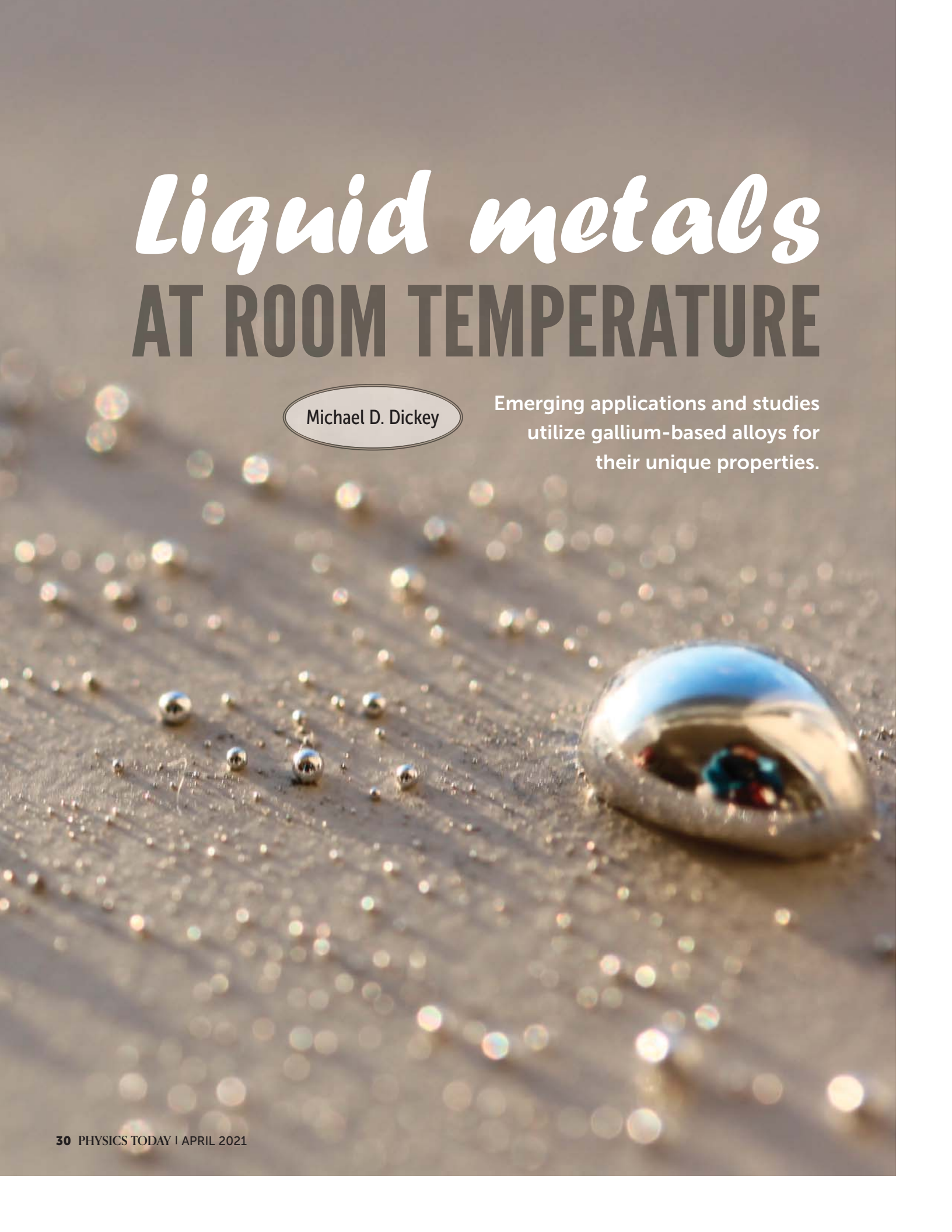




# *Liquid metals* **AT ROOM TEMPERATURE**

Michael D. Dickey

Emerging applications and studies  
utilize gallium-based alloys for  
their unique properties.

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he phrase “liquid metal” readily evokes images of toxic mercury, mad hatters, and the menacing villain from the movie *Terminator 2*. (Incidentally, the villain’s computer rendering was based on mercury.) Suffice it to say, the phrase often carries negative connotations.

However, there is hope for liquid metals: Gallium has a melting point near room temperature and doesn’t share Hg’s toxicity. When Ga was discovered in 1875, Hg had already been known for more than 1000 years and was being used in thermometers, electrochemical reactions, and dental fillings. But because Ga reacts readily with oxygen to form a thin oxide crust on its surface, it could not readily replace toxic Hg.

The formation of surface oxides is common. Noble metals such as platinum and gold are rare examples of metals that do not readily oxidize. In contrast, Ga oxidizes almost instantly—likely within microseconds in air—much like aluminum, its neighbor on the periodic table. Surface oxides can be beneficial: They protect the underlying metal from further oxidation. Known as passivation, the formation of thin surface oxides shields metals like Al and stainless steel from O in the air and thereby prevents rusting.

The surface oxide on Ga is problematic, however, for applications that require a free-flowing liquid. It can also impede electrochemical reactions, and that explains why chemists still opt for Hg rather than Ga as an electrode in certain experiments. Ga also corrodes in water, one of several reasons why dentists continued for many years to fill cavities with Hg amalgams. Despite its toxicity, Hg is not easy to replace.

Over the past decade, Ga and its liquid alloys have received renewed interest. They have a wide range of interesting properties that researchers are now exploring. Simply stated, Ga is a solution looking for the right problems.

### The most interesting element?

The electrical and thermal properties of Ga are metallic, yet its melting temperature is just 30 °C—low enough that it would melt if you held it in your hand. That temperature can be lowered further by adding other metals, such as indium or tin. The two most popular options are eutectic gallium indium (EGaIn) and gallium indium tin (Galinstan).

Conceptually, the melting and freezing point of ma-

terials should be the same. One might thus expect Ga and its alloys to freeze on a cold day. Yet the liquids tend to become supercooled, meaning they freeze at temperatures well below their melting points. Consequently, once melted, Ga and

many of its alloys remain liquid at or below room temperature. For example, for months researchers in my laboratory have left EGaIn in a freezer at –15 °C—a remarkable 30 °C below the material’s melting point. It has yet to freeze. The supercooling effect becomes even more pronounced in small particles.

Like water, Ga is one of the few materials that expands in volume when frozen. It therefore becomes more electrically conductive in the liquid state, which is also unusual for metals. The remarkable phase behavior and low melting point can be attributed to Ga’s unique bonding: Rather than form bonds between atoms, as other metals do, Ga forms bonds between covalently paired dimers.

Ga has effectively zero vapor pressure at room temperature. In fact, it must be heated to above 2400 °C before it will boil. Whereas water, ethanol, and other familiar liquids will evaporate at ambient conditions, Ga will not. Why does that matter? Ga can be handled openly outside a safety hood without fear of inhalation. It can even be placed in the very low-pressure vacuum environments that scientists often use to study materials. Normally those low pressures would cause liquids to evaporate, but not Ga.

Like most molten metals, Ga has a low bulk viscosity. In fact, its viscosity is just twice that of water. And at 500 mN/m, Ga’s surface tension is the largest of any liquid at room temperature; for comparison, water’s surface tension is 72 mN/m, and ethanol’s is 22 mN/m. Thus, in the absence of a surface oxide layer, the metal flows like water due to its low viscosity and naturally forms spherical shapes due to its high surface tension.

Importantly, Ga has low toxicity. Its salts have been approved by the US Food and Drug Administration for human use in applications such as MRI contrast imaging. Although it should still be handled with care since it is not a regular dietary nutrient, Ga appears to be safe because the body has the ability to remove it.

Although Ga is relatively abundant in the earth, it is difficult to mine on its own. Instead, it is found as an impurity in alumina—the precursor to aluminum—which

makes it expensive despite its abundance; one gram costs around \$0.25–\$1.00. Ga has industrial applications as a precursor for compound semiconductors such as Ga arsenide and Ga nitride. Researchers are exploring gallium (III) oxide ( $\text{Ga}_2\text{O}_3$ ), a wide bandgap semiconductor, as a promising material for power electronics—that is, solid-state semiconductor devices that control electric power. Such devices are becoming increasingly important for electric vehicles and renewable energy. Commercial uses of liquid Ga are still in the early stages of development, but several companies are beginning to harness its unique properties. This article briefly explains some of these emerging applications.<sup>1</sup>

## Printing and patterning

Perhaps Ga's most important property for applications is its ability to rapidly form an oxide skin on its surface.<sup>2</sup> The oxide layer is a few nanometers thick; for reference, the diameter of a human hair is about 30 000 times thicker. As mentioned above, the native oxide layer was historically found to be a nuisance. However, it enables patterning of liquid metal into shapes that would not be possible with conventional liquids, especially ones with low viscosity and high surface tension. The rapidly formed surface oxide shell is behind the shapes shown in figure 1.

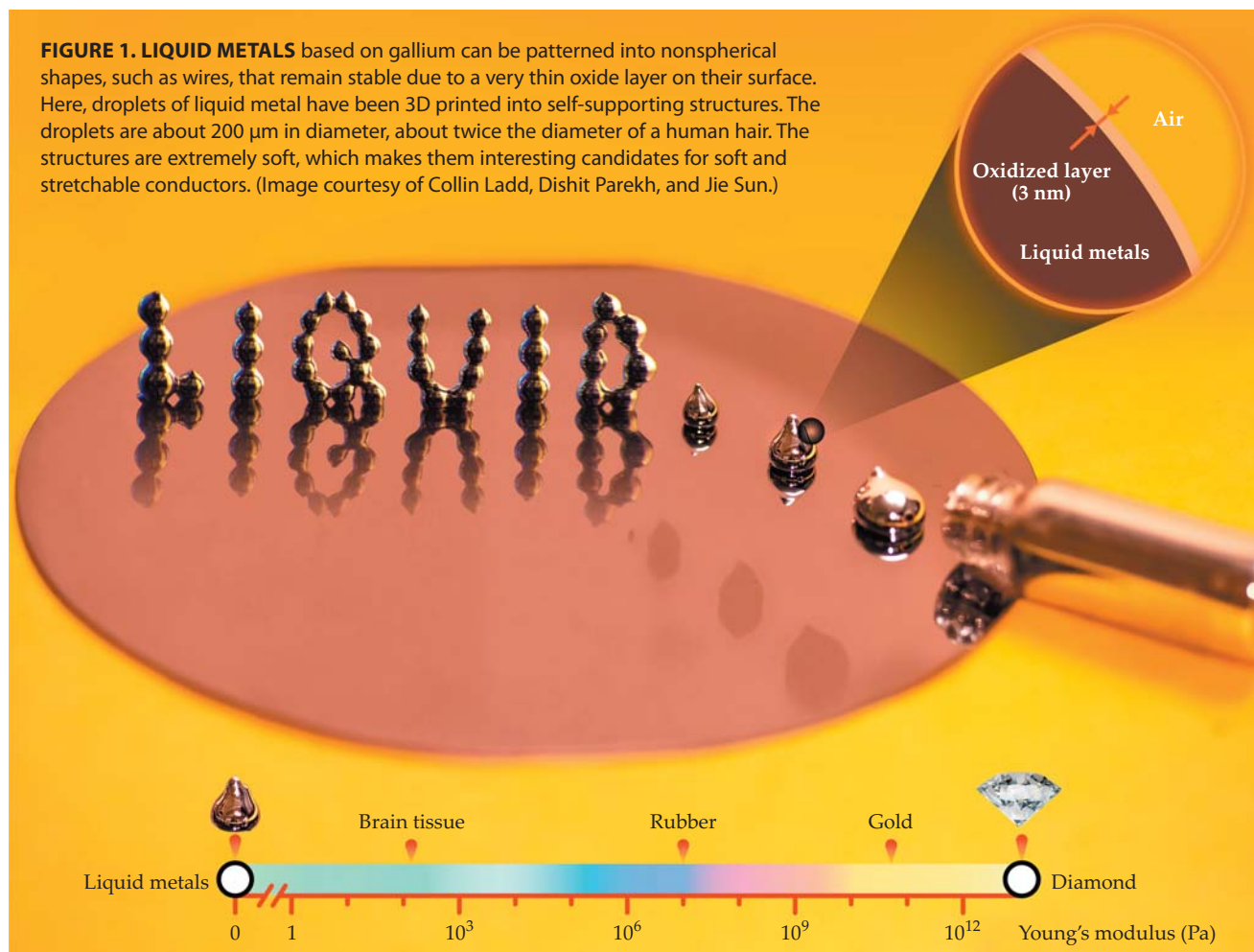
Liquid metals can be printed and patterned in ways that

simply are not possible with conventional solid metals.<sup>3</sup> Those that are liquid at room-temperature can be, for example, injected, painted, smeared, wetted, molded, and printed. (Figure 1 shows one example of printing.) Despite being thin, the oxide layer stabilizes the resulting structures. Above a critical surface stress, however, the oxide layer breaks and the low-viscosity metal flows readily.

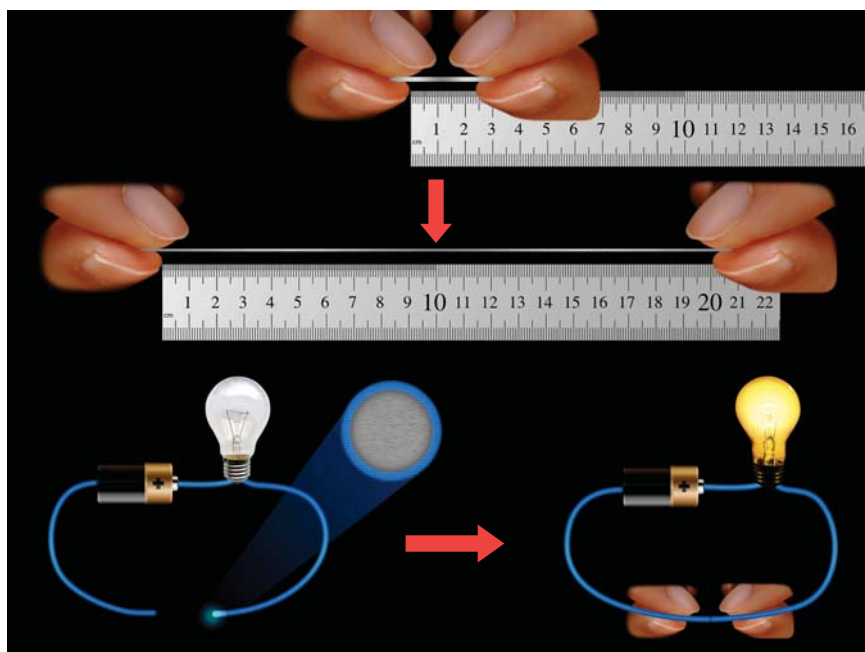
The critical surface stress, a force per length, is a material property of the oxide that can be combined with the curvature of a surface to determine the critical stress—force per area—required to break the oxide. Gravitational forces can exceed the critical stress of a spherical structure when its diameter exceeds just a few millimeters, whereas a 100- $\mu\text{m}$ -diameter vertical cylinder can grow to be several cm tall without collapsing.

In the absence of stress, an oxide layer forms rapidly and helps maintain the shape of the metal. It is similar to a scaled-down waterbed mattress—a thin, solid barrier contains the liquid. But a waterbed would leak if punctured, whereas the liquid Ga's shell can reseal when broken. The ability of the metal to flow by breaking the oxide combined with the ability of the oxide to re-form allows patterning of the liquid metal.

Perhaps the simplest way to pattern the metal is to inject it into tubing. If the tubing has a diameter smaller than about a millimeter, then it is considered a microchannel, which is useful for manipulating fluids for various applications. Among







**FIGURE 2. WIRES** made from liquid metal can have the best of both worlds: the conductivity of a metal and the mechanical properties of rubber. A hollow elastomeric fiber filled with liquid metal (top) can be stretched to 10 times its original length. Its stretchiness is limited only by the properties of the polymer. Liquid metal can also form circuits (bottom) that electrically self-heal after being cut. The metal remains flush with the cut interface because it forms an oxide layer when exposed to air, and the interfaces merge when put in contact. Encasing the metal in an insulating shell of self-healing polymer (blue) allows the circuit to heal mechanically. (Image courtesy of Jie Sun.)

them are so-called lab-on-a-chip devices that can, for example, miniaturize assays of biological liquids. The ability to inject liquid metal into such channels is a simple way to create electrodes, pumps, valves, and other microfluidic components.<sup>4</sup>

Liquid metal can also be used in 3D printing, which is a popular technique for creating structures in an additive manner. Most commercial 3D printers utilize polymers, although the resulting polymeric structures' utility could potentially be increased through multimaterial printing. The ability to print liquid metals at room temperature is enticing because the metal can be incorporated into structures with plastics, elastomers, and other temperature-sensitive materials.

The surface oxide that forms on liquid metals causes the materials to adhere to most surfaces, a property that is necessary for maintaining a printed shape. In the absence of the oxide, the metal beads up to form spherical shapes that minimize surface energy. However, there are a few surfaces to which liquid Ga can adhere without its oxide layer. For example, it can reactively wet solid metal substrates by forming metal-metal bonds.

## Soft and stretchable metal

Conductors made from liquid metal adopt the mechanical properties of the encasing material. In other words, placing liquid metal inside a rubber tube produces a wire that can maintain metallic conductivity while being stretched like a piece of rubber. That property is useful for creating soft, stretchable

electronics.<sup>5</sup> It also eliminates a long-standing trade-off encountered in conductive composites: Adding solid conductors such as metallic or carbon particles to rubber increases its conductivity but changes its mechanical properties. Liquid metals, on the other hand, do not significantly alter the rubber's mechanical properties. That ability has been exploited to create wires that can stretch to nearly 10 times their original lengths while maintaining their metallic conductivity, as shown in figure 2.

Likewise, liquid metal has been utilized to form stretchable electric interconnects between small, rigid chips embedded in elastomer. The overall soft devices harness the sophistication and capabilities of microelectronics and maintain functionality during stretching. Liquid metal thus promises to advance technology such as wearable electronics,

skin-mountable devices, and soft sensors that mimic skin's mechanical properties.

Liquid Ga conductors can be designed to heal themselves when damaged.<sup>6</sup> As illustrated in figure 2, when a liquid-metal wire is cut, it will rapidly form an oxide skin that keeps the material from leaking out of a circuit. When the broken wire ends are brought back together, the exposed interfaces merge—the thin oxide on each side breaks and the liquid reconnects—to re-form the electrical connection. If the metal wires are encased in a special self-healing polymer shell, the entire circuit can heal when brought into contact.

Soft electrodes for probing surfaces can also benefit from liquid metal.<sup>7</sup> Rather than depositing metal electrodes using expensive equipment that often requires high temperature and vacuum, the liquid metal is simply placed against a surface where it makes gentle contact. The electrode can then measure the electrical properties of molecules on the surface. That ability has helped advance the field of molecular electronics in which molecules are investigated as the smallest building blocks for electronic devices such as transistors.

Traditional wires, such as those made from copper, can move and bend when touched but do not change their cross-sectional geometries. Liquid-metal conductors, on the other hand, can change their geometries in response to deformation. Such changes can alter a device's capacitance or resistance, depending on the design, and can be used to detect touch, strain, and other modes of deformation. Antennas made from liquid metal can shift their resonant frequency in response to strain.

Recently, students in my research group harnessed touch-responsive circuitry to create soft materials that performed simple logic operations without the use of conventional transistors.<sup>8</sup> We were motivated by the octopus: The neurons distributed throughout the animals' arms eliminate the need for complex neuronal wiring to send signals back and forth between sensors (their arms) and a centralized processor such as the brain.

To demonstrate the concept of "materials logic," we created circuits composed of liquid-metal wires in which electricity can

travel along multiple paths. Pressing a given path decreases the cross-sectional area of the wire and thus increases the local resistance. That change can divert current to other paths or alter the potential drops through parts of the circuit. With proper design, such a soft circuit can generate a response that depends uniquely on the location and number of touch points. The concept may be useful for designing smart materials that respond to tactile inputs in complex and appropriate ways. (For more about tactile circuits, see the Quick Study by Adam Fortais, *PHYSICS TODAY*, November 2020, page 62.)

## Surface tension modulation

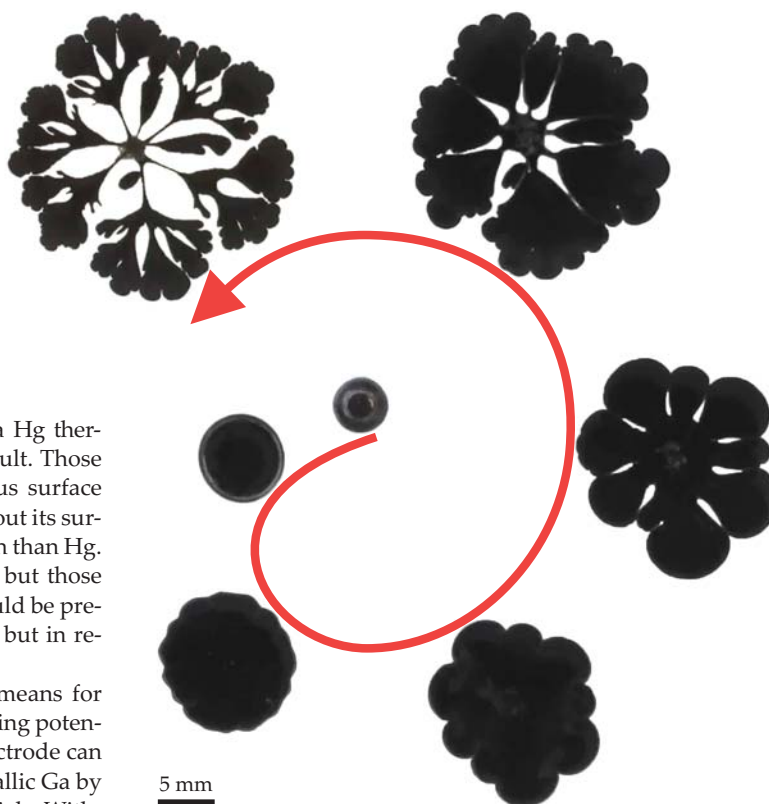
Anyone who has had the misfortune of breaking a Hg thermometer knows about the spherical droplets that result. Those droplets form because liquid metals have enormous surface tensions in the absence of native oxides. In fact, without its surface oxide layer, Ga has an even larger surface tension than Hg. A native oxide can be removed by an acid or base, but those liquids are corrosive. In principle, the oxide layer could be prevented by working in an oxygen-free environment, but in reality oxygen is difficult to avoid.

Electrochemical reduction provides a practical means for removing Ga's oxide layer. Applying a modest reducing potential of, say,  $-1$  V to the metal relative to a counter electrode can convert the  $\text{Ga}^{+3}$  on the oxidized surface back to metallic Ga by providing electrons at energetically favorable potentials. Without the oxide, the metal readily beads up (figure 3, center). The oxide spontaneously re-forms once the potential is turned off, although the metal can be kept oxide-free if the experiments are performed in acidic or basic electrolytes.

My research group discovered an unexpected phenomenon that occurs on applying a positive potential of, say,  $+1$  V to a droplet of liquid Ga in a basic solution of 1 molar sodium hydroxide: The droplet spreads out into fractals,<sup>9</sup> as shown in figure 3. Snowflakes can form fractals of ice crystals, but when melted, they bead up into a droplet of water due to surface tension. How, then, is it possible to form a fractal with a liquid that has nearly 10 times the tension of water?

Applying a positive potential drives the formation of the surface oxide. One might expect the oxide layer to form a crust on the surface of the metal and restrict its flow. We found, however, that during electrochemical oxidation, the droplets behave as if their surface tension is very low.<sup>10</sup> The NaOH slowly but continuously dissolves the oxide being deposited on the droplet's surface, so the metal can flow despite the oxide formation. With the tension significantly lowered through electrochemical oxidation, gravity flattens the normally spherical drop and small gradients in surface tension cause so-called Marangoni flows that contribute to the unusual fractal patterns.

In a well-known phenomenon called electrocapillarity, charge that gathers across a metal–electrolyte interface can modestly lower a metal droplet's surface tension. However, the observed behavior cannot be explained by electrocapillarity alone for several reasons—most notably that the magnitude of the change in tension, from more than  $500$  mN/m to near zero, is too large to be caused by an approximately  $1$  V potential; such a small potential would only reduce the tension to about  $400$  mN/m. Our experiments establish that electrochemical



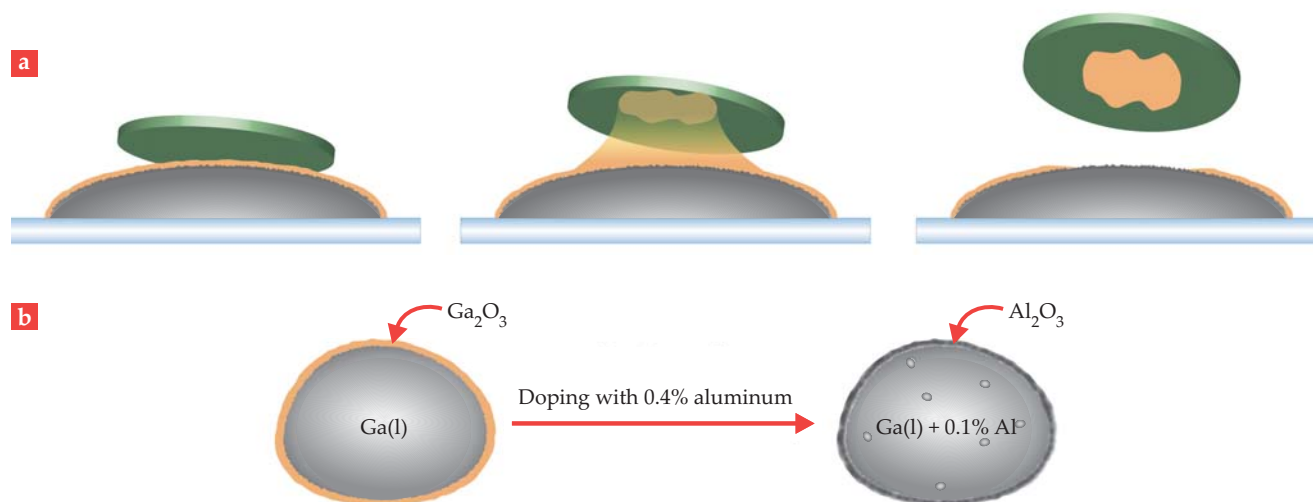
**FIGURE 3. GALLIUM DROPLETS** have enormous surface tension in the absence of a surface oxide layer and therefore form spheres (center). However, putting a droplet in an electrolyte and applying a positive potential drives surface oxidation. Here, a droplet is connected to a small wire from below (not shown) and submerged in 1 molar sodium hydroxide electrolyte; it is photographed from the top down and appears black because it is backlit. The oxidation process causes the metal to spread into fractals, which suggests that the effective tension is near zero under the conditions shown. (Image courtesy of Collin Eaker and Jie Sun.)

oxidation lowers the metal's surface tension.<sup>9</sup> Understanding the complex behavior is an ongoing area of research.

## Liquid-metal reactors

An intriguing recent discovery suggests that the thin oxide layer that forms on liquid metal can be removed by exfoliation.<sup>11</sup> The technique is an attractive way to deposit thin oxide films onto surfaces at room temperature, and it can be utilized for transferring thin insulators, conductors (including indium tin oxide), and semiconductors onto arbitrary surfaces, as illustrated in figure 4a.

Once deposited, the oxide layers can be chemically transformed into other species—for example, gallium oxide can become gallium sulfide. Another way to alter the composition of the surface oxide is by doping the liquid Ga droplet with small amounts of other metals prior to exfoliation. If the formation of the dopant metal's oxide is more energetically favorable, it can form preferentially over  $\text{Ga}_2\text{O}_3$ . For example, adding trace amounts of Al to Ga can produce  $\text{Al}_2\text{O}_3$  on the surface of the metal (figure 4b). Liquid metals can also be used as substrates to grow two-dimensional materials, such as



**FIGURE 4. OXIDE SPECIES** form when liquid metal reacts with air. **(a)** Those species can be transferred to other surfaces by exfoliation. The process offers a simple route for creating ultrathin oxide films at room temperature. **(b)** Adding small amounts of a reactive dopant to liquid gallium can transform the surface from the native oxide,  $\text{Ga}_2\text{O}_3$ , into a different chemical species. For example, adding 0.4% aluminum causes the surface to become  $\text{Al}_2\text{O}_3$ . (Images courtesy of Jie Sun.)

graphene, and may offer a facile way to transfer them to other surfaces.

The ability to alter the surface chemistry of liquid metal may be useful for catalysis or electrochemistry. For example, recent experiments show that trace amounts of cerium added to Ga naturally segregate to the surface of the liquid and lower the energy required to reduce carbon dioxide into solid carbonaceous species.<sup>12</sup> In addition, the carbon species do not adhere to the liquid metal, which prevents them from “coking,” or building up on the droplets and blocking reaction sites. Improving the efficiency of  $\text{CO}_2$  reduction is of great practical

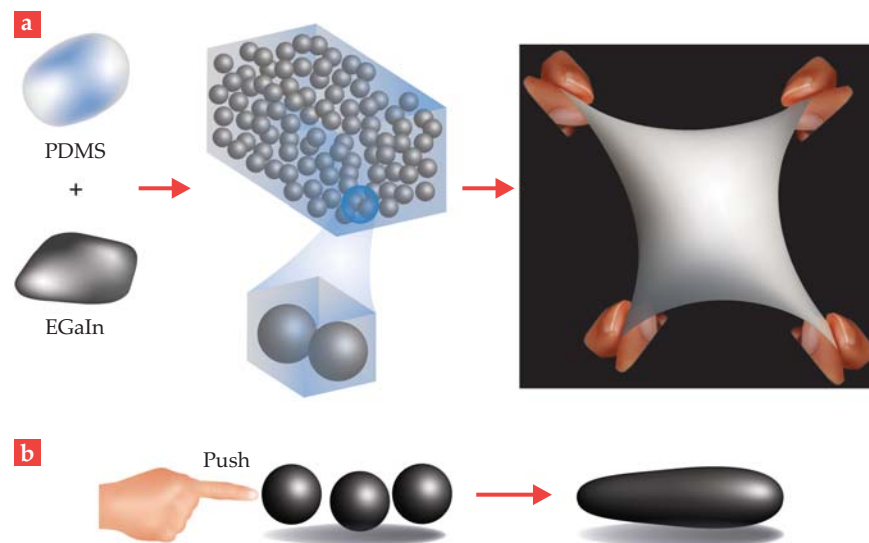
interest considering its impact as a greenhouse gas. Liquid-metal nanoparticles have also been shown recently to initiate polymerization—that is, to cause monomeric molecules to react and form polymers.

## Droplets and composites

Liquid metals can be mixed into polymer matrices to form composites with new or enhanced properties.<sup>13</sup> It is well-known that adding solid particles to a polymer can significantly change the polymer’s mechanical properties; for example, tire makers toughen rubber tires by adding carbon particles. Yet the same solid particles can make elastomers—rubbery materials—less stretchy. In contrast, liquid-metal particles have a minimal impact on rubber’s extensibility because the particles themselves are liquid (see figure 5).

Depending on the particle loading and size, liquid-metal particles can have non-negligible effects on an elastomer’s mechanics, and understanding those effects is an ongoing area of research. Interestingly, adding liquid metal can significantly increase an elastomer’s tear strength by dulling cracks, which is where stress concentrates and leads to failure; consider how much easier it is to tear fabric if it is first nicked with scissors. (For more on how elastomers tear, see *PHYSICS TODAY*, February 2021, page 14.)

Adding liquid-metal particles to elastomers can increase the resulting composite’s conductivity. Stretching rubbery composites loaded with solid particles, such as silver flakes, causes the particles to move apart and thereby increases the material’s thermal and electrical resistance. In contrast, elongation of rubber loaded with liquid-metal particles causes the particles to elongate. The transition from spheres to ellipsoids generates anisotropic



**FIGURE 5. STABLE PARTICLES** of liquid metals can be formed by simply stirring the metal in the presence of another liquid. **(a)** Mixing liquid metal (eutectic gallium indium; EGaIn) into silicone (polydimethylsiloxane; PDMS) creates a soft composite upon curing the silicone. Adding solid particles to a rubber normally makes it stiffer, but with liquid particles, the composite remains soft. **(b)** Liquid particles can easily be mechanically sintered by pushing them together (shown here in an oversimplified schematic). Likewise, straining or compressing composites that contain liquid metals can lead to unusual “piezo” properties—those that change when the material is squeezed—due to the particles’ geometric changes within the elastomer. (Images courtesy of Jie Sun.)



thermal conductivity—that is, the ability to conduct heat in the direction of strain is enhanced.<sup>14</sup>

Recent studies show that adding magnetic particles such as iron to liquid-metal composites can result in piezoconductivity, meaning the material becomes more conductive when strained; most composites instead possess piezoresistivity. In addition, composites loaded with liquid-metal particles can self-heal electrically when cut because the metal particles smear across the damaged region.

Liquid-metal particles formed in liquid media can have diameters with length scales from tens of nanometers to hundreds of microns. Sonication—agitation by ultrasonic vibrations—can break the metal into smaller droplets that can be stabilized by an oxide layer or by polymers grafted to the surface. The many applications for such particles in nanotechnology include self-propelled particles, new types of phase behavior, dual liquid–solid particles, drug delivery, catalysis, and optics.<sup>15</sup>

## A better reputation

Ga is one of the most interesting elements on the periodic table because of its low melting point, negligible vapor pressure, high surface tension, low viscosity, and metallic properties. Its reactivity has historically been considered a hindrance, since the liquid metal rapidly forms a thin surface oxide that precludes certain applications.

In the right context, however, both the oxide and the surface reactivity can be beneficial. The oxide skin that forms on liquid Ga allows for the assembly of soft and stretchable conductors that can maintain metallic conductivity at unprecedented lev-

els of strain. It also enables 3D printing and other patterning methods that would be impossible with solid metals, and it stabilizes droplets inside composite materials to generate unique thermal, electrical, and mechanical properties. Furthermore, liquid Ga permits electrochemical reactions that dramatically modulate the material's interfacial tension. The metal can be used as a “reactor” that sheds thin oxide sheets and presents reactive species on its surface.

Physicists have many opportunities to contribute to the fundamental understanding of liquid Ga's interesting properties and the applications they enable. With such a bright future, the term “liquid metal” should shed its once-negative connotation.

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