

ALLOYED FORCES LAID BARE

Nanotechnology relies on the fact that there can be significant differences between the properties of a material in the bulk and those at the sub-microscopic (nano) level. Low-melting metal alloys for instance, in the bulk, are seemingly the same throughout, behaving as near-perfect liquids when heated. However, at the nano level of metal clusters and surface atoms, several of these alloy compounds display odd behavior that seemingly goes against the grain, including surface layering, capillary action, demixing, and surface freezing. Understanding such nanoscale behavior might allow researchers to control it and exploit it in the production of novel materials with tailored properties. Such an understanding is the goal of a group of researchers from Harvard University, Bar-Ilan University, Brookhaven National Laboratory, and The University of Chicago, whose investigations into the behavior of a particular alloy provide new information about what occurs on the material's surface.

In this study, the researchers studied an alloy of bismuth and tin. The material, a less-toxic alternative to lead-based solder, has the chemical formula $\text{Bi}_{43}\text{Sn}_{57}$, and apparently behaves as a near-perfect liquid—at least when viewed on the bulk scale. However, the researchers used resonant x-ray reflectivity on the ChemMatCARS 15-ID beamline to take a much closer look at the surface of this material. Their findings suggest an altogether more deviant behavior.

They obtained a liquid $\text{Bi}_{43}\text{Sn}_{57}$ sample of 99.99% purity and prepared it under ultra-high vacuum conditions, scraping off stray impurities from the surface to render it “atomically clean” and then blasting it with high-energy argon ions to knock out any stragglers. They then carried out measurements on the liquid surface diffractometer at the ChemMatCARS beamline at a sample temperature of 142°C , which is 4 degrees above the temperature at which $\text{Bi}_{43}\text{Sn}_{57}$ melts—its eutectic point. The researchers then fitted the results to a computer model to reveal any organization in the liquid.

In the bulk liquid, the bismuth and tin atoms are distributed evenly, albeit randomly, throughout, just as one would expect of particles in a liquid mixture. Near the surface, however, the researchers found something quite shocking for a liquid: *order*. Rather than the random metal atoms being fully mixed, they separate out into atomic layers with alternating compositions. The top layer is mostly bismuth; below that is tin, then another layer of bismuth and so on, with the atoms gradually becoming more mixed as depth increases. Their results gave an excellent fit to the model for three ordered layers, but one and two layers coincided very poorly with the model predictions.

Researchers have, in the past, observed a similar surface segregation in other liquid alloys, such as gallium indium, mercury gold, and bismuth indium, but the separating out of the two liquid-metal components was limited to a single layer at the sur-

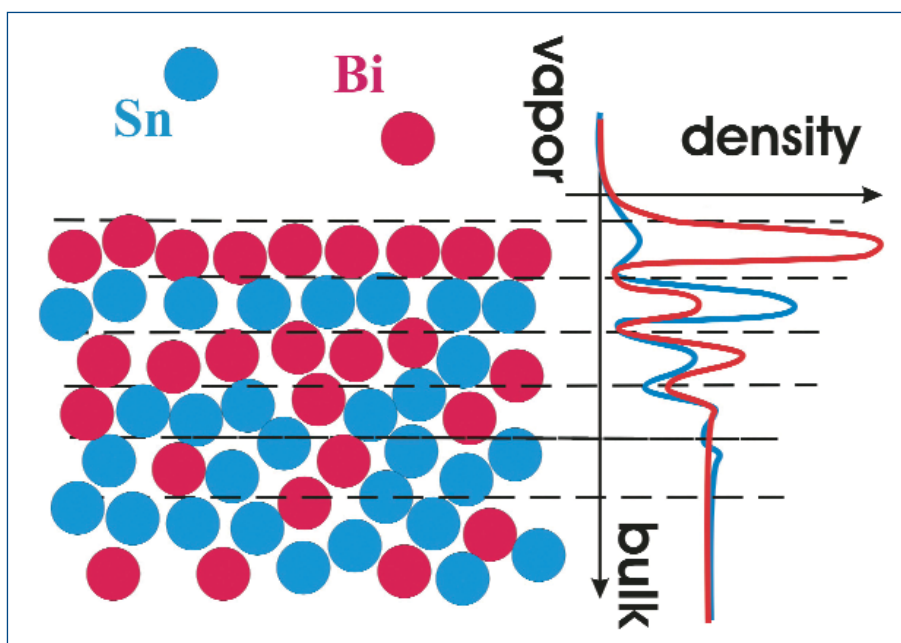


Fig. 1. On the surface, x-ray reflectivity reveals just how organized are liquid metal alloys.

face. Scientists explained this phenomenon in terms of the energetics of the liquid near the surface. However, this is the first time anyone has observed such demixing extending deeper into a liquid than the uppermost monolayer. The power of synchrotron-based x-ray reflectivity using hard x-rays and atomic resolution reveals a phenomenon. On the one hand, immiscible liquids such as oil and water, which repel each other, quickly demix, but miscible liquids—ones in which the components are strongly attractive—do not.

Improved understanding of surface demixing and other phenomena—such as wetting, spreading, and reactivity—is essential to the use of novel materials, such as multicomponent alloys. Researchers might be able to tailor these materials to specific applications, such as lead-free solders and hybrid nanostructures (e.g., core-shell nanoparticles). It might also be possible to “lock-in” the surface order by cooling the liquid back

to its solid form, resulting in a modified surface. The way surfaces in the liquid interact with nanoscale particles that impinge on it could also be important in tribology applications, where significant recent research has focused on incorporating such nanoparticles into lubricants to help reduce friction and wear.

— David Bradley

See: Oleg G. Shpyrko¹, Alexei Yu. Grigoriev¹, Reinhard Streitel¹, Diego Pontoni¹, Peter S. Pershan¹, Moshe Deutsch², Ben Ocko³, Mati Meron⁴, and Binhua Lin⁴, "Atomic-scale Surface Demixing in a Eutectic Liquid BiSn Alloy," *Phys. Rev. Lett.* **95**, 106103 (2005).

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NEW INSIGHTS INTO THE STRUCTURE OF SUPERCOOLED LIQUID SILICON

The structure of supercooled liquid silicon (Si) as it transforms from a metallic dense-packed structure at high temperatures to a semiconducting open network at lower temperatures has remained a controversial topic for several decades. Much of the controversy has focused on the postulated existence of a first-order liquid-liquid phase transition in the supercooled state. While some computer simulations have produced such a transition, others have not. Experimental studies using various containerless techniques have likewise yielded conflicting results. To resolve the question, researchers from Washington University, Iowa State University/Ames Laboratory, the University of Massachusetts, the University of Alabama, and the NASA Marshall Space Flight Center performed time-resolved *in situ* high-energy x-ray diffraction measurements of liquid Si by using the recently developed beamline electrostatic levitation (BESL) technique. Their results provide new insights into the existence (or lack) of a liquid-liquid phase transition.

Small spheres (2.2 to 2.5 mm in diameter) of high-purity Si, prepared by arc melting in a high-purity argon atmosphere, were levitated in a BESL chamber at high vacuum (10^{-7} to 10^{-8} torr) on the MU-CAT 6-ID-D beamline at the APS. The levitated samples were heated and melted by using 30-W diode and CO₂ lasers. Optical pyrometers with a 1.45- to 1.8- μm wavelength range were used to measure the sample temperature to an accuracy of 1K. Because of the high thermal conductivity of liquid silicon, the samples were in thermal equilibrium over the measured temperature range, with the maximum difference between the temperature at the center of the samples and that at the surface being less than 1K.

The diffraction measurements obtained at the APS offered important improvements over previous investigations. First, the use of high-energy x-rays (125 keV) ensured that the experiments were performed in a transmission geometry, so that the sample volume was probed. The use of high-energy x-rays also minimized data corrections caused by sample absorption and multiple scattering. Secondly, BESL offered a distinct advantage over electromagnetic and aerodynamic levitation, in that the processes of heating and positioning are

decoupled, eliminating the need for cooling or levitating gases. The high-vacuum environment of BESL also minimizes environmental contamination of the sample, which can lead to heterogeneous nucleation. This allowed high-quality structural data to be extended more deeply into the supercooled regime of liquid silicon than has been possible before, to 316K below the melting point. Finally, the use of fast area detector technology in combination with the high-energy x-rays permitted rapid data acquisition (~ 100 ms for a complete pattern) over a reasonably wide momentum transfer range ($q_{\text{max}} \sim 10 \text{ \AA}^{-1}$), allowing the researchers to take advantage of the deep supercooling obtained in BESL without needing to hold samples at a set temperature for a prolonged period of time. Rather than obtaining only 5 to 10 data sets spaced over the entire temperature range, the researchers were able to continuously monitor structural changes over temperatures from 1815K to 1369K.

The researchers found that, in contradiction to several existing experimental studies and many simulations using the Stillinger-Weber potential, the coordination number of liquid Si

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