Surface studies of water: Are all liquids intrinsically layered?

Oleg Shpyrko[1], Masa Fukuto[1], Peter Pershan[1], Ben Ocko[2], Moshe Deutsch[3], Thomas Gog[4], Ivan Kuzmenko[4]

[1]Department of Physics, Harvard University, Cambridge, MA; [2]Brookhaven National Lab, Upton, NY; [3]Bar-Ilan University, Israel, [4]Argonne National Lab, Argonne, IL

Abstract

• Experimental measurements: free surfaces of liquid metals and alloys are always layered, regardless of composition and surface tension

• Are non-metallic liquids layered?

• Our x-ray measurements:

No observable surface-induced layering in water

• Fundamental difference between dielectric and metallic liquids

Introduction

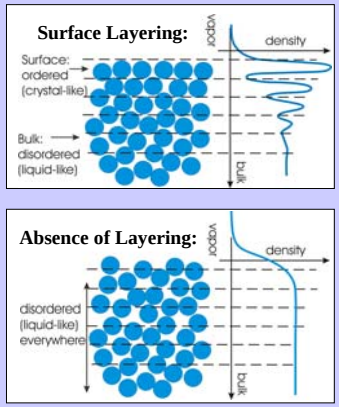
Background

What is surface-induced layering?

- Well-ordered atomic layers at the surface
- Manifested in a Bragg-like peak in x-ray reflectivity
- Observed for:
  - high-surface tension metals (Ga, In, Hg, Sn)
  - alkalis (K, KNa), with low surface tension (similar to that of dielectric liquids, such as water)
- Is it possible that dielectric liquids are layered too?
- Does layering exist in something as common as water?

❑ Cons: Capillary waves obscures surface structure, stronger for low-surface tension liquids

❑ Pros: Theory experimentally confirmed for other liquids, can be applied to deconvolve structure



Our results:

✓ Capillary wave theory successfully describes the surface of water, using only known values of temperature, surface tension and resolution

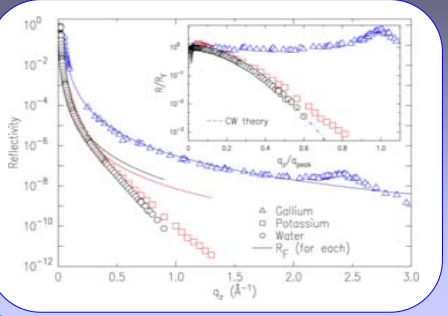
✓ X-ray reflectivity can only be obtained up to $q_z = 0.95Å^{-1}$, due to Debye-Waller like limit

✓ Capillary Theory ⟹ Structure deconvolved: No evidence of surface layering for water!

✓ Dielectric vs. Metallic liquids:
- Surface structure is different!

✓ Layering not defined by Surface Tension

X-Ray Reflectivity



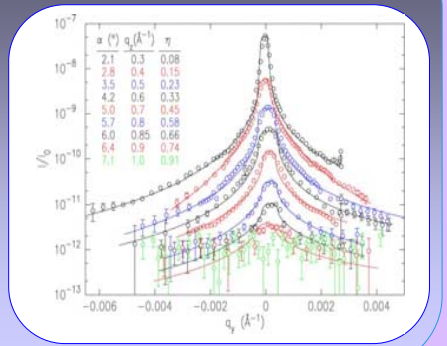
• Data for liquid Ga, K and water, along with theoretically predicted Fresnel reflectivity lines. Inset: the same data, normalized to Fresnel.

• Ga: Surface layering self-evident (Bragg-like peak at $q_z=2.5Å^{-1}$)

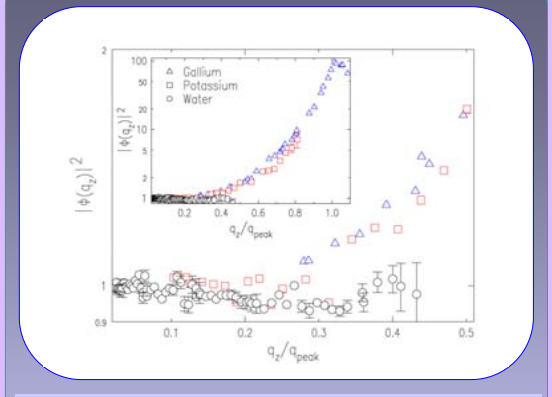
• K and water:
- Structure effects subtler
- Debye-Waller-like effect much stronger
- Full layering peak measurements impossible
- Need to deconvolve capillary wave contributions

Capillary Wave Theory Confirmed

- X-ray diffuse scattering: data agrees with theory with no adjustable parameters
- Structure can be deconvolved from reflectivity
- At $q_z = 1.0Å^{-1}$ it is no longer possible to distinguish specular signal from diffuse wings. Thermal effects can be accounted for and removed.



Surface Stucture Factor



Surface Structure Factor (Squared): Fresnel-normalized reflectivity with thermal (capillary) effects taken out, for Ga, K, water

- Ga: high surface tension ⟹ full layering structure
- K, water: low surface tension ⟹ partial structure
- Ga and K: rise of structure factor above 1
- Water: structure factor remains unchanged

⇩

• **Water surface is not layered!**

Summary

Surface Layering in Liquids:

✓ High surface tension metallic liquids: Ga, In, Hg, Sn, alloys…….. Layered

✓ Low surface tension metallic liquids: K, KNa…….. Layered

✓ Low surface tension dielectric liquids: Water…….. Not Layered

• Metallic vs. Dielectric: Important
• Surface Tension: Not as important

Future Studies:

Rare gases (Ne, Ar, Kr)?

• Pros – simple atomic structure, developed theory

• Cons – low temperatures, surface tension ⟹ high capillary fluctuations

Acknowledgements

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