Eutectic Gallium-Indium (EGaIn): A Liquid Metal Alloy for the Formation of Stable Structures in Microchannels at Room Temperature**

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This paper describes the rheological behavior of the liquid metal eutectic gallium-indium (EGaIn) as it is injected into microfluidic channels to form stable microstructures of liquid metal. EGaIn is well-suited for this application because of its rheological properties at room temperature: it behaves like an elastic material until it experiences a critical surface stress, at which point it yields and flows readily. These properties allow EGaIn to fill microchannels rapidly when sufficient pressure is applied to the inlet of the channels, yet maintain structural stability within the channels once ambient pressure is restored. Experiments conducted in microfluidic channels, and in a parallel-plate rheometer, suggest that EGaIn's behavior is dictated by the properties of its surface (predominantly gallium oxide, as determined by Auger measurements); these two experiments both yield approximately the same number for the critical surface stress required to induce EGaIn to flow (~0.5 N/m). This analysis–which shows that the pressure that must be exceeded for EGaIn to flow through a microchannel is inversely proportional to the critical (i.e., smallest) dimension of the channel–is useful to guide future fabrication of microfluidic channels to mold EGaIn into functional microstructures.

1. Introduction

This paper describes a study of the behavior of the electrically conductive fluid metal eutectic, gallium-indium (EGaIn, 75% Ga 25% In by weight, ~15.5 °C melting point) when injected into microfluidic channels at room temperature (RT).

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The ability to inject metal into microchannels is important for the co-fabrication[1] of low-cost, flexible electronic components such as microscale wires, circuit elements, electrodes, and electromagnets.[2] We show here that EGaIn i) rapidly flows into and fills microchannels at RT when a critical pressure — the value of which depends on the geometry of the channel — is applied to the inlet of the channel, and ii) maintains structural stability (i.e., does not spontaneously retract from the channel) when this pressure is relieved. In some applications, EGaIn may have an advantage over molten solders (used in a set of methodologies called "microsolidics"[2,3]), which require heating and cooling steps that increase the time needed for the fabrication process, and make it incompatible with heat-sensitive materials such as organics. For most applications requiring a liquid metal, EGaIn is superior to Hg, which readily fills microchannels at RT, but is toxic and forms unstable structures that spontaneously retract from the channels to minimize interfacial free energy. In this work, quantitative analysis of the behavior of EGaIn i) injected into a channel whose width varied along its length, and ii) in a parallel plate rheometer, allowed us to determine both the critical stress required to induce EGaIn to fill a channel of known cross-sectional dimensions, and the primary origin of EGaIn's rheological properties: a thin skin (mostly comprised of oxides of Ga, as determined by Auger spectroscopy) on its surface. This analysis provides guidelines for the design of microfluidic channels as molds for EGaIn.

1.1. Background

1.1.1. Metal (Solders) in Microchannels for Electronics

Injecting molten solder — typically, a low-melting solder such as In (melting point 157 °C) — into a microchannel, and allowing it to solidify by cooling, creates metallic microstructures. Solders, however, have three limitations: i) The temperatures required to melt even "low-melting" solders are too high to be compatible with many organic materials (especially biopolymers) of real or potential interest in devices. ii) The heating and cooling steps increase the processing time necessary to form the device. iii) The solidification of the solder produces mechanical stresses that result in structures that are susceptible to cracking and mechanical fatigue. Solders are self-healing (i.e., reheating mends cracks), but, for microfluidic applications, a material — for example, a fluid metal — that either never fails, or continually self-heals, is preferable.

1.1.2. EGaIn

The use of EGaIn in microchannels is, potentially, a room-temperature extension of the techniques used in microsolidics that addresses the limitations of conventional, higher-melting metals and alloys such as solders. EGaIn is a commercially available liquid metal alloy with the following attributes:

i) EGaIn is electrically conductive. The resistivity of EGaIn is $\sim 29.4 \times 10^{-6}\,\Omega\text{-cm}$;[4,5] this property allows EGaIn to be used as a contact electrode for the electrical characterization of thin-film organic and semiconductor devices.[6,7]

ii) The surface of EGaIn is covered with a thin "skin". The skin is apparent to the un-aided eye when a drop of EGaIn is placed on a substrate and the substrate is tilted (see movie M1 in the Supporting Information for a demonstration of this behavior); gravitational forces cause the EGaIn to redistribute (i.e. flow) underneath the confines of the skin. We analyze the composition of the skin in the Results and Discussion section.

iii) EGaIn is moldable. We define "moldability" as the ability to shape a material into free-standing, stable structures in which the surface free energy is not minimized. For example, small, stable cones (with tips as small as 1 μm in diameter) of EGaIn can be formed by bifurcating a drop of EGaIn under tension.[7] Notably, we have only been able to mold EGaIn on the μm-to-mm size scale (i.e., on the macroscopic scale, EGaIn is not moldable). This observation suggests that its moldability is a function of the ratio of surface area to volume (a ratio which increases as the size of the structure decreases), and is therefore attributable to the properties of its skin.

iv) EGaIn is a low-viscosity fluid in the absence of the skin. The bulk viscosity of EGaIn is $1.99 \times 10^{-3}\,\text{Pa·s}$ ($\sim$a factor of two greater than that of water).[8] This low viscosity allows it to be used as an electrically conductive, thermally stable lubricant,[9] and explains why it flows readily — within the confines of its skin — when a drop is placed on a tilted substrate (see movie M1 in Supporting Information).

v) According to the CRC Handbook, the components of EGaIn have "low orders of toxicity".[10] Indium has been used in dental fillings and Ga is a trace nutrient. Indium is also ubiquitous (as a solder) in the semiconductor industry.

1.2. Experimental Design

1.2.1. Surface Characterization

In order to characterize (chemically) the surface of EGaIn, we used Auger Electron Spectroscopy, a technique that monitors the emission of electrons — due to bombardment with X-rays — from only the first few atomic layers of a sample (unlike X-ray photoelectron spectroscopy, which probes as deep as 15 nm into a sample).

1.2.2. Forming Stable Metallic Microstructures in Fluidic Channels

We sought to study the conditions under which EGaIn would fill microchannels, and determine the stability of the resulting structures.

EGaIn is only moldable on the microscale. We therefore hypothesized that, although EGaIn pours readily out of a bottle, the ability to inject EGaIn into a micron-scale channel would depend on the pressure applied to EGaIn in the channel; this pressure, in turn, should depend on the cross-sectional dimensions of the channel. To test this hypothesis, we designed a microfluidic channel with constant height but narrowing width. This simple design — in which the width of the channel decreased continuously — allowed us to study the relationship between the critical pressure required to induce flow and this critical dimension, and from this relationship deduce the critical surface stress (i.e., the stress that must be exceeded before EGaIn flows). We made the channels out of PDMS using standard soft lithography techniques because these techniques are simple and widely used (and therefore easily adaptable by others). The channels were $\sim$40 μm deep (a dimension used previously with solders[2]), and the narrowest channel was $\sim$20 μm wide (limited by the height:width aspect ratio that can be achieved readily by photolithography).

We hypothesized that the skin on EGaIn would provide structural stability to the liquid metal once it filled the channel. To highlight the influence of the skin of EGaIn on its behavior in the channels, we also injected EGaIn into channels that were pre-filled with 10 wt% aqueous HCl, which removes the skin.[4]

We compared the behavior of EGaIn with Hg because Hg is, like EGaIn, a liquid metal at room temperature. Mercury is, however, a low-viscosity, Newtonian fluid (a fluid, like water or oil, with no elastic properties), and does not oxidize readily (i.e., does not form a skin) under ambient conditions.[10]

1.2.3. Rheological Characterization

We sought to quantify the response of EGaIn to stress — and thereby provide insight into the behavior of EGaIn

injected into microchannels — by performing parallel-plate rheometry.[11]

2. Results and Discussion

2.1. The Nature of the Surface of EGaIn

To determine the chemical composition of the skin of EGaIn under different conditions, we used Auger spectroscopy (Physical Electronics Model 660 Scanning Auger Microscope) to analyze samples of EGaIn i) as purchased (straight from the bottle, purchased from Aldrich), ii) after "in situ" sputtering with argon (that is, we sputtered the EGaIn without removing it from the high vacuum conditions — $\sim 5 \times 10^{-9}$ torr — found within the chamber of the spectrometer), and iii) after exposure to air for approximately one minute after sputtering. We compared the measured elemental ratios on the surface versus those in the bulk (1:5 atomic ratio of In:Ga). The Supporting Information (Figure S3) contains the Auger spectra from these three samples, along with the relative atomic percentages of In, Ga, and O in each sample.

The "as purchased" EGaIn showed an enhanced amount Ga and O at the surface (atomic % ratio In:Ga:O = 1:15:17) compared to the bulk, suggesting that the skin primarily consists of oxides of gallium; this result is consistent with the fact that Ga is highly reactive towards oxygen at room temperature. This finding is also consistent with previous studies: X-ray studies on pure Ga,[12] the majority component of EGaIn, and galinstan[13] — a eutectic alloy of 68.5% Ga, 21.5% In, and 10% Sn by weight that is also a liquid at room temperature — showed that both materials formed a skin of gallium oxide after even a brief exposure to air (180 L of oxygen, where 1 L = 10^{-6} Torr s), and that the oxide skin formed a highly uniform passivating layer that protected the bulk material from further oxidation (much like aluminum).[12]

A prior X-ray study of EGaIn — done under ultra-high vacuum — showed that the outermost layer of the surface of EGaIn became enriched with In after the ambient skin was sputtered off (this result is reasonable since In has a lower surface energy than Ga by $\sim 30\%$).[14] We performed Auger spectroscopy on EGaIn after in-situ sputtering and also found that the skin became enriched with In (atomic % ratio In:Ga:O = 5:6:1). Indium has been shown to cover as much as 94% of the surface of EGaIn after sputtering in ultra-high vacuum,[15] but, unlike Ga, In is slow to oxidize when it is exposed to oxygen.[16] When the indium does oxidize, it does not form a passivating layer on the surface of EGaIn.[16] We sought to test if the surface of the EGaIn reverts back to the initial state (i.e., enriched with Ga and O) by exposing the as-sputtered EGaIn to ambient air. Indeed, the surface of the EGaIn — after exposure to ambient air for one minute — returned to a state enriched with gallium and oxygen (atomic % ratio In:Ga:O = 1:10:14). The observation that gallium oxide dominated the surface of EGaIn after the sputtered surface was exposed to air implies that either i) the monolayer of In

was permeable to oxygen, such that gallium near the surface oxidized and then displaced In at the surface, or ii) oxygen reacted with the small amount of gallium in the monolayer, oxidized gallium, and gallium oxide then displaced In at the surface. Regardless of the mechanism, these results suggest that in the presence of air (i.e., in the ambient) the surface of EGaIn will be predominately covered with oxides of gallium.

Our conclusion that a surface oxide (in particular, gallium oxide) is responsible for the rigid skin agrees with previously reported[4] measurements of the surface tension of a pendant drop of EGaIn: The surface tension of EGaIn at ambient conditions is ~ 624 mN/m,[4] whereas the surface tension of EGaIn during exposure to aqueous HCl (which presumably causes acid-promoted dissolution of the oxide) is ~ 435 mN/m. The high surface tension of EGaIn measured under ambient conditions may therefore be explained by the presence of a surface oxide that is capable of supporting more weight from a pendant drop.

2.2. Behavior of EGaIn in Microchannels, and Comparison with Hg

We fabricated microchannels from PDMS, which is highly permeable to oxygen, by established soft-lithographic techniques.[17] A top-down schematic of the channel is included at the top of Figure 1. The channel consisted of a narrow portion (20 µm wide ×40 µm deep ×1 mm long) that connected symmetric inlet and outlet, both of which widened (to 1 mm wide ×40 µm deep) over a length of ~ 3 mm.

We filled individual microfluidic channels with EGaIn and Hg by dispensing a droplet (~ 0.1 mL) of the metal from a syringe into the inlet of the channel, and applying pressure to the inlet using regulated, pressurized nitrogen, while allowing the outlet to remain at atmospheric pressure. A digital pressure gauge, placed upstream of the inlet, measured the nitrogen pressure. We did not have to pre-treat the PDMS channels (with silanes, for example) to fill them with EGaIn or Hg. We used the PDMS channels immediately after exposing them to a plasma of air for one minute (pressure = ~ 500 mtorr), but those channels that sat in air for one week exhibited the same behavior.

2.2.1. Behavior of EGaIn and Hg Under Applied Pressure

Figure 1a is a back-lit, top-down optical micrograph of a channel partially filled with EGaIn in which the applied pressure was 85 kPa.[18] The EGaIn (which is opaque and therefore dark in this image) filled the inlet channel rapidly (in <1 s), but stopped at the entrance to the narrow channels. At pressures below 85 kPa, the EGaIn stopped short of the entrance to the narrow channels. Hg (right side of Figure 1a) behaved similarly to EGaIn, but only required 54 kPa to reach the narrow portion of the channel. Despite the application of pressure to the inlet, both images in Figure 1a are static: the center of mass of the metal was not moving when the image was taken because the pressure at the metal-air interface balanced
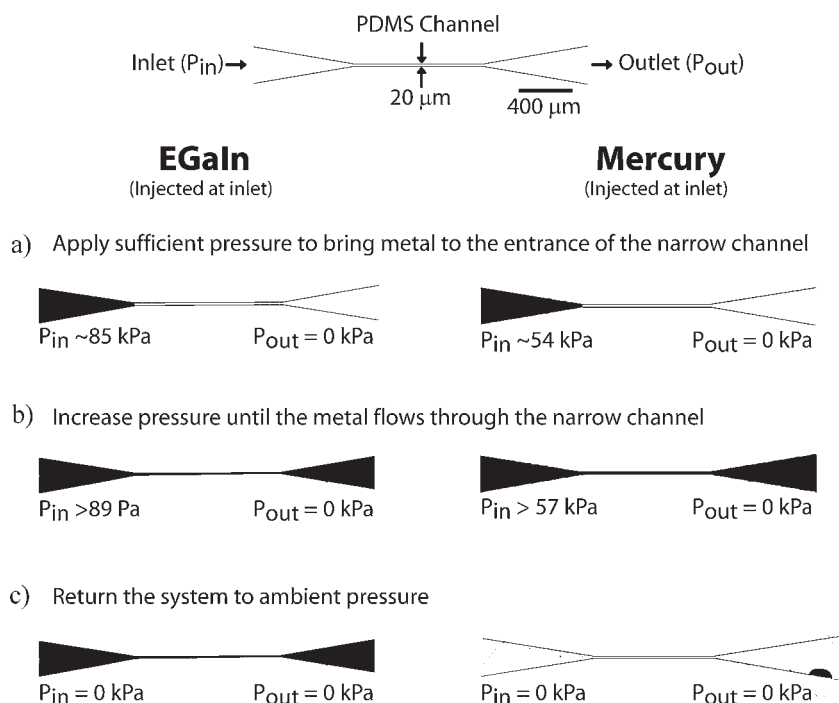
Figure 1. Examples of liquid metals in microchannels and their dependence on pressure. The dimensions of the channels fabricated from PDMS are labeled at the top of the figure. The remaining images are back-lit, top-down optical photographs of EGaIn (left column) and Hg (right column) in PDMS microfluidic channels. The PDMS is transparent, whereas the metals block the light and consequently appear dark. i) Both metals filled the channels until they reached the narrow portion of the channel. ii) When a critical pressure was exceeded, both metals rapidly (in < 1 sec) filled the channels. iii) When the system was returned to ambient pressure, the EGaIn structure was stable, whereas the Hg instantaneously (<1 s) withdrew from the channel. All pressures are gauge pressures.

EGaIn stopped flowing for a given pressure; Figure 2 shows P vs. 1/W.

According to Eq. 1, the slope (which we found to be 1.1 N/m) of the linear fit to these data is $2\gamma\cos(\theta)$. We estimated the angle between the EGaIn and the side-wall of the channel to be ~150°, based on a top down, optical image of the EGaIn in the channel (see Supporting Information Figure S4), so $\gamma = $~630 mN/m; this value is indistinguishable from the value reported for what was interpreted to be the "surface tension" of EGaIn in ambient conditions (624 mN/m).[4] A similar analysis performed for Hg ($2\gamma\cos(\theta) = 0.7$ N/m, contact angle ~140°) yielded a surface tension of ~450 mN/m, only slightly less than the value reported in the literature (480 mN/m).[10] Although these two values for Hg are within experimental error of each other — the contact angle estimation is accurate to within +/− 5°, and a contact angle of 136° would give a surface tension of 480 mN/m — it is possible that the Hg surface had adsorbed contaminants (e.g., thiols) that would cause us to observe a lower surface energy than that of pure Hg.

The intercepts of the linear fits to the data in Figure 2 (29.1 kPa for EGaIn, 18.3 kPa for Hg) are the pressures required to inject the fluid metal into an infinitely wide channel (i.e., one in which the 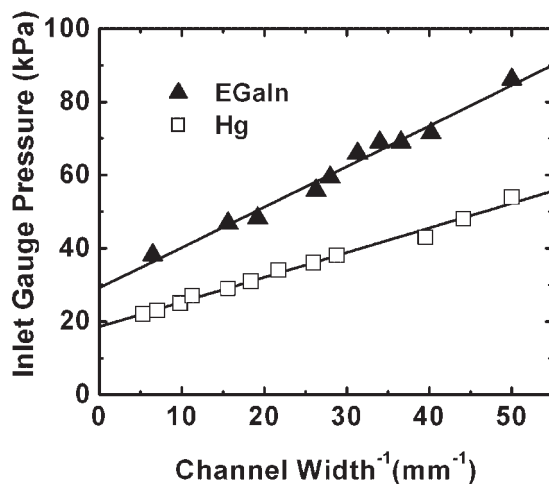only dimension of consequence is the pressure applied at the inlet, and stopped the metal from moving further through the channel. Increasing the pressure applied at the inlet to ~89 kPa caused the EGaIn to flow rapidly through the narrow channel toward the outlet (Figure 1b, left side). The Hg filled the narrow channel rapidly (<1 sec) when the applied pressure exceeded ~57 kPa (Figure 1b, right side).

We can express the pressure drop (P, Pa) across the metal-air interface using the Young's-LaPlace equation (eq. 1). In this equation, W and H are the width and height (m)

$$P = 2\gamma\cos(\theta)(1/W + 1/H) \qquad (1)$$

respectively, of the channel at the metal-air interface, and θ is the contact angle between the liquid and the walls of the channel. The phenomenological parameter γ (N/m) is, in the most general sense, a measure of interfacial force per unit length of the interface, but its physical origin is system-specific. For a liquid, this parameter is the surface tension. For a solid-like film (such as that at the surface of the EGaIn), the value of γ depends on the mechanical properties of the film. We applied a series of pressures (P) to the inlet, and measured the width (W) of the channel at the point at which

Figure 2. A plot of pressure (P_{in}) applied to the inlet of the channels as a function of the inverse of the smallest width (1/W) of the channel filled by EGaIn and Hg. The slope of the linear fit is proportional to γ (a measure of force per unit length of the interface, N/m) and the intercept is equal to the pressure required to inject the metal into an infinitely wide channel. The slope of the best fit line to the data for EGaIn is 1.1 N/m and the intercept is 29.1 kPa. The slope of the best fit line to the data for Hg is 0.7 N/m and the intercept is 28.3 kPa. This plot illustrates the inverse relationship between pressure and critical dimension.

the depth of the channel). This pressure is specific to the geometry of the channels used in these experiments and, according to eq. 1, should equal the slope divided by the height of the channels (H). The intercepts from Figure 2 yielded a value for H of ∼38.1 μm for EGaIn and ∼37.5 μm for Hg. These values — as expected — are roughly equal to the pre-determined height of the channel (38 μm, as measured by profilometry).

Based on this analysis, we can develop an expression (Eq. 2) for the critical pressure, P_c (Pa)

$$P_c \times CD \propto 1.1 \qquad (2)$$

required to force EGaIn through a channel of critical dimension CD (m). In eq. 2, the units of 1.1 are N/m.

2.2.2. Behavior of EGaIn and Hg upon Returning the System to Ambient Pressure

When we relieved the pressure at the inlet, the EGaIn did not reflow or reorganize within the channel, but rather remained in the shape pictured in Figure 1c indefinitely. EGaIn's moldability (which allows for the formation of structurally stable microstructures in channels at room temperature) distinguishes it from Hg, which reflowed immediately upon our returning the system to ambient pressure (Figure 1c, right side). EGaIn does not reflow despite having the same two characteristics that destabilize Hg: i) *Non-wetting*. EGaIn does not wet the walls of the channel: As shown in Figure S3 in Supporting Information, the metal-air interface in the middle of the channel protrudes towards the outlet. ii) *Large surface energy*. Similar to Hg, the interfacial free energy of EGaIn is large (>600 mN/m, based on the measurements in this study).

Why then are structures of EGaIn stable while Hg instantaneously reflows? We suspect that EGaIn's stability is due to the skin of gallium oxide on its surface. To test this hypothesis, we injected EGaIn into a channel pre-filled with 10 wt% aqueous HCl, which removes the skin by dissolving the oxide (see Figure S2 in Supporting Information). The EGaIn, in the presence of HCl, behaved similarly to Hg: it rapidly withdrew from the channel when the inlet returned to ambient pressure. Furthermore, we found that the surface tension of EGaIn in the presence of HCl dropped to ∼444 mN/m (based on Eq. 1), similar to that previously reported for EGaIn in the presence of HCl (432 mN/m).[4]

2.3. The Rheological Characterization of EGaIn

The stability of microstructures of EGaIn in channels, and the loss of this stability when EGaIn is exposed to HCl, suggests that EGaIn's oxide skin dictates its rheological behavior. Little is known about the mechanical properties of oxide skins on liquid substrates. We sought to quantitatively characterized the mechanical properties of EGaIn using a rheometer equipped with parallel-plates (Bohlin Gemini HR

Nano from Malvern Instruments, see Supporting Information for additional experimental details). The rheometer — which precisely measures the deformation response of EGaIn to an applied stress under controlled conditions — allowed us to measure the visco-elastic properties of the skin, determine the critical stress required to yield the skin, and characterize the properties of its flow once it yielded. The Supporting Information contains a glossary of rheology terms and equations for all of the quantities discussed here.

We dispensed a small volume (∼0.4 mL) of EGaIn between the two parallel plates separated by ∼1.2 mm. The top plate was attached to a low-friction bearing capable of applying a wide range of torques (about the axis normal to the plane of the plate, while the bottom plate remained stationary) and was also equipped with an optical encoder that tracks the radial displacement, θ, of the top plate. We monitored the torque required to oscillate the top plate sinusoidally with a constant frequency ω (1 rad/s), as shown in Eq. 3, where R is the radius of the plate (10-mm)

$$\gamma_s = \frac{R\theta}{d} = \gamma_0 \sin(\omega t) \qquad (3)$$

d is the gap between the plates (1.2 mm), and t (s) is time. Equation 3 also defines the surface strain (γ_s) — which is a measure of deformation of the EGaIn — and the strain amplitude (γ_0).

We recorded the torque required to maintain the constant oscillatory frequency (described by Eq. 3) while increasing the strain amplitude. The torque is a measure of the total stress required to deform the sample; here, we assume that the bulk of the sample is a low viscosity liquid, while the surface exhibits solid-like properties. In this case, the torque, τ (N·m), is proportional to the surface stress (σ_s, N/m) applied to the EGaIn, as shown in Eq. 4, in which the surface stress is integrated around the circumference, l (m) of the top plate.

$$\tau = \int \sigma_s R \, dl = 2\pi \sigma_s R^2 \qquad (4)$$

We thus determined the viscoelastic properties of surface of the EGaIn — the surface elastic modulus (G'_s, N/m) and the surface viscous modulus (G''_s, N/m) — by relating the strain amplitude (γ_0) to the corresponding surface stress (σ_s), as shown in Equation 5.

$$\sigma_s = \gamma_0(G'_s \sin(\omega t) + G''_s \cos(\omega t)) \qquad (5)$$

A perfectly elastic material, such as a highly cross-linked gel, behaves like a spring, while a perfectly viscous material, such as water or Hg, behaves like a dampener. Similar behavior will also occur for an interface; in that case, the interface can possess either perfectly elastic ($G''_s \sim 0$) or perfectly viscous ($G'_s \sim 0$) behavior. The skin of EGaIn has both elastic and viscous characteristics over a large range of values of strain, so both G'_s and G''_s are non-zero.
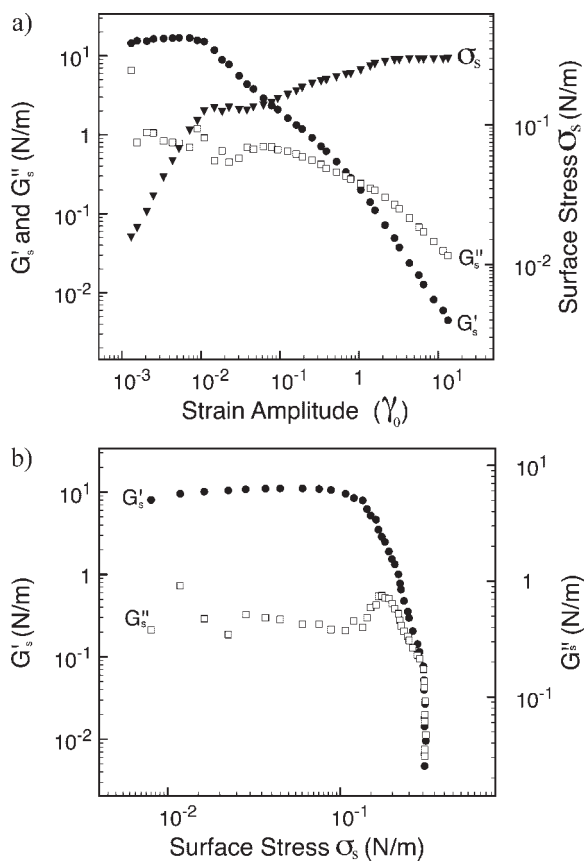
Figure 3. Visco-elastic rheological plots of EGaIn. **a)** A plot of the surface shear stress (σ_s, N/m), the surface elastic modulus (G'_s, N/m), and the surface viscous modulus (G''_s, N/m) vs. strain amplitude (γ_0) for EGaIn. At low values of strain amplitude (<0.01), EGaIn has elastic like behavior ($G'_s \gg G''_s$). Notably, the stress did not increase significantly beyond a strain of 0.1; this result suggests that the EGaIn flows readily once it yields. **b)** A plot of G'_s and G''_s vs. stress for EGaIn. The data shows that the EGaIn flows readily beyond a critical surface stress (~0.5 N/m).

2.3.1. Results of the Parallel Plate Measurements

Figure 3a includes a plot of the surface stress (σ_s) as a function of the amplitude of the surface strain (γ_0) for EGaIn.[19] As expected, stress increased with strain, because the EGaIn resisted the movement of the plates through i) elastic restoring forces and ii) viscous dissipation (although this component is close to zero for EGaIn). Figure 3a shows the surface elastic and viscous moduli for EGaIn plotted as a function of the surface strain. The values of G'_s and G''_s were independent of strain for strain amplitudes less than 0.01 (a strain of 0.01 means the upper plate deformed the material by 1% of its thickness). In this "low-strain" regime, the interface of the EGaIn was primarily elastic ($G'_s \gg G''_s$). At strains greater than 0.01, the decrease in G'_s indicates that EGaIn became less elastic, and began to yield (or flow).

At the onset of yielding (strain amplitude >0.01), the surface stress (σ_s) leveled off at ~0.5 N/m. This plateau suggests that i) the skin could only support ~0.5 N/m of surface stress, and beyond this value, ii) only a small amount of additional stress

was needed to strain EGaIn further because the resistance to flow only arises from the skin, which has yielded and begun to flow. Bulk EGaIn has a low viscosity, which imparts an insignificant resistance to the oscillations (we estimate that the contribution of the bulk viscosity to the applied torque is approximately six orders of magnitude lower than that required to yield the EGaIn). Thus, once the skin yields, there is minimal resistance to flow and the stress required to increase the strain amplitude plateaus. In this plateau region, the skin "slips" — that is, it either detaches from the rheometer plate or it cracks open at the EGaIn-air interface; it is within these small regions that all of the flow appears to occur. The plateau behavior of the stress explains why the EGaIn filled the narrow portion of the microchannel (Figure 1b) so rapidly once a critical pressure was exceeded.

The value of the stress at which EGaIn yields is readily apparent in a plot of G'_s and G''_s as a function of surface stress (σ_s), Figure 3b. Both moduli decreased rapidly at ~0.5 N/m; this trend implies that EGaIn yielded at this value of surface stress and we therefore define this value as the critical surface stress. The skin cannot support stresses larger than ~0.5 N/m; any additional stress that is applied simply makes the EGaIn flow faster.

We repeated the rheological measurements after leaving the EGaIn between the two parallel plates for ~24 hours to determine whether the rheological properties change with time. We could not detect a change in the yield stress, moduli, and general shape of the plots shown in Figure 3 after 24 hours of exposure of the EGaIn to the ambient; this result provides indirect evidence that the thickness of the skin does not change significantly over the time scales of our experiments, and corroborates previous X-ray measurements that show that the oxide layer is passivating.[12]

From sample to sample, the absolute values of the moduli varied, but the shapes of the plots (and the value of the strain at which the EGaIn yielded) were the same. The Supporting Information contains a discussion of this variation.

2.4. Evidence that the Properties of the Surface of EGaIn Dictates its Rheological Behavior

In the aforementioned rheological measurements, the rheometer recorded the torque required to oscillate the top plate. In principle, the resistance to deformation (i.e. the required torque) can arise from both the skin and the bulk, but our analysis assumes that the surface properties dominate (i.e. the bulk contribution is insignificant). We believe that this approach is justified based on the following phenomenological and quantitative evidence:

i) The expected contribution of bulk EGaIn—which is a low viscosity fluid[8]—to the measured torque is approximately six orders of magnitude lower than those recorded in these experiments; this result suggests that the resistance of EGaIn to deformation, including its elastic response, arises primarily

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from the skin. The elastic properties of the skin suggest it is solid-like, which is consistent with previous observations of the gallium oxide skin on liquid gallium.[12]

ii) This skin is visually apparent at the interface between the EGaIn and air during the parallel-plate measurements (see movie M2 in Supporting Information). Figure 4 contains three frames of this interface taken with the top plate rotating counter-clockwise[20] (Figure 4a), centered at its starting position (Figure 4b), and rotating clockwise (Figure 4c). The skin deformed in synchrony with the oscillations (Figures 4a, 4c) and appeared crumpled after returning to the center position (Figure 4b), probably because of buckling and cracking.

iii) Moduli are physical properties of a material that should be independent of the size of the plate since the surface moduli are normalized by the perimeter of the plate (units of force per length). As expected, the surface moduli were the same for both 20 and 40 mm diameter plates (see Figure S1), but the bulk moduli (which are normalized by the surface area of the plate), changed by a factor of two. This result suggests that surface moduli are the relevant parameters, and that the elastic behavior is due to the rheological properties of species present at the surface of EGaIn (and not in the bulk).

iv) The critical surface stress required for EGaIn to yield in the parallel plate configuration was ∼0.5 N/m (Figure 3). We obtained the same critical surface stress when using a larger plate (40 mm) for the measurement. This value (∼0.5 N/m) is remarkably similar to both the "surface tension" of EGaIn in

air (0.63 N/m) measured by the pendant drop method[4] and the critical surface stress required to force the EGaIn through the microfluidic channels (∼0.6 N/m, the product of the pressure applied at the inlet and half of the critical dimension of the channel, Eq. 2).

The agreement between the values of critical surface yield stress obtained from the behavior in the channels and the rheological measurements support our hypothesis that the observed rheological properties of EGaIn are dominated by the species at the surface, and are not a property of the bulk material. A Newtonian fluid, such as Hg or water, does not behave elastically, nor do they have a critical surface yield stress. These fluids do require a critical pressure to inject them into channels, the value of which depends on the surface tension and contact angle (Eq. 1). EGaIn's behavior, however, is due to its skin, which is elastic. The elasticity of the skin allows EGaIn to maintain post-injection structural stability, whereas Hg continually reorganizes to minimize its interfacial free energy.

3. Summary and Conclusions

3.1. The Connection between the Rheological Properties of EGaIn and its Behavior in Microchannels

The rheological measurements demonstrated that EGaIn has the properties of an elastic material until an applied critical surface stress (∼0.5 N/m) is exceeded, at which point it flows readily; this result is consistent with the observation that EGaIn can be forced to fill channels rapidly when a critical pressure is exceeded for a given channel critical dimension. In other words, EGaIn can only support surface stresses below ∼0.5 N/m. We obtained this critical stress value both by rheological measurements (Figure 3) and by studying the critical pressure required to inject EGaIn into a microchannel of known geometry (Figures 1 and 2). The critical surface stress required to inject EGaIn into channels, and the stability of the EGaIn in the channels after injection, arises from a skin on the surface of the EGaIn. Auger spectroscopy showed that this skin is composed of oxides of gallium (Figure S3).

The ability of the EGaIn to fill the channels rapidly once it yields is consistent with the rheological observation that a negligible amount of additional stress is required to induce EGaIn to flow faster once the material yields (specifically, the "plateau" in the plot of stress vs. strain amplitude in Figure 3a).

The elastic nature of EGaIn under low-strain (or, equivalently, low-stress) conditions explains the stability of the EGaIn structures within the microfluidic channels once the pressure through the channels is relieved (Figure 1c). The stability is due to the skin, as shown by the instability of EGaIn in channels pre-filled with HCl. For the design of future microfluidic systems to mold EGaIn, we can use the critical surface stress (∼0.5 N/m) to i) estimate the pressure required to yield EGaIn from an elastic material to a flowing fluid in a
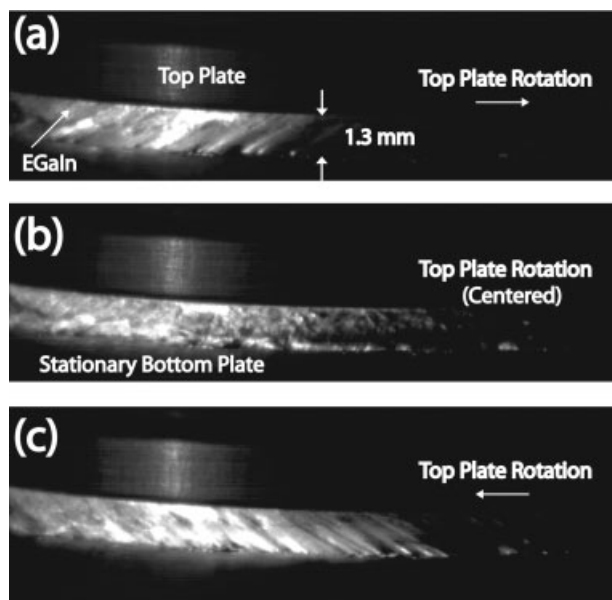

Figure 4. A series of side-view snapshots of EGaIn between the two parallel plates of the rheometer. The images illustrate how the "skin" on the EGaIn surface deformed (the full movie, M2, is available in Supporting Information) during the oscillation of the top plate about the axis normal to the plane of the plate (the bottom plate was stationary). a) The plate rotated to the right of the center position, and the creases in the skin slanted in concert with the rotation. b) The plate returned to its initial center position, and the relaxed skin appeared crumpled after being stretched (rotationally extended). c) The plate rotated to the left of the center position, and the creases of the skin slanted accordingly.

channel of given dimensions, or alternatively ii) estimate the critical dimension of the channel required to block the passage of EGaIn for a given pressure drop. The required pressure to yield EGaIn is inversely proportional to the smallest dimension of the channel, as dictated by the critical surface stress (Eq. 1).

3.2. Outlook

The analysis in this paper may be relevant to the characterization of other solders and liquid metals for which surface oxides dictate behavior below a critical stress. These oxides are often considered a nuisance and are therefore removed prior to rheometry; here, we showed that the skin can be beneficial for certain applications. EGaIn is different from many metals, however, because it is a liquid at room temperature and has a passivating oxide skin (similar to Al).

The elastic skin of EGaIn allows it to be molded at room temperature, but flow rapidly once a critical stress is exceeded. This property could be harnessed to enable several applications:

i) The formation of conformal electrodes for metal-molecule-metal junctions incorporating self-assembled monolayers or other thin organic films.[7] The moldability of EGaIn allows it to form small cones with tips with diameters as small as 1 μm: these electrodes are much smaller than those formed using a drop of Hg, and are therefore less likely to contact defects in the organic film. In addition, EGaIn can be deposited at room temperature, so fabrication of EGaIn junctions does not subject the organic film to bombardment with hot, evaporated metal.

ii) The formation of metal microstructures by injecting EGaIn into microchannels. The stability of the structures facilitates the formation of functional components — such as heaters, coils, etc – within the channels. Because these structures are fabricated at room temperature, they could be used as metal-organic contacts or interconnects for organic sensors or field-effect transistors.

iii) The injection of EGaIn a predetermined distance into a channel by rationally designing the cross-sectional dimensions of the channel. Using this technique, metal-fluid junctions can be formed in channels that may be useful as sensors or electrodes.

iv) The switching of the behavior of EGaIn in channels from that of a liquid to that of an elastic solid through modulation of pressure. This technique has implications for the development of self-healing materials.

[1] Co-fabrication is a strategy for simplifying the fabrication of complex microfluidic devices by combining multiple functional components — heaters, electrodes, optical waveguides, etc. — and microfluidic channels in a single step of microfabrication using one layer of lithography.

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[19] The strain is directly proportional to strain rate (s^{-1}) since the frequency of rotation is constant.

[20] The orientation of rotation is defined relative to a top-down view of the plates.