X-ray reflectivity study of temperature-dependent surface layering in liquid Hg

E. DiMasi*

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000

H. Tostmann

Division of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts 02138

B. M. Ocko

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000

P. S. Pershan

Division of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts 02138

M. Deutsch

Department of Physics, Bar-Ilan University, Ramat-Gan 52100, Israel

(Received 26 August 1998)

We report x-ray reflectivity measurements of liquid mercury between $-36\,°C$ and $+25\,°C$. The surface structure can be described by a layered density profile convolved with a thermal roughness σ_T. The layering has a spacing of 2.72 Å and an exponential decay length of 5.0 Å. Surprisingly, σ_T is found to increase considerably faster with temperature than the $\sqrt{T}$ behavior predicted by capillary wave theory, in contrast with previous measurements on Ga and dielectric liquids. [S0163-1829(98)52144-3]

The effect of temperature on the surface structure of a liquid is quite different from that of a solid surface. In the liquid, thermal surface waves are excited at all wavelengths from the particle spacing to a long wavelength gravitational cutoff, and produce a surface roughness on the order of the particle spacing. For nonmetallic liquids, these capillary waves broaden the liquid-vapor interface, which is a monotonically decreasing density profile with a width of several Å.[1]

Metallic liquids exhibit a more complex surface structure in which the atoms are stratified parallel to the liquid-vapor interface in layers that persist into the bulk for a few atomic diameters. This layering arises from the strongly density-dependent nonlocal interionic potential[2] and is unique to metallic liquids. Nevertheless, the effect of temperature is still expected to be principally in the form of capillary waves, which roughen the surface-normal profile and diminish the layering amplitude. X-ray reflectivity measurements have confirmed the existence of surface layering in liquid Hg,[3] Ga,[4] In,[5] and several alloys.[6,7] Models based on capillary waves as the only mechanism for surface roughening were found to describe the temperature-dependent layering of liquid Ga[8] as well as diffuse scattering measured from the liquid In surface.[5]

In previous comparisons of the x-ray reflectivity of liquid Hg and Ga,[9] two important differences were identified. Although reflectivities for both metals exhibit quasi-Bragg peaks indicative of surface layering, the Hg data have a minimum at low-momentum transfer ($q_z \approx 0.6\ \text{Å}^{-1}$) not found in Ga (see Fig. 2 in Ref. 9). To describe this minimum, the model for the surface structure had to be more complex than that of Ga. One successful model incorporated a low density region persisting a few Å into the vapor side of the interface.

This feature was taken to be intrinsic to Hg. In addition, the room-temperature layering peak appeared to be broader for Hg than for Ga, leading to the conclusion that in Hg, surface layering decayed over a much shorter length scale.

Subsequent measurements yielded variations in this low-q_z minimum, prompting us to address the possible effect of impurities at the surface. An important difference between experiments on Hg and Ga is that due to the low vapor pressure, Ga can be measured under ultra-high-vacuum (UHV) conditions and cleaned *in situ* by argon sputtering, which is not possible for Hg. In this work, we compare Hg measured in a reducing H_2 atmosphere[10] to measurements taken in a UHV compatible chamber having a very low oxygen partial pressure.

The present temperature-dependent study has an important advantage over previous room-temperature measurements. Near the melting point, the layering peak has a large amplitude and is easily distinguished from the region of the low-q_z minimum. This allows a robust determination of the layering decay length that is not affected by the details of the models in the near-surface region. This is not the case at room temperature, where the shallow peak and pronounced minimum yield more ambiguous fits. We conclude in the present work that Ga and Hg have comparable layering decay lengths. This underscores the value of temperature-dependent measurements for comparisons of liquid metals' surface structure.

X-ray reflectivity measurements[1] were carried out using the liquid surface spectrometer at beamline X22B at the National Synchrotron Light Source, at an x-ray wavelength of 1.24 Å and resolution of 0.035 Å^{-1}.[11] The background intensity, due mainly to scattering from the bulk liquid, was subtracted from the specular signal by rocking the detector out of the reflection plane.

Liquid mercury was prepared in two different sample chambers. In the first, the Hg sample[12] was contained in a glass reservoir with a Teflon stopcock and glass filling capillary, mounted on a high vacuum chamber comprised of a cylindrical thin-walled Be can mating to stainless steel flanges with viton o-ring seals. After several cycles of evacuating the chamber to 10^{-4} Torr and backfilling with 900 Torr of dry H_2 gas, the liquid Hg was poured from the reservoir into a ceramic sample pan. Surfaces appeared clean to the eye and yielded reproducible reflectivity measurements for as long as 4 days. When the sample was deliberately exposed to air, the reflectivity exhibited deep oscillations characteristic of rapid oxide formation.[13]

A second Hg reservoir, capillary and valve made from stainless steel was mounted on top of a UHV chamber. Following a bakeout, the sample was poured, with the Hg vapor pressure of about 10^{-2} Torr then determining the total pressure in the chamber. Small patches of oxide were initially observed, but disappeared from the surface within a few hours. Hg oxide is expected to decompose due to the low oxygen partial pressure in this pseudo-UHV environment.[14] In addition, we observe a continuous evaporation and recondensation of Hg, constantly renewing the Hg surface.[15] The resulting Hg surface was stable, as determined by x-ray reflectivity, for 11 days.

In both chambers, a copper cold finger extended from the bottom of the sample pan into a liquid nitrogen dewar. Temperature was monitored near the sample pan, and calibrated in separate experiments with a sensor immersed in the Hg. Corrected sample temperatures are reported with relative errors of ± 1 °C. For the UHV chamber, the gradient between sample and thermometer was greater, and there is an additional systematic error that may be as large as 8 °C. Both chambers rested on an active vibration isolation unit.

Our x-ray reflectivity measurements reveal that the surface induced layering is strongly temperature dependent. Figure 1(a) shows the reflectivity as a function of q_z measured in the glass chamber for three temperatures between -35 °C and room temperature. The quasi-Bragg peak observed at $q_z \approx 2.2$ Å^{-1} indicates that the liquid metal is stratified near the surface. The peak position, amplitude, and width give the length scales for the surface induced layering, which extends several Å into the bulk liquid. The other main feature of the data is the minimum in the reflectivity at $q_z \approx 0.6–1.2$ Å^{-1}, the depth of which differs between samples. This minimum is much more pronounced under the high-pressure H_2 environment (900 Torr) than under the Hg vapor pressure of 10^{-2} Torr, as shown for two sets of room-temperature measurements in Fig. 1(b). These low-q_z data indicate that the details of the electron density within 5 Å of the surface are affected by the sample environment.

We have quantified the surface layering by constructing a model for the surface-normal density profile, parametrized as reported previously,[3,4,8] and fitting the reflectivity calculated from the model to the experimental data. The surface-normal density profile is constructed from slabs of electron density parallel to the liquid-vapor interface. The slabs represent planes of atoms separated by a distance d, which are disordered in plane, and which have mean-squared surface-normal displacements increasing with depth. The electron density profile is composed of a sum of Gaussian terms:
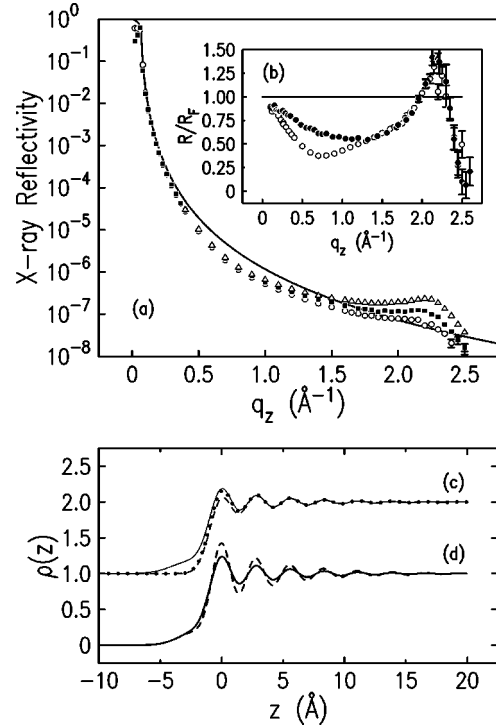

FIG. 1. (a) X-ray reflectivity of liquid Hg. $\triangle$: -35°C; $\blacksquare$: 0 °C; $\bigcirc$: $+23$ °C; (—): calculated Fresnel reflectivity R_F. (b) Room-temperature reflectivity normalized by R_F (—) for two Hg samples. $\bigcirc$: glass chamber with H_2 gas. $\bullet$: UHV chamber. (c) Calculated local layering profiles having $d=2.72$ Å, $\bar{\sigma}=0.46$ Å, and $\sigma_T=1.0$ Å. ($\cdots$): no surface modification. (—): adlayer model. (- - -): surface depletion model. (d) Best-fit profiles for vacuum data. (—): Room temperature ($\sigma_T=1.0$ Å). (- - -): $T=-36$ °C ($\sigma_T=0.8$ Å).

$$\rho(z)=\rho_\infty \sum_{n=0}^{\infty} \frac{d/\sigma_n}{\sqrt{2\pi}} \exp[-(z-d)^2/2\sigma_n^2],$$

where ρ_∞ is the electron density of bulk Hg, and we represent the mean-squared displacements in the nth layer by $\sigma_n^2 = n\bar{\sigma}^2 + \sigma_T^2$, where σ_T characterizes the roughness of the layer nearest the surface. Far into the bulk, $n\bar{\sigma}^2$ becomes large, and no layering is present, so that $\bar{\sigma}$ quantifies a layering decay length. With this form for $\rho(z)$, the reflectivity, proportional to the Fresnel reflectivity R_F of an abruptly terminated homogeneous electron density, can be calculated analytically and yields

$$\frac{R(q_z)}{R_F} = \left| \frac{1}{\rho_\infty} \int_{-\infty}^{+\infty} (\partial\rho/\partial z)\exp(iq_z z)\,dz \right|^2$$

$$= F^2 (q_z d)^2 \exp(-\sigma_T^2 q_z^2)[1-2\exp(-q_z^2\bar{\sigma}^2/2)$$

$$\times \cos(q_z d) + \exp(-q_z^2\bar{\sigma}^2)]^{-1},$$

where the reduced scattering form factor $F=(f(q_z)+f')/(Z+f')$ has been inserted, as presented previously.[16]

The parameters σ_T, $\bar{\sigma}$, and d control the height, width, and position of the layering peak, and characterize a simple local layering profile [Fig. 1(c), dotted line]. Although this model is sufficient for liquid Ga (Refs. 4 and 8) and In,[5] it does not yield a good fit to the the low-q_z reflectivity of liquid Hg. To account for the low-q_z reflectivity we have

consideredprofiles that incorporate density terms in addition to the layered model, modifying the first Hg layer, the first several layers, and/or the region several Å towards the vapor side of the interface. These additional features are independent of temperature. The modification having the best fit for all data is a single additive Gaussian term $f_A \rho_\infty (d/\sigma_A \sqrt{2\pi}) \exp[-(z-z_A)/2\sigma_A^2]$, positioned a few Å into the vapor region, with a width $\sigma_A \approx 1.5$ Å and a density f_A relative to the bulk varying from 0.1–0.3 between samples [Fig. 1(c), solid line]. However, this model is difficult to distinguish mathematically from one in which the density of the first Hg layer is decreased. In particular, the data with the most exaggerated low-q_z minima can be fit by models with a broadened, depleted first Hg layer and an expanded spacing between the first two layers [Fig. 1(c), dashed line]. Models having alternating long and short layer spacings, as might result from atomic pairing, do yield destructive interference at low q_z but do not fit the data well.

Deviations from the simple oscillatory profile are smaller for samples poured in a UHV chamber at 10^{-7} Torr following a bakeout than for measurements in a glass chamber evacuated to only 10^{-4} Torr. To explain this difference, we attribute the modified density profile to the presence of impurities. In recent self-consistent quantum Monte Carlo simulations of the Hg-vapor interface, no vapor-side tail or appreciable modification of the surface layer was observed in the computed density profile.[17] As discussed above, we believe the presence of macroscopic oxide is unlikely, although oxygen, water, or other contaminants introduced with the Hg sample may be present in small amounts. These may form a passivated, low-density adlayer or incorporate themselves into the first Hg layer to alter its density.

Although the available x-ray data do not allow a unique determination of the near-surface region, we obtain reliable information on the temperature dependence of the surface-normal density profile. All Hg data are described by local layering parameters $d = 2.72 \pm 0.02$ Å and $\bar\sigma = 0.46 \pm 0.05$ Å. These values are obtained for both H_2 and vacuum measurements, and are independent of the model surface modification. The temperature dependence of the reflectivity can be quantified solely by the variation of σ_T, as shown in Fig. 2(a) for measurements in H_2 atmosphere. This parameter controls the amplitude of the layering peak and is directly related to the amplitude of the density oscillations at the surface, as shown in Fig. 1(d) for vacuum measurements, varying from 0.8 Å near the melting point to about 1.0 Å at room temperature. The other parameters, if allowed to vary for each temperature independently, show no systematic dependence on T.

In particular, this means that the layering decay length of 5.0 ± 0.5 Å for Hg is independent of temperature, as was previously shown for Ga.[8] This is somewhat surprising, since it is not obvious that layering should persist over essentially the same length scale in the face of thermal roughening that effectively broadens the interfacial width. Such a model, in which the local surface-normal density profile is independent of the surface height fluctuations, is intrinsic to the analyses long used for calculating the scattering cross section from rough surfaces.[18,19] Previous observations on liquid metals demonstrated that such an interpretation appears to be justified.[5,8] In fact, it has been thought that the liquid metal
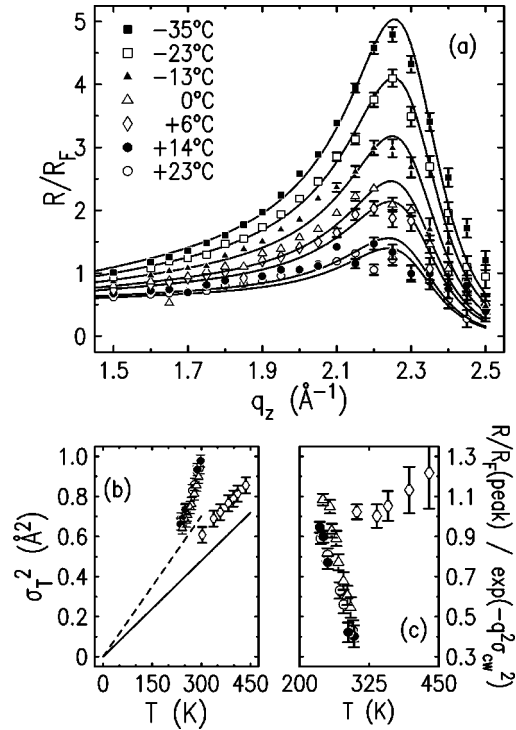

FIG. 2. (a) R/R_F for different temperatures, from sample measured in H_2 atmosphere. Solid lines are fit curves for which σ_T has been varied. (b) Temperature dependence of σ_T^2. △: Measurement in vacuum. ○: Measurement in H_2 gas. ●: Second sample measured in H_2 gas. ◇: Ga data from Ref. 8. Lines: Capillary wave form $\sigma_{cw}^2(T)$ for Hg (- - -) and Ga (—). (c) Temperature dependence of $(R/R_F)/\exp(-q^2\sigma_{cw}^2)$ at the layering peak, normalized at the melting point, for Ga (◇) and Hg [symbols as in (b)].

surface may provide the best justification of this approach, since the measured reflectivity peak is a dramatic structural feature that is both straightforward to characterize and strongly affected by surface height fluctuations that vary considerably with temperature.

In the capillary wave model, thermally excited surface waves produce mean-squared displacements for which the restoring force is due to the surface tension γ:

$$\sigma_{cw}^2(T) = \frac{k_B T}{2\pi\gamma} \ln\left(\frac{k_{max}}{k_{min}}\right),$$

where $k_{max} = 1.2$ Å^{-1} and $k_{min} = 7.4 \times 10^{-3}$ Å^{-1} are wave-vector cutoffs determined by the atomic size and the instrumental resolution, respectively.[1] This model has been successfully applied to dielectric liquids[1,20] and to liquid Ga.[8] Figure 2(b) compares σ_{cw}^2 calculated as a function of temperature for Hg and Ga (dashed and solid lines), for appropriate values of the surface tension,[21] bulk inter-atomic spacing,[21] and instrumental resolution, to the surface roughness σ_T^2 extracted from reflectivity measurements of Hg and Ga (symbols). The temperature dependence of σ_T differs fundamentally between Hg and Ga. For Ga, the slope of the experimental points matches that of the capillary wave model, offset only by a constant term $\sigma_0 \approx 0.3$ Å, attributed to an intrinsic roughness.[8] This allows the quantity σ_T for Ga (denoted in Ref. 8 by σ_c) to be written as $\sigma_T^2 = \sigma_0^2 + \sigma_{cw}^2$.

Liquid Ga, therefore, has a temperature-independent local surface layering profile, roughened by capillary waves.

By contrast, $\sigma_T^2(T)$ for Hg has a much steeper slope than predicted by capillary wave theory, exhibiting an additional temperature-dependent roughness. This result is independent of the local layering model, as shown in Fig. 2(c), where we plot $(R/R_F)/\exp(-q^2\sigma_{cw}^2)$ for Hg and Ga at their layering peaks vs T, normalized at the melting point. The Ga data increase only slightly with T, within their scatter of about 15%. The Hg data exhibit a steep slope far exceeding the $\approx 15\%$ scatter. The temperature dependence of the Hg-vapor interface roughness has also been extracted from recent self-consistent quantum Monte Carlo simulations.[17] While similar linear behavior of $\sigma_T^2(T)$ is observed, direct comparison of the slope is complicated by the differences in capillary wave cutoffs and surface tension between the experimental and simulation samples.

The temperature dependence of γ, even considering the possible effects of impurities, can be ruled out as a cause. For pure Hg, $d\gamma/dT \approx -0.2\times10^{-3}$ N/mK,[21] an order of magnitude too small to explain our observations. Optical measurements on Hg surfaces with varying degrees of cleanliness have found $d\gamma/dT$ in the range of -0.7×10^{-3} to $+0.3\times10^{-3}$ N/mK depending on the method of sample preparation.[22] The observation that oxide or contamination can produce $d\gamma/dT > 0$ for Hg is notable, but this would cause a reduction of σ_T with increasing T rather than the increase observed, and so cannot account for our results.

We conclude that the surface structure of liquid Hg has a temperature-dependent component in addition to capillary wave roughening. This may take the form of temperature-dependent height fluctuations that increase the mean-squared atomic displacements beyond the effect of capillary waves, or of a temperature-dependent local density profile. The specular reflectivity measurements presented here cannot distinguish between these two cases. Measurements of diffuse scattering from the Hg surface may provide further information. These results reemphasize the fact that roughness intrinsic to the surface-normal density profile in general cannot be unambiguously separated from height fluctuations, despite previous treatments of scattering from the liquid surface.

---

*Author to whom correspondence should be addressed. Electronic address: dimasi@bnl.gov

[1] A. Braslau, P. S. Pershan, G. Swislow, B. M. Ocko, and J. Als-Nielsen, Phys. Rev. A **38**, 2457 (1988).

[2] S. A. Rice, J. Non-Cryst. Solids **205–207**, 755 (1996).

[3] O. M. Magnussen, B. M. Ocko, M. J. Regan, K. Penanen, P. S. Pershan, and M. Deutsch, Phys. Rev. Lett. **74**, 4444 (1995).

[4] M. J. Regan, E. H. Kawamoto, S. Lee, P. S. Pershan, N. Maskii, M. Deutsch, O. M. Magnussen, B. M. Ocko, and L. E. Berman, Phys. Rev. Lett. **75**, 2498 (1995).

[5] H. Tostmann, E. DiMasi, P. S. Pershan, B. M. Ocko, O. G. Shpyrko, and M. Deutsch (to be published).

[6] H. Tostmann, E. DiMasi, O. G. Shpyrko, P. S. Pershan, B. M. Ocko, and M. Deutsch, Ber. Bunsenges. Phys. Chem. **102**, 1136 (1998).

[7] N. Lei, Z. Huang and S. A. Rice, J. Chem. Phys. **104**, 4802 (1996); **l07**, 4051 (1997); M. J. Regan, P. S. Pershan, O. M. Magnussen, B. M. Ocko, M. Deutsch, and L. E. Berman, Phys. Rev. B **55**, 15 874 (1997).

[8] M. J. Regan, P. S. Pershan, O. M. Magnussen, B. M. Ocko, M. Deutsch, and L. E. Berman, Phys. Rev. B **54**, 9730 (1996).

[9] M. J. Regan, O. M. Magnussen, E. H. Kawamoto, P. S. Pershan, B. M. Ocko, N. Maskil, M. Deutsch, S. Lee, K. Penanen, and L. E. Berman, J. Non-Cryst. Solids **205–207**, 762 (1996).

[10] D. Turnbull (private communication). More recently it has been recognized that passivation of Hg oxide occurs only at elevated temperatures: V. Kolevzon (private communication).

[11] The reflectivity measured for $q_z \gtrsim 1.2$ Å^{-1} varies by a few percent depending on the choice of vertical detector resolution, due to diffuse scattering near the specular condition that arises from surface fluctuations. We have not incorporated this small effect into our analysis of the reflectivity. A detailed discussion is given in Ref. 5.

[12] Quadruple distilled Hg with <1 ppm metal impurities, Bethlehem Apparatus Co., Inc., Front and Depot Streets, Hellertown, PA 18055.

[13] H. Tostmann, E. DiMasi, B. M. Ocko, M. Deutsch, and P. S. Pershan, J. Non-Cryst. Solids (to be published).

[14] B. N. Thomas, S. W. Barton, F. Novak, and S. A. Rice, J. Chem. Phys. **86**, 1036 (1987).

[15] B. C. Lu and S. A. Rice, J. Chem. Phys. **68**, 5558 (1978).

[16] In this paper, we consistently use $n=0$ to refer to the surface layer. This produces discrepancies with the equations given in Ref. 3.

[17] D. S. Chekmarev, M. Zhao, and S. A. Rice, Phys. Rev. E (to be published).

[18] S. K. Sinha, E. B. Sirota, S. Garoff, and H. B. Stanley, Phys. Rev. B **38**, 2297 (1988).

[19] M. K. Sanyal, S. K. Sinha, K. G. Huang, and B. M. Ocko, Phys. Rev. Lett. **66**, 628 (1991).

[20] M. Fukuto, R. K. Heilmann, P. S. Pershan, J. A. Griffiths, S. M. Yu, and D. A. Tirrell (unpublished).

[21] T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Oxford University Press, Oxford, 1993).

[22] V. Kolevzon and G. Pozdniakov, J. Phys.: Condens. Matter **9**, 6815 (1997), and references therein.