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Journal of Non-Crystalline Solids 205–207 (1996) 762–766

JOURNAL OF
NON-CRYSTALLINE SOLIDS

X-ray studies of atomic layering at liquid metal surfaces

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Abstract

Surface-induced layering has been observed in liquid gallium and mercury using X-ray reflectivity. The specular reflectivity $R(q_z)$ has been measured to wavevector transfers as large as $q_z = 3.0$ Å^{-1}. For Ga, the only major deviations from Fresnel theory R_f are near $q_z = 2.4$ Å^{-1}, where there is a peak in the ratio R/R_f. For Hg, there is a broad peak near 2.15 Å^{-1}. The data have been collected on a sputtered clean, ultra-high vacuum Ga surface and on a Hg surface in a reducing atmosphere of hydrogen. The data can be explained with a layered liquid/vapor interface that is roughened by thermally excited capillary waves. The layer spacing is similar to the Ga or Hg atomic dimensions, extending into the bulk with an exponential decay length of 6 Å for Ga and 3 Å for Hg.

1. Introduction

Liquid metals differ from most simple, non-metallic liquids since they have to be described in terms of two charged interacting liquids, the classical ionic liquid and a quantum conduction liquid [1,2]. Numerous theoretical, both analytic [3–5] and molecular simulation [3] [6,7], studies have investigated liquid metal surfaces. Although the bulk structure for metallic and non-metallic liquids are similar, the surface structures are expected to be quite different. In liquid metals the delocalization of the near surface conduction electrons coupled with the dominating Coulombic interactions suppresses positional fluctuations of the near surface ion cores. As a result, it is predicted that the top several layers of atoms parallel to the surface will be ordered, resulting in a damped oscillatory electron density profile, in contrast to the monotonic profile of non-metallic liquid surfaces. Although this prediction is now over two decades old, it was hitherto not rigorously tested experimentally in spite of substantial efforts by a number of groups [8–10].

We have recently used X-ray reflectivity to unambiguously demonstrate surface-induced layering in liquid gallium [11] and mercury [12] with atomic-scale resolution. X-ray specular reflectivity is a technique which probes the average structure along the surface normal [13] and direct observation of atomic

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PII S0022-3093(96)00303-1

layering requires that reflectivity measurements extend to a wavevector transfer $q_z = 2\pi/d \approx 2.5$ Å^{-1}, where d is of the order of the atomic diameter. The reflectivity at these large q_z is weak and mandates the use of a synchrotron source. Previous measurements did not extend past $q_z = 0.75$ A^{-1}, and thus could not show unambiguous proof for layering [8–10].

Since it is not clear to what extent variations in bulk properties manifest themselves at the free surface, we have studied two liquid metals, gallium and mercury, which are the most convenient since both are liquid at relatively low temperatures. Gallium exhibits several unique qualities which distinguish it from Hg and most other liquid metals. When compared to Hg, Ga has a smaller atomic diameter, much higher surface tension, an extremely small vapor pressure, an exceptionally large liquid range (~ 2000°C), a smaller supercooling range (~ 30°C), and short distance bond orientational correlations [14,15].

Despite these differences, for both Ga and Hg we observe peaks in the reflectivity which indicate atomic layering with a layer spacing similar to their atomic diameters. There are important differences in the layering, however. First, the peak widths indicate that the exponential decay of layer penetration into the bulk for Ga (6 Å) is almost a factor of two greater than that for Hg (3 Å). Second, there are qualitative differences in the small angle X-ray reflectivities that imply differences in the near surface structure. We will begin by reviewing the experimental methods, and then results on bare Ga and Hg surfaces will be presented, with a discussion of ongoing and future experiments.

2. Experimental

X-ray reflectivity experiments were carried out at the National Synchrotron Light Source beam lines X25 with a new liquid surface reflectometer and X22B with the Harvard/Brookhaven liquid reflectometer. For these reflectometers the liquid sample is horizontal and the incident beam is deflected downward using Bragg reflection optics. The reflectivity data were collected on a shallow liquid Ga film (melting point at 29.8°C) supported by a Mo substrate. The thin layer (~ 0.2 mm thick) is necessary for suppression, by viscous drag at the Ga–Mo interface, of mechanically excited surface waves. Samples were prepared at Harvard and frozen in a nitrogen environment, and then transported to the NSLS, melted and placed into a customized UHV chamber where X-ray measurements were made at O_2 partial pressures less than 10^{-11} Torr. Surface oxides that form during transport, when the samples are exposed to air, are removed by sputtering with 2-keV Ar ions. Although contact angles as small as ~ 10° (as judged by eye) were possible, the large surface tension for Ga leads to a curved surface, with the measured radius of curvature at the top of the drop on the order of 300 mm. A detailed analysis of X-ray reflectometry from curved surfaces will be published elsewhere [16].

The measurements on Hg are somewhat simplified due to its relatively small reduction potential. In this case, UHV techniques are not required, and the surface can be kept oxide free by enclosing it in a reducing atmosphere of H_2 gas. The Hg was placed in a trough enclosed in a H_2-filled glass chamber. In this trough, the surface curvature is negligible, and the mechanical vibrations were suppressed by mounting the lightweight chamber on an active vibration isolation table.

Since reflectivity to large wavevectors ($q_z \sim 2.5$ Å^{-1}) must be measured to observe atomic layering, an appreciable background develops that is dominated by diffuse scattering from the bulk pair correlations described by the liquid structure factor $S(q)$. In view of the fact that $S(q)$ peaks at approximately the same wavevector magnitude as the specular reflection, subtraction procedures are employed to isolate the specular reflection [11,12]. Since $S(q)$ is isotropic while the reflection signal is confined to the line $\boldsymbol{q} = (0,\ 0,\ q_z)$ (sample normal along z), the obvious method to distinguish the specular reflection from $S(q)$ is to move the detector off the specular condition by several resolution widths, either in the plane of reflection or normal to it. In either case, the isotropic bulk scattering is essentially unchanged, whereas the reflection strongly depends on the orientation of $\boldsymbol{q}$.

3. Reflectivity results

Fig. 1 shows the absolute reflectivity $R(q_z)$ of liquid gallium [11] contained under UHV conditions

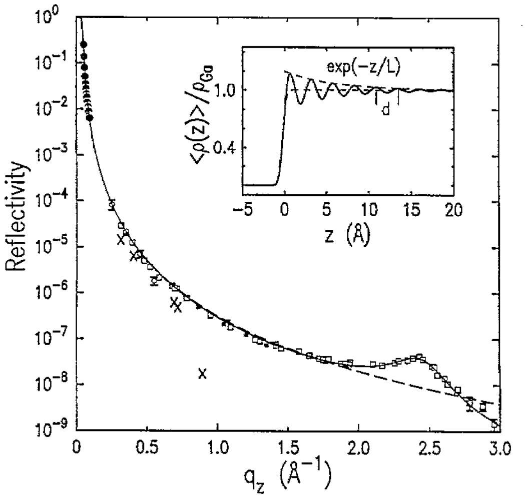

Fig. 1. (a) Measured X-ray reflectivity for liquid Ga. Data marked with an × were collected prior to the sample cleaning procedure; ■ collected during the sputter cleaning procedure; □ from the clean surface after the sputter cleaning was completed; ● using the low q_z method described in Ref. [8]; ○ are data from Ref. [8]. The Fresnel reflectivity is denoted by a dashed line, and the solid line is the best-fit to the exponentially decaying sine-wave model. The corresponding electron density profile is shown as the inset.

at room temperature. The dashed line is the theoretical reflectivity $R_f(q_z)$ for a perfectly flat surface, calculated from the Fresnel law of optics. The reflectivity data obtained on the clean Ga show no appreciable deviation from Fresnel theory except for $q_z > 2.0$ Å^{-1}, where a well defined maximum is evident near $q_z \sim 2.4$ Å^{-1}. This is a clear indication of atomic layering at the surface. The importance of in-situ surface cleaning is demonstrated by comparison of the data collected on oxidized Ga surfaces and then on sputtered clean surfaces as shown in Fig. 1. The marked difference in reflectivity from a dirty surface, which is much less than $R_f(q_z)$ and was not measurable for $q_z > 1$ Å^{-1}, and then from a clean one, highlights the importance of maintaining a UHV-clean, oxide-free surface for Ga.

When scaled by the Fresnel theory (Fig. 2), the data are of a rather simple form. The ratio $R(q_z)/R_f(q_z)$ can be generally described by as few as four parameters in real-space that are equivalent to the amplitude, decay length, and spacing of the electron density oscillations into the bulk liquid, and the interfacial roughness. One of the simplest layering profiles that can be constructed is based on an error-function interface (width σ and offset by z_0) modulated by an exponentially decaying sine wave:

$$\frac{\langle \rho(z)\rangle}{\rho_\infty} = \mathrm{erf}\left(\frac{z-z_0}{\sigma}\right) + \theta(z)\, A \sin\left(\frac{2\pi z}{d}\right) e^{-z/L}; \qquad (1)$$

$\theta(z)$ is the step function, d is the interlayer spacing, L is the exponential decay length, and A is the amplitude. A fit to this model is shown in Fig. 1 (solid line), with $d = 2.56 \pm 0.01$ Å, $L = 5.8 \pm 0.4$ Å, $A = 0.20 \pm 0.02$, $\sigma = 0.50 \pm 0.04$ Å and $z_0 = -0.24 \pm 0.06$ Å. The electron density profile $\langle \rho(z)\rangle/\rho_\infty$ is shown as the inset to Fig. 1. Profiles computed within the errors of the parameters would be indistinguishable in the figure.

For Hg, the results are quite different and indicate fundamental differences in the surface structure (Fig. 2). The Hg reflectivity [12] falls from close to unity below the critical angle to 10^{-9} at $q_z \approx 2.8$ Å^{-1}, yet it remains within a factor of two of $R_f(q_z)$ for

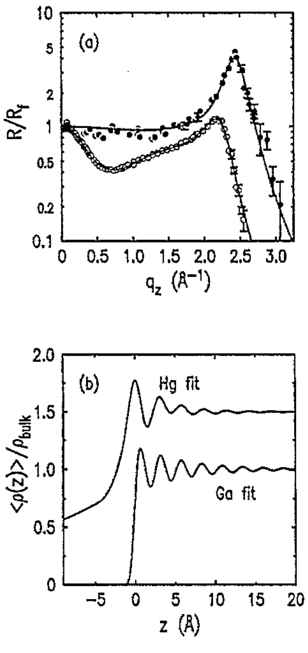

Fig. 2. (a) The normalized reflectivity $R(q_z)/R_f(q_z)$ for Ga (●) and for Hg (○) at room temperature. (b) Corresponding best-fit electron density profiles for Ga and Hg (vertically offset for clarity).

$q_z < 2.3$ Å^{-1}. The interesting deviation from Fresnel theory at small q_z is an important, reproducible observation that is not seen for Ga and will be discussed in more detail later. The position of the broad peak at $q_z = 2.15$ Å^{-1}, smaller than the 2.4 Å^{-1} recorded for Ga, is expected for atomic layering since the Hg atomic radius is greater than for Ga. The peak in $R(q_z)/R_f(q_z)$ is broader for Hg than in Ga and indicates that the surface layering decay length is significantly larger in Ga. The Hg fit, to one of the various density profile models to be discussed below, confirms this expectation, leading to an exponential decay length of only 3–3.5 Å^{-1}.

It is important to note that although the liquid phase of Hg is stable at room temperature. Ga is only liquid at this temperature as a metastable supercooled phase. Although there is no theoretical prediction that the surface order of the supercooled phase should be different from that of the stable phase, we have recently carried out measurements of the Ga surface between 24 and ~ 100°C (Fig. 3) [16]. The Ga was heated radiatively using a lamp through an accessible viewport of the UHV chamber. The height of the peak at $q_z \approx 2.4$ Å^{-1}, which is $R(q_z)/R_f(q_z) \approx 4$ at room temperature, decreases to ≈ 1.2 with no appreciable variation in the width of the peak. This indicates that for these changes in temperature the layering decay length is unchanged, but the amplitude of the density variation is clearly reduced with increasing temperature, presumably through increased surface roughness. Quantitative measurements using an internal heater with improved temperature sensing are currently underway.

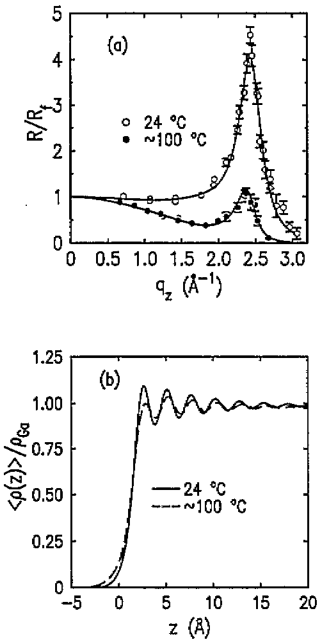

Fig. 3. (a) The normalized measured reflectivity $R(q_z)/R_f(q_z)$ for gallium above and below the melting point (29.8°C), and the fits to the model discussed in the text (solid lines). (b) Corresponding best-fit electron density profiles.

4. Discussion

The simple model of an exponentially decaying sine wave is sufficient to explain the basic features of the atomic layering, but a more sophisticated model is required for Hg to explain the small q_z behavior. One such model of the liquid vapor interface is a truncated solid in which the root-mean-square (rms) deviations of atoms in each layer is described by a Gaussian whose width increases with increasing distance from the interface [12]. The fits to this model are illustrated in Fig. 2 along with the corresponding density profiles. These fits clearly show that the exponential decay length for Hg is twice as small as for Ga and that the top-most layer rms deviations are less than 1 Å, in agreement with those expected from the thermally excited capillary wave model [17,18]. The Ga and Hg interlayer spacings are slightly less than their near neighbor spacing in the bulk liquid, which is expected from the stacking of neighboring layers.

The origin of the dip at $q_z = 0.6$ Å^{-1} for Hg can be explained in terms of an expanded spacing of the top-most layer, which extends several tenths of an Angstrom into the vapor, and a slightly asymmetric top-most layer density. Similar lattice expansions have been observed at reconstructed solid metal surfaces [19,20]. These deviations are not present on the Ga surface, which in fact is quite sharp at the surface. This effect may be related to the much higher vapor pressure of Hg.

To assess the influence of adsorption on the layering, we have recently studied self-assembled monolayer films of thiol molecules (a sulfur terminated alkane chain) on the liquid Hg surface [21]. Clear modulations are observed in the reflectivity curve, indicating a dense monolayer, the thickness of which is commensurate with the fully extended, vertically oriented thiol molecule. Remarkably, essential features of the reflectivity, including the peak at large q_z and the dip at small q_z are identical with and without the thiol monolayer. This clearly indicates that the surface layering is an intrinsic feature of the Hg surface. Further measurements are in progress to elucidate the detailed structure of the thiol monolayer, and its dependence on molecular-length and temperature.

5. Conclusions

Atomic layering has been observed at the free surface of liquid Ga and Hg using X-ray reflectivity. The interlayer spacings are similar to the respective atomic radii, and the widths are consistent with capillary wave theory. An important distinction between Ga and Hg liquid surfaces is the exponential decay length, which is two times greater in Ga (6 Å) than Hg (3 Å). The low q_z data indicate a rather sharp, abrupt surface for Ga, while for Hg they suggest unique surface structure at the topmost layer. These results provide strong confirmation for the principle theoretical predictions in liquid metals and raise important new scientific issues as well. Ongoing and future experiments are planned to study the temperature dependence of the atomic layering and any modification of the layering with the addition of self-assembled monolayers.

Acknowledgements

This work has been supported by grants from the US Department of Energy, DE-FG02-88-ER45379 and the National Science Foundation, DMR-94-00396 and DMR-91-13782. Brookhaven National Laboratory is supported by DOE Contract No. DE-AC02-76CH00016. Support from the US–Israel Binational Science Foundation, Jerusalem, is gratefully acknowledged.

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