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# A New Low: Lilliputian pipette releases tiniest drops

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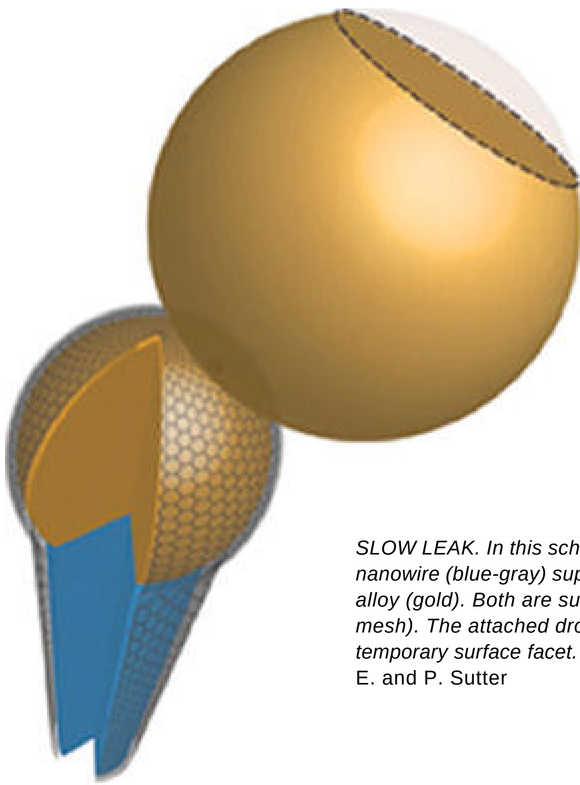
Physicists have constructed a pipette that dispenses a billionth of a trillionth of a liter, a droplet that's a thousand times as small as volumes previously achieved. The behavior of these zeptoliter-size drops challenges an accepted theory describing how drops crystallize as they cool, the researchers say.



*SLOW LEAK. In this schematic of the pipette, the germanium nanowire (blue-gray) supports a reservoir of gold-germanium alloy (gold). Both are surrounded by a carbon shell (dark mesh). The attached droplet of melted alloy shows a temporary surface facet.*
E. and P. Sutter

To build the pipette, Eli A. Sutter and Peter W. Sutter of the Brookhaven National Laboratory in Upton, N.Y., started with a germanium nanowire. It supports an initially solid reservoir of a gold-germanium alloy. A carbon shell encapsulates the assembly, which is about 2 micrometers long.

The researchers place the pipette in a vacuum chamber within a transmission-electron microscope. To dispense liquid, they melt the reservoir of gold-germanium alloy and then focus a beam of electrons on the tip.

The beam punctures the carbon shell, Peter Sutter says.

The liquid alloy oozes through the hole and slowly forms a drop up to 40 nanometers in diameter and 35 zeptoliters in volume. "It's the smallest amount of fluid that, to our knowledge, anybody has dispensed in a controlled fashion," Peter Sutter says.

A filament of liquid alloy connects the drop to the tip. Having the drop almost free of contact makes it useful for studies of crystallization, explains Peter Sutter. Typically, researchers have supported drops on another surface, which influences how they crystallize.

For their crystallization studies, the researchers slowly cooled the pipette and its drop until they were a few degrees above the liquid alloy's freezing temperature of 300°C. At this temperature, the electron microscope images show that inside the drop, the alloy remained liquid. But "what used to be a round drop all of a sudden isn't round anymore," Peter Sutter says. Areas on the drop's surface developed facets, a property associated with solids.

The facets disappeared and reappeared across the surface until the alloy reached its freezing temperature, at which point the drop solidified completely.

These experiments call into question the common view that crystallization in liquid drops proceeds from the inside out. "We see at the surface that solidlike behavior sets in at a temperature where the interior of the drop is still liquid," Peter Sutter says.

The observed mechanism may govern the crystallization of nanometer-size metal-alloy drops in general and possibly the freezing of other liquid drops, the researchers report online and in an upcoming *Nature Materials*.

The report combines a "very nice" technical achievement with a convincing finding, comments Uzi Landman, a physicist at the Georgia Institute of Technology in Atlanta.

"It's the first experimental proof" of this mode of crystallization, Landman says. To determine how general the effect is, "it would be nice to see more examples of different types of materials," he adds.

The Brookhaven scientists say that they have begun building pipettes that dispense different metal alloys.