

## Capillary-wave roughening of surface-induced layering in liquid gallium

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The temperature dependence of surface-induced atomic layering in liquid gallium has been investigated with x-ray reflectivity. The prominent layering peak at  $q_z = 2.4 \text{ \AA}^{-1}$  decreases dramatically upon heating from 22 to 170 °C, but its width stays, unexpectedly, unchanged. The decrease is traced to the temperature dependence of capillary-wave induced surface roughness. The constant width indicates a temperature-independent layering decay length. The measured layering amplitudes are found to be significantly underestimated by existing theory and molecular simulations. [S0163-1829(96)02337-5]

The complex two-fluid nature and strong Coulombic interactions in liquid metals were long predicted by theory<sup>1-3</sup> and simulation<sup>4-7</sup> to give rise to an atomic layering at the free surface. This important central prediction was verified very recently by our x-ray reflectivity measurements on liquid mercury<sup>8</sup> and gallium.<sup>9</sup> For Hg, a layering decay length of  $\sim 3\text{--}3.5 \text{ \AA}$  was found to coincide with the bulk atomic correlation length, indicating a possible common origin for both effects. In Ga, however, the layering decay length was found, surprisingly, to be twice the bulk correlation length, indicating possible additional ordering mechanisms. A general prediction of statistical mechanics is that quasi-two-dimensional surfaces should exhibit less tendency to order than the corresponding three-dimensional bulk. Hence examples of surfaces with a large degree of excess surface order are rarely observed.

The most prominent example of surface-induced ordering are liquid crystals, where smectic surface layers, often extending hundreds of angstroms into the bulk, coexist with either a nematic or an isotropic bulk.<sup>10,11</sup> Here the layering decay length increases as the transition to the bulk smectic phase is approached, and in some cases it diverges. The unique layering and mesophases are generally attributed to the anisotropy of the liquid crystal molecules, the lengths of which are typically many times their molecular diameters. In gallium, the molecules are isotropic and the statistical physics of the surface, and its manifestation in the temperature dependence of the layering, are therefore likely to be fundamentally different. Our previous Ga surface layering measurements were only done at room temperature, where the sample is supercooled by about 8 °C. Temperature dependence measurements of the surface profile in liquid gallium are therefore highly desirable to determine the behavior of the layering decay length and the possible influence of supercooling on the layering.

Such measurements should also provide new insight into the capillary-wave theory of liquid interfaces. According to this theory, the interface between a liquid and its vapor is roughened by thermal capillary waves and this gives rise to a characteristic interfacial width of the density profile. For simple liquids<sup>12-15</sup> and liquid alkanes,<sup>16</sup> the dependence of the measured width on temperature and spectrometer resolution and the angular distribution of the capillary-wave induced diffuse scattering were shown experimentally to agree well with those predicted by this theory. While our room temperature measurements for Hg and Ga lead to widths which are consistent with capillary-wave theory as well, a definitive attribution of the width to capillary waves will require measurements at more than a single temperature. Furthermore it is not known whether, and how, surface order such as the observed layering influences the capillary-wave spectrum and its manifestation in the surface width.

Here we report x-ray reflectivity measurements from the Ga surface between room temperature and 170 °C. The high surface tension, small atomic size, convenient (near-room) melting temperature, exceptionally large liquid range and very low vapor pressure render Ga an almost ideal sample for studying the issues discussed above by x-ray reflectometry, since they allow for measurements over a wide range of temperatures and reflectivity wave vector  $q_z$ . Our results show unambiguously that the layering decay length is *independent* of temperature, and that the capillary-wave theory predictions are followed, unmodified by the order, and valid for our sample at all temperatures measured. This is in contrast to recent results on oxidized Ga surfaces, where capillary waves are suppressed, over a similar temperature range as reported here, by a uniform 6 Å gallium-oxide layer.<sup>17</sup> Being able to separate out the temperature-dependent capillary wave effects, that are not included in the theory of the local order at one point on the surface, allows us also a direct

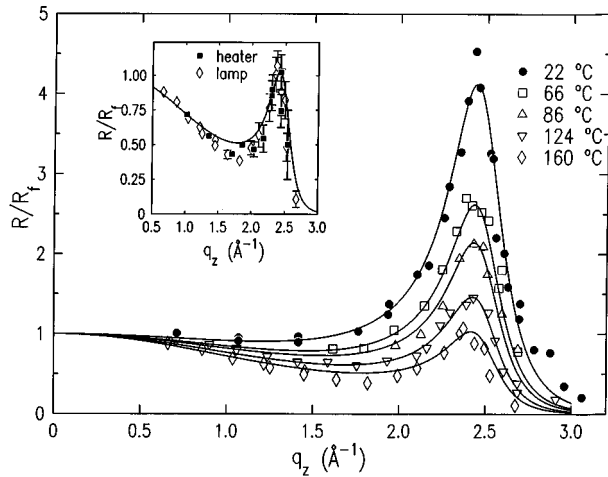


FIG. 1. Measured reflectivity curves for liquid Ga at various temperatures, normalized to the Fresnel Law of Optics. The fits to the data are from the three-parameter layered capillary-wave model discussed in the text. For clarity, error bars are not shown for these data, but typical error bars are included on the data in the inset. The inset shows that similar  $R/R_f$  data are collected when varying the temperature with either lamp illumination or resistive heater ( $T=160$  °C).

comparison of the measurements with theory. We find that existing theories significantly underestimate the degree of ordering as reflected in the amplitude of the layering in the local density profile for liquid metals.

X-ray reflectivity measurements were carried out at the wiggler beamline X-25 at the NSLS using a toroidal mirror and a liquid reflectometer with a water-cooled Ge(220) crystal monochromator set to reflect at  $\lambda=0.6532$  Å. Details of the sample preparation, surface cleaning, data collection and analysis procedures have been presented elsewhere.<sup>9,18</sup> The Ga sample was heated either by illumination through a viewport in the UHV chamber using a powerful halogen lamp or by a resistive heater installed inside the chamber under the sample holder. Identical results were obtained by both methods. The temperature was measured using a thermocouple placed beneath the sample holder and calibrated within  $\pm 3$  °C using a similar thermocouple placed in the liquid Ga.

Figure 1 shows the basic results of the x-ray specular reflectivity experiments, where the measured reflectivity is normalized to the Fresnel theory. As noted previously,<sup>9</sup> a peak is observed at  $q_z \sim 2.4$  Å<sup>-1</sup>, indicating atomic layering with a layer spacing  $d \approx 2\pi/q_z = 2.6$  Å, and its corresponding peak width is consistent with atomic layering extending an exponential decay length of  $\sim 3$ – $4$  atomic diameters into the bulk. The striking feature is that, in contrast to the effect of temperature on surface layering for liquid crystals<sup>10,11</sup> where the decrease in the peak height is invariably accompanied by an increase in the peak width, the temperature increase in our case reduces the peak height but leaves its width unchanged. This suggests that with increasing temperature the layering decay length is unchanged, and the amplitude of the density variations are simply reduced. Although various models can and have been constructed to describe the profile and quantify its variation with temperature, the model-independent features that must always be present are a temperature independent layering decay length

of  $\sim 3$ – $4$  atomic diameters and a temperature-dependent density variation amplitude. The surface roughness, included in every model as a Debye-Waller-like factor, shows also a model-independent behavior by yielding an identical temperature dependence for all models. Since this fully accounts for the amplitude variation, we conclude that all temperature effects are introduced via the roughness. In turn, the temperature variation of the roughness is found to agree with that predicted by capillary-wave theory.

To make this discussion more quantitative, we note that for wave vectors  $q_z$  larger than 4–5 times the critical wave vector, the reflectivity is related to the average electron density along the surface normal,  $\langle \rho(z) \rangle$ , by

$$\frac{R(q_z)}{R_f(q_z)} \approx \left| \frac{1}{\rho_\infty} \int \left[ \frac{d\langle \rho(z) \rangle}{dz} \right] e^{iq_z z} dz \right|^2, \quad (1)$$

with  $\rho_\infty$  the known bulk electron density and  $R_f$  the theoretical reflectivity for a perfectly flat surface calculated from the Fresnel Law of Optics. A simple layered density model, based on Gaussian functions, has been applied to Hg (Ref. 8) and Ga (Ref. 9) and is modified here to include the effects from thermally induced capillary waves. This “distorted crystalline model” is composed of equally-spaced atomic layers where the density distribution along the surface normal of each layer is broadened by mean square displacements (MSD) that increase with distance into the bulk liquid. This leads to an oscillatory profile close to the surface and a uniform density beneath it. To account for the temperature dependent capillary-induced surface roughness, the atomic distribution of the distorted crystalline model is convoluted with  $\exp(-\sigma_c^2 q_z^2)$ , where  $\sigma_c$  is the contribution to the MSD due to capillary waves. Since this procedure smears the whole profile uniformly, the convoluted profile has a smaller layering amplitude, but no change in the decay length. The simplest way of including the temperature dependence in the model is, thus, to represent the MSD of the  $n$ th layer as

$$\sigma_n^2 = n\bar{\sigma}^2 + \sigma_c^2 = n\bar{\sigma}^2 + \sigma_0^2 + \frac{k_B T}{2\pi\gamma} \ln\left(\frac{k_{\max}}{k_{\min}}\right), \quad (2)$$

where  $n=0, 1, 2, \dots$ ,  $\bar{\sigma}$  is a measure of the increasing root-mean displacement as the density approaches the bulk liquid and  $\sigma_0$  is an intrinsic contribution which, along with the final term, makes up the contribution from the thermal capillary-wave displacement.<sup>19,20</sup>

In general the capillary contribution is determined by balancing the thermal energy,  $k_B T$ , with the surface tension  $\gamma$  and gravity. The logarithmic term in Eq. (2) arises from the  $1/k^2$  dependence of the contribution of surface tension to the energy of a surface capillary wave with wave vector  $\mathbf{k}$ . The short and long wavelength cutoffs,  $k_{\max}$  and  $k_{\min}$ , respectively, are determined by the molecular size  $d$  ( $k_{\max} = \pi/d = 1.26$  Å<sup>-1</sup>) and gravity ( $k_{\min} \propto \sqrt{\Delta\rho g/\gamma}$  with  $\Delta\rho$  the mass density difference between the liquid and vapor). However, for the present x-ray measurements carried out on a curved sample, the longest coherence length that can be measured is  $4\pi/(q_z \Delta\beta)$ , with  $\Delta\beta$  determined by the local radius of curvature ( $R \sim 150 \pm 30$  mm for the Ga samples measured here) and the beam height at the sample position ( $h \sim 0.1$  mm), leading to  $k_{\min} = 2\pi h/(R\lambda) = 0.0064$  Å<sup>-1</sup>.<sup>18</sup> With a uniform layer spacing  $d$  the reflectivity is

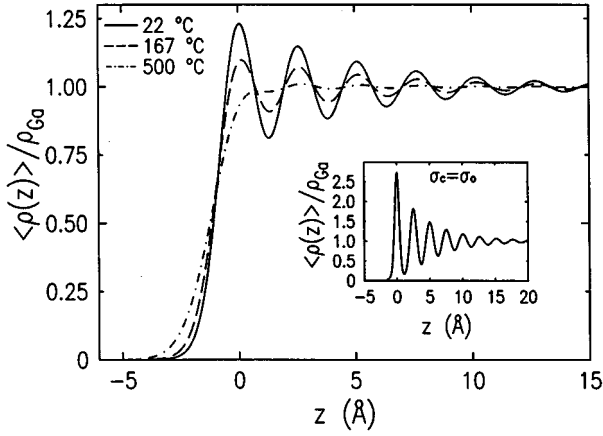


FIG. 2. Electron density profiles for the Ga liquid/vapor interface at 22 and 167 °C generated from the three-parameter layered capillary-wave model discussed in the text. Also included is the electron density profile from our fits extrapolated to a temperature of 500 °C, which shows the diminution of the layering at the higher temperatures. The inset shows the intrinsic gallium layering profile prior to including the temperature dependence of the capillary width (i.e.,  $\sigma_c = \sigma_0$ ).

$$\frac{R(q_z)}{R_f(q_z)} = e^{-q_z^2 \sigma_c^2} \left| \frac{f(q_z) q_z d}{Z} \right|^2 |e^{q_z^2 \bar{\sigma}^2} e^{-iq_z d} - 1|^{-2}, \quad (3)$$

where  $f(q_z)$  is the atomic scattering factor.

Over the temperature range measured, there is excellent agreement between this simple three-parameter model and the measured reflectivity. Figure 1 shows the model fit to the Ga data. The fact that all five data sets can be fit with the same three parameters,  $d = 2.504 \pm 0.006$  Å,  $\sigma_0 = 0.37 \pm 0.027$  Å, and  $\bar{\sigma} = 0.393 \pm 0.005$  Å, strongly supports the conclusion that all temperature variation is indeed due to capillary waves, not to variations in the local surface layering. The temperature dependence of the surface tension  $\gamma$  is included from Ref. 21, although it does not vary by more than 2% over this temperature range.

The corresponding electron density profiles at the lowest and highest recorded temperatures are shown in Fig. 2, which illustrates that the layering decay length does not change with temperature whereas the amplitudes of the layers do. The decrease of the amplitudes with increasing temperature results from averaging the intrinsic oscillations, with fixed decay length, over an increasingly broader roughness width. Note that in spite of this thermal smearing we still observe appreciable layering even at  $\sim 150$  °C above the Ga melting point. To permit quantitative measurements at even higher temperatures, flatter samples are required. The present curved Ga sample leads to a degradation of the signal-to-noise ratio that is equivalent to a coarse detector resolution for a flat sample; it increases the detected intensity from bulk diffuse scattering relative to the specular peak. For our model, extrapolation of the current measurements to  $\sim 500$  °C leads to a layering modulation amplitude that is only 1% of the average density, as compared to 25% at room temperature. At this level, even for a flat sample, the reflectivity peak would be extremely difficult to detect experimentally. At the other extreme, for the  $T \rightarrow 0$  limit, the intrinsic gallium layering profile is unmodified by capillary waves

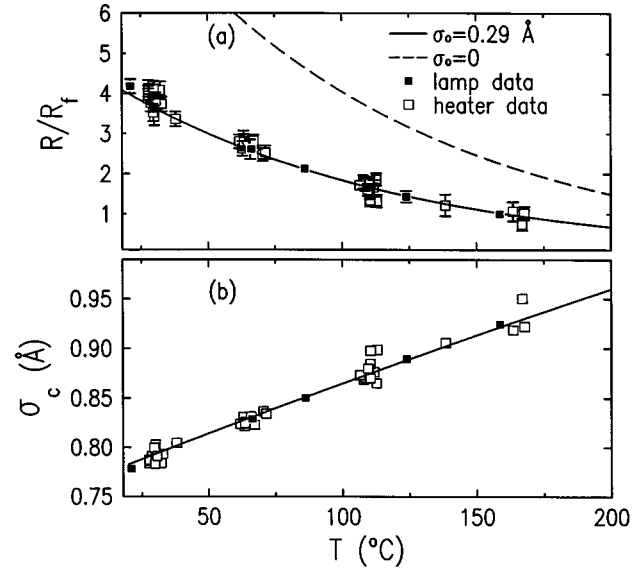


FIG. 3. (a) The variation of the  $R/R_f$  peak ( $q_z = 2.4$  Å $^{-1}$ ) with temperature. The solid line is from the layered capillary-wave model with the parameters from the fit of Fig. 1, and the dashed line is with  $\sigma_0 = 0$ . (b) The variation of  $\sigma_c$  with temperature as computed from the data in (a) using Eq. (3) with  $q_z = 2.4$  Å $^{-1}$  and the model in the text. The solid line is the variation expected from capillary-wave theory. Note the excellent agreement.

( $\sigma_c = \sigma_0$ ) and is shown as the inset to Fig. 2. The layering is very prominent indeed, with the height of the first layer at 2.8, as compared with 5.8 for a crystalline layer at room temperature calculated from the Debye-Waller factor for solid Ga and the atomic scattering factor.

To further describe the variation in  $R/R_f$  with temperature, we show in Fig. 3(a) the amplitude of the  $R/R_f$  peak ( $q_z = 2.4$  Å $^{-1}$ ) as a function of temperature. As with the spectra fit in Fig. 1, there is excellent agreement between the peak amplitude and that predicted from the three-parameter layered capillary-wave model discussed previously (solid line). The importance of including an intrinsic width  $\sigma_0$  to the profile is also clearly demonstrated by the broken line which illustrates that without this additional displacement, the capillary width would be insufficient to account for the full interfacial width, and the predicted  $R/R_f$  peak amplitudes would be significantly greater. The origin of  $\sigma_0$  is likely from the finite atomic size; however, contributions due to local deviations of the atomic centers from the ideal flat plane assumed in the existing model [Eq. (2)] are also possible. These could conceivably result from the same nonisotropic nearest-neighbor atomic distributions that give rise to the shoulder in the structure factor for bulk liquid Ga.<sup>22</sup> Finally, Fig. 3(b) shows the variation of  $\sigma_c$  with temperature. The  $\sigma_c$  are calculated directly from the  $R/R_f$  peak amplitudes in Fig. 3(a) using Eq. (3) and the best-fit values of  $d$  and  $\bar{\sigma}$  from Fig. 1. In comparison, the solid line is the capillary width, with  $\sigma_0$  also from the best fit of the data shown in Fig. 1. The temperature dependence relies solely on the capillary-wave contribution, and there is good agreement.

These results show quite conclusively that over the measured temperature range the variation of the density profile with temperature is due exclusively to the corresponding temperature dependence of the capillary waves, and, in con-

trast to liquid crystals, no variation in the intrinsic layering occurs. Note that in spite of this excellent agreement with capillary-wave theory, the present temperature range and coarse resolution are insufficient to distinguish between various capillary-wave models.<sup>19,20</sup>

A quantitative comparison of our results with theory, and in particular with the extensive simulations done for various liquid metals, is complicated by the fact that molecular simulations are done on relatively small model systems that necessarily cut off the long wavelength capillary waves. With one exception, that of liquid Hg,<sup>5</sup> the amplitudes of the surface oscillations obtained from our measurements on liquid Ga are larger than those obtained by any theory<sup>1-3</sup> or simulation.<sup>4,6,7</sup> However, to make the comparison more meaningful we have convoluted the Ga intrinsic profile, shown as the inset in Fig. 2, with a capillary wave roughness in which the long-wavelength cutoff  $k_{\min}$  is given by  $\pi/L$ , where  $L$  is the length scale of the particular simulation. When the comparison is made in this way the amplitudes of the resultant surface oscillations from our measurement are even larger. In fact, this is even true for the only (although unpublished) simulation that we are aware of on liquid Ga.<sup>23</sup> Although the amplitude of the predicted surface oscillations for liquid Hg are comparable to what we observe for Ga and present an exception to our claim that all simulations underestimate the amplitude of the surface layering, the quantitative significance of this is not clear. For example, the peak

amplitude of the first layer in the experimentally measured Hg profile is only about 50% of that of Ga, and since this means it is also 50% of the simulation for Hg, it follows that the simulations and measurements for Hg are not mutually consistent.

Clearly, there is need for further theoretical study, simulations, and experimental measurements. In particular, extending the present meager body of measurements to other liquid metals is crucial for determining the fundamental layering features common to all liquid metals. An extension of these measurements to higher melting point metals (e.g., Au, Pt) or those with a relatively small surface tension (e.g., Cs), may not be, however, straightforward. The capillary-wave contribution in these cases will be much greater than for Ga, significantly damping any intrinsic density oscillations. It is not clear if the capillary widths will dominate and completely smear the layering profiles for these metals, as projected for Ga at 500 °C (Fig. 2), or if the intrinsic profile will compensate and lead to a strong layering as we observe for Ga at room temperature.

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