

Complementarity of Smoothing Procedures for a Smoothed Groove-Tracking Method

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The complementarity of smoothing procedures for a smoothed groove-tracking method (SGTM) is essential in realistic experimental cases. A strategy of using successively smoothing procedures based on cubic-spline interpolation, averaging processes and Fourier transformation at various stages in SGTM is proposed. The mathematical basis of SGTM and the strategy of invoking various smoothing procedures are discussed. Application of this strategy is demonstrated on experimental data from a liquid crystal and C₆₀-amine adducts at the interface between air and water.

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I. Introduction

Techniques involving X-ray specular reflectivity and neutron scattering are widely used to probe surface structure along the surface normal in diverse materials [1]. Analysis of such reflectivity data involves methods both either dependent or independent of a model [2, 3]. Because reflectivity data lack phase information and because the q_z range over which reflectivity is measured is limited, all these methods for analysis of X-ray reflectivity inherently fail to yield unique profiles of the electronic density [4]. In model dependent methods, a model profile of electronic density of a particular sample must be established in advance. Experimental data of X-ray reflectivity are used to adjust the value of each parameter of the model. For some samples prior information of the profile within the surface region is lacking; to construct a profile then becomes difficult and use of model-dependent methods to analyze X-ray reflectivity data is precluded. Schemes independent of a model for analysis of reflectivity data are thus crucial because with the latter methods one can retrieve profiles of electronic density directly from reflectivity data. Furthermore, such methods help reveal physical phenomena of surface structures that might be overlooked in related theories and speculations [5].

Zhou and Chen [6, 7] demonstrated that, when good data exist for the region of small q_z , the relation between the physical profile and reflectivity contains phase information that eliminates some ambiguities in the extracted profiles. They therefore developed a model-independent groove-tracking method (GTM) [6] that employs recursive equations derived by Parratt [8] to construct a step-like profile to outline the smooth profiles of the samples. In the GTM, the density profile is first approximated by a few steps of equal width and

independent height. The reflectivity for this model interface is computed, compared to experimental data with a cost function defined in Ref. [6] and the density of each step is then independently varied to minimize the cost function. Successive approximations are made by subdividing each step and then repeating the process while allowing subsequent amplitudes for narrower steps to vary. The procedure is completed as soon as the calculated cost function attains an acceptable value.

Although the GTM has proved applicable to many samples, we invented a smoothed groove-tracking method (SGTM) [9], which is based on improving the original GTM by imposing the requirement that the profile of electronic density be smooth. In the SGTM, the surface region of a sample is divided into much thinner layers and then the reflectivity is calculated more precisely with Parratt's formula. Moreover, a subtle iteration of improved GTM and successive smoothing procedures is utilized to extrapolate reasonably the reflectivity data beyond $q_{z,\max}$, yielding more physically reasonable profiles than typically jagged, discontinuous profiles generated with the original GTM. Hence the SGTM makes the original GTM significantly more practical particularly in cases in which experimental data are measured within a limited range of q_z .

The fitting procedure in the original GTM is found to be flawed and sometimes causes problems of local minima, although a cost function is defined prudently to drive plausibly the fitting procedures in the original GTM. To eliminate this deficiency, a modified groove-tracking method (MGTM) [10], taking account of the relation between thickness of divided layers and the range of q_z of data at each stage of fitting, is proposed. Applying MGTM and SGTM to experimental data of X-ray reflectivity from liquid mercury, we construct a new electron density profile at the interface between mercury liquid and vapor. This work [5] not only provides the first significant evidence of a layer of adsorbed atoms above the surface of liquid Hg, as D'Evelyn and Rice predicted [11], but also successfully demonstrates usage of the MGTM and SGTM. The latter methods are also applicable to data of neutron reflectivity and are available to analyze reflectance with phase information if the phase problem is solved with the aid of actual measurements of phase [12].

To make the SGTM more practicable, we developed two new smoothing procedures [13] to diminish the number of iterations, but we must utilize all smoothing procedures in an appropriate series because profiles of manifold samples possess individual features and because no experimental data are measured in an completely ideal way. In this paper, we present an essential strategy of successive utilization of various smoothing procedures for SGTM. We also examine a mathematical basis of the SGTM and its smoothing strategy, after the original GTM fitting procedures, of which mathematical details are investigated carefully [6], are found to be flawed.

II. Theory of SGTM and smoothing procedures

The surface region, of depth d , of interest is divided into N equal sections, each of which has thickness D such that $ND = d$. d must be large enough that all features of electronic density profile are distributed within this region. The profile of electronic density within each slice is regarded as a constant equal to the average electronic density in this slice. N must be large so that the real density of electronic density $\rho(z)$ is replaced safely by a discretized $\mathbf{\rho}_N = [\rho_1, \rho_2, \rho_3, \rho_N]$.

Being a function of the free-space wave number $k_o = (2\pi/\lambda) \sin \theta$, with θ denoting the grazing angle and λ the free space wavelength of the wave, the theoretical reflectance of N uniform slices is given in terms of the profile ρ_N through a recurrence relation [8],

$$r_i = \frac{R_{i+1} + r_{i+1} \exp(2ik_{i+1}\Delta Z_{i+1})}{1 + R_{i+1}r_{i+1} \exp(2ik_{i+1}\Delta Z_{i+1})} \quad (1)$$

in which $\Delta Z_{i+1} = D$ is the thickness of layer $i + 1$ and $i = N - 1, N - 2, 2, 1, 0$,

$$k_{i+1} = \sqrt{(k_o^2 - 4\pi\rho_{i+1})} \quad (2)$$

the wave number in layer $i + 1$, $R_{i+1} = (k_i - k_{i+1})/(k_i + k_{i+1})$ the Fresnel reflectance of the interface between the layers i and $i + 1$, and $r_N = (k_N - k_\infty)/(k_N + k_\infty)$ the Fresnel reflectance of the interface between the layer N and the bulk. Therefore, $r_o(k_o)$ is the reflectance of the entire N -layer assembly and the reflectivity is expressed as $|r_o(k_o)|^2$ for a given ρ_N .

According to Born's approximation, $R_i \ll 1$, and Fresnel reflectance is expressed as

$$R_{i+1} \approx \frac{4\pi(\rho_{i+1} - \rho_i)}{(2k_o)^2} \quad (3)$$

Therefore, Eq. (1) becomes

$$r_i \approx R_{i+1} + r_{i+1} \exp(2ik_{i+1}\Delta Z_{i+1}). \quad (4)$$

Neglecting the variation of k_{i+1} among slices, for which electronic density differs, i.e., $k_{i+1} \approx k_o$ for all i , and denoting k_{i+1} as k_o , we obtain the reflectance

$$r(q_z) = \frac{4\pi}{q_z^2} \int \frac{\partial \rho(z)}{\partial z} e^{iq_z z} dz, \quad (5)$$

with $q_z = 2k_o$. After integrating Eq. (5) by parts, we obtain the reflectance

$$r(q_z) = \frac{-4\pi i}{q_z} \int \rho(z) e^{iq_z z} dz, \quad (6)$$

and the reflectivity

$$R(q_z) = \left| \frac{-4\pi i}{q_z} \int \rho(z) e^{iq_z z} dz \right|^2. \quad (7)$$

In SGTm and MGTm, X-ray reflectivity is calculated with Eq. (1), but the result of the calculation is almost equal to Eq. (7) derived according to Born's approximation. Therefore the latter approximation is sufficiently accurate for interpolation of how the MGTm and the smoothing procedures function. In experiments, data are measured within a finite range from q_c to $q_{z,\max}$. In the fitting procedure of MGTm a function is constructed for a profile $\kappa(z)$ that generates the reflectivity spectrum and fits satisfactorily the experimental reflectivity data of the real profile $\rho(z)$ just within $q_{z,\max}$. Even in an ideal case in which the fitted reflectivity spectrum agrees with experimental data within $q_{z,\max}$, it is still possible that $\kappa(z)$ differs from $\rho(z)$. According to Eq. (7), the difference between the reflectivity of an obtained profile $\kappa(z)$ and the experimental reflectivity of the real profile $\rho(z)$ can be explicitly expressed as

$$2|\tau(q_z)||\mathcal{H}(q_z)|\cos(\alpha - \beta) + |\mathcal{H}(q_z)|^2 \quad (8)$$

in which

$$\mathcal{H}(q_z) = \frac{-4\pi i}{q_z} \int \Delta(z)e^{iq_z z} dz, \quad (9)$$

where α and β are the phases of $\tau(q_z)$ and $\mathcal{H}(q_z)$. $A(z)$ is a function indicating the difference between the real profile $p(z)$ and $\kappa(z)$. During fitting of GMTM, the reflectivity spectrum is computed to agree with experimental data satisfactorily within $q_{z,\max}$, i.e., Eq. (8) must approach zero within $q_{z,\max}$. $\Delta(z)$ is formed as a quasi-periodic function with period $\tau \sim \pi/q_{z,\max}$ and a finite coherence length, and a step-like profile $\kappa(z)$ is constructed so that $\mathcal{H}(q_z)$ has a bump appearing about $2\pi/\tau$ and both Eq. (9) and (8) approach zero within $q_{z,\max}$. Differing from the real profile $\rho(z)$ by a quasi-periodic function $A(z)$, $\kappa(z)$ crosses the real profile $\rho(z)$ periodically to outline it. Various methods independent or dependent of model can yield disparate $\kappa(z)$ functions and create various artificial features of reflectivity beyond $q_{z,\max}$. Thus the fitted reflectivity differs from reflectivity data of the real profile of electronic density beyond $q_{z,\max}$. To choose or to create another function $A(z)$ is equivalent to various extrapolations for fitted reflectivity beyond $q_{z,\max}$. For a sample with a smooth profile, artificial features of reflectivity are unexpected. In SGTm, smoothing procedures are undertaken to avoid such unexpected features.

Figures. 1 illustrates the result of applying GMTM and SGTm to simulated data of X-ray reflectivity within $q_{z,\max} = 3.0\text{\AA}^{-1}$ from the surface of liquid Ga at room temperature. The dashed line in Fig. 1(a) represents the fitted reflectivity spectrum obtained by GMTM and the full line illustrates the result of the SGTm procedure. Both fit the simulated spectrum well within $q_{z,\max} \sim 3.0\text{\AA}^{-1}$. An inset shows the step-like profile $\kappa(z)$, obtained with GMTM, and the smoothed profile, constructed with SGTm. Both are superimposed on the original profile that produces simulated data of reflectivity. The extrapolated reflectivity spectra of the SGTm profile and of the GMTM profile, depicted in the inset of Fig. 1(a), are calculated according to Parratt's formula and are shown as solid and dotted lines in Fig. 1(b). Unexpected artificial features of the extrapolated GMTM reflectivity are significant whereas differences between simulated spectra and the extrapolated SGTm reflectivity are smaller.

Based on mathematics explained above, we learn the relation between a step-like profile $\kappa(z)$ and a real profile $p(z)$. Therefore, on using a smoothing procedure based on cubic-spline interpolation we obtain efficiently a smoothed profile denoted $\mathbf{A}(z)$ to approach the real profile. Obviously, the smoothed profile $\mathbf{A}(z)$ may differ from the real profile $p(z)$ by a smooth function $S(z)$. The remaining task is to discover $S(z)$ so as to obtain $p(z)$.

Successive fitting procedures of SGTm indicate a new profile $\kappa(z)$ expressed as $\mathbf{A}(z) + \mathcal{D}(z)$, whereas the real profile $p(z)$ can be expressed as $\mathbf{A}(z) + S(z)$. $\mathcal{D}(z)$, unlike $\Delta(z)$, is no longer a quasi-periodic function. In the ideal case in which the following SGTm procedure can make the fitting perfect, i.e., $\mathcal{D}(z)$ possesses the following characteristic [13]:

$$\int \mathcal{S}(z)e^{iq_z z} dz \approx \int \mathcal{D}(z)e^{iq_z z} dz \quad (10)$$

within $q_{z,\max}$.

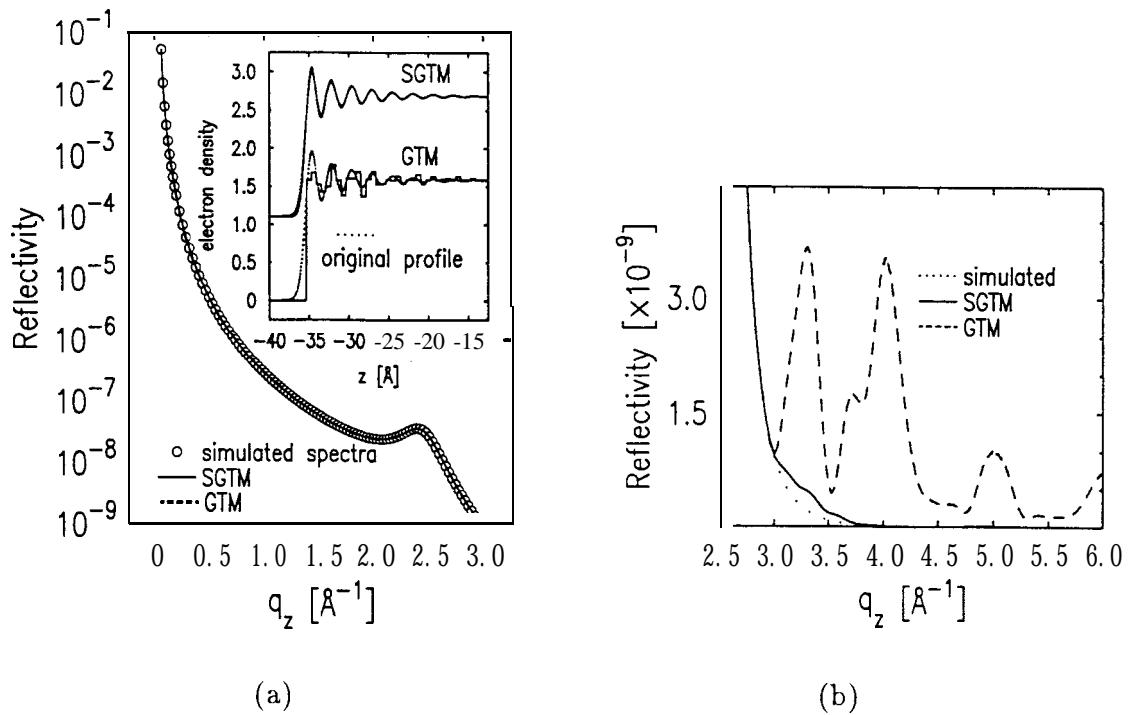


FIG. 1. (a) Simulated reflectivity data for original model profile, shown in the inset, of liquid Ga at room temperature (circle) compared with reflectivity spectra fitted with SGTM (solid line) and GTM (dashed line). (Inset) Density profiles constructed with SGTM and GTM to produce the fitted reflectivity spectra shown in (a) along with the original model profile. (b) Simulated reflectivity (dotted line) for extrapolated wave vectors, $q_z \geq q_{z, \max} = 3.0 \text{ \AA}^{-1}$, compared with the reflectivity spectrum with artificial features fitted by GTM (dashed line) and with the reflectivity spectrum, resembling simulated data, fitted with SGTM (solid line).

The profile of electronic density in the surface region of each and varied samples has individual features unexpected beforehand in many cases. The value of $q_{z, \max}$ that can be reached in experiment depends mainly on experimental conditions for each case and is sometimes limited. Furthermore, depth d , into which the surface region is divided in many thin slices when the SGTM is employed to analyze reflectivity, is a constant. This constant is given with only principal consideration whether it is large enough to cover all features of the profile of electronic density. Therefore, in practice perhaps the MGTM might not function ideally to outline the unknown profile; then the smoothing method based on cubic-spline interpolation can not function perfectly. There is no assurance that $S(z) (= \rho(z) - A(z))$ and the step-like function $D(z)$ indicated from the subsequent SGTM procedure can satisfy Eq. (10). This condition implies that this subsequent SGTM procedure can not make the fitting perfect. Moreover, because instead of a periodic function $A(z)$ the difference function between $\kappa(z)$ and $p(z)$ is just a step-like function $D(z)$ (see Fig. (2)), to repeat the cubic-spline smoothing procedure is generally futile here.

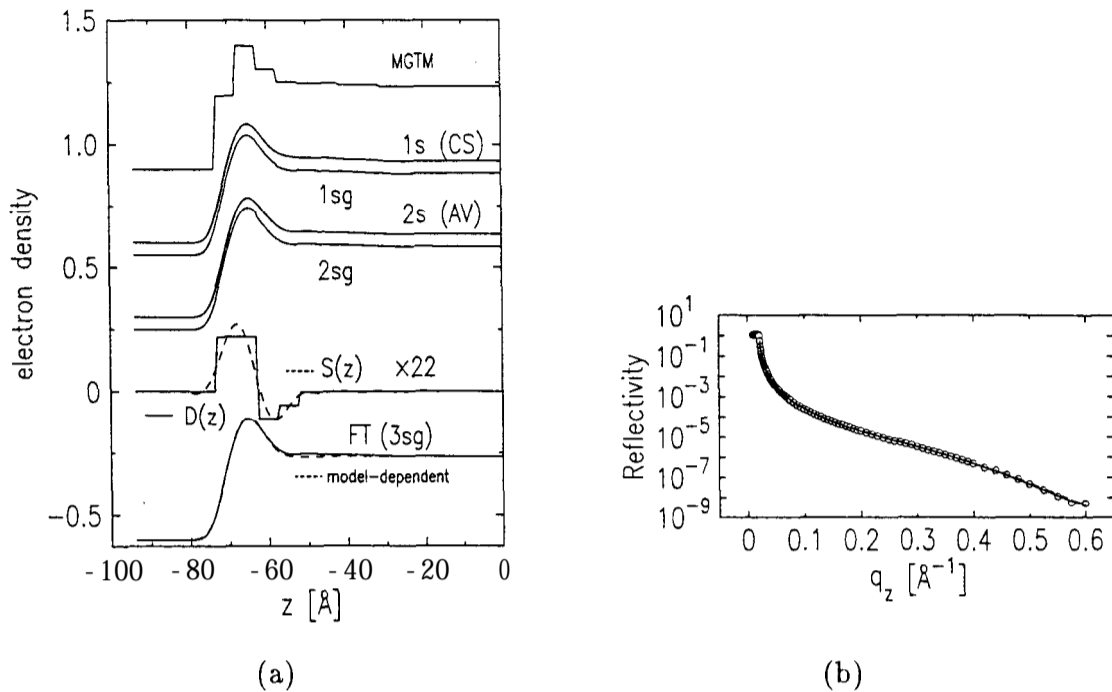


FIG. 2. (a) Profiles at successive stages of SGTM procedure with the new strategy of smoothing procedures. "CS" indicates the first smoothing operation based on cubic-spline interpolation and "1sg" refers to application of a successive SGTM procedure to "1s (CS)" profile (notation similar for subsequent iterations). "AV" refers to the second smoothing operation based on averaging. On applying the smoothing procedure based on averaging once, $D(z)$ (multiplied by 22) are obtained with a subsequent SGTM procedure and $S(z)$ (multiplied by 22) is obtained according to Eq. (11). "3sg (FT)" refers to the resultant profile obtained on smoothing based on Fourier transformation and verified with a succeeding SGTM procedure. The dashed line superimposed on the "3sg (FT)" profile is constructed with a model-dependent method. (b) Reflectivity spectra fitted with the step-like "MGTM" profile, shown in (a), and of the "3sg" profile agree satisfactorily with experimental reflectivity data.

Thus, at this stage an iteration of the smoothing procedure based on averaging processes is necessarily undertaken to modify $A(r)$ and to make it approach gradually the real profile. Therefore, the difference function $S(z)$ gradually decreases. When fitted reflectivity data agree satisfactorily with experimental data, the function $D(z)$ satisfying Eq. (10) is obtained and $S(z)$ is thereby obtained from the following formula

$$S(z) = \frac{1}{\sqrt{2\pi}} \int_{-q_{z,\max}}^{q_{z,\max}} \left[\frac{1}{\sqrt{2\pi}} \int D(z') e^{iq_z z'} dz' \right] e^{-iq_z z} dq_z. \quad (11)$$

The real profile becomes expressed as $A(z) + S(z)$. The chi-square with the final smoothed profile $A(z) + S(z)$ is subject to minimization again on invoking the SGTM procedure. In

general no physically meaningful change in this profile is found and $A(r) \cdot t S(z)$ is safely regarded as the real profile.

III. Applications of the strategy

Fig. 2 shows experimental reflectivity data for C_{60} -amine adducts at an interface between air and water [14] near 300 K with profiles retrieved with a model-dependent method and with SGTm with our new smoothing strategy. The MGTm profile, of which the computed reflectivity spectrum (dashed curve in (b)) fits satisfactorily the experimental data (circles in (b)), is shown in (a). Then, the SGTm iteration is utilized to discern key features and details of the profile of electronic density of this sample. By employing a smoothing procedure based on cubic-spline interpolation, we construct a smooth profile that reveals the outline of the real profile, although the following SGTm procedure indicates additional modifications on this constructed profile. In some cases [13] iterating the cubic-spline smoothing procedures improves fits successively, but according to the mathematical discussion above, at following stages utilizing a smoothing method based on averaging is mathematically reasonable and efficient. Here, the smoothing procedure based on averaging processes is employed only once and in the following SGTm procedure the computed reflectivity of the constructed profile, denoted "2sg" in (a), fits satisfactorily the experimental data. Hence the function $D(z)$ and $S(z)$ satisfy Eq. (10). Using the smoothing procedure based on Eq. (11) we extract $S(z)$ together with a smoothed profile, denoted "FT" in (a). The successive SGTm procedure yields a profile denoted "3sg", which is the same as the FT profile. The resultant computed reflectivity (solid curve in (b)) of 3sg profile fits the data as well as MGTm reflectivity does. The solid and dashed curves are scarcely distinct. Nevertheless, compared with the model-dependent method, SGTm has the advantages of flexibly revealing details of the unknown profile from experimental data. Therefore, a minute discrepancy between the model profile and the 3sg profile is observed about $\sim -40 \sim -60$ Å.

Fig. 3 presents experimental reflectivity data of a liquid crystal [15] and results of successive application of SGTm with the new strategy. A smooth profile (1s in (a)), constructed on applying a cubic-spline smoothing procedure to the MGTm profile only once, resembles the resultant profile, denoted "6sg", but the computed reflectivity from lsg profile does not yet fit the experimental data well. The inset in Fig. 3(b) shows the differences between the computed reflectivity spectra from lsg profile and from 6sg profile with the experimental reflectivity. Employing a smoothing procedure based on averaging and the SGTm procedure succeeding each smoothing procedure four times (2s-5s), we obtain the 5sg profile of which the computed reflectivity fits satisfactorily the experimental data. Then the smoothing procedure based on Fourier transformation yields a smoothed profile (6s) and the successive SGTm procedure indicates a 6sg profile that is the same as the 6s profile. SGTm either with the original smoothing procedures or with the new smoothing strategy, makes the fit superior to that with a model-dependent method [9]; moreover, the number of iterations in the SGTm is profoundly diminished on using the new smoothing strategy.

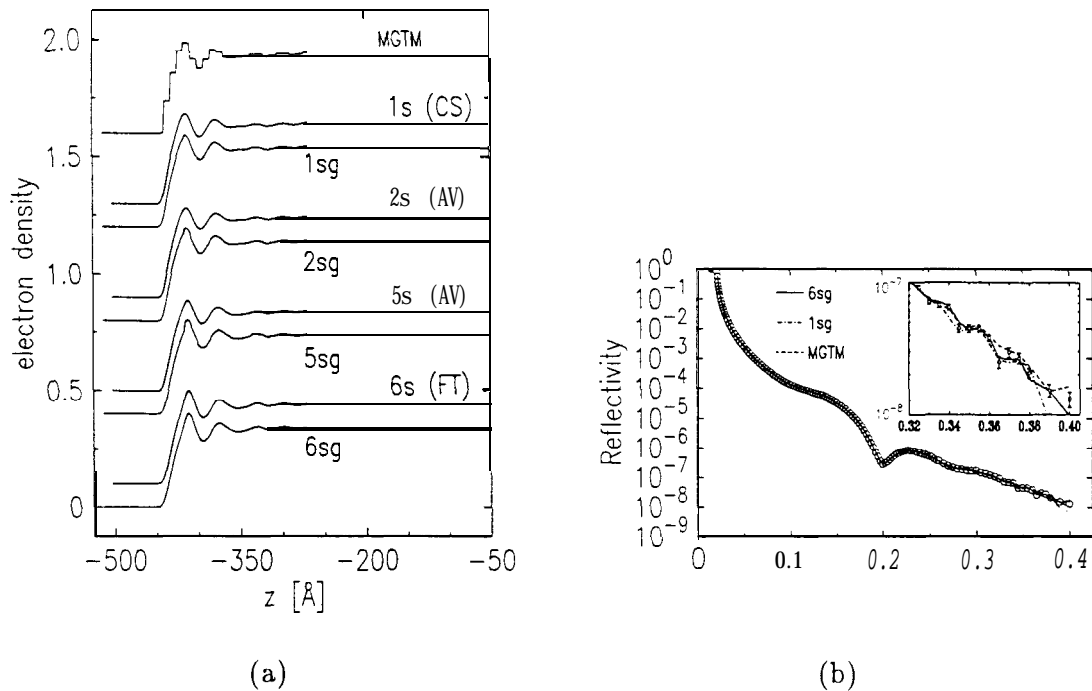


FIG. 3. (a) SGTM approach with the new strategy of using smoothing methods to obtain the resultant profile (6sg) from the MGMT profile shown as the step-like curve. “CS” refers to the first smoothing based on cubic-spline interpolation and “1sg” refers to application of succeeding SGTM to “1s” profile (notation similar for subsequent iterations). “AV” refers to smoothing based on averaging. “FT” refers to smoothing based on averaging. (b) Fitted reflectivity spectra of the step-like “MGTM” profile, “1sg” profile and “6sg” profile, shown in (a), compared with experimental data (circle). The inset shows details of these reflectivity spectra at $q_z \geq 0.32 \text{ \AA}^{-1}$.

IV. Conclusion

A strategy of using various smoothing procedures, which are based on cubic-spline interpolation, averaging processes, and Fourier transformation, is proposed in this paper. The mathematical details indicate why the various smoothing proposed cedures are employed in the order suggested in this strategy. As demonstrated on applying the strategy to data of a liquid crystal and C_{60} , the new strategy helps to decrease the number of iterations in SGTM. The improvement results from the fact that each smoothing procedure makes the obtained profile at each stage of SGTM approach the real profile efficiently and mathematically reasonably.

In this strategy, a smoothing procedure based on cubic-spline interpolation is first utilized to construct a smoothed profile $A(z)$ from the obtained MGMT profile $\kappa(z)$, because the function of the real profile $p(z)$ must cross the step-like profile $\kappa(z)$ periodically. This smoothed profile $A(z)$ might differ from the real profile slightly by a smooth function $S(z)$.

At this stage, however, the successive SGTm procedure indicates a modification function $D(z)$ on $A(z)$ but might be unable to make the computed reflectivity of the obtained profile: expressed by $A(z) + D(z)$, fit experimental data satisfactorily. Hence the difference function $S(z)$ and the modification function $D(z)$ might not satisfy Eq. (10). Therefore, a smoothing procedure based on averaging is used repeatedly to reform flexibly the function $A(z)$ and thereby the difference function $S(z)$. The iteration of this smoothing procedure and successive SGTm procedures continues until the fitted reflectivity data agree with the experimental reflectivity data satisfactorily while Eq. (10) is satisfied. Finally, the smoothing procedure based on Fourier transformation is undertaken to extract $S(z)$ from the finally obtained $D(z)$. The unknown real profile of the sample is retrieved reliably as $S(z) + A(z)$.

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