Model-independent reconstruction of smooth electron density profiles from reflectivity data of liquid surfaces

Chien-Heng Chou,* M. J. Regan, and P. S. Pershan
Division of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts 02138

X.-L. Zhou
Department of Nuclear Engineering, 24-215, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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A smoothed groove-tracking method (SGTM) is developed for the construction of the electron density profiles of liquid surfaces from reflectivity data. This work is based on improving the groove-tracking method (GTM) previously published by one of us (X.-L. Zhou) [X.-L. Zhou and S. H. Chen, Phys. Rev. E **47**, 3174 (1993)] by imposing the requirement that the electron density profile be smooth. Application of the method is demonstrated on both simulated reflectivity data with model density profiles and experimental data from liquid metal, liquid crystal, and water surfaces. Comparisons are made among results obtained by the SGTM, the original GTM, and published model density functions for both monotonic and layered density profiles. We find that the requirement for a smooth profile leads to more physically reasonable profiles than the often jagged, discontinuous profiles generated by the GTM. Although model-independent methods, by their nature, cannot yield unique density profiles and may converge to local minima, these techniques are quite useful for suggesting new profiles when little *a priori* information is available. [S1063-651X(97)04006-3]

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I. INTRODUCTION

The method of x-ray specular reflectivity has been widely used in the last several years for probing surface structure along the surface normal in a variety of materials [1–4]. Unfortunately, as a consequence of both the familiar phase problem and the finite range of angles over which reflectivity is measured, it is not possible to directly invert the reflectivity data in order to obtain the unique surface electron density profile [5,6]. Typically, one fits the reflectivity data to an assumed profile based on physical ideas, usually constructed from Gaussians, error functions, hyperbolic functions, etc.; however, there is no certain proof that any ''best fit'' is unique and confidence in any one model is usually dependent on other physical considerations. Nevertheless, in the last several years a number of model free fitting methods have been developed [7–11]. Although these do not necessarily resolve the ''uniqueness'' issue, Zhou and Chen [8] have demonstrated that when there is good data in the small angle region, the relation between the physical profile and the reflectivity does contain phase information that eliminates some ambiguities in the extracted profiles.

With these considerations in mind, Zhou and Chen [8] developed the model-independent groove-tracking method (GTM) for obtaining a real profile from reflectivity data. In the GTM, the density profile is first approximated by a small number of steps of equal width and independent height. The reflectivity for this model interface is computed, compared to the experimental data with a cost function defined in Ref. [8] or a χ^2 and then the density of each step is independently varied to minimize the cost function. Successive approximations are made by subdividing each step and then repeating the process while allowing the subsequent amplitudes for the narrower steps to vary. The procedure is completed as soon as the calculated cost function or χ^2 attains an acceptable value.

Figure 1 illustrates the result for applying this method to x-ray reflectivity measurements from the surface of water. The dashed line in Fig. 1(a) represents the published physical model [12] based on capillary wave induced Gaussian roughness, and the full lines illustrate the result of the GTM procedure where the surface region is approximated by an increasing number of subdivisions. By the time the width of the GTM steps are ~ 5 Å, the fit to the reflectivity data is very good, and the cost function does not decrease significantly upon subdividing the density profile any further. This result is not surprising, since the smallest length L that can be probed from the data is determined from the maximum wave vector transfer $q_{z,\max}$, where $L \sim \pi/q_{z,\max} = 5$ Å for these data. To further divide the slices into even thinner slices (smaller than L) to try to achieve a better fit is unjustified from the data and leads to no additional insight.

The physical content of the profile obtained by the GTM, however, is not particularly satisfying. This problem arises from the fact that the GTM procedure leads to a density profile that is made of relatively few discrete steps separated by sizable unphysical discontinuities. In addition, it should be noted that as a result of the sharp discontinuities in the GTM profile, the computed reflectivity for wave vectors extrapolated for $q_z > q_{z,\max}$ contains artificial information, in many cases large oscillations that are due to the discretization scheme employed by the GTM, and not physically justified. In this paper we demonstrate that both of the problems, the physically unsatisfying discontinuities in the step

*Present address: Dept. of Physics, National Taiwan University, Taipei 107, Taiwan.

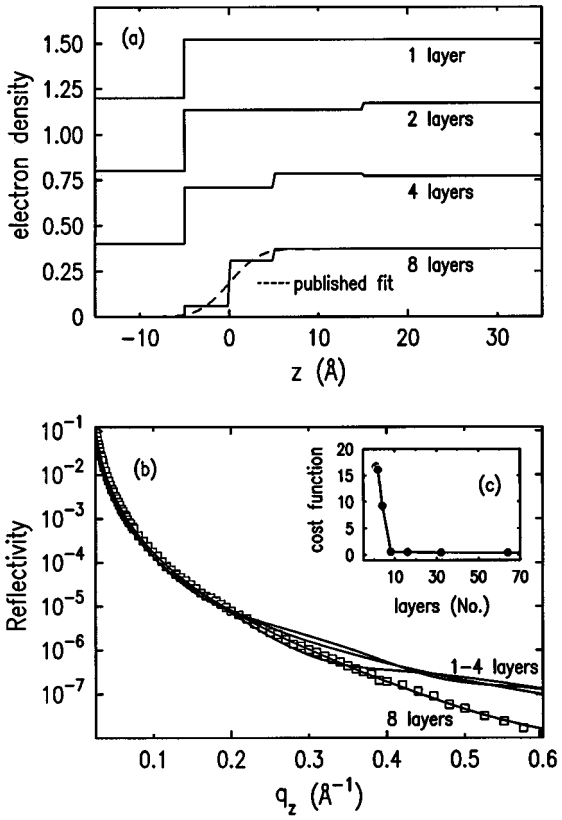

FIG. 1. (a) Density profiles obtained by the GTM for $N=1$, 2, 4, and 8 layers (solid line) compared to the model profile of pure water (dashed line). (b) Reflectivity data for water compared with the reflectivity computed for the profiles shown in (a). (c) Variation of cost function with the number of layers N. For $N>8$, there is no significant improvement in the fit to the data.

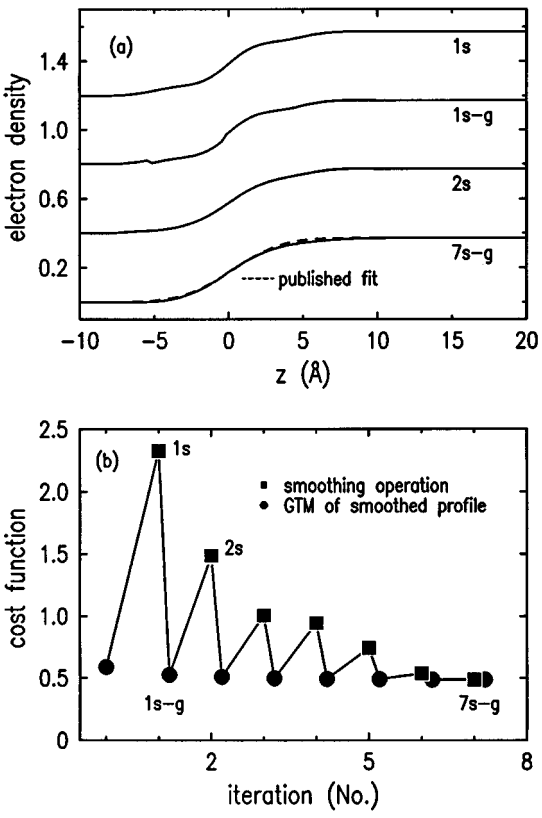

FIG. 2. SGTM approach to obtain a smooth electron density profile of a water surface from the $N=8$ GTM fit of Fig. 1. (a) Outline of the procedure for fitting with the SGTM. ''1s'' refers to the first smoothing operation, and ''1s-g'' refers to the application of GTM to 1s (notation similar for subsequent iterations). By the 7th iteration, the smoothed profile is very similar to the published fit. (b) Variation of the cost function with the application of the smoothing and GTM procedures. The two converge at approximately the 7th iteration.

model and the discrepancies at large q_z, can be eliminated by requiring that the density profile be smooth.

The importance of obtaining a smooth profile has been discussed by Pedersen and Hamley [9]. In this approach, the density profile is parameterized using either cubic splines or a series of sine and cosine terms. The coefficients are then related to the reflectivity data and determined by constrained nonlinear least-squares methods. In these methods, a smoothness factor has to be inserted in the equations to help the equations converge to a meaningful solution. In fact, it is also a smoothness criterion that we propose here for the GTM method. Either of these model-independent methods works very well in that they obtain *a profile* that will represent the observed reflectivity without assuming any particular functional form of the density profile. Obviously, they present a powerful method to extract meaningful information from any given reflectivity data and may provide useful suggestions for new models. However, it should be pointed out that model-independent profiles are inherently nonunique [5,6], and there is no guarantee that these profiles, or any others, have converged to an absolute, rather than to a local, minimum.

II. SMOOTHED GROOVE-TRACKING METHOD [13]

The mathematical basis of the GTM is discussed in detail in the work of Zhou and Chen [8]. We demonstrate here how a straightforward modification of that method can be applied to construct a physically more appealing, smoothed profile from the GTM.

In the GTM, the maximum thickness for the surface region, where the electron density is allowed to differ from the bulk density, is arbitrarily chosen to be D_s. As a practical matter, D_s can safely be chosen to be of the order of some multiple of the reciprocal of $1/q_c$, where q_c is the wave vector corresponding to the x-ray critical angle; however, it can be smaller if the reflectivity is a slowly varying function of q_z. The surface region D_s is divided into $i=1,\ldots,N$ sections of thickness D_s/N, and the N values of the uniform density $\{\rho_i\}$ within each layer are optimized be invoking a nonlinear least-squares procedure to minimize the difference of the cost-function and/or the χ^2 difference between the model reflectivity $R(q_z)$ and the measured reflectivity. If the reflectivity near q_c is important, the theoretical reflectance of the N slices can be computed with Parratt's recurrence relation [14], but if that is not the case, the kinematical approximation can be applied [15]. Starting from a small value of N the procedure is repeated with increasing N until the fit to the measured reflectivity satisfies some goodness criteria.

To illustrate the smoothed groove-tracking method (SGTM) consider, for example, the GTM profile for water

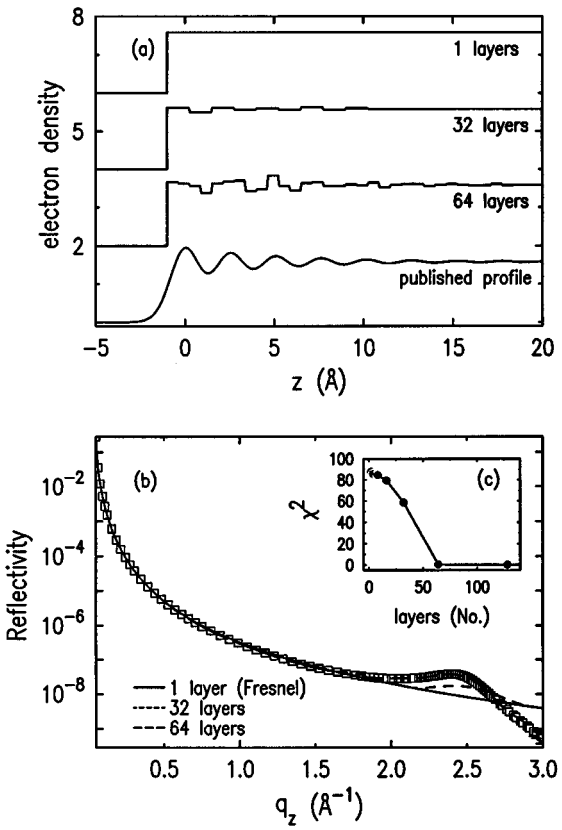

FIG. 3. (a) Density profiles for liquid gallium at room temperature obtained by the GTM ($N=1$, 32, and 64 layers; solid line) and compared to the model profile (dashed line). (b) Reflectivity data for Ga compared with the reflectivity computed for the profiles shown in (a). (c) Variation of χ^2 with the number of layers N. For $N>64$, there is no significant improvement in the fit to the data.

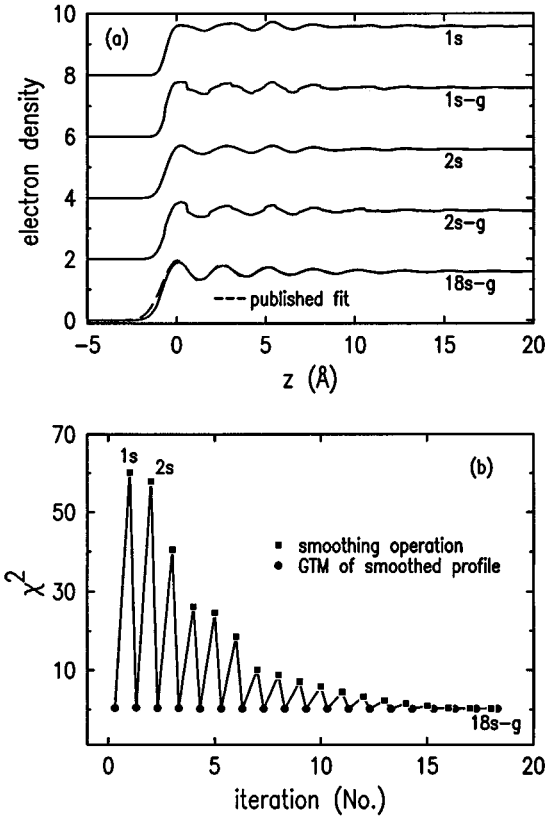

FIG. 4. SGTM approach to obtain a smooth electron density profile for liquid Ga from the $N=64$ GTM fit of Fig. 3. (a) Profiles at different stages of the SGTM procedure. By the 18th iteration, the smoothed profile is very similar to the published fit. (b) Variation of χ^2 with the application of the smoothing and GTM procedures. The two converge at approximately the 16–18th iteration.

illustrated for $N=8$ in Fig. 1(a). There are many ways to smooth any given profile; the very simple approach that is developed and used here proceeds as follows. First, each of the original GTM layers for the water surface is further divided into an arbitrary number of layers. In practice subdivision into 16 layers has proven practical, so that the width of each sublayer is $D_s/(16N)$. Then, the value of the electron density in each of the sublayers $\{\rho_{i,i+1,m}\}$ $(m=1\ldots16)$ is altered by successive iterations in which the density within each sublayer is replaced by the average with its nearest neighbors. This smoothes the abrupt discontinuity between the original N layers; however, the value of the cost-function and/or χ^2 difference between this averaged profile and the data is generally increased over the value previously obtained by the GTM process with N uniform layers. The averaging iteration process is halted when the value of the cost function for the smoothed profile becomes equal to or less than the value obtained by the GTM process for $N/2$ uniform layers. The value of the cost function computed for the $1s$ profile is shown in Fig. 2(b), and, as expected, the consequence of the smoothing operation is to cause the fit to the data to become worse.

In the next step, this cost function, with the averaged profile, is again minimized by invoking the GTM procedure, allowing only the N values of $\{\rho_i\}$ to vary. Within the GTM fitting procedure, the shape of the smoothed interface between the layers is maintained by scaling the density of the sublayers $\{\rho_{i,i+1,m}\}$ to the varying $\{\rho_i\}$. The best-fit profile from this iteration is shown as "$1s$-g" in Fig. 2. The value of the cost function, as indicated in Fig. 2(b), is considerably smaller than the $1s$ value although it is not significantly better than the starting value obtained by the GTM procedure. Note, however, that there are still small discontinuities in the $1s$-g profile. By iterating this procedure of smoothing and fitting with the GTM approach, a stable, smooth profile is eventually obtained. The procedure is stopped when the change in the cost function between the fitted and smoothed profiles satisfies an arbitrarily set convergence criteria. As demonstrated in Fig. 2, after seven iterations of smoothing and using the GTM procedure, the profile for water is quite smooth and is very similar to the published fit. It should be noted that there are a variety of smoothing procedures that could be applied, and certain smoothing procedures might optimize the number of iterations required for the convergence illustrated in Fig. 2 for water. However, this was not investigated here and is the subject of future work.

III. SGTM FOR LAYERED DENSITY PROFILES

In order to demonstrate the effectiveness of the SGTM approach, we have applied it to several problems of current interest. The SGTM works well for simple monotonic pro-

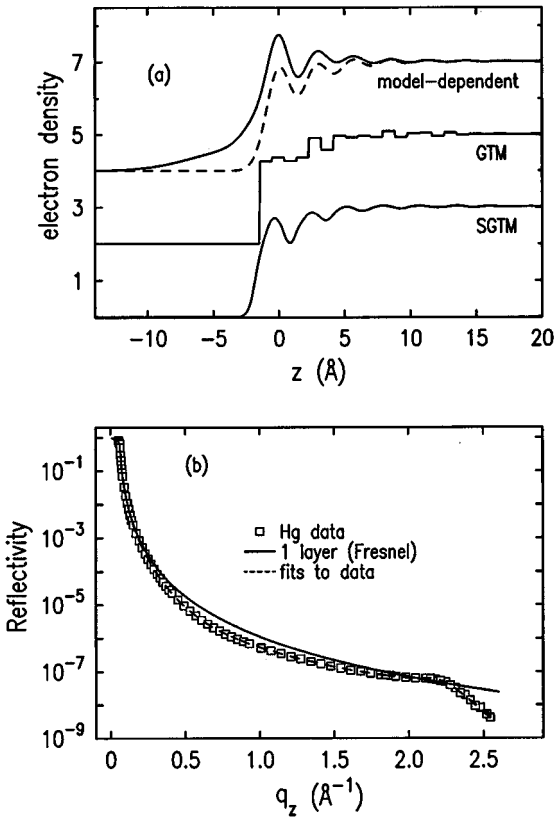

FIG. 5. (a) Summary of the GTM and SGTM results for the mercury liquid-vapor interface at room temperature. It is difficult to discern the atomic layering with the GTM profile, but the SGTM clearly demonstrates layering, converging to one of the two model-dependent profiles for liquid Hg. (b) Reflectivity data compared to the computed reflectivity for the model profiles in (a) illustrate that there is excellent agreement between the data and the GTM and SGTM profiles.

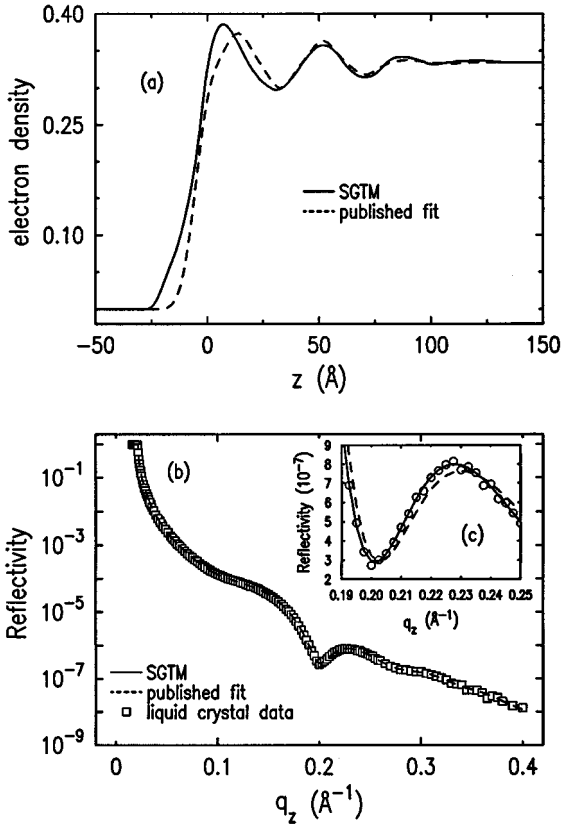

FIG. 6. (a) Density profiles obtained by the SGTM and compared to the model-dependent profile for a liquid crystal surface. (b) The SGTM and model-dependent fit agree nicely with the reflectivity data. However, in (c) it is clear that the SGTM fits the data better near the local minima and maxima corresponding to $q_z = 0.20–0.23$ Å^{-1}. The better fit from the SGTM approach is perhaps due to the enlarged interlayer spacing of the topmost layer in (a) which the published, model-dependent fit does not have the flexibility to model (as it is constructed).

files exhibited by simple dielectric liquid surfaces [12], as demonstrated in Figs. 1 and 2, but it also works similarly well on reflectivity data from layered density profiles. In this section, SGTM fits to simulated and experimental data are presented for liquid metal surfaces (Ga and Hg) and a liquid crystal surface. When there is layering, we show how the effectiveness of the original GTM is greatly improved with the SGTM procedure.

A. Liquid gallium

The liquid-vapor electron density profile of liquid gallium has been measured at room temperature with x-ray reflectivity ($q_{z,\max}=3$ Å^{-1}), leading to the observation of atomic layering at liquid metal surfaces [16]. Figure 3 shows the reflectivity computed from the published model profile [16] at room temperature, and the GTM profile for $N=1$, 32, and 64 layers. Due to the discrete nature of the GTM approach, jagged edges and apparent kinks make it difficult to discern the key features of the layering phenomena even though the fit to the data with $N=64$ layers is as good as the published profile. Figure 4 shows the results of the successive application of the SGTM to the GTM profile. By 18 iterations, the χ^2 of the smoothed profile converges to that from the GTM, and there is good agreement with the published profile based on model-dependent methods.

B. Liquid mercury

The SGTM has been applied successfully on experimental reflectivity data when atomic layering is present. Figure 5 shows the reflectivity data for the surface of liquid Hg [17] at room temperature along with the profiles computed from model-dependent methods, GTM, and SGTM. In contrast to liquid Ga, where the reflectivity closely follows the Fresnel theory for small q_z wave vectors, the data from the liquid Hg surface shows a deviation from the Fresnel theory near $q_z \sim 0.5–1.0$ Å^{-1}, indicating additional surface structure on the order of $\sim 5–10$ Å. This feature in the data has been considered by model-dependent methods (Fig. 5) as either resulting from a density excess above the topmost layer, leading to a density tail that extends into the vapor [17], or from a density deficit that exists in the topmost surface layers. Since these models fit the data equally well, without supplementary information or physical reasoning it is not possible to determine the unique profile.

The GTM can reproduce the reflectivity data, but it is difficult to observe the key features in the density profile due to the sharp, jagged features in the steps. With the SGTM, we find that the reconstructed profile is in excellent agreement with one of the model-dependent profiles that have

been constructed to fit the reflectivity. The convergence of the SGTM to one of two equally valid profiles highlights the issue of nonuniqueness to the model-independent profiles. Presumably, with a different starting profile (i.e., at $N=1$) or with other model-independent methods, convergence to the excess density model is also possible.

C. Liquid crystal surface

As a final example, we consider the reflectivity data from a liquid crystal [18], shown in Fig. 6(b) with the model-dependent and SGTM fits in Fig. 6(a). From the best-fit density profiles, both the reconstructed profile and model profile exhibit three similar peaks at similar positions. The SGTM fit to the data is slightly better, however, especially near the local minima and maxima corresponding to $q_z = 0.20-0.23$ Å^{-1} in Fig. 6(c). The better fit from the SGTM approach is perhaps due to the enlarged interlayer spacing of the topmost layer that is shown in Fig. 6(a), which the published, model-dependent fit does not have the flexibility to model. Of course, if the model-dependent method, by its mathematical construct, had the flexibility to vary the interlayer spacing from layer to layer as the SGTM, then its fit to the data in Fig. 6(c) would be presumably equally good.

IV. CONCLUSION

We have modified the GTM on the basic premise that the density profiles of liquid surfaces should be smooth. By iterating a simple smoothing procedure with the GTM, we have obtained several smooth profiles that agree nicely with the reflectivity data and the published profiles. The applicability of the improved method has been demonstrated by examples on simulated and real experimental data for simple monotonic and more complicated layered profiles. These examples have also been chosen to illustrate the weaknesses of the GTM which, however, is quite useful to extract surface profiles. The SGTM approach should help further refine the previous GTM results. Although the scope of this work has included only x-ray reflectivity data, the approach is also valid for neutron reflectivity data where the electron density is replaced with the neutron scattering length.

It should be noted that the SGTM and GTM procedures lead to essentially equivalent fits to the reflectivity data over the measured q_z range. We have chosen the smoothed profiles that result from the SGTM as the more physically acceptable since the sharp features in the GTM are unrealistic. These sharp features lead to reflectivity peaks when computed for extrapolated wave vectors, $q_z > q_{z,\max}$, which are consistent with the length scale D imposed by the discretization procedure of the GTM. These artificial reflectivity peaks are an artifact that lead to the immediate rejection of the GTM profile; they are not observed in the SGTM and published model-dependent profiles. Of course, since data have not been collected at wave vectors larger than $q_{z,\max}$, one cannot rule out that the oscillations present in the GTM actually exist. But, for liquid surfaces where the density is a smooth, slowly varying function of position in the bulk liquid, the sharp features in the GTM are not expected.

Finally, we have not addressed the issue of uniqueness in these profiles. With either a model-dependent or model-independent treatment of reflectivity data, there is no guarantee that one has obtained the correct density profile [5,6]. With the well-known phase problem, various, unrelated profiles can give rise to similar reflectivity data, and the fitting procedure may converge to a local minimum which is not physically correct. Typically, one can guess at the profile and use model-dependent methods. However, a model-independent treatment can provide suggestions for profiles when little *a priori* information is available.

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