CHARACTERIZATION OF LIQUID-METAL GALINSTAN® FOR DROPLET APPLICATIONS

Tingyi "Leo" Liu, Prosenjit Sen and Chang-Jin "CJ" Kim
University of California, Los Angeles (UCLA), California, U.S.A.

ABSTRACT

We report our characterization of nontoxic liquid-metal alloy Galinstan® on its potential for substituting mercury droplets in miniature devices. To combat the super fast oxidation, which has been hindering the studies of Galinstan®, our entire experiments are performed in a nitrogen-filled glove box. Galinstan® droplets are found to behave like a true liquid, indicating a good liquid-air interface, only if the oxygen traces stay below 1 ppm. Surface tension of Galinstan® is measured to be 534.6±10.7 mN/m in nitrogen at 28ºC using a pendant drop method. Advancing/receding contact angles on glass and Teflon surfaces are found to be 146.8°/121.5° and 161.2°/144.4°, respectively. The electrowetting on dielectric (EWOD) mechanism of Galinstan® is also demonstrated.

INTRODUCTION

Galinstan® – a eutectic alloy of 68.5% gallium, 21.5% indium and 10% tin – is the only readily available liquid metal that retains a liquid state well below 0ºC other than mercury. Due to its nontoxicity and a very low vapor pressure ($<10^{-6}$ Pa at 500°C), it has been replacing mercury in many applications (e.g., thermometer). In MEMS, it has already been used [1] or is in line to replace mercury in due course [2, 3]. However, Galinstan® has not produced many success stories in MEMS as initially anticipated, partly because, being relatively new, its properties are not well known. Some information on the Internet (e.g., Galinstan® wets glass), unfortunately, lack rigor and could be misleading. Out of the need to replace mercury droplets, we have investigated the key properties of Galinstan® that are essential in designing droplet microdevices. Electrical actuation of Galinstan® droplets was also tested. The fact that Galinstan® gets oxidized so easily and fast has been the key challenge of characterizing Galinstan® especially as small droplets. Prevention of oxidation will stay as a main issue in developing microdevices that involve its droplets.

THEORY AND METHODS

Surface tension measurement

Surface tension at the interface between a liquid and a gas or vapor, can be measured by various methods (e.g., the capillary rise method, pendant drop method, Wilhelmy slide method [4]). We have adopted the pendant method, because it suited our need the best: building the entire setup and performing the entire experimental procedure inside a glove box. In the pendant method, surface tension is determined from the shape analysis of a static drop or bubble when gravitational and surface tensional forces are comparable [4]. As a pendant/sessile drop is created, its profile follows the Young-Laplace equation (Eq. 1), which depicts the pressure difference caused by the curvature of the surface.

$$\Delta p = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \tag{1}$$

where Δp is the pressure difference between the liquid and gas, γ is the surface tension of the liquid, and R_1 and R_2 are the two principle radii of curvature of the surface at a specific point.

The two radii of curvature are equal at the apex owing to the cylindrical symmetry of the pendant/sessile drop, i.e., $R_1 = R_2 = R$, resulting $\Delta p = 2\gamma/R$ at the apex. Hence, considering gravity g, the pressure difference at height z from the apex is expressed as $\Delta p = 2\gamma/R - \Delta\rho g z$, where $\Delta\rho = \rho_{liquid} - \rho_{gas}$, and ρ is density. Combining it with Eq. 1 yields,

$$\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = \frac{2\gamma}{R} - \Delta\rho g z \tag{2}$$

By defining Bond number as $\beta = -\Delta\rho g R^2/\gamma$ and calculating β and R from the empirical fitting polynomials given in [5], a theoretical profile of the drop is generated from the numerical solution of Eq. 2 to compare with the points on the experimental profile [5]. An objective function (sum of squares of the normal distance between the experimental to the generated theoretical profile) is then used to seek the optimum β and R that are best fit to the experimental data by varying them in a certain range. The surface tension γ is then calculated from the optimum β and R.

Note that the above algorithm applies to both the pendant and sessile drop method as far as the coordinate system originates at the apex and the z-axis points upward.

Contact angles

It is known that the contact angle at an advancing meniscus of a liquid is greater than that at a receding meniscus. Any static droplet formed on a surface has a contact angle between advancing and receding contact angles. The difference between advancing and receding contact angles is referred to as contact-angle hysteresis. By adding or subtracting liquid from the droplet continuously, advancing or receding contact angle, respectively, can be found at the moment right before the contact line moves.

Electrowetting-on-dielectric (EWOD) actuation

Surface tensions between the three phases (gas, liquid,

solid) give rise to different wetting conditions of different liquids on a solid. The wetting condition can be controlled by various means including electrical (i.e., electrowetting), with the mechanism and configuration of EWOD currently being the most popular for microdevices. The phenomenon of electrowetting under the configuration of EWOD is illustrated in Figure 1.

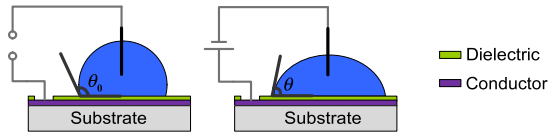

Figure 1. EWOD actuation of liquid on a microdevice

The mathematical relation between the applied voltage and the change of contact angle is expressed as the Lippmann-Young's equation [6],

$$\cos\theta = \cos\theta_0 + \frac{1}{2\gamma} cV^2 \qquad (3)$$

where θ_0 is the initial ($V = 0$) contact angle of the liquid on a solid surface, γ is the liquid-gas surface tension, c is the unit-area capacitance, θ is the contact angle when the applied voltage between the liquid and the conductor is V.

EXPERIMENT PROCEDURE

Prevention of oxidation of Galinstan®

The main difficulty in handling Galinstan® is its severely fast oxidation in air, which becomes especially significant in microscale because of the large area-to-volume ratio, so much so that 1-2 mm diameter droplets would form a distinctively non-spherical shape, as seen in Figure 2(a), even at only 0.2% oxygen in a nitrogen-filled glove box (VAC 101965). Furthermore, the droplets behave like a gel rather than a true liquid even at mere ~20 ppm of oxygen trace. This super-fast oxidation is one reason the properties of Galinstan® are scarce and device development using its droplets has been slow in MEMS. Galinstan® droplets finally showed no apparent effect of oxidation when the oxygen trace neared the limit of the glove box (~0.1 ppm). Our observations are listed in Table 1. This condition allowed us, for the first time, to accurately measure the surface tension of Galinstan® and its contact angles on solid surfaces. Our setup was built and measurements were done inside the glove box at below 0.5 ppm of oxygen and moisture.

Table 1. Behavior of Galinstan® droplet at different oxygen trace levels

Oxygen	Observation
0.2-20.9%	Droplet is distinctively non-spherical by instantaneous surface oxidation even at the moment of dispensing
~20 ppm	Droplet is spherical Droplet behaves like gel rather than true liquid
<1 ppm	Droplet behaves like true liquid
<0.5 ppm	Droplet behaves like true liquid The condition for all data in this report

(a) (b)

Figure 2. (a) Galinstan® droplet (~2 mm in diameter) gets oxidized instantaneously as being dispensed (~0.25 s), forming a non-spherical shape, even when the oxygen trace is only ~0.2%, (b) Galinstan® droplet is formed spherical and behaves as liquid at oxygen trace below 1 ppm.

Surface tension measurement

Following earlier works [5, 7] the experiments were carefully designed to prevent minor specifics that lead to errors, such as lighting condition, vibration, camera tilt, edge detection failure of small droplets due to limited resolution. To precisely measure the surface tension of Galinstan® by the pendant method, all the experimental apparatuses were set up on a vibration isolation plate. A plumb bob was used as a reference vertical line to correct the slight camera tilt. Drop with an equator was desirable and made as large as possible to avoid pixel error from the finite resolution of the camera. The experimental setup for surface tension measurement using pendant drop method is shown in Figure 3.

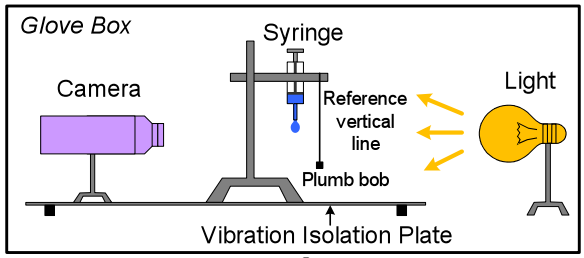

Figure 3. Schematic of Galinstan® surface tension measurement using pendant drop method

The detailed procedure for this measurement is given as follows. The optimum size of the pipette/syringe tip was first calculated for an elongated shape of the hanging drop. Then, a stable hanging drop was made using a syringe with a glass pipette tip. The whole process of droplet growth was recorded on video until the droplet falls down. Snapshots were then captured from this video. Finally, the image was rotated, correcting the asymmetry of the profile caused by camera tilt before sending all pictures to a computer program for calculation.

The surface tension measurement using sessile drop method follows a same procedure as that using pendant drop method. Since line tension affects the shape of droplets that are much smaller than the capillary length and gravity distorts droplets that are larger than the capillary length, droplets with dimensions close to the capillary length were used to improve accuracy.

Contact angles

A syringe with needle (Hamilton syringe with removable stainless-steel needles) were used to generate Galinstan®

droplets on the surface of interest. After the droplet-forming step, Galinstan® was pumped into or sucked from the droplet continuously and slowly, so as to minimize any dynamic effects, and the evolution of the droplet was recorded by the camera at a rate of 28 frames per second. Note that the needle tip must be small compared to the drop so that fluid adhesion does not distort the droplet shape [8].

Investigating the video frame by frame, snapshots were taken at the frame right before the contact line of the droplet advanced or receded. Then the advancing and receding contact angles were calculated by an automatic contact angle computational program developed in-house.

Electrowetting-on-dielectric (EWOD) actuation

An EWOD test setup was built inside the glove box. A tungsten probe was used for an electrical activation for its chemical inertness with Galinstan®. The DC power source was turned on only when the snapshot was taken to minimize dielectric charging.

RESULTS AND DISCUSSION

Surface tension measurement

In the pendant drop case, in order to make a hanging drop (elongated by gravity) fill the picture frame (width:height = 30:47) fully for maximum data points on the profile, the optimum diameter of the pipette was calculated to be between 0.72 mm and 2.04 mm for this case. Note that the diameter obtained here is the inner diameter of the pipette, since in our experiments Galinstan® was found to be nonwetting on bare glass. Even though Galinstan® is usually thought to wet almost all surfaces including glass, we conclude, based on our experiments, that the widely spread view is incorrect. It is the oxidation of Galinstan® that produces the appearance of wetting. Similar behavior where oxidation leads to enhanced wetting has also been reported for gallium [9].

We randomly cut an 80 minutes video clip from our ~90 minutes record and take snapshots every 1 second. Hence, 4800 snapshots were acquired, and the resulting 4800 data points allowed us to use statistical analysis to achieve statistically accurate results. Box plot (Figure 4) was chosen to graphically depict the differences between calculation results without making any assumptions of the underlying statistical distribution. Note that the large population of our data may make multiple outliers appear as one plus sign in Figure 4(a). In order to reveal its distribution more clearly, a normal probability plot is drawn in Figure 5. It shows that the results fit pretty well with a normal distribution, which agrees with the common assumption that observational errors are normally distributed. The measurement was repeated over time (more than 2 hours), and its invariant results indicated no oxidation effect.

Pixel error is the biggest error for surface tension measurement using digital images. It is recognized that one pixel error is the limit of digital images. Hence, the error in our final results is about ±2.0%. It is worth noting that the role of the vibration isolation plate was significant. When the vibration isolation plate was not used, results scattered about ±5.3% even though only the data that seem to have less vibration effect were manually selected.

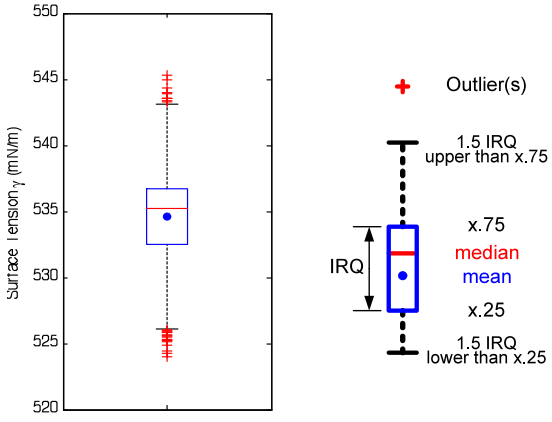

Figure 4. (a) Box plot of the results of surface tension measurement of Galinstan® (b) Meaning of the box plot

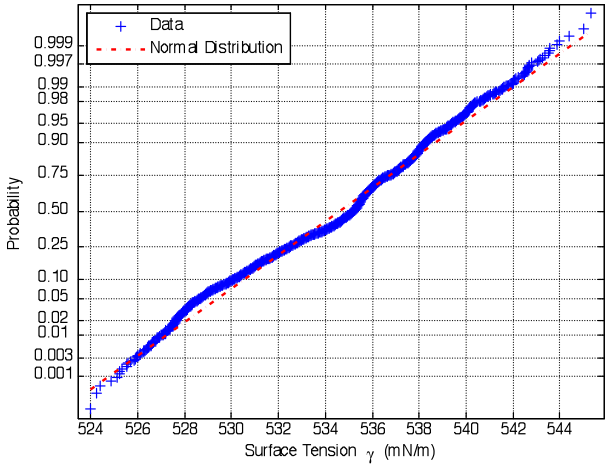

Figure 5. The normal probability plot of results of surface tension measure of Galinstan®

Using a pendant drop method as described above, the surface tension of Galinstan® in nitrogen at 28.0ºC (measured by Ever-Safe N16B glass organic filled MCT classical thermometer) was measured to be 534.6±10.7 mN/m.

Compared with the pendant drop method, the sessile drop method has an inherent shortcoming in which one has to calibrate the camera to accurately obtain the scale factor, which converts the pixels to physical length. Yet a slight shift of the optical elements between calibration and measurement can introduce errors which vitiate any advantage gained by the enlargement of the drop image [10]. Although difficulties are found to accurately determine the scale factor under our current equipments, we still measured the surface tension using the sessile drop method as another reference. The sessile drop method gave a mean value of 576.2±27.2 mN/m, slightly larger than the data from the pendant drop method.

Contact angles

On a glass surface (soda lime glass, Fisherfinest® microscope slides), the advancing and receding contact angle were measured to be 146.8° and 121.5°, respectively. On a Teflon surface (~1700Å-thick Teflon AF prepared by spin-coating on ~4500Å-thick silicon nitride on an ITO-coated glass substrate and baked at 2000°C for 2 hours), on the other hand, the advancing and receding contact angle were 161.2° and 144.4°, respectively. The error of contact angle calculation program in our experiments is within 1°.

Electrowetting-on-dielectric (EWOD) actuation

The device configuration for EWOD testing is illustrated in Figure 6, and the result of EWOD actuation test for Galinstan® is shown in Figure 7. The diamond marks in Figure 7 give the experimental data of contact angle changes versus the applied voltage. The contact angle was ~151° initially (0 V) and decreased to ~113° when the voltage increased to 120 V. The measured data are compared with two theoretical (Eq. 3, Lippmann-Young's equation) curves plotted using the surface tension result (534.6±10.7 mN/m) obtained from pendant drop method and the initial contact angle with no voltage applied (i.e., 0 V). The black solid line was generated by using the contact angle measured while the tungsten probe was inserted into the droplet but at 0 V (151.5°). The red dashed line, on the other hand, was generated by using the average static contact angles of randomly deposited droplets without inserting the probe tip (155.9°).

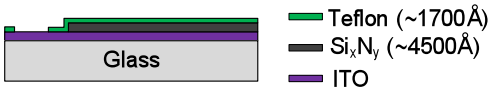

Figure 6. Device configuration for EWOD actuation test

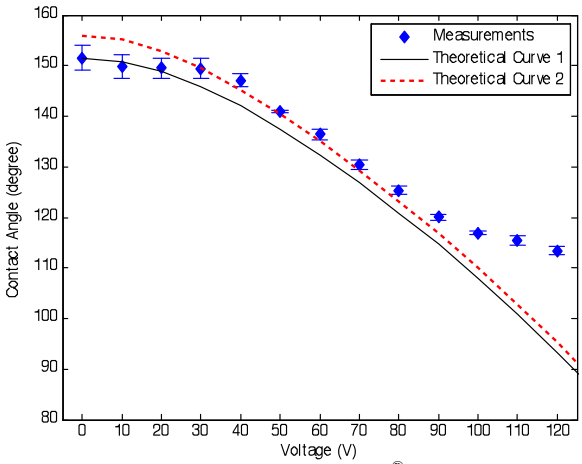

Figure 7. Result of EWOD test for Galinstan®. Theoretical curves are generated using the properties obtained in this report.

CONCLUSION

We have presented our investigation to characterize Galinstan® for droplet applications. Even though Galinstan® is highly prone to fast oxidation in ambient air, we have finally achieved its droplets behaving as a true liquid (i.e., not affected by surface oxidation) by using a nitrogen-filled glove box with oxygen trace controlled below 1 ppm. Galinstan® droplets showed no apparent effect of oxidation for more than 2 hours during our experiments with oxygen trace <0.5 ppm.

The oxygen-free condition allowed us to measure the surface tension and contact angles of Galinstan® accurately and further verify its EWOD mechanism for the first time. We reported that the surface tension of Galinstan® in nitrogen at 28.0ºC is measured to be 534.6±10.7 mN/m using the pendant drop method. Contact angles (advancing/receding contact angles) of Galinstan® on a glass and Teflon surface were measured to be 146.8°/121.5° and 161.2°/144.4°, respectively. The contact angle changes of Galinstan® using EWOD was confirmed and measured to be ~38º before saturation. All of the above suggest that Galinstan® can eventually replace mercury for the microdevices using liquid-metal droplets.

ACKNOWLEDGEMENT

This work was supported by the DARPA HERMIT program. The authors would like to thank Mr. Zhiyu Chen for the fabrication of the devices and Mr. James Jenkins for the assistance on experiments in the glove box.

REFERENCES

[1] Cao, A., P. Yuen, and L. Lin, "Microrelays With Bidirectional Electrothermal Electromagnetic Actuators and Liquid Metal Wetted Contacts," *J. MEMS*, 2007. **16**(3): p. 700-708.

[2] Sen, P. and C.-J. Kim, "A Fast Liquid-Metal Droplet Microswitch Using EWOD-Driven Contact-Line Sliding," *J. MEMS*, 2009. **18**(1): p. 174-185.

[3] Sen, P. and C.-J. Kim, "A Liquid–Solid Direct Contact Low-Loss RF Micro Switch," *J. MEMS*, 2009. **18**(5): p. 990-997.

[4] Adamson, A.W. and A.P. Gast, *Physical Chemistry of Surfaces*, 6th ed. New York: Wiley, 1997.

[5] Lin, S.-Y., et al., "An Examination on the Accuracy of Interfacial Tension Measurement from Pendant Drop Profiles," *Langmuir*, 1995. **11**(10): p. 4159-4166.

[6] Lee, J., et al., "Electrowetting and electrowetting-on-dielectric for microscale liquid handling," *Sens. Actuators, A*, 2002. **95**(2-3): p. 259-268.

[7] Andreas, J.M., E.A. Hauser, and W.B. Tucker, "Boundary Tension by Pendant Drops," *J. Phys. Chem.*, 1938. **42**(8): p. 1001-1019.

[8] Woodward, R.P., "Contact Angle Measurements Using the Drop Shape Method," First Ten Angstroms.

[9] Burton, R.G. and R.A. Burton, "Gallium alloy as lubricant for high current density brushes," *IEEE Trans. Components, Hybrids, and Manufacturing Technology*, 1988. **11**(1): p. 112-115.

[10] Butler, J.N. and B.H. Bloom, "A curve-fitting method for calculating interfacial tension from the shape of a sessile drop," *Surf. Sci.*, 1966. **4**(1): p. 1-17.