STICKY LIQUID METALS

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Introduction

Liquid metals are interesting because they have the ability to flow like a fluid, yet have metallic electrical, thermal, and optical properties. Most metals melt at significantly elevated temperatures, which is impractical for handling or interfacing molten metals with materials of interest to the adhesion community (e.g. polymers). Mercury is the most familiar liquid metal with a low melting point, but it is notoriously toxic.

Our group has been studying gallium and its alloys. Gallium melts at approximately 30 °C and thus would melt if you held it in your hand. It is possible to add other metals to gallium (e.g. indium, tin) to lower the melting point below room temperature. Gallium is considered to have low toxicity and its vapor pressure approaches zero at room temperature, which means it will not evaporate and therefore is safe to handle without worry of inhalation. Its viscosity is water-like (approximately twice that of water). It has an electrical conductivity that is an order of magnitude lower than copper, but orders of magnitude higher than other liquids (e.g. salt water).

Importance of the 'Sticky' Surface Oxide

For the applications explored by our group, the most important property of gallium is its ability to react rapidly with oxygen in the air to form a thin (~3 nm thick) native oxide composed of gallium oxide. Most metals react with air to form an oxide, so by itself, that result is not surprising. Nevertheless, the presence of the oxide has significant implications on the way the metal flows and adheres to surfaces. Liquid metals have enormous surface tension, which is why mercury forms spherical shapes. However, the presence of the surface oxide allows the metal to maintain shapes that would normally be prohibited due to surface tension. **Figure 1** shows an example in which the liquid metal is stabilized in non-spherical shapes due to the oxide. The oxide layer is passivating, which means it should not get thicker with time. It is a few nanometers in thickness, but has a profound impact on the way the metal behaves at small (sub-mm) length scales.

Applications

We have taken advantage of this property to enable 3D printing of the liquid metal[1] into shapes such as wires, electrodes, and antennas that would not be possible using existing methods to pattern metals[2]. **Figure 2** shows an example of the NC State logo printed on a surface with liquid metal. The patterning can be done entirely at room temperature using a variety of techniques (e.g. screen printing, stencil printing, microfluidic injection, etc.)[3]. The liquid metal features can be encased and then sacrificially removed to create microchannels or microvasculature (which can then be used to flow in other fluids)[4]. The metal can also be injected into capillaries[5], microchannels[6], and 3D printed parts[7] to add metallic functionality to plastic objects[8]. We have used this process to create electrodes[9] and antennas[10], for example. If the plastic object is composed of a polymer that can self-heal, then it is possible to create self-healing liquid metal wires that can regain electrical continuity after being cut[11]. In addition, liquid metal wires are stretchable. Normally if you add metal to a polymer to render it conductive, you alter the overall mechanical properties. In contrast, the addition of the liquid metal to the polymer has no influence on the overall mechanical properties because the metal is a liquid. As a result, it is possible to create wires that maintain metallic conductivity up to hundreds of percent strain (i.e. if you inject the metal into a rubbery material, you will achieve a rubbery wire).[12] These types of stretchable wires may be useful for stretchable electronics, wearables, and even soft electronics (e.g. for emerging classes of soft robotics).[13]

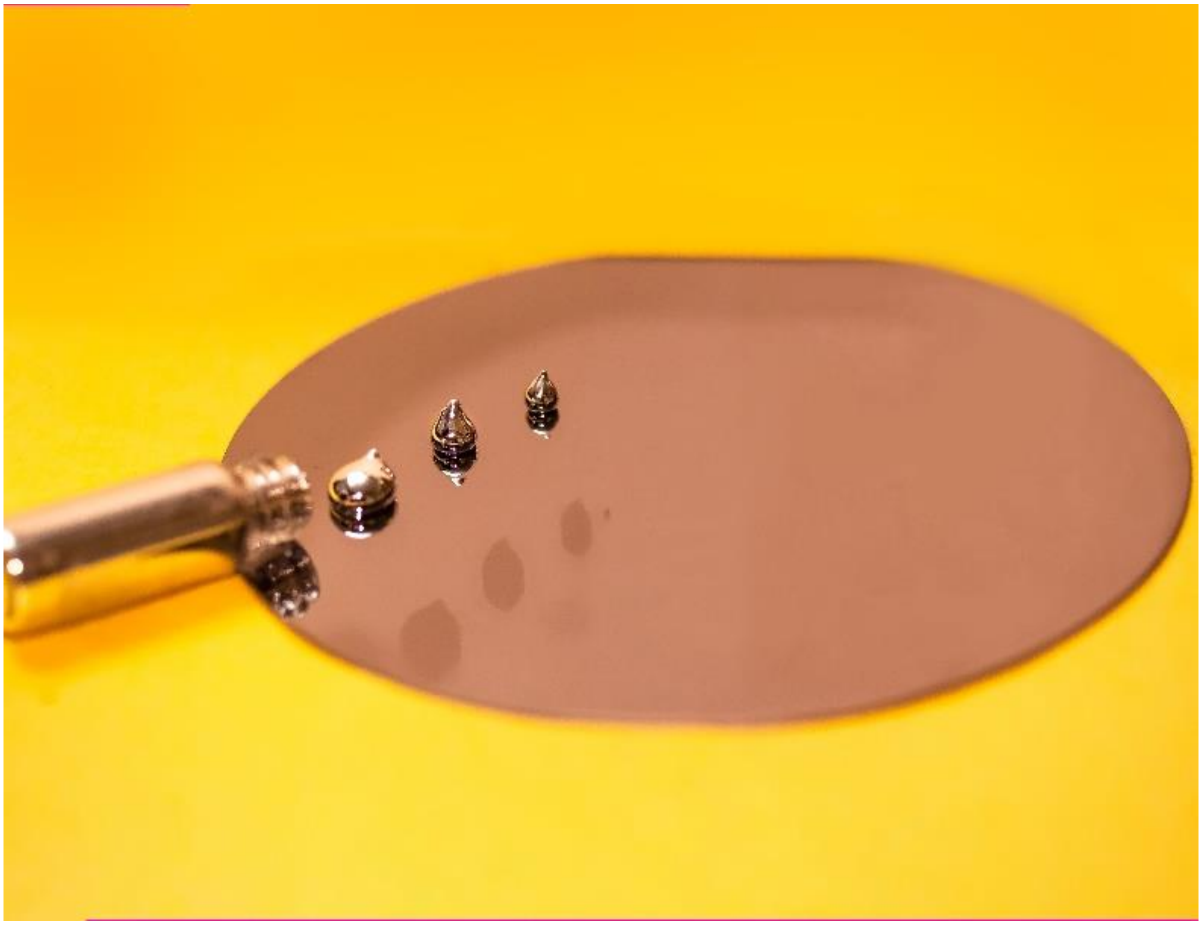

Figure 1. (Left) Droplets of liquid metal maintain non-spherical shapes due to the presence of the nm-thick oxide layer. Normally, droplets of liquid would assume spherical shapes due to surface tension.

Adhesion

The presence of the oxide has significant implications for the adhesion of the metal to surfaces. Normally, liquid metals would not adhere to most surfaces due to its large surface energy. However, the presence of the oxide allows the metal to adhere to almost all surfaces. Other groups have utilized this property to make conductive adhesives[14].

We have utilized electrochemistry to remove and deposit the surface oxide[15]. Removing the oxide (by applying a reducing potential of ~ -1 V to the metal in the presence of electrolyte) creates a bare metal with high surface tension[15,16]. Surprisingly, depositing the oxide (by applying an oxidative potential of ~ +1V to the metal in the presence of electrolyte) causes the effective interfacial tension to drop significantly[17,18]. Our results suggest the tension can approach zero due to the deposition of the oxide. The ability to modify surface tension is an attractive way to move and manipulate the shape of liquid metals[19]; for example, it is possible to create shape reconfigurable antennas in this way[20,21].

Figure 2. Liquid metal printed in the NC State logo. This shape is maintained solely due to the native oxide that helps preserve the shape and adhere the metal to the surface.

Conclusions

Liquid metals are exciting materials because they have such unique properties. For the work in our group, the native oxide that forms on the metal is critical to enable adhesion of the metal to surfaces and the ability to pattern the metal into non-spherical shapes. This makes it possible to 3D print the metal and shape the metal into useful geometries such as wires, electrodes, and antennas using microfluidic injection. The resulting structures are liquid and therefore the devices that utilize these structures adopt the mechanical properties of the encasing materials. Thus, it is possible to make stretchable wires. There are many exciting future applications of this special material.

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