CHINESE JOURNAL OF PHYSICS VOL. 36, NO. 2-I APRIL 1998

Non-Unique Electron Density Profiles of Liquid Mercury from a Smoothed Groove Tracking Method

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(Received Janurary 5, 1998)

The modified groove tracking method (MGTM) along with the smoothed groove tracking method (SGTM) are applied to X-ray reflectivity data of liquid mercury at room temperature. It is demonstrated that it is possible to obtain non-unique profiles, which are physically reasonable, by SGTM. The SGTM yields independently an electron density profile which does contain the essential features of the electron density profile of liquid mercury proposed by D'Evelyn and Rice. [M. P. D'Evelyn and S. A. Rice, *J. Chem. Phys.* ***78, 5081*** (1983)]

PACS. 61.25.Mv − Liquid metals and alloys.
PACS. 61.10.–i − X-ray diffraction and scattering.

I. Introduction

The method of X-ray (or neutron) specular reflectivity has been widely utilized in the last several years for probing surface structure along the surface normal in a variety of materials [1,2]. Due to the consequences, of both the familiar phase problem and the finite range of angles over which reflectivity is measured, all of the model-free [3,4] and model-dependent methods inherently cannot suggest unique electron density profiles [5,6]. For an unambiguous analysis of surface structures by X-ray (or neutron) reflection, one must determine the full complex reflection coefficient, that is, not only its absolute square, the reflectivity, but also its phase. The phase problem will hopefully find its solution when experimental considerations have led to a practical method for determining the phase [7,8]. The possible ambiguity due to the lack of complete phase information may be helpful in giving rise to a whole family of acceptable "reflectivity-equivalent scattering length density profiles" [6], although some of these profiles may not appear reasonable from a physical point of view. In the model-free methods the profiles are retrieved directly from the measured reflectivity data. Therefore, the model-free methods are helpful for experimentally revealing the physical phenomena of the surface structures, which may be neglected or undiscovered in the theory, and are not just used for adjusting the values of the parameters in the model known beforehand. The model-free fitting techniques which can reveal non-unique profiles are extremely important for suggesting new profiles, specially when only a little prior information is available.

It has been demonstrated, by Zhou and Chen, that when there are 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 [9]. With these considerations in mind, they developed the model-free groove tracking method (GTM), which employs the recursive equations derived by Parratt, for constructing a step-like profile. GTM is applicable to many samples of which the electron density profiles are smooth [9,10,11].

Recently we found that the fitting procedure in the original GTM is flawed and causes a local minimum problem in some cases. A straightforward yet necessary correction was proposed to eliminate this defect of the original GTM [12]. So as to have adequate flexibility, the modified groove tracking method (MGTM) can reveal non-unique profiles that generate a reflectivity fitting the experimental data well. Moreover, we developed a smoothed groove tracking method (SGTM) [13] by imposing the requirement that the electron density profile be smooth and by iterating a smoothing process with the GTM. It has been demonstrated that the SGTM leads to more physically reasonable profiles than the often jagged, discontinuous profiles generated by the original GTM.

In this paper, using the MGTM and the SGTM we make it possible to obtain two reasonable profiles of liquid mercury. One of the new obtained profiles does contain many of the essential features of the theoretical profile previously published [14,15] and provides the only experimental evidence of the existence of the vaporized Hg atom layer in the theoretical profile.

II. MGTM and SGTM

In reflection experiments, the reflectivity is measured as 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. Suppose M data $E(k_{oi})$ (i = 1, 2, 3, ... M) are obtained at distinct values k_{oj} (i = 1, 2, 3, ... M). The surface region, with depth d, of interest is equally divided into N sections, each of which has the same thickness D such that ND = d. The electron density profile within each slice is regarded as a constant equal to the average electron density profile in this slice. The continuous profile $\rho(z)$ is then replaced by the discretized $\rho_N = [\rho_1, \rho_2, \rho_3, \rho_N]$.

The theoretical reflectance of the N uniform slices is given in terms of the profile ρ_N through a recurrence relation [9],

$$r_i = \frac{R_{i+1} + r_{i+1}\exp(2ik_{i+1}D_{i+1})}{1 + R_{i+1}r_{i+1}\exp(2ik_{i+1}D_{i+1})}, \tag{1}$$

where $D_{i+1}(=D)$ is the thickness of layer i+1 for i=N-1, N-2, ... 2, 1, 0,

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

is the wave number in layer i+1,

$$R_{i+1} = \frac{k_i - k_{i+1}}{k_i + k_{i+1}} \tag{3}$$

is the Fresnel reflectance of the interface between the layers i and i+1, and

$$r_N = \frac{k_N - k_\infty}{k_N + k_\infty} \qquad (4)$$

is the Fresnel reflectance of the interface between the N-th layer and the bulk. Obviously, r_o is the reflectance of the entire N-layer assembly, and to calculate reflectivity, denoted by $|r_o(k_o)|^2(k_o = k_{o1}, k_{o2}, k_{o3}, \ldots k_{oM})$, for a given ρ_N using Eq. (1) is straightforward.

Now the task of the data processing is to determine the ρ_N characterizing the samples by using the GTM to make the difference between $|r_o(k_o)|^2$ and $E(k_{oi})$ (in this paper: the x-ray reflectivity data recorded as a function of $q_z = 2k_o$) as small as possible.

In the GTM, the density profile is first approximated by a small number of slices of equal width. The reflectivity for this interface is computed according to Eq. (1), compared to the experimental data with a cost function defined in Ref. [10] or a χ^2 and then the density of each slice is independently varied to minimize the cost function. Successive approximations are made by subdividing each slice and then repeating the process while allowing the subsequent amplitudes for the narrower steps to vary. The procedure is complete as soon as the calculated cost function or χ^2 attains an acceptable value. the MGTM is sensitive to the relation between the thickness D of the divided layers and the q_z range of the data taken into consideration for fitting in each stage of the GTM. In SGTM, each of the MGTM layers is further divided into a number of layers. In practice, subdivision into 8-16 layers has proven practical. Then, the value of the electron density in each of the sub-layers 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. In the next step, this cost function, with the averaged profile, is again minimized by invoking the GTM procedure. Therefore, the value of the cost function becomes considerably smaller again. 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.

III. Data analysis

Fig. 1 shows the two different evolutions of the step-like profiles obtained by the MGTM in successive stages. The surface region, which thickness d being 39.5168 Å, of the liquid mercury is divided into N layers. Hence, the thickness D of the divided layers is 39.5168/N Å for N = **1, 2, 4, 8, 16, 32.** In each stage only the data points distributed within π/D are taken into consideration for fitting. The rigorous mathematical reason why the effectiveness of the original GTM is greatly improved with the MGTM procedure is addressed in reference 12. The mathematical basis of the GTM in each stage is discussed in detail in the work of Zhou and Chen [10,11]. Because the MGTM with the necessary modification is mathematically sound, it has adequate flexibility to retrieve non-unique profiles. At the fourth stage, in which the starting Ap [10] is 1.0 and the number of data points taken into consideration is 31, a new profile (referred to as profile II in the figures), which generates the reflectivity data fitting the experimental data well, is constructed. In Fig. 1 the solid curves (c-e) present the new profiles and the dashed curves superimposed

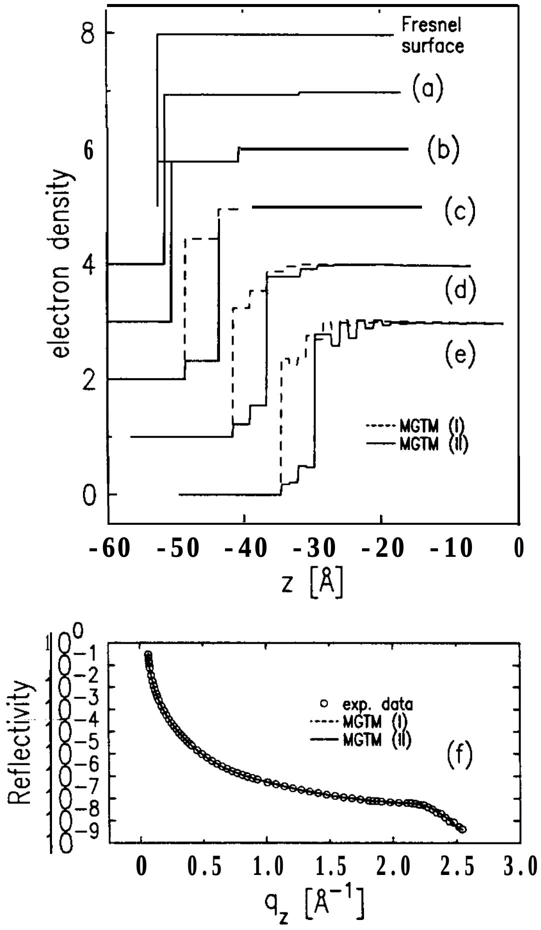

FIG. 1. The two different evolutions of the retrieved profiles in the MGTM while the surface region of liquid mercury is divided into 1 layer (Fresnel surface), 2 layers (a), 4 layers (b), 8 layers (c), 16 layers (d), and 32 layers (e). The curves have been shifted vertically and horizontally for clarity. (f) The fitted reflectivity spectra of the two MGTM profiles shown in (e) agree nicely with the reflectivity data.

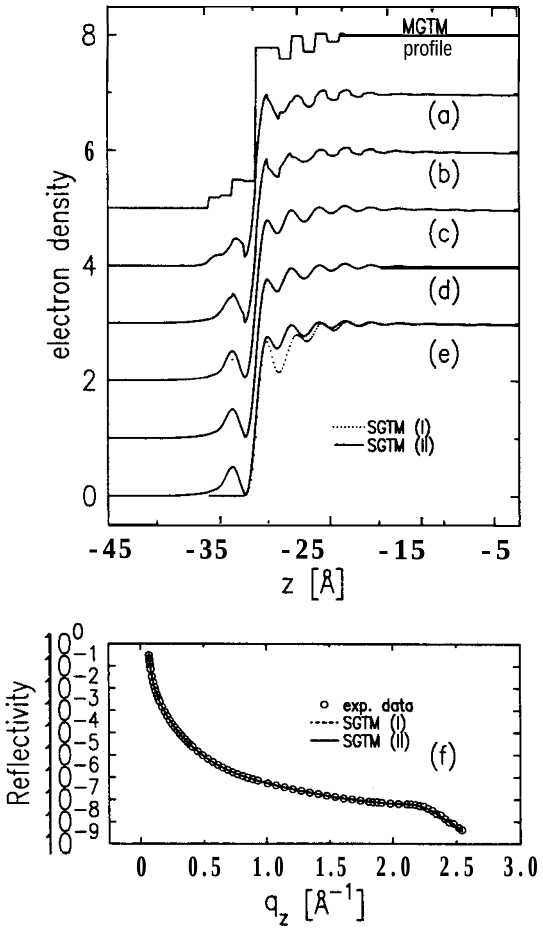

FIG. 2 The SGTM approach to obtain the smooth electron density profile for liquid mercury from the MGTM profile shown as the solid curve in Fig. 1(e). The profiles obtained in different stages in the SGTM (a-e) compared to the SGTM profile obtained previously (dotted curve superimposed over the solid curve shown in (e)). (f) Reflectivity data compared to the computed reflectivity spectra shown as the solid curve and the dashed curve (obscure) from the two smoothed profiles in (e).

over them represent the profiles (profile I) obtained previously from MGTM [13]. Depending on the resolution $\pi/q_{z\max}$ = 1.2349 A, the finest MGTM profiles are obtained and shown in Fig. l(e). It is notable that the computed reflectivity of both profiles fit the experimental data well (see Fig. l(f)).

Then the SGTM [13] is applied to the MGTM profiles. In order to make the smoothing procedures more efficient, the new smoothing methods, based on cubic spline interpolation and Fourier transformation [16], are employed. Fig. 2 illustrates the evolution of the new profiles obtained by the SGTM at various stages. The first profile, obtained by applying the smoothing method based on cubic spline interpolation and by invoking the successive GTM, is depicted in Fig. 2(a). The curves (b-e) present the last four profiles separately. By 12 iterations, a new smooth profile, shown as the solid curve in (e), is obtained. The corresponding reflectivity of this SGTM profile is shown as the solid curve in Fig. 2(f). The tiny variations, which are not readily apparent but really present in the solid curves (c-e), are crucial to finally achieve a good fit. For comparison, the old SGTM profile is plotted as the dotted curve superimposed over the solid curve (e). Despite the vastly different shapes of these two profiles obtained by SGTM, both profiles give excellent, almost indistinguishable fits fo the experimental reflectivity data, shown in Fig. 2(f). Minor deviations of the fitting reflectivity spectra are seen only beyond $q_z \approx$ 2.3 Å^{-1} where the experimental error is large.

IV. Discussion

As demonstrated by the dotted and solid curves shown in Fig. 2(e), the main differences between the SGTM profiles are as follows: The first interlayer spacing of the previous profile is enlarged while the interlayer spacing of the new profile obtained in this paper is almost uniform. Contrary to the previous profile, which does not has a low-density layer, the new profile does have such a layer on top of the first liquid layer. The density of each peak of the new profile is more or less larger than that of the previous profile.

Monte Carlo (MC) simulations of Hg clusters by D'Evelyn and Rice [14] lead to a theoretical profile which exhibits at least six layers with a uniform spacing of about 3.0 Å and a low-density layer of vaporized Hg atom on top of the first liquid layer. This absorbed vapor layer is a particular feature of this theoretical profile of liquid Hg; thus the Hg surface transition zone is not typical of all liquid metals. After being appropriately parameterized, this theoretical profile, shown in Fig. 12 in reference 14, yielded agreement with the earlier experimental data of Bosio and Oumezine [17].

Three models of the electron density profile, based on the model-dependent method, were vecently proposed by Pershan *et al.* [13,18], after the q_z range of the measured reflectivity data reached 2.5 Å^{-1}. Two of the models, being extremely analogous to each other, exhibit significant layering with a spacing of about 3.05 Å between the first and the second layer and about 2.76 Å spacing between all subsequent layers. The first layer of the two models is asymmetric with a broader tail toward the interface. The two models are supposed to resemble the theoretical profile in spite of two conflicting facts [18]: The models exhibit a broader tail toward the interface, instead of the vapor layer adsorbed on the surface of liquid Hg, i.e., the vapor layer predicted by the theory is not portrayed precisely in the model profiles. Moreover, the first interlayer spacing of the models is enlarged but the spacing of the liquid layers in the theoretical profile is uniform. A third model of the liquid Hg surface profile was proposed very recently [13]. This model, being similar to the previous SGTM profile, does not exhibit the asymmetric broader tail toward the interface and also contradics the theoretical profile.

The new SGTM profile differs from all the three profiles obtained from model-dependent methods, but is quite similar to the theoretical model. The new SGTM profile and the theoretical profile share the following properties: These two profiles exhibit similar layers at similar positions. The density of the first liquid layer is smaller than that of the second liquid layer. Of particular interest is that the new SGTM profile does have the vaporized Hg atoms layer absorbed on the surface of liquid Hg. In addition, the gap where the density is almost zero between vaporized layer and the outmost liquid layer indeed exists. With the exception of the spacing between the vapor layer and the outmost liquid layer, the interlayer spacings are uniform. Nevertheless, the differences between the new SGTM profile and the theoretical profile, which may have subtle implications for the details of the proposed theory, also have been observed. The corresponding amplitudes of the oscillations of the SGTM profile are about 1/4 of those of the well ordered layers in the theoretical profile. Each spacing between adjacent layers in the new SGTM profile is slightly smaller than that of the corresponding layers in the theoretical model. These discrepancies may be due to an inaccurate finite size of the Hg cluster and the thermally excited capillary waves used in the simulations.

V. Conclusion

-This phase problem can be solved only with the help of actual measurements of the phase as proposed in [19]. Therefore, the task of analyzing the reflectivity data, which lack sufficient phase information, is to construct the non-unique profiles in order to reveal all the information that the experimental data possess. The recent work of G. Reiss and R. Lipperheide [6] shows that people can induce seemingly arbitrary changes in the profile, which all preserve the fit to the measured reflectivity, and some of these "reflectivity-equivalent profiles" may not appear reasonable from a physical point of view. However, in the SGTM the possible non-unique profiles obtained shall be physically reasonable because of the nature of the fitting strategy in this method. By using the SGTM we have successfully obtained two of the physically reasonable profiles of liquid mercury to date.

The new SGTM profile is consistent with the theoretical profile based on a Monte Carlo simulation [14]. It should be noted that both the non-unique profiles obtained by the SGTM make the reflectivity fitting satisfactory and, to rule out the possibility of other explanations, such as contamination of the liquid Hg sample, requires additional versatility. Our work is apparently the first in which the new profiles obtained from the SGTM provides significant evidence for the existence of the absorbed atom layer on top of the surface of liquid Hg, just as D'Evelyn and Rice predicted.

Acknowledgments

I would like to thank Professor P. S. Pershan and Professor X.-L. Zhou for insightful discussions. This work was supported by the National Science Council of the Republic of China on Taiwan under grant No. NSC 86-2112-M-002-034-T.

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