

Surface Layering of Liquids: Is Surface Tension the Dominant Factor?

O. Shpyrko,¹ M. Fukuto,¹ P. Pershan,¹ B. Ocko,² I. Kuzmenko,³ T. Gog,³ M. Deutsch⁴

¹Department of Physics, Harvard University, Cambridge MA, U.S.A.

²Department of Physics, Brookhaven National Lab, Upton NY, U.S.A.

³CMC-CAT, Argonne National Lab, Argonne, IL, U.S.A.

⁴Department of Physics, Bar-Ilan University, Ramat-Gan, Israel

Introduction

Recent measurements show that the free surfaces of liquid metals and alloys are always layered, regardless of composition and surface tension, a result supported by three decades of simulations and theory. Recent theoretical work claims, however, that at low enough temperatures the free surfaces of *all* liquids should become layered, unless preempted by bulk freezing. Using x-ray reflectivity and diffuse scattering measurements, we show that surface-induced layering does not occur in water at $T=298\text{K}$, thus highlighting a fundamental difference between dielectric and metallic liquids. The implications of this result for the question in the title are discussed.

The free surface of liquid metals and alloys were demonstrated experimentally over the last few years to be layered, i.e., to exhibit an atomic-scale oscillatory surface-normal density profile. This is manifested by the appearance of a Bragg-like peak in the x-ray reflectivity (XR) curve, $R(q_z)$, as shown in Fig. 1 for Ga [1]. The layered interface is in a marked contrast with the theoretical description of the liquid-vapour interface of a simple liquid, which predicts a step-wise but monotonic change between the low density of the vapor and the high density of the bulk liquid [2]. Early simulations demonstrate that atomic layering is ubiquitous near a hard flat surface, and at first it is tempting to think that the large surface tension of liquid metals like mercury, gallium and indium might be the explanation for the surface layering (SL) observed at their liquid/vapor interface. This assumption is partially mitigated by the observation of SL at the free surface of liquid potassium, whose surface tension is nearly an order of magnitude smaller than that of Ga, In and Hg. In this paper we report x-ray scattering results that show the free surface of water, which has nearly the same surface tension as potassium, does not exhibit SL, thereby proving that surface tension by itself is not the explanation.

The explanation for SL is still an open question. Unfortunately, one of the major problems is that the measurable q_z -range is more often than not limited to values much less than q_{peak} by the strong off-specular diffuse scattering caused by thermal capillary waves. The effect of the capillary waves is to induce a surface roughness, which is proportional to the square root of

surface tension. The consequence of this, which is shown in Fig.1 for three liquids at room temperature, is to reduce the reflectivity $R(q_z)$ below that of the theoretical Fresnel reflectivity from an interface with an idealized flat, step-like density profile. For low-surface-tension liquids like water (70 mN/m) and potassium (100 mN/m), the reduction is significant, while for gallium (750 mN/m) the effect is almost negligible at room temperature [1].

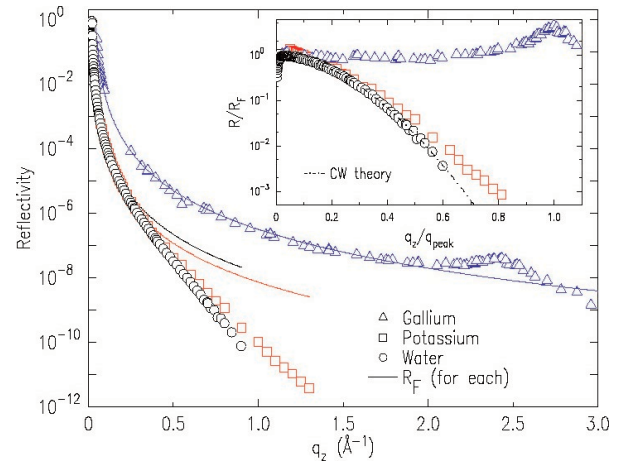


FIG. 1. X-ray reflectivity from free liquid surfaces of the indicated samples. Points- measured $R(q_z)$, lines - calculated for an ideally flat and step-like interface, $R_F(q_z)$. The inset shows the ratio of the two.

In spite of the fact that the rapid fall off that prevents $R(q_z)/R_F(q_z)$ from being measured at the position of the SL peak for water, our recent studies of liquid K [3] demonstrated that if surface layering is present the effect can still be observed even in low ($\sim 100\text{mN/m}$) liquids by carefully accounting for the effects of capillary waves, based on diffuse x-ray scattering (DS) measurements. We present here an x-ray study of the surface structure of water including diffuse scattering over the most extended q_z range published to date [4]. For the present measurements the intrinsic surface structure factor of water can be extracted directly from the raw $R(q_z)$ without resorting to any structural model

for the interface. Comparison between the water surface structure factor, for which there is no evidence of SL, and that of potassium and gallium conclusively establishes that surface tension is not the dominant cause of the effect in metals.

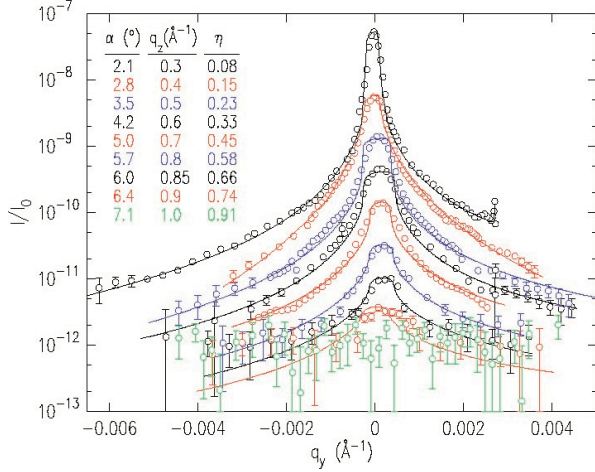


FIG. 2. Comparison of measured diffuse scattering (open circles) with capillary wave theory predictions for the angles of incidence α listed. The q_z values correspond to the specular condition $q_y = 0$. η is the diffuse scattering lineshape exponent.

The theoretical curves in Fig. 2 that were calculated using capillary wave theory with $T=298\text{K}$ and $\gamma=72\text{ mN/m}$ are shown as lines. As q_z increases, so do both $\eta \sim q_z^2$ and the intensity of the off-specular power-law wings relative to that of the specular peak at $q_y = 0$. The curve at $q_z = 1\text{ Å}^{-1}$ demonstrates the capillary-wave-imposed limit where the specular signal at $q_y = 0$, which contains the surface structure information, becomes indistinguishable from the DS signal at $q_y > 0$. In principal this limit arises from the fact that for $\eta > 2$ the singularity at $q_{xy} = 0$ in $d\sigma/d\Omega$ vanishes, and there is no longer any criterion by which the surface scattering can be differentiated from other sources of diffuse scattering. In practice the fact that the projection of the resolution function on the horizontal x-y plane is very much wider transverse to the plane of incidence than within the plane of incidence reduces this limit to a value closer to $\eta \sim 1$. Fig. 2 exhibits excellent agreement between the theoretical DS curves calculated with capillary wave theory with the measured DS over several decades in intensity and one decade in η , without any adjustable parameters. This confirms the applicability of the capillary wave theory for the surface of water over the q_z range studied here, $0 < q_z < 0.9\text{ Å}^{-1}$.

The results for the surface structure factor $|\Phi(q_z)|^2$ thus obtained for water are shown by the black open circles in both the inset and the main part of Fig. 3 along

with previously measured results for $|\Phi(q_z)|^2$ for potassium and gallium. The abscissa in the inset is normalized to the values of q_z at which one expects a surface layering peak. For water q_{peak} was taken to be 1.6 Å^{-1} .

For Ga the rise of the $|\Phi(q_z)|^2$ to ~ 100 at q_{peak} due to layering can be clearly seen on the inset to Fig. 3. For potassium, the capillary-wave-imposed limit only allows obtaining $|\Phi(q_z)|^2$ for $q_z < 0.8 q_{\text{peak}}$. On the other hand, the value of $|\Phi(q_z)|$ for potassium starts to deviate from unity for values of $q_z/q_{\text{peak}} \sim 0.3$. Furthermore, over the range for which it can be measured, it is basically identical to the structure factor for gallium. This is a clear indication that the surface of liquid potassium has essentially the same SL as that of gallium, which is also nearly identical to that of the other liquid metals that have been studied to date, indium and tin.

For water, however, no deviation of $|\Phi(q_z)|$ from unity is observed even at the highest measurable $q_z/q_{\text{peak}} \sim 0.6$. This indicates clearly and confidently that surface-induced layering does not occur at the surface of water. The different behavior, in spite of the similar γ of water and potassium, strongly supports the conclusion that the surface layering in potassium is not simply a consequence of its surface tension. The absence of layering in water, and its presence in potassium, seems at first sight to corroborate Rice et al.'s [5] claim that layering is a property arising from the metallic interaction of the liquid. On the other hand, Chacon et al. [6], who maintain that surface-induced layering is a general property of all liquids, regardless

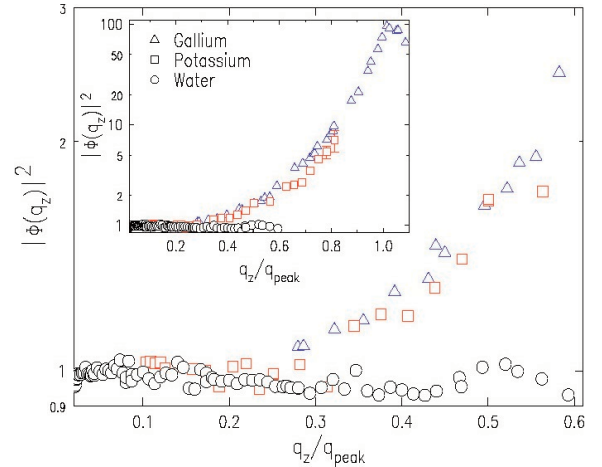


FIG. 3. Comparison of the structure factor squared $|\Phi(q_z)|^2$ for water (circles), liquid potassium (squares) and liquid gallium (triangles). The wave vector q_z is normalized to the expected position of the layering peak q_{peak} of each sample. The inset shows the data on an extended scale. For discussion see text.

of their interactions, predict that layering should occur only at temperatures $T/T_c < 0.2$, where T_c is the critical temperature of the liquid. Although supercooling is often possible the practical limit for most reflectivity measurements is the melting temperature T_m . Thus the smallest T/T_c for any liquid is on the order of T_m/T_c . For liquid metals T_m/T_c is 0.15 (K), 0.13 (Hg), 0.07 (In), 0.066 (Sn) and 0.043 (Ga). Since these values are < 0.2 , by Chacon's criteria surface layering is expected, and indeed demonstrated experimentally to occur, in all of them [1, 3, 7]. By contrast, for water of $T_m/T_c = 0.42 > 0.2$, Chacon's criteria predict that for water the appearance of surface layering is preempted by bulk freezing.

Summary

First, the surface of water has been shown to not exhibit SL even though its surface tension is not significantly different from that of liquid potassium for which layering is observed. Although this would seem to support Rice's argument that the metallic phase is essential for SL. On the other hand, SL at the liquid vapor interface is exhibited by both liquid crystals and other large organic molecules. Consequently, there are other criteria for SL aside from those proposed by Rice. One of the possibilities is the proposal by Chacon et al. that SL should be ubiquitous for all liquids that can be cooled to temperatures of the order of $0.2 T_c$. Unfortunately, this is a difficult proposition to test since suitable liquids are rather scarce.

Acknowledgments

This work has been supported by the U.S. Department of Energy Grant No. DE-FG02-88-ER45379, the National Science Foundation Grant No. DMR-01-12494 and the U.S.—Israel Binational Science Foundation, Jerusalem. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. We would also like to acknowledge CMC-CAT for providing help with this experiment.

References

- [1] M.J. Regan et al., Phys. Rev. Lett. **75**, 501 (1995).
- [2] F.P. Buff et al., Phys. Rev. Lett. **15**, 621 (1965); F.H. Stillinger and J.D. Weeks, J. Phys. Chem. **99**, 2807 (1995); J. S. Rowlinson and B. Widom, "Molecular Theory of Capillarity" (Oxford University Press, Oxford, 1982).
- [3] O.G. Shpyrko et al., Phys. Rev. B **67**, 115405 (2003).
- [4] A. Braslau et al., Phys. Rev. Lett. **54**, 114, 17 (1995); D.K. Schwartz et al., Phys. Rev. A **41**, 5687 (1990).
- [5] S.A. Rice et al., *Adv. Chem. Phys.* XXVII (Wiley, Chichester, 1974, p. 543); M.P. D'Evelyn and S.A. Rice, J. Chem. Phys. **78**, 5225 (1983).
- [6] E. Chacon et al., Phys. Rev. Lett. **87**, 166101 (2001); E. Velasco et al., J. Chem. Phys. **117**, 10777 (2002).
- [7] O.M. Magnussen et al., Phys. Rev. Lett. **74**, 4444 (1995); H. Tostmann et al., Phys. Rev. B **59**, 783,791 (1999); O.G. Shpyrko et al. (*in preparation*, 2003).