Breaking the Gibbs Adsorption Rule: Resonant X-ray Reflectivity from a Liquid Bismuth-Indium Alloy

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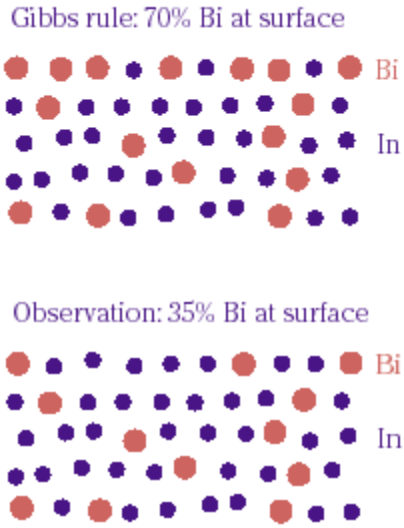
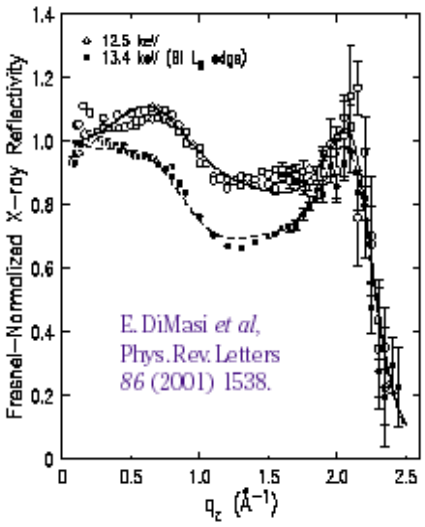
Binary liquids are supposed to follow a simple rule, formulated by Gibbs in 1878: the species having the lowest surface tension should segregate into a separate monolayer at the surface. However, this picture assumes that interactions between atoms can be disregarded. What happens in alloy-forming mixtures with attractive interactions between atoms?

To answer this question, we performed resonant x-ray reflectivity measurements from a liquid Bismuth-Indium mixture having 22 at% Bi in the bulk. By tuning the incident x-ray energy through the Bi L_{III} absorption edge, we can determine the ratio of Bi to In at the surface. The Gibbs rule for the noninteracting system predicts segregation of 70% Bismuth at the surface.

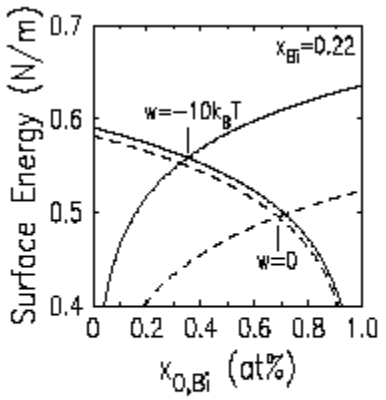




We find a Bi enrichment of 35 at% in the surface layer, compared to the 22 at% in the bulk. This is considerably less Bi than would be expected in the absence of attractive Bi-In interactions, which we find must be on the order of 10 kBT to explain our data.

This work quantifies, for the first time, the extent to which attractive interactions can compete with Gibbs adsorption.

These are the first resonant x-ray reflectivity measurements ever achieved on a liquid surface, and were made possible by specialized instrumentation at the National Synchrotron Light Source at BNL.



Surface free energy condition equating surface tension and entropic terms for In and Bi as functions of concentration.

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