Vibration-enabled mobility of liquid metal

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Abstract

Directed liquid metal (gallium-based) manipulation and actuation are paramount for copious applications, including soft robotics, soft electronics, and targeted drug delivery. Although there are several strategies available to achieve mobility of liquid metals in a “wet” environment. Strategies to achieve and improve mobility of liquid metal droplets and puddles in a “dry” environment have been scarce and rely on metallophobic surface design or liquid metal marbles. Here, we discover high mobility of Galinstan achieved by combining metallophobic surface design and vertical vibrations. Vibration frequencies between 20 and 30 Hz were conducive to droplet movement and threshold inclination angles of 0.5 to 1° were observed upon actuation by the vibrations. The method itself is applicable for a wide range of droplet sizes (30 and 2000 µL) and very robust. The droplet movement typically comprises of periodic receding and advancing of the droplet and commences via a rolling mechanism rather than a gliding mechanism. Finally, we show that small (0.5 mm height) obstacles can be traversed by this method, indicating that it can be used in concert with other strategies, such as surface structuring strategies, which open up pathways for mobility and controlled actuation of liquid metal droplets in air.

1. Introduction

Control and manipulation of liquids play fundamental roles in microfluidics, water harvesting, chemical reactions, and biomedical analysis. In recent years, droplet-based motion has garnered considerable attention, perhaps due to the fact that it can transport liquids counterintuitively against gravity.\textsuperscript{[1]} Indeed, Chaudhury and Whiteside showed that water droplets move uphill due to a chemical gradient or (better) a wettability gradient. From these beginnings, many different actuation and manipulation methods have been established and controlled direction transport has been achieved for many liquids, including water and organic liquids, in the past via a plethora of methods. These methods may rely on passive or active driving forces. Both general means necessitate a reason for directional movement, which arises due to asymmetry. Passive driving forces are the aforementioned chemical gradients and topographical gradients.\textsuperscript{[1–3]} Active mechanisms for movement rely on external energy input, such as electric, magnetic, light, heat (i.e., Marangoni effect based), and vibrations,\textsuperscript{[4–7]} albeit the driving force may be derived from an asymmetry in the surface texture/structure\textsuperscript{[4, 6]} or the external energy.\textsuperscript{[8–9]} These kinds of water transport methods are already long in use by nature, for instance, the feeding mechanism of capillary feeding shorebirds relies on ratcheting of tiny droplets by time dependent changes in beak geometry, a combination of a passive (geometry) and active (change in geometry of the beak).\textsuperscript{[10]} Vibrations have shown interesting features, such as the ability to move liquid upward a slope at specific drive frequencies and amplitudes.\textsuperscript{[11]} Further, directed water droplet motion was achieved by using texture ratchets in combination with vertical vibrations.\textsuperscript{[6]} Similarly, liquid infused ratchets in combination with horizontal vibrations were recently used to drive water droplet motion for droplet volumes from 0.05–2000 µL,\textsuperscript{[12]} showing significant progress in directed transport of liquids. While there are many methods to move and manipulate water and organic liquid droplets, manipulation of liquid metals is more demanding.
Liquid metals, metals and alloys liquid at or near room temperature, have garnered attention in the scientific community due to an interesting combination of properties. Granted the long-used liquid metal mercury has been phased out due to safety concerns, see Minamata convention.\[13\] Nowadays, mercury has been substituted by gallium-based liquid metals. These metals and alloys feature electrical and thermal conductivity, low viscosity, low toxicity, and a reactive and regenerating surface.\[14–15\] Therefore, their potential for application as chemical reaction environments,\[16\] in soft electronics,\[17\] and in soft robotics is scrutinized.\[18–19\] For many applications, especially, for soft electronics (i.e., patterning methods), biomedical applications (i.e., controlled drug delivery), and soft robotics, reliable and controlled movement or manipulation (i.e., deformation) of liquid metal is essential.

Mobility and directed transport of gallium-based liquid metals are more challenging than for ‘conventional’ liquids. This difficulty arises from the reactivity of gallium towards oxygen, as these liquid metals form a self-limiting oxide skin. This oxide skin is sticky toward most surfaces while featuring yield stress.\[20\] Because of the sticky nature of the liquid metal oxide, liquid metals are often actuated in liquids, where one can exploit the slip layer.\[20–21\] Liquid metals do not stick to smooth surfaces when a thin layer of water or organic solvent is deposited on the surface first. Interestingly, slip layers can also be used to achieve rebound of liquid metals. Here, the slip layer thickness was found to impact the rebound of liquid metal droplets while helping to avoid the adhesion of the liquid metal.\[22\] Generally, actuation of liquid metals is easier in liquids than in air. Actuation means in liquid or on a liquid layer rely on magnetic fields,\[18,23\] electric fields,\[24\] chemical gradients (chemotaxis),\[25\] fuel,\[26\] and ultrasound (low µm-scale object).\[27–28\] Though the latter three methods have only been shown for small droplets. Furthermore, without an exterior second liquid phase, controlled actuation of liquid metals becomes arduous, as the liquid sticks to other materials. Therefore non-stick, so-called metallophobic, surfaces have been established, which rely on hierarchical roughness of the surface minimizing the contact area between the liquid metal oxide and the substrate.\[29–30\] Another method involves decorating small liquid metal droplets with micro- or nanoparticles, generating liquid metal marbles. Both methods can be used to achieve limited mobility of the liquid metal.\[31–33\] The latter is impacted by particle detachment and generation of pristine surface areas under stresses for larger droplets (ca. bigger than 100 µL). Movement and deformation of liquid metal droplets “in air” have been generally obtained by gravity (tilting the sample) or by magnetic actuation. In our experience, both methods are rather unreliable, as the shape of the droplet dictates the necessary force (i.e., tilting angle). Further, actuation of a magnetic liquid metal droplets by a magnetic field can deform the liquid metal droplet substantially, and perhaps rendering it unresponsive due to adhesion induced by the forces acting on the liquid metal, i.e., by forced wetting.\[20\]

Herein, we showcase a new paradigm to actuate liquid metal droplets (Galinstan, a eutectic alloy of gallium, indium, and tin; denoted EGaInSn) in air (without another liquid, i.e., without slip layer). The method encompasses the combined use of a metallophobic substrate and vertical vibrations. The method features great repeatability, control of the movement speed by control of the tilting angle, and a large transport volume range, from 30 µL to 2000 µL and potentially even greater. Further, we show that only minute inclination angles can be employed to actuate the liquid metal droplets. There are many
possible combinations of vibration frequencies and amplitudes, inclination angles, and droplet size. Therefore, initially, the vertical vibration was optimized for each droplet size, namely, the frequency and amplitude. Then, the threshold inclination angle and the droplet movement speed at a fixed vibration were analyzed. Finally, the movement mechanism was analyzed and the ability of liquid metal droplets to cross obstacles investigated. Due to the high mobility induced by the vertical vibrations, this method can be used in conjunction with other actuation methods, i.e., magnetic actuation,\textsuperscript{[18]} or with textures to enable controlled and on demand directed movement of liquid metals.

2. Methods

Materials

The eutectic alloy of gallium, indium, and tin (EGaInSn) with a composition of Ga 68.5 wt\%, In 21.5 wt\%, Sn 10 wt\%, denoted in literature as Galinstan, was used in all experiments. The alloy was purchased from Dongguan Wochang Metal Products Co. (Dongguan, China). 90 mm standard polystyrene petri dishes were used as substrates (Biosharp, Hefei, China), and were coated by the liquid metal phobic (metallophobic) coating Neverwet (Rust-Oleum, Vernon Hills, United States).\textsuperscript{[34]} A structured and rough diamond coating was generated with specific liquid metal phobic morphology on a Si-sample according to a procedure outlined earlier.\textsuperscript{[35–36]}

Characterization

Scanning electron microscopy (SEM) micrographs and energy-dispersive X-ray spectroscopy (EDS) mappings were taken with the APREO S (Thermo Fisher Scientific) at an acceleration voltage of 5 kV. Micro-Raman scattering was measured with the HORIBA LabRAM HR800 Evolution Raman spectrometer employing an excitation wavelength of 532 nm.

Fabrication of liquid metal phobic samples via Neverwet coating

Polystyrene petri dishes were cut (the outer rim was trimmed) to obtain flat PS disks from single use petri dishes and glued to cardboard. Then, the base coat (Neverwet) was applied twice and left to dry for at least 30 min in the fume hood (step denoted as step 1 in the instructions). Subsequently, the top coat (step 2) was applied two times and the sample was left to dry overnight (12 h). The coating was applied from an approx. distance of 20 cm. More information on the coating procedure and some key points to keep in mind can be found in the instructions manual of the commercial coating and the article by the Dickey group.\textsuperscript{[34]}

Setup and workflow of vibration-induced movement of the liquid metal: A Frederiksen Vibration generator no 218500 with circular Chladni plate was used to generate precise and defined vibrations (Frederiksen Scientific, Drammen, Norway). The Chladni plate was outfitted with a paper coating to protect it from liquid metal attachment and corrosion. On this protective paper coating the liquid metal phobic samples were placed (glued). A Keysight 33210A Function/Arbitrary Waveform Generator (Keysight Technologies,
Santa Rosa, United States) was employed to generate square shaped waves with frequencies ranging from 1 to 60 Hz at amplitudes ranging between 0.1 and 10 Volt (later denoted V). The function generator was directly connected to the vibration generator. Furthermore, the vibration generator was placed on a manual tilting stage, which can measure the tilting angle between −20° to 20°. For liquid metal droplet deposition on the sample, the tilting stage was set to 0°. Then, the sample (attached to the vibration generator) was placed below a self-built dispensing unit, comprising a fluorocarbon tip, a 20 cm long silicone rubber peristalsis tube, and the Leadfluid TYD01 syringe pump (Baoding Lead Fluid Technology Co., Ltd., Hebei, China) outfitted with a 10 mL syringe. The 10 mL syringe was initially filled with EGaInSn and the pump was used to control the liquid metal droplet volume. We estimate the deviation of the droplet volume to around 15 µL. A certain volume, between 30 and 2000 µL, was dispensed by the pump and placed carefully on the sample at a distance less than 1 cm between the nozzle and the sample. Then, the horizontal level of the Chladni plate was assessed and aligned by use of a spirit level (in both directions, x and y). Subsequently, the tilting stage was set to the desired tilting angle and vibrations applied to move the droplets. The vertical vibrations are schematically shown in Fig. 1. As blank experiments, droplets were moved by only tilting the stage or by tilting the stage after flattening the drops by using vibrations (i.e., strong vibrations: 4–6 V at 20 to 30 Hz). After the experiment, the horizontal level of the Chladni plate was ascertained a second time. Movement of the droplets was captured in a top-view (or rarely: side view) setup by a Nikon D7100 camera (Nikon Corporation, Tokyo, Japan) at an acquisition rate of 29 Hz (29 pictures per second) with a Nikon AF-S DX Nikkor 35 mm f1.8G lens (Nikon Corporation, Tokyo, Japan) or in a side-view configuration by a high-speed camera (Phantom Miro Lab 110, Vision Research, Wayne, United States) at an acquisition rate of 400 Hz, a resolution of 768 pixels x 768 pixels, and an exposure time of 2400 µs.

3. Results and Discussion

3.1 Metallophobic nature of the coatings

Although this work does not focus on the study of liquid metal phobic or better liquid metal oxide phobic (metallophobic) surfaces, a short overview of the two different liquid metal phobic surfaces and the origin of their liquid metal repellency are given here briefly.

Gallium-based liquid metals react with oxygen rapidly and form gallium oxide (mixed oxides of Ga$_2$O$_3$ and Ga$_2$O).\textsuperscript{37} This oxide skin is considered to be sticky on many substrates.\textsuperscript{20} Many methods have been established to avoid adhesion of liquid metals, but most of them are only applicable in liquid surroundings. One rationale to inhibit the adhesion of liquid metal (with oxide skin) in air without the use of surrounding liquids is the use of roughness combined with hydrophobic or even superhydrophobic surfaces.\textsuperscript{20} A high roughness reduces the contact area between the liquid metal and the surface substrate drastically, which is ascribed to the yield stress of the oxide skin. The liquid metal oxide is in the case of a rough substrate only in contact with surface protrusion and does not infiltrate pits between protrusion as long as the pit and protrusion dimensions are favorable.\textsuperscript{38–39} Notably, wettability also
plays a role but a small change in wettability is not that impactful. Consequently, several rough surfaces feature liquid metal repellency. Here, the Neverwet coating and structured diamond coatings were used. The former was used due to the ease of access and fabrication, while the latter was chosen due to the low friction coefficient of diamond. Furthermore, during experiments leading to a previous report on the surface tension of the liquid metal oxide skin,[35] we found that liquid metal droplets, especially larger ones, were very mobile on structured diamond coatings upon exposition to vibrations.

In Fig. 2, the surface morphology of the Neverwet and diamond coatings are shown. The Neverwet coating appears to be homogeneously (Fig. 2a) and comprises of two layers of roughness. The microscale roughness originates from clusters or aggregates spaced out hundreds of micrometers. These clusters have a height of tens of micrometers, as discussed by the Dickey group.[34] The second layer of roughness originates from hills of nanoparticles with 100 nm or less and comprise of silica nanoparticles (ca. 20 nm). Further characterization of such a Neverwet coating can be found in the article by the Dickey group.[34] It should be noted that this kind of coating is F-terminated. The F-termination in combination with the rough and porous structure of Neverwet leads to the high water contact angles (superhydrophobic surface).

Similarly, the diamond coating features hierarchical roughness. The coating comprises of diamond hemispheres of approx. 2 µm height and 2.2 ± 0.5 µm width, the coating itself is nanocrystalline (50 to 250 nm grain size), and it is continuous. The hemisphere density on the sample is an important parameter for liquid metal repellency and was chosen to be close to that employed for the superhydrophobic diamond coating in our previous article.[35] In comparison to the previous published coating, the density of the hemispheres is slightly higher, leading to somewhat coalesced diamond hemispheres, as seen in Fig. 2d. The observed surface structure arises from the two-step deposition process and the prior intricate seeding procedures, as outlined previously.[36] Briefly, in a first seeding step, nanodiamond seeds are stabilized by oxalic acid, leading to controlled low seeding densities on the substrate. Then, the diamond is grown by hot filament chemical deposition (HFCVD), resulting in the growth of hemispheres due to the growth mechanism of diamond (Vollmer-Weber; also known as island growth).[40] Subsequently, a second seeding procedure with a highly stable nanodiamond colloid (and conducive surface charge, that is positive Zetapotential of the nanoparticles) was executed, yielding a high seeding density on the sample. Finally, a second HFCVD growth process was executed, resulting in the growth of a coalesced diamond film on the sample. To verify the identity of the coating, Raman spectra of were measured (Figure S2). The peak at 1333 cm$^{-1}$ verifies the presence of diamond. Further, the shoulder at 1350 cm$^{-1}$ and the peak at 1582 cm$^{-1}$ signify the presence of graphite (or graphitic material) and correspond to the D and G bands, respectively,[41] a common by-product during the diamond synthesis.

Both coatings feature hierarchical roughness and are good candidates for liquid metal repellent surfaces. To signify the excellent liquid metal repellency of the Neverwet coating, an SEM micrograph in combination with EDS maps were taken after the movement experiments below were concluded. Notably,
no cleaning of the samples was conducted before SEM and EDS measurements. Neither in the SEM micrograph nor in the EDS maps or the EDS spectrum the presence of liquid metal (gallium, indium, or tin) could be ascertained (see Figure S3), signifying the excellent liquid metal repellency of the Neverwet coating. For the superhydrophobic diamond coating similar behavior is expected as long as the coating is H-terminated (hydrophobic). Besides the advantage of low friction coefficient of the diamond coating it also possesses a high chemical resistance and can be easily cleaned by acid or base if contaminated by liquid metal (oxide) adhesion. Notably, these two structured surfaces only serve as examples of usable materials and were chosen due to their availability rather than their performance. We anticipate that other liquid metal repellent surfaces (likely based on hierarchical roughness\textsuperscript{20,29,42–44}) can be used in a similar fashion and might even show better performance than the coatings featured here.

### 3.2 Liquid metal movement on inclined surfaces by vibrations

In general, it is difficult to move liquid metal in air, as it is outfitted with the sticky oxide skin and features yield stress. Further liquid metal droplet movement is commencing via rolling, and the issue of the yield stress of the oxide is that non-equilibrium shapes, for instance, ovaloid or flattened shapes, are often obtained due to an impact of the droplet on the surface. Similarly, flattening can be caused by vibrations, and this flattening has an impact on the scroll off angle (mobility). This makes reliable and repeatable measurement of scroll off angles even for very small droplets challenging. To set the stage, the necessary inclination angles for liquid metal droplets rolling off samples was determined on the Neverwet coated polystyrene, as shown in Fig. 3a. Small droplets (30 µL) scroll or roll off the sample at an inclination angle of around 13.5 ± 0.5°. However, flattened droplets show an increased scroll off angle of around 19.7 ± 1.0°. Relatively low roll off angles have been published for round liquid metal droplets deposited very gentle (or by improving their roundness) on metallophobic surfaces and liquid metal marbles, i.e., ca. 12° for magnetically controllable liquid metal marbles, 5–8° for graphene coated and 2° for polytetrafluoroethylene coated liquid metal marbles as well as ≤ 12° for liquid metallophobic surfaces.\textsuperscript{31–32,45–47} Maybe overlooked in this context is the fact that the scroll off angle is dependent on the droplet volume and droplets and marbles deform upon deposition. Non-circular objects generally need a higher inclination angle in order to roll off (see Fig. 3a). The higher inclination angle for flattened droplets arises from the mechanism of movement, which is a rolling motion. The necessary inclination angle increases for droplets of 100 µL and then, decreases for bigger droplets to around 6.8 ± 0.2° (2000 µL). The higher inclination angle for 100 µL stems from the non-circularity of the droplet as it appears ovaloid. Bigger droplets are more flattened but necessitate a much lower inclination angle due to their high mass. This is due to the fact that the liquid in the oxide skin shifts the weight to the lower region of the droplet and this mass is able to move the oxide skin in the process. It should be noted that this motion is still a “rolling” motion and not a sliding motion (see Section “Motion mechanism”). One can see this for semimetallophobic surfaces, such as paper, where larger liquid metal droplets roll down while leaving a liquid metal oxide trail behind them on the paper.\textsuperscript{48}
Shifting to vibration enabled movement. In Fig. 3b, the minimum inclination angle necessary to actuate a droplet downwards is plotted versus the droplet volume for the Neverwet and the diamond coating when the droplet is actuated by vibrations. For this measurement, the vibration frequency and amplitude were optimized, as shown in Fig. 3c. As frequency, 27.5 Hz was used for the measurement, while the amplitude and inclination angle were varied. Generally, the amplitude was varied between 2 and 6 V, but most of the times, 2 to 3 V would move droplets once the inclination threshold for movement was reached. The minimum inclination angle for the liquid metal to move on Neverwet is with ca. 1 ± 0.3° across all drop sizes slightly higher than that on the diamond coating (0.5 ± 0.3°). As an example for movement of liquid metal on the diamond sample, Figure S1 in the supporting information shows video stills from the droplet movement at an inclination angle of 0.5°: droplet volume 600 µL, vibration 27.5 Hz and 3 V. Due to the low inclination angle the droplet movement is very slow. The slightly lower threshold inclination angle for diamond may originate from the low friction coefficient of diamond.[40,49] Interestingly, the threshold inclination angle is rather independent of the droplet volume, suggesting a somewhat different mode of motion than ‘normal rolling’ (see Section “Motion mechanism”). An exception to this may be very small droplets with volumes (30 µL or less), as they appear to necessitate a lower inclination angle (Neverwet coating) than the bigger droplets. For each droplet volume, several parameters need to be optimized, namely, the drive amplitude (between 0.5 and 10 V), the frequency (between 5 and 60 Hz), and the inclination angle. In Fig. 3c, the inclination angle was set to 3° and the drive amplitude, frequency, and the droplet volume varied. For droplets (≤ 650 µL), an optimal frequency range between 20 and 30 Hz is observed, and the necessary drive amplitudes are ca. 2 V. For lower frequencies, the necessary drive amplitude increases rapidly. Similarly, for higher frequencies, the threshold amplitude increases, yet the droplets remain relatively mobile. For instance, movement can still be obtained by a higher inclination angle or manually tilting. Though, the motion itself remains relatively slow compared to the movement observed in the optimal frequency range, and it does not appear to depend on the drive amplitude at these higher frequencies. For bigger droplets (or puddles; ≥ 1000 µL), the liquid metal moves even at low (i.e., 5 Hz) and high frequencies (i.e., 60 Hz) at driving amplitudes of 4 V or lower. However, the optimal frequency range remains between 20 to 30 Hz, unaltered from the optimal range for the smaller droplets, and driving voltages around 1 V are only necessary to induce movement of the liquid metal on the Neverwet coating. That the optimal frequency range for mobile liquid metal droplets remains constant is surprising as for water droplets application of resonance frequencies improves droplet mobility (speed), and the resonance frequencies are dependent on the droplet size/volume.[6,50] Notably, the threshold driving voltage necessary to induce movement on the inclined sample is lower the higher the volume of the droplet is, perhaps related to the higher driving force (due to higher mass of the droplet).

As an example of droplet movement, Fig. 4 shows the top view of droplet motion of 30 µL and 1000 µL liquid metal droplets on Neverwet coated polystyrene. In the Supporting information (movies 1 and 2), movies of droplet motion are shown, which correspond to the stills shown in Fig. 4. Figure 4a shows the movement of a 30 µL droplet down an incline of 2°. The vibration used here is defined by a frequency of 27.5 Hz and an amplitude of 6 V. The droplet crossed the distance of the sample (ca. 7 cm) in less than 1 s. The stills of the taken video suggest that the droplet detaches from the surface (3rd and 6th stills), as
the droplets become smaller (due to the high surface tension of ca. 365 mN/m).[35] Furthermore, one can observe a flattened droplet with higher surface area than the original one in the third still, suggesting impact of the droplet. However, this is difficult to ascertain from top view videos. Further, vibration patterns can be observed on the other stills. For the big droplet with a volume of 1000 µL, movement of the droplet appears to be a bit slower, and the video as well as the stills do not suggest that the droplet detaches from the surface. Again, vibration patterns can be observed. Similar vibration patterns have been described by Zhao et al. for liquid metal in alkaline aqueous solution[51] and by Steen et al. for water droplets.[52] Beside these patterns, one can observe liquid metal scattering and dispersal for larger droplets at high amplitudes (≥ 6 V) when the frequency is between 20 and 30 Hz. For instance, as shown in movie 3 in the supporting information for a 1000 µL droplet excited with a vibration of 27.5 Hz and 8 V. Droplets may be ejected in the middle or at the side of the liquid metal puddle. Therefore, the drive amplitude needs to be controlled rigorously.

### 3.3 Dependence of the liquid metal movement speed on inclination angle and droplet volume

Figure 5 has a closer look at the liquid metal movement on the inclined Neverwet coating upon actuation with vibrations. Here, the vibration frequency was set to 27.5 Hz and the vibration amplitude was generally set to 2 V, except for the smallest droplet size of 30 µL, as this droplet size did not reliably move upon use of a drive amplitude of 2 V. In Fig. 5a and c, the time-displacement curves for droplets with volumes of 30 µL and 1000 µL are shown while Fig. 5b and d depict the corresponding velocity. Upon excitation with the specific vibration, the 30 µL droplet moves downwards. Initial displacement is slow and acceleration is observed in the time-displacement curve in the first 0.2 s. Then, the velocity (displacement versus time) remains constant, which can be ascertained by the linear region in the graphs (Fig. 5a). The impact of the inclination angle is directly visible in the time-displacement curves and in the average velocity graph in Fig. 5b. At minute inclinations (i.e., 0.5°), the movement is very slow with a velocity of 2.5 ± 0.5 cm/s. The velocity increases with inclination linearly up to a velocity of 14.3 ± 1.4 cm/s at an inclination angle of 5°. Higher inclination angles were not measured, as for bigger droplets movement might arise at angles higher than 5° due to jitter stemming from manual adjustment of the tilting stage. At first glance, the droplet movement of 1000 µL droplets appears similar to that of the 30 µL droplets. However, a longer run in time of ca. 0.3 s is needed and the velocity is lower with 0.7 ± 0.3 cm/s (1°) and 7.7 ± 0.8 cm/s (5°), as seen in Fig. 5c and d. Figure 5e and f suggest that this is a general trend. The droplet movement is for the 30 µL droplet much faster than for the bigger ones. Interestingly, droplet movement speed does not appear to be dependent on the droplet size in the range from 100 to 2000 µL, as the velocities for different droplet sizes are scattered around 5.5 cm/s for a set inclination angle of 4°. The similar velocity irrespective of the droplet volume might stem from a common movement mode. The movement is either sliding/gliding or “rolling” (see Section Movement mechanism). Bigger droplets have a higher mass, which increases the driving force due to the tilted surface, but they are also encumbered with higher friction/adhesion counteracting the movement due to the bigger contact area (or better? pinned contact line length) and mass. The higher velocity observed for the small droplet is
ascribed to the different movement mode, “jumping movement”, arising from the different vibration amplitude used. During jumping movement, the droplet is not in contact with the surface, which alleviates friction and adhesion forces with the surface counteracting the driving force of droplet motion and the droplet is able to move faster.

3.4 Movement mechanism

In this article, it was hinted that the mechanism for movement is different for an inclined surface and the vibration induced movement. From experience with liquid metal marbles, we know that liquid metal marbles roll down an inclined surface, even at rather low inclination angles. However, rolling off is impeded by a low roundness of the droplets and large droplets are difficult to move, as they might leave behind their liquid metal oxide patina. In Fig. 3a it was shown that a considerable tilting angle is needed to actuate liquid metal down a slope, even when the surface is metallophobic. The reason for the relatively high roll off angles measured above are the movement mechanism, which is a rolling motion (see also Fig. 6 and the corresponding videos: Movie S4 and S5), and the fact that roundness of the droplets was not improved by a prior rolling procedure (compare to liquid metal marbles). The rolling motion is also observed for the bigger droplets. For instance, the 1000 µL liquid metal droplet shows this ‘rolling’ motion. Upon inclining the tilting stage, the liquid inside the oxide skin is moved toward the lower part of the droplet, thereby pushing the oxide skin towards the ground. Concurrently, less bulk liquid metal is located at the higher section of the liquid metal droplet. Due to the tilted surface, gravity exerts a driving force toward the lower part of the sample. As the liquid metal now moves downwards, the oxide skin at the higher part of the droplet is lifted (detaches from the surface). This lifting results from the high yield stress of the oxide skin, operating in a similar way as rubber encapsulation or liquid marbles. For liquid puddles (or liquid marbles) movement has been shown to work via rolling in a mixture of free surface and caterpillar motion (depending on the volume of the droplet).

Liquid metal movement induced by vibrations either commences via jumping and ‘rolling’ or via ‘rolling’. In Fig. 7 (and the supporting information Movie S6 and S7), the movement of 30 µL and 1000 µL droplets is shown. The former was excited by 27.5 Hz, 6 V vibration, the latter by 27.5 Hz, 2 V vibration while in both cases the inclination angle was set to 3°. For the smaller droplet, one can see in the image at t = 0 s that the droplet is compressed and flattened during upward movement of the vibrating plate. Once the plate moves downwards, the liquid metal droplet is expelled from the surface, as seen in the images at t = 0.0075 s and 0.0275 s. During the time the liquid metal droplet is airborne, it travels a fair distance downward the inclined sample and impacts the substrate after ca. 2 oscillations of the sample (see image: t = 0.0650 s). A slight droplet movement downward the sample is also observed during contact with the sample. In an additional experiment, the liquid metal oxide skin was marked with silica beads and rolling of the whole droplet (30 µL) was observed while airborne and while in contact with the surface. The large droplet (1000 µL) does not detach from the surface, rather it appears to slide on the surface, as shown in Fig. 7. At the beginning (t = 0 s), the vibrating plate moves upwards, and the droplet (or puddle) is compressed. Once the plate moves downwards, the liquid metal maintains some momentum, and the center of mass is lifted. Concurrently, the elevated (receding) contact line recedes.
while the lower contact line (advancing contact line) is maintained. At 0.0275 s, the plate moves upwards and the puddle is compressed by the substrate surface, resulting in a bigger puddle area. This time, the lower (advancing) contact line advances, while the receding contact line is maintained. The process can be summarized as periodic receding (uphill) and advancing (downhill) of the droplet. We assumed that larger liquid metal droplets slide down a slope once actuated with vibrations rather than rolling down. To validate or disprove this hypothesis, the 1000 µL liquid metal puddle was marked with silica beads, as shown in the supporting information Figure S4. Beads remaining stationary on the liquid metal puddle would indicate that the liquid metal puddle moves via a sliding mechanism. However, the silica beads moved in the same direction as the liquid metal droplet. The silica bead located at bottom (middle) moved much faster than the beads located at the right and left side. All these facts indicate that the droplet ‘rolls’ down by periodic lifting the oxide skin (detaching from substrate) at the receding end of the puddle and lowering of the liquid metal oxide skin at the advancing section of the puddle, where it would contact the substrate.

Notably, droplets were also able to cross small obstacles. For instance, the 650 µL droplet could cross an edge with a height of 0.5 mm, as shown in Fig. 8. The droplet was actuated for this traversal with 27.5 Hz at 2 V vibration at an inclination angle of 5°. The stills in Fig. 8 (and the Movie S8) show that the droplet moves from the Neverwet coated sample (white) to the diamond coated sample (black) and crosses the obstacle very rapidly. This traversal is related to projection of some mass of the liquid metal across the edge (0.1 s) and the tilting angle combined with gravity resulting in a net downwards force. We also tested an obstacle height of 0.8 mm. However, traversal of such a high obstacle by droplets was unreliable. Still, these results indicate that with surface design and surface structuring techniques one may be able to establish motion without employing a general tilting angle, but by using structures, such as (texture) ratchets. One may also consider horizontal vibration instead of vertical vibrations, asymmetric horizontal or vertical vibrations, or a combination of horizontal and vertical vibrations for this purpose.

Conclusion

In this work we presented a facile method to achieve high mobility of liquid metal (Galinstan) droplets in air by coupling metallophobic surface design with horizontal vibrations. As metallophobic surfaces, hierarchical structured Neverwet and diamond coatings were used while the optimal vibration frequency was 27.5 Hz across all droplet sizes. Notably, with this method we were able to actuate a broad range of droplet sizes with the aid of only minute inclination angles, as the threshold inclination angles were between 0.5 and 1°. Furthermore, the movement speed was homogeneous and with ca. 5.5 cm/s at an inclination angle of 4° high. Further, the movement speed was rather independent of the droplet volume (≥ 100 µL). The movement mechanism was found to be a rolling mechanism, based on periodic receding (uphill) and advancing (downhill) of the droplet during vibration. Finally, we showed that liquid metal puddles are able to traverse small (height 0.5 mm) obstacles, indicating that it can be combined with surface structuring to achieve more directed motion. In regard to directed motion, other vibrations, such
as horizontal vibrations, asymmetric vibrations, and combination of these, and their combination with surface structures are anticipated to further improve liquid metal manipulation and directed liquid metal transport.

Declarations

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Author contributions S. Handschuh-Wang conceive the project. S. Handschuh-Wang, and T. Gan performed the experiments and analyzed data under the supervision of and X. Zhou, B. He, and P. Han. S. Handschuh-Wang, T. Gan, and T. Wang prepared the samples. Data analysis was performed by T. Gan, S. Handschuh-Wang, and F. J. Stadler. All authors discussed and interpreted the results. S. Handschuh-Wang and F. J. Stadler wrote the manuscript with the assistance of the other authors. X. Zhou, P. Han, and B. He provided financial support.

References


Figures

Figure 1

Schematic showing the movement of a liquid metal droplet due to vertical vibrations when the sample is inclined at an inclination angle (α).
Figure 2

Morphology of the liquid metal repellent surfaces. (a) SEM micrograph of the Neverwet coating on polystyrene and its magnification (b). (c) SEM micrograph of the structured diamond coating on Si and its magnification (d).

![Figure 2](image)

Figure 3

(a) Scroll off angle of liquid metal droplets dependent on the droplet volume for both normal deposited and flattened droplets, the liquid metal phobic sample was the Neverwet coated polystyrene. (b) Minimum inclination angle necessary to move liquid metal droplets on Neverwet or diamond when exposed to vibrations (frequency 27.5 Hz, 2 to 6 V amplitude). (c) Minimum amplitude (in V) necessary to move a liquid metal droplet dependent on the frequency and droplet volume. The inclination angle of the sample (Neverwet coating) was set to 3°.
Figure 4

Sequence of photographs illustrating droplet motion induced by vibrations. (a) Motion of a 30 µL droplet actuated by a vibration at 27.5 Hz and 6 V. (b) Motion of a 1000 µL droplet (or puddle) actuated by a vibration at 27.5 Hz and 2 V. Both movements were recorded at an inclination angle of 2°.
Figure 5

Movement of EGaInSn on the Neverwet coating upon application of vibrations. (a) Time-displacement curve of EGaInSn droplets with a volume of 30 µL dependent on the inclination angle of the sample upon actuation with vibrations (27.5 Hz, 6 V amplitude) and (b) the corresponding velocity versus inclination angle diagram. (c) Time-displacement curve of EGaInSn droplets with a volume of 1000 µL dependent on the inclination angle of the sample upon actuation with vibrations (27.5 Hz, 2 V amplitude) and (d) the corresponding velocity versus inclination angle diagram. (e) Comparison of time-displacement curves of liquid metal droplets; the droplet volume was varied between 30 µL and 2000 µL. The inclination angle was maintained at 4°. The vibration used was 27.5 Hz, 2 V amplitude, except for 30 µL droplet (27.5 Hz, 6 V amplitude). (f) Velocity of droplet movement versus droplet size at fixed inclination angle of 4°. The vibration used was 27.5 Hz, 2 V amplitude, except for 30 µL droplet (27.5 Hz, 6 V amplitude).
Figure 6

Droplets moving down a slope on a metallophobic diamond coated Si sample. The red arrows indicate that the movement is commencing via a rolling motion.
Figure 7

Movement of liquid metal droplets on Neverwet coated PS upon exposition to vibrations. The 30 µL droplet was exposed to 27.5 Hz at 6 V and the 1000 µL droplet to 27.5 Hz at 2 V. The inclination angle was set to 3°. The arrows depict the movement direction of the substrate while the numbers in the image depict the elapsed time. Further, the advancing and receding contact line is indicated in the image with a red dotted line.
Figure 8

Droplet movement across an obstacle (0.5 mm edge height). For this experiment, a 650 µL EGaInSn droplet was used, an inclination angle of 5° was set, and the vibration used was 27.5 Hz at 2 V. The height of the obstacle (black substrate) is 0.5 mm and the obstacle material is a diamond coated Si sample. The white sample is the Neverwet coated PS.

Supplementary Files

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