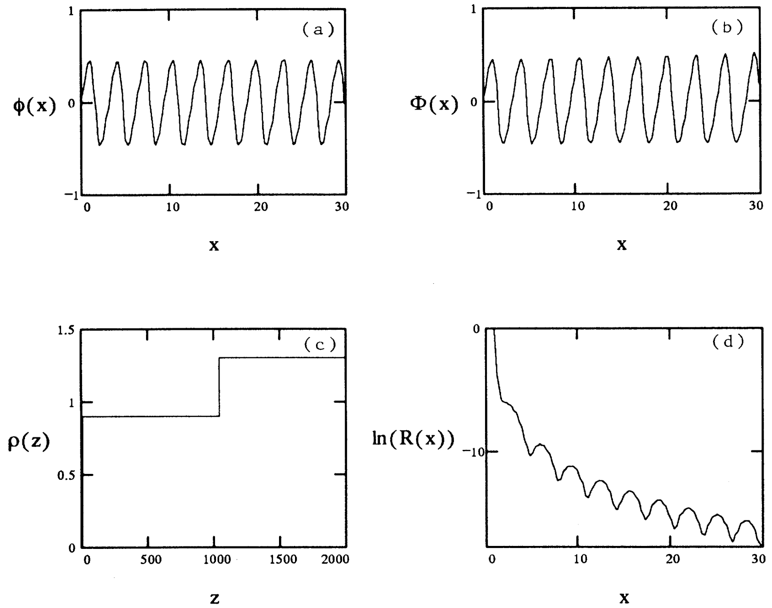

FIG. 2. Same as Fig. 1 for the profile depicted.

But if $\Delta\rho_2 > \Delta\rho_1$, then a line of zeros exists parallel to the real axis at $q = n\pi/d$ and $\kappa d = \ln|\Delta\rho_2/\Delta\rho_1|$ because $|\Delta\rho_1/\Delta\rho_2|$ is now less than one and Eq. (13) is satisfied for any set of all even or all odd integers depending on the sign of the ratio.

We next derive a sufficient condition that any sharp interface profile will have a structure factor that has no zeros in the UHP.

Let the mth interface have the largest value of $\Delta\rho$, i.e., $|\Delta\rho_m| > |\Delta\rho_n|$ for all n. Thus, since $\kappa > 0$ for the UHP, a necessary condition for $F(\mathbf{q})$ to have a zero in the UHP is $\mathrm{Re}F(\mathbf{q}) = 0$ for some $\kappa > 0$. This requires

$$\Delta\rho_m + \sum_{n \neq m} \Delta\rho_n \cos(qz_n) e^{-\kappa z_n} = 0 , \tag{14}$$

where we have taken $z_m = 0$ and $z_n > 0$ for all n. But if we then choose

$$|\Delta\rho_m| > \sum_n |\Delta\rho_n| > \left|\sum_n \Delta\rho_n \cos(qz_n) e^{-\kappa z_n}\right| ,$$

Eq. (14) can *never* be satisfied. Hence the inequality

$$|\Delta\rho_m| > \sum_{n \neq m} |\Delta\rho_n| \tag{15}$$

is a sufficient condition to ensure that the profile has a

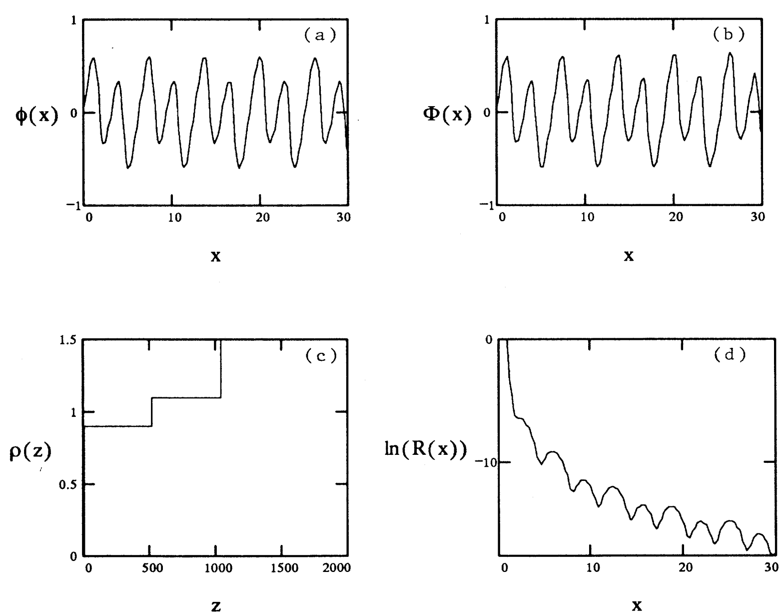

FIG. 3. Same as Fig. 1 for the profile depicted.

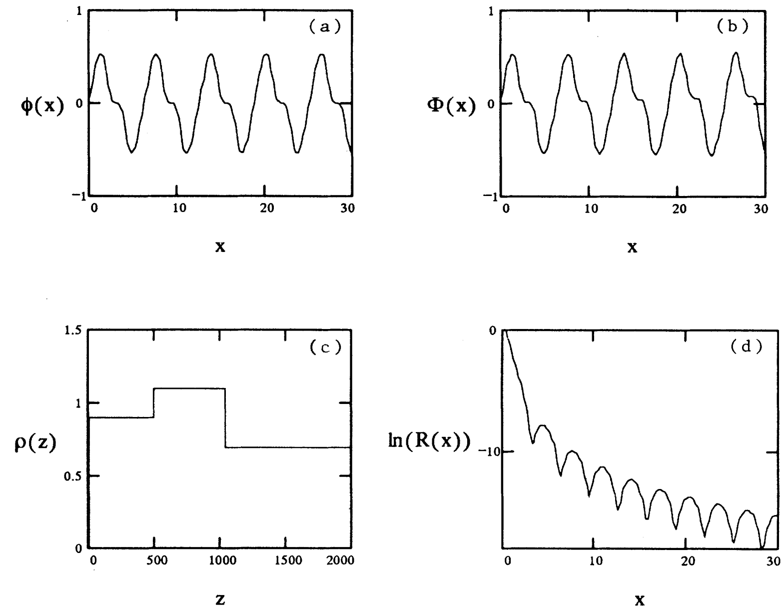

FIG. 4. Same as Fig. 1 for the profile depicted.

zero-less structure factor in the UHP. This remarkable result implies that one should be able to fabricate layered structures that allow complete phase determination from measurements of $R(q)$ alone.[11]

We have numerically tested this result in a series of calculations on simulated profiles in Figs. 1–5.

Our final application shows how the theoretical results presented here also apply to real systems. In Fig. 6 modeled neutron reflectivity data for a 1042 Å Ni film on a float glass substrate are shown.[8] The sharp model profile is displayed in Fig. 6(c), and Fig. 6(d) shows the log of the reflectivity. It is seen that this profile satisfies our condition that $|\Delta\rho_1| > |\Delta\rho_2|$. Thus the phase of the structure factor should be completely determined by the Hilbert phase of Eq. (4). In Figs. 6(b) and 6(a) we plot the model Hilbert phase compared to the exact calculated phase from the model. The latter, of course, can be calculated exactly from the one-dimensional Schrödinger equation, i.e., $\phi = \tan^{-1}[\mathrm{Im}(F)/\mathrm{Re}(F)]$ where F is the exact scattering amplitude of the one-dimensional barrier problem shown, normalized to the Fresnel amplitude for the Ni interface.[12]

Figure 6 shows results for sharp interfaces since the Ni vacuum and Ni substrate roughnesses are only 10 and 1 Å, respectively.[8,13]

In summary we have shown, using logarithmic disper-

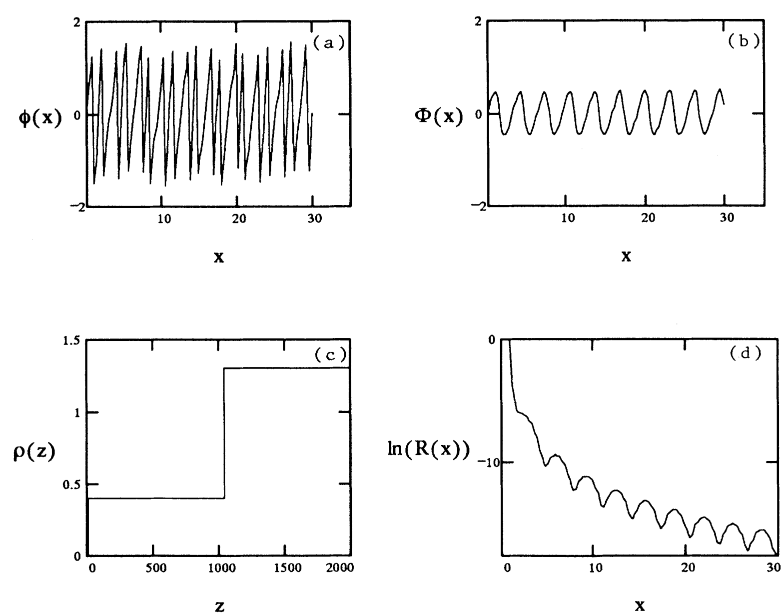

FIG. 5. Same as Fig. 1 for the profile depicted. Note here however that (a) and (b) do not agree because the condition $|\Delta\rho_1| > |\Delta\rho_2|$ is violated and $F(q)$ will have zeros in the UHP.

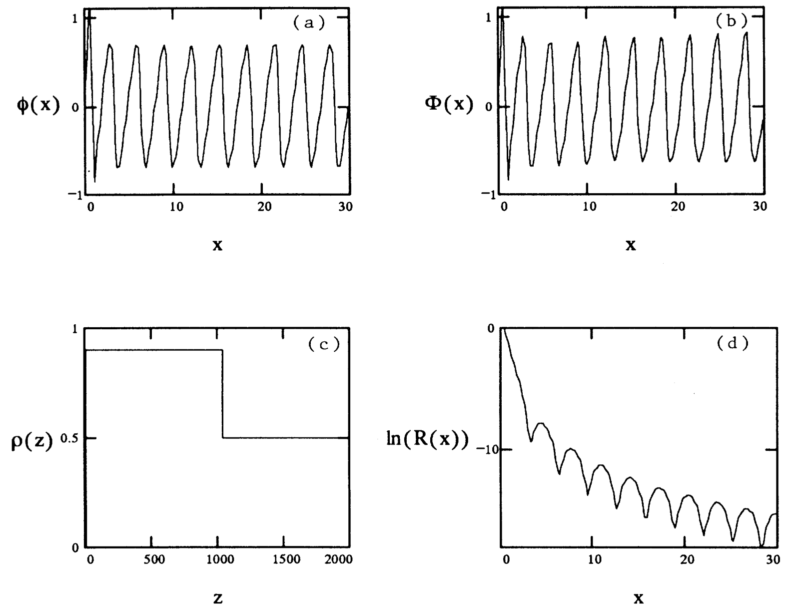

FIG. 6. Structure factor derived for exact scattering amplitude described in the text. Otherwise the figure depicts the same information as in previous figures.

sion relations, that the phase of the reflection amplitude in reflectivity experiments can be completely and relatively easily recovered, at least for certain profiles. The problem of zeros in the complex momentum-transfer plane can be completely avoided in many important physically realizable cases. The theoretical foundation of these results is the Titchmarsh theorem for causal transforms. Remarkably, the finite sample size in x space implies the analyticity of the scattering amplitude in q space and thus plays the role of causality in Kramers-Kronig ω-t dispersion relations.

---

[1]J. S. Toll, Phys. Rev. **104**, 1760 (1956).

[2]R. Oderico, Nuovo Cimento **54**, 96 (1968); J. A. McClure and L. E. Pitts, Phys. Rev. D **5**, 109 (1972).

[3]R. E. Burge, M. A. Fiddy, A. H. Greenaway, and G. Ross, Proc. R. Soc. London Ser. A **350**, 191 (1976). Also an informative discussion in the context of crystallography occurs in B. Kaufmann, Acta Crystallogr. Sect. A **4**, 152 (1985).

[4]The Kramers-Kronig relations are the most celebrated. A detailed mathematical discussion can be found in F. W. Byron and R. W. Fuller, *Mathematics of Classical and Quantum Physics* (Addison-Wesley, Reading, MA, 1970). We recall that the Kramers-Kronig relations are integral conditions (Hilbert transforms) relating the real and imaginary parts of a susceptibility $\chi(\omega)$. The conditions result because the Fourier transform of $\chi(\omega)$, a response function $G(\tau)$, must satisfy a causality condition in the time domain [e.g., $G(\tau)\equiv 0$ for $\tau<0$]. This condition in turn implies analyticity of the Fourier transform of G, namely $\chi(\omega)$, in the complex-frequency plane [i.e., $\chi(\omega)$ is a causal transform]. By comparison in the present problem, finiteness of the scattering target [e.g., $\rho(z)\equiv 0$ for $z<0$] implies analyticity of the structure factor $F(q)$ in the complex q plane. Thus the conditions we use here are the direct analog of Kramers-Kronig relations where ω-τ is replaced by q-z and LDR are used rather than the ordinary dispersion relations because of the importance of the phase.

[5]C. F. Majkrzak, N. F. Berk, J. F. Ankner, S. I. Satija, and T. P. Russell, Proc. SPIE **1738**, 282 (1992). For a review see C. F. Majkrzak, in *Handbook of Neutron Scattering,* edited by W. Glaser (Springer-Verlag, Berlin, 1991), Chap. 13.

[6]J. Als-Nielsen, *Topics in Current Physics, Structure and Dynamics of Surfaces* (Springer-Verlag, Berlin, 1986), Vol. 2; P. S. Pershan, Faraday Discuss. Chem. Soc. **89**, 231 (1990).

[7]In all calculations we used the following definitions: $x\equiv qa$, $x_c\equiv q_c a$, $x_1\equiv(x^2-x_c^2)^{1/2}$, $R_F\equiv|(x-x_1)/(x+x_1)|^2$, $q=2k$, $k\equiv[(2m/\hbar^2)(E-V_0)]^{1/2}$.

[8]J. F. Ankner and C. F. Majkrzak, Proc. SPIE **1738**, 260 (1992).

[9]D. S. Sivia and R. Pynn, Proc. SPIE **1738**, 305 (1992).

[10]S. K. Sinha *et al.*, in *Surface X-ray and Neutron Scattering,* edited by H. Zabel and I. K. Robinson (Springer-Verlag, Berlin, 1992), p. 85.

[11]For the simulated profiles presented in this paper the value of $\Delta\rho$ is, of course, known in advance and the point of this work is to present numerical examples testifying to the credibility of the theory. Even in real experimental situations one can, with modern techniques, fabricate surfaces that satisfy the requirements of Eq. (15) so that the theory can be tested in the laboratory. For unknown structures, I envision this theory as playing a complementary role to modeling techniques.

[12]For the sharp barrier of thickness a, the exact reflection coefficient is given by

$$B(x)=[R_{F_1}^{1/2}+R_{F_2}^{1/2}\exp(ix)]/[1+R_{F_1}^{1/2}R_{F_2}^{1/2}\exp(ix)]\ .$$

[13]W. L. Clinton (unpublished), wherein we show that the scattering potential $V(z)=V_0(1+e^{-\alpha z})^{-1}$, where α^{-1} is the roughness parameter, can be solved exactly for multiple nonoverlapping interfaces. We also incorporate the instrumental Gaussian broadening (Ref. 8).