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Liquid Metal Soft Machines

Principles and Applications

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Liquid Metal Soft Machines

Principles and Applications



Springer

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Preface

In recent years, a group of very fundamental discoveries were continuously made on liquid metals which paved new ways for making new generation soft machines even highly advanced transformable robots. Unlike former endeavors of tackling pure liquid metal matters, the new findings revealed that hybrid components with both liquid metal and related solution including certain solid elements together would enable rather complicated machine styles. Along this direction, many pivotal findings were being achieved on shape changeable liquid metals or smart transformers.

Particularly, owing to the discovery of the extraordinary self-powered liquid metal effect, a group of long-lasting and quickly running soft machines which run just like a biomimetic mollusk became now also possible. This new generation machine owns the capabilities of autonomous convergence or divergence during chasing which are hard to image otherwise by conventional machines, even biological systems. And more liquid metal smart machines are still on the way.

In a large extent, the finding of artificial liquid metal machines opens an exciting platform for designing future soft robot, microfluidic systems, and may eventually lead to the envisioned dynamically reconfigurable intelligent soft robots. Aiming for this goal, several years before, we had ever initiated a program named as SMILE (soft machine based on intelligence, liquid metal, and electronics). Clearly, all these machine or robot styles are based on the soft, fluidic, and multi-physical and chemical capabilities of liquid metal.

In fact, with many outstanding material merits inside, the liquid metal is rather promising in making various complicated machine styles whose ultimate goal is definitely biology like robots. The next step for advancing liquid metal machine is therefore to just fully simulate nature. Meanwhile, some newly emerging liquid metal 3D printing methods will also aid for such machine fabrications. It is expected that a wonderful world of liquid metal soft robots will come true in the near future.

To push forward further researches and possible applications along the above important frontier, this book is dedicated to draft a new machine category: the liquid metal soft machines or motors. The major advancements as achieved before will be

summarized and future directions worth of pursuing will be outlined. Representative applications enabled by liquid metal machines from both fundamental and practical aspects will be reviewed. Perspective for future development in the area of liquid metal soft machine was given.

The present book is an output of our lab's more than 10 years' continuous academic endeavors. Over the past few years, a group of our faculties, postdoctoral research fellows, graduate students, and collaborators have made important contributions to mold this new area of liquid metal robots. The authors would like to take this chance to express their sincere appreciations to those people who have offered their professional contribution: Dr. Jie Zhang, Dr. Bin Yuan, Dr. Jianbo Tang, Dr. Lei Wang, Dr. Sicong Tan, Dr. Qian Wang, Dr. Yang Yu, Dr. Liting Yi, Dr. Liang Hu, Dr. Shuting Liang, Mr. Youyou Yao, Mr. Xiaohu Yang, Mr. Hongzhang Wang, Mr. Sen Chen, Mr. Yujie Ding, and Mr. Wenqiang Fang. Lastly but not least, the senior author of this book would like to acknowledge the generous support from the NSFC Key Project under Grant No. 91748206, the Frontier Project of the Chinese Academy of Sciences, Special Foundation of President of the Chinese Academy of Sciences, and Tsinghua University Initiative Scientific Research Program. Thanks for all these valuable supports, the present book could now become a reality.

We humbly hope that this book could serve as a start point for the academics to quickly grasp the basics of the liquid metal soft machine and thus better advance the area. We would very much welcome any critical comments and constructive suggestions from the readers for us to further enhance our book which would be incorporated into its future possible updated version.

Beijing, China
July 2018

Jing Liu
Lei Sheng
Zhi-Zhu He

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Abstract

This book is to present the core principles and practical applications of a latest machine category: The liquid metal soft machines or robots. Along with a brief introduction on the conventional soft robot and its allied materials, the new conceptual liquid metal machines were introduced to revolutionize existing rigid robots either in large or small size. Typical features of the soft liquid metal materials were outlined. Various transformational and locomotion capabilities of liquid metal machines under either external fields or intrinsic driving fuels were illustrated. Meanwhile, a series of unusual phenomena thus disclosed toward making the shape changeable smart soft machines were presented. The related physical or chemical mechanisms to control the liquid metal transformers were interpreted. Important strategies were explained to construct a group of different advanced functional liquid metal soft machines or robots which are hard to fabricate otherwise via rigid metal or conventional materials. With both fundamental and practical importance, this book is expected to serve as basic reference for making future generation smart soft machine or accompanying robots.

Keywords Liquid metal • Soft machine • Transformable robot
Smart materials

Chapter 1

Introduction



Abstract Making soft robots that can flexibly transform among different morphologies has long been a dream in both science and engineering areas. With outstanding versatile capabilities, liquid metals are opening breakthrough strategies for molding future smart soft robots that had never been anticipated before or hardly achievable by a rigid metal or conventional material. All the evidences collected so far pointed out that liquid metal machine is evolving via a rather quick way. The latest discoveries on a group of very fundamental phenomena of liquid metals and technological advances thus enabled significantly strengthened this endeavor. Clearly, combining allied components with the liquid metal systems is offering many brand new machine roles as well as incubating future highly advanced robots. In fact, capabilities as offered by liquid metals are far much profound than one can expect. There is plenty of space to explore in the area. This chapter gives a brief overview of soft robots and some unconventional opportunities that liquid metal could provide for innovating the soft machine science and technology.

Keywords Liquid metal • Robot • Soft machine • Smart material

Making soft robots that can flexibly transform among different morphologies has long been a dream in both science and engineering areas. With outstanding versatile capabilities, liquid metals are opening breakthrough strategies for molding future smart soft robots that had never been anticipated before or hardly achievable by a rigid metal or conventional material. All the evidences collected so far pointed out that liquid metal machine is evolving via a rather quick way. The latest discoveries on a group of very fundamental phenomena of liquid metals and technological advances thus enabled significantly strengthened this endeavor. Clearly, combining allied components with the liquid metal systems is offering many brand new machine roles as well as incubating future highly advanced robots. In fact, capabilities as offered by liquid metals are far much profound than one can expect. There is plenty of space to explore in the area. This chapter gives a brief overview of soft robots and some unconventional opportunities that liquid metal could provide for innovating the soft machine science and technology.

1.1 Basics About Robots

Robotics is a comprehensive discipline of engineering and science that generally includes mechanical engineering, material science, electrical engineering, computer science, and more other areas. It deals with the design, construction, operation, and application of robots, as well as computer systems for their control, sensory feedback, and information processing. These technologies are assumed to make machines that can substitute for humans [1]. Robots can serve in any situation and for any purpose, but today many are used in dangerous environments (including bomb detection and deactivation), manufacturing processes, or where humans cannot survive. Robots can take on any form but some are just made to resemble humans in appearance. This is said to help in the acceptance of a robot in certain replicative behaviors usually conducted by people. Such robots attempt to replicate walking, lifting, speech, cognition, and basically anything a human can do. In fact, many of today's robots are inspired by nature, contributing to the field of bioinspired robotics [1].

The concept of creating machines that can operate autonomously dates back to classical times, but research into the functionality and potential uses of robots did not grow substantially until the twentieth century. Throughout history, it has long been frequently assumed that robots will one day be able to mimic human behavior and manage tasks in a human-like fashion [1]. Today, robotics comes into a rapidly growing era, as technological advances continue. Researching, designing, and building new robots are expected to serve for various practical purposes, whether domestically, commercially, or militarily. Many robots are built to do jobs that are hazardous to people such as defusing bombs, finding survivors in unstable ruins, and exploring mines and shipwrecks. Robotics is also used in education about science, technology, engineering, and mathematics as a teaching aid. Several typical modern robots used in multiple areas can already be autonomous or semiautonomous and range from humanoids to industrial robots, medical operating robots, patient assist robots, partner robots, and even microscopic nano-robots [1].

While most robots today are installed in factories or homes, performing labor or life-saving jobs, many new types of robot are being developed in laboratories around the world. Much of the research in robotics focuses not only on specific industrial tasks, but also on investigations into new types of robot, alternative ways to think about or design robots, and new ways to manufacture them. It is expected that these new types of robot will be able to solve real-world problems when they are finally realized. One approach to designing robots is to base them on animals, especially for designing soft robot.

1.2 Rise of Soft Machine

In nature, a great many trials have been made on the designing of devices that can flexibly transform among different morphologies and freely move via a controllable way to perform desired tasks. This spans in diverse scientific and technological areas

ranging from mechanics, biology to physics. Tremendous efforts have therefore been invested to explore promising strategies to design various kinds of soft machine to perform more special, advanced or dangerous tasks. Such robots should be able to deform timely according to human needs. Passing through the narrow channel, and even spread to the building door (access target internal), then restore and continue to perform the task, such superpower robot has been described in a science fiction blockbuster “Terminator” in the United States which had ever brought to people infinite imagination. In fact, in the practice of medicine, developing soft robots to perform desired medical tasks in human body, such as free movement over the blood vessels, has always been a rather realistic and important scientific goal in the pursuit of the frontier of electronic machinery and modern medicine. It is not hard to perceive that the research scope of the deformable robot beyond the traditional mode is extremely vivid and rich, covering a wide range of fields, such as biology, physics, materials, machinery, and electronics. The connotation of such research is quite intersecting and the applications involved can be seen in various walks of life.

Obviously, to achieve human-like functional bionic soft robot, one must break through the existing technological barrier to the maximum extent, and thoroughly innovate the traditional thoughts. To this end, the scientific community has in fact made a series of important advancements over the past few years which are full of future color. In 2002, researchers from Carnegie Mellon University carried out a quite imaginative exploration, named as “electronic clay” project. It aimed at the goal that under manual control, the machine can arbitrarily change its shape, size, and characteristics, through the program control, to realize the movement of the corresponding electronic clay and the mutual adhesion, and then, with the aid of thousands of electronic clay components, building unimaginable complex objects and implementing various functions. Unfortunately, the above ideas are based more on imagination rather than real technology. Until now, no ideal solution has yet been found. However, the researches on finding the deformable machine have never been interrupted. After 2007, the U.S. Defense Advanced Research Projects Agency (DARPA) launched a campaign competition to develop a flexible “chemical robot” (ChemBot) as the goal and provides a \$3.3 million research contract for the University of Tufts, in order to find new materials and design new kind of robot which not only can move freely, but also can change its shape under the electromagnetic field, acoustic effects, chemicals and other forces. This kind of robot can be engaged in a series of complex space explorations, such as climbing along the rope and performing other activities. It is widely believed that once such a technology is established, its contribution to human activities will be much far bigger than that of the existing robots. Unfortunately, due to the limitation of the materials, such goal has again not yet shown substantial breakthroughs in the development of various shapes of robots.

In recent years, over the processes in investigating various advanced machines, there appear some innovative thoughts in the academic societies. Among them, researchers from Massachusetts Institute of Technology put forward a concept called 4D printing, aiming to achieve self-deformation and assembly of materials. Such research aroused big attentions over the world. At the same time, a joint team from Harvard University, Pittsburgh University and UIUC received a large funding from

the US Army Research Office to develop new materials that can change in shape. The related research is stepping forward, but the focus still lies in the category through varying the conventional materials. In early 2014, the Internet giant Google bought a number of technological companies related to intelligent robots. The company firmly believed that intelligent robots will be the commanding heights of technology and economic growth in the coming future. Obviously, regarding the most advanced intelligent robot, a basic feature on deformable and flexible capability is a key. These trends indicate the great scientific significance and application prospects of the advanced robots.

1.3 Advancements in Soft Robot

Robots used for manufacturing are usually designed to be stiff, composed of rigid materials like alloys, metals, and magnets. The robots based on the rigid materials are perfect for repetitive work due to their fast, precise and strong operation. The natural world is highly different, ranging from the fully soft-bodied octopus to living beings with stiff endo–exoskeleton or exoskeletons. Soft robotics is a growing new field that focuses on the mechanical qualities such as the capacity of the large deformation, the integration of materials, structures, and software, and the application in the field that the rigid materials-based robots cannot adapt to work. Besides, various components to make soft robotics such as sensors and brakes embedded in them are not connected in rigid form, but are printed by 3D, laminate or adhesive [1]. So far, various kinds of principles have been developed in the scientific community to design soft robotics [2, 3]. The control methods involve the form of light [4], magnetic field [5], bionic [6], and electrical [7]. Earlier, a series of soft machines and mollusk robots have been developed by scientists all over the world [8–10], including the worm and worm-like robot [11–13], caterpillar and caterpillar-like robot [14–17], octopus, and octopus-like robot [18, 19], which however still belongs to a plurality of stiff unit bodies. There is currently a considerable distance from designing flexible, pervasive deformation and even fusion soft robots.

Recent work of the robotic systems based on soft technologies has been greatly inspired by the study of soft-bodied animals [20], which is important for developing new robotic mechanisms, actuation techniques, and algorithms. Thus, the new active soft materials were urgently determined to construct soft robots, which could implement the biomechanical intelligence of soft-bodied animals. Many commonly used functional materials include shape memory alloys, elastic material, hydrogel, and dielectric elastomer, ion exchange polymer metal composite and colloidal particles have been tried. It is noteworthy that developing soft muscle-like actuation technology is still one major challenge in the creation of fully soft-bodied robots that can move, deform their body, and modulate body stiffness [20]. So far, the available soft robot is gradually developed along the route from the original rigid machine to semiflexible semirigid until finally full flexibility. In particular, a joint group from Harvard University reported in 2016 a completely soft machine, which formed the

soft octopus by 3D rapid manufacturing technology of elastomeric materials. Such machine was driven by gas expansion that generated through decomposition of fuel inside the internal layout of pipeline [21].

Over the last ten years, various forms of soft robot technology have been proposed. Although new technologies emerge endlessly, there are still great challenges in the soft robot, no matter whether it is material, engine or function. Softness is one of the most essential characteristics of soft robots, and currently, soft robots are hard to achieve the “soft” characteristics of structures and functions at the same time, especially in terms of functional aspects. Soft materials open up new prospects for bioengineered and hybrid devices. A tissue-engineered jellyfish through growing cardiac muscle cells has been developed to swim like a fish. Minimally invasive surgery (MIS) is another very important application of soft robot. MIS soft robot has less tissue trauma than rigid instruments during insertion and navigation through soft tissues and complex organ geometries [20]. The features of the soft biomaterials for soft medical machine include flexible function, transient electronics and a tissue growth scaffold made from biopolymers such as silk [20]. 3D printed hydrogel structure has also been used to fabricate the locomotive “bio-robot”. In addition, a soft robot for tissue repair could be designed to release therapeutic agents locally or deposit materials [20]. The soft robots could be prepared by using 3D printing fabrication methods. It thus also has great potential for performing tasks that require disposable devices or swarm-like interactions. New challenges include the selection of appropriate tissue sources and the flexible interaction with synthetic materials and electronics [20]. A new generation of soft robots adapted to the real-world situations requires seamless integration of various disparate fields such as material science, electrical, mechanical, manufacturing technology, bioengineering and medicine [20].

1.4 About New Generation Soft and Smart Materials of Liquid Metal

With a group of unique properties such as fluidic [22] (low viscosity and high surface tension), thermal (low melting point and high conductivity) and electrical conductivity (high conductivity) attributes (as shown in Fig. 1.1), the room temperature liquid metals are being increasingly used in extremely broad categories. In fact, research in this area is recently becoming a major stream in rather diverse frontiers. The present lab is lucky enough to have worked in this area for more than 17 years. Our earliest endeavor can be dated back to 2001 which initially was mainly focused on developing liquid metal chip cooling technologies which later were extended into a series of profound scientific situations such as printed electronics, 3D printing, biomaterial technologies, and soft robot. Especially in recent years, it has been revealed that liquid metal is opening big potential for developing new generation of soft robots. A group of very fundamental discoveries were continuously made which in fact paved the ways for molding various soft machines even robots. In the summer of 2015,

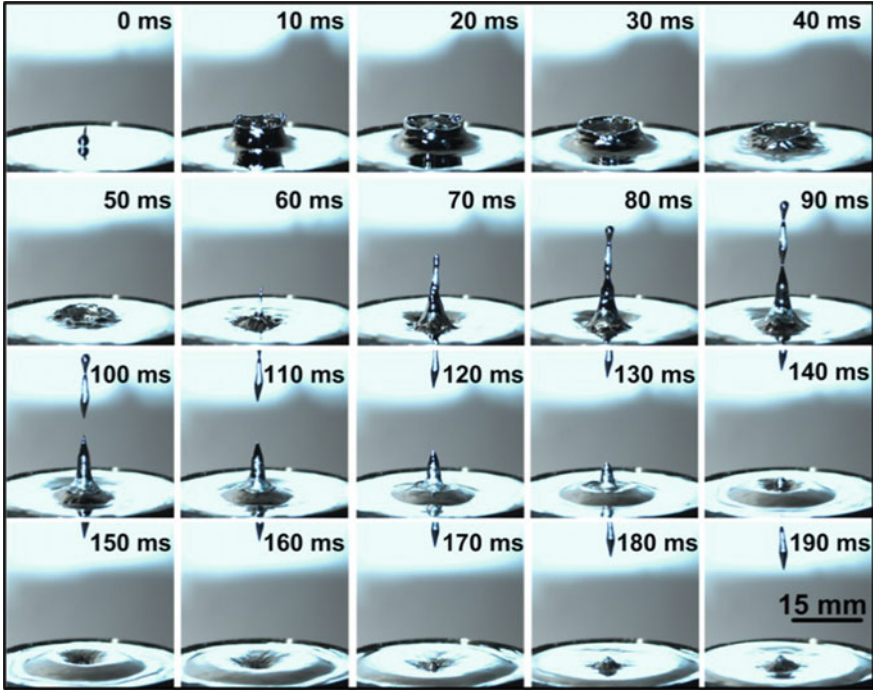


Fig. 1.1 Liquid metal striking on the same metal pool [22]. Picture is reproduced with permission

under support from the Chinese Academy of Sciences, this lab had ever initiated a project termed as SMILE (soft machine based on intelligence, liquid metal and electronics). All these machine or robot styles are based on liquid metal's soft, fluidic, multi-physical and chemical capabilities.

In the multiphase system containing liquid metal at room temperature, the flow and deformation of metal droplets often show unconventional physical properties. For example, the flow behavior of liquid metal induced by external field will become very complex. The electrodynamic complexity of a multiphase fluid is mainly caused due to discontinuity of the Maxwell electrical stress caused by the charge of the interface (or nearby). Typical fluid electrodynamic mechanisms include electrowetting, electroosmosis, electrophoresis, electrospray, and electrospinning. They are critical in fluid flow and deformation control. At room temperature, the liquid metal can switch between the wetting and nonwetting states with the dielectric substrate to achieve the power generation. In air, the liquid metal surface at room temperature would form a convex singular point (curvature tends to infinity) under the action of high-intensity electric field, but for water and other media, the convex top has limited curvature and ruptures under the action of larger electric field. The mechanism of this strange phenomenon lies in that the perfect conductor property of room temperature liquid metal makes the electric field line vertical and terminates on the surface of

liquid metal, so that the force on the surface is spherically symmetric and uniformly concentrated at a certain point, eventually leading to the formation of the tip. The conductive liquid in the dielectric would deform along the direction of the external electric field, and the surplus charge on the surface can also promote the droplet to move along the direction of the electric field. However, because of the electric field polarization and the formation of double electric layer near the interface of conductive droplets in electrolyte, the mechanism of conductive droplet deformation and electrolyte fluid dynamics is far from being clear so far.

At present, the rise of liquid metal science and technology can be attributed to the discovery of a series of unique attributes lying behind. One of the major differences between room temperature and high-temperature liquid metals lies in the application scenarios. For example, the interaction between room temperature liquid metal and aqueous solution is difficult to reproduce in high-temperature liquid metal experiment. Therefore, the physical and chemical mechanism from the traditional high-temperature liquid metal is not applicable to that of the liquid metals at room temperature. On the other hand, both the room temperature liquid metal (or alloy), single-phase fluid or the multiphase system formed by room temperature liquid metal and other media have different flow and deformation characteristics compared with the traditional fluid medium. For liquid metal at room temperature, electromagnetic effects not only can drive the flow and deformation, but also realize the conversion between various forms of energy (such as acoustic electric conversion), and the surface oxidation layers strengthen the liquid metal wetting characteristics.

Clearly, many novel applications of liquid metals at room temperature are closely related to their flow and deformation properties. However, understanding and practices of liquid metals are still in the beginning stage, which are far from being fully and systematically explored. Over the last 10 years of unremitting exploration, a series of phenomena of large-scale deformation and motion of liquid metals which have never been anticipated before were discovered. The shape transformable liquid metal machine is showing great promise in the development of future soft robots even construction of liquid machines.

1.5 Emergence of Liquid Metal Soft Robot

If giving a thorough review on the various advanced machine prototypes that have been conceived by human beings over the past few decades, the most impressive one is perhaps the whole liquid metal robot that has never been defeated in the Hollywood science fiction film “Terminator”. Such highly advanced robot can change its shape, present a variety of appearances and is very futuristic. Unfortunately, it is purely scientific fantasy, which however does make us change our classical concept on robot. Then, people would like to ask such a basic question: Is it possible for a liquid metal robot to be really made in theory and technology? This question and the technical feasibility did appear to be hard to answer previously. However, with

a series of latest progresses on investigating the liquid metal matter, realization of such possible technology is becoming clearer and clearer in reality.

With outstanding versatile capabilities, liquid metals are opening breakthrough strategies for molding future smart soft robots that are hard to anticipate before or hardly achievable by a rigid metal or conventional materials. All the evidences collected so far pointed out that liquid metal machine is evolving via a rather quick way [23]. Through more than ten years' continuous academic endeavors, researchers in China and over the world have achieved a group of very fundamental discoveries on the effects and phenomena of transformational liquid metal machines [24, 25]. These breakthrough findings are expected to play pivotal roles in developing new generation soft robots. Further, some latest works [26–28] offer the way for easily manipulating liquid metal through introducing graphite as special functional substrate. Due to interactions on the interface, liquid metal in alkaline electrolyte can be fixed into any desired stable shapes like flat, dull and sharp angle [25]. Besides, unique transformations and worm-like antigravity upslope liquid metal locomotion were also made possible. The supernormal deformation and crawling characteristics provide very convenient methods for the development of a deformable robot. However, the singular behavior of liquid metal is far more than that. For example, the liquid metal has similar biological effects like endocytosis, phagocytosis of micro/nanoscale metal particles [29] and self-growing and serpentine locomotion behavior when induced by copper ions [29, 30].

A most surprising discovery in liquid metal science is perhaps the extraordinary phenomenon of self-powered liquid metal machine [31]. Such long-lasting and quickly running soft machines work just like a biomimetic mollusk since they closely resemble the nature by “eating” aluminum as “food”, and can change shape through closely conforming to the geometrical space they voyage in. This new generation machine owns the capabilities of autonomous convergence or divergence during chasing which are hardly achievable otherwise by conventional machines, even biological systems [32]. The self-driving liquid metal micro motor group can form high-speed cooperative motion characteristics in the electric field [33]. It can move as a deformable machine for a long time. Unlike former trials on pure liquid metal, the new findings revealed that hybrid structures with both liquid and solid elements together would enable more complicated functions [34]. The magnetic solid–liquid composite machine can also realize movement to stop, steering and acceleration through the field [35]. By using liquid metal wheel, a 3D print mini vehicle can also be driven to achieve more complex locomotion [36]. It is worth noting that the series of liquid metal sensing technology provides a new way of building the future soft robot [37]. More theoretical and experiments indicate that liquid metals can present almost all forms of deformation and movement [38]. Through building the basic unit of robot, the corresponding technology also owns great value in many aspects such as electronics manufacturing [39], sensing technology and biological medical treatment [40]. If dividing the liquid machine basic units into groups and guaranteeing them to be controllable [24], this will establish a very practical and feasible technical way for the realization of programmable flexible intelligent robot, which will change the appearance of the traditional robots. It should be said that such special deformable

functions are almost impossible to realize with only rigid materials or traditional fluid materials.

These discoveries have opened up unconventional way for the design and manufacture of new kinds of soft robots based on liquid metal, and preliminarily established the theoretical foundation of the new generation deformable soft robots, which has both scientific significance and profound application prospects. Because liquid metal has its unique advantages in controllable deformation, it stimulates a lot of researches throughout the world. Among them, Royal Melbourne Institute of Technology University in Australia is a representative group. They have achieved the electronically controlled liquid metal micro-pump [25] and ion concentration difference-driven liquid metal movement [41]. The University of Hawaii team realized a self-driving liquid metal based on the redox reaction [42]. After other team's earlier discoveries on electrically induced transformation of liquid metals in either free space, patterned flowing path and bridge [24] or capillary tube [43], a group at State University of North Carolina also tested the issue of using electric field to fill liquid metal in the microfluidic channel [44]. At the diverse scale, the transient state liquid metal machine which can transform from tremendous autonomous running tiny motors to a larger single machine were also introduced [45]. It is worth pointing out that in recent years, liquid metal has also played a great role in flexible electronic technology [37].

Lastly, if taking a deep thinking about nature, it would be interesting to note that all living systems including both plants and animals own such a basic feature: "soft". Liquid metal machine perfectly mimics this power in nature. It is "soft" that distinguishes the biology or liquid metal machine from the abiotic matter and enables a wonderfully vibrant world. In this sense, Liu [23] had ever proposed a basic concept that by defining "softness" as another dimension apart from the classical definition on time and geometries. This is because with soft property inside, material can change shape, dimensions, and undertake the tough task. For example, a liquid metal wire packed in plastic pipe could be easily stretched or separated. While for a liquid metal sphere immersed in aqueous solution, external fields such as electricity would be able to induce its interior circulation. In that case, although size, weight, and even shape do not vary, the dimension of the object has already been changed. Therefore, "soft" serves well to characterize the new dimension. And softness spanning from 0 to 1 could provide more quantifications on such dimensional behavior. For example, liquid metal may stay in completely soft state which can reorganize into any different shapes. While for a perfect rigid material, its softness is just zero. It means that such object could not change shape unless machined. For soft robots composed of liquid metal and other materials, the desired softness in 0–1 can be obtained. Thus, there is plenty of space in innovating liquid metal and aligned materials to compose advanced soft robots.

1.6 Conclusion

In a word, it is one of the major topics of science and engineering to realize the really free and controllable conversion of soft robots among different forms. However, the currently existing technology often encounters big challenges in realizing large-scale controllable deformation of subjects, especially in terms of soft deformation and flexible perception, where liquid metals show great potential in both of these two aspects. The next step for advancing liquid metal machine is to just fully simulate nature. Meanwhile, some newly emerging discoveries and technologies on liquid metal and its allied materials will also aid for such machine fabrications. It is expected that a wonderful world of liquid metal soft robots will come true in the near future.

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Chapter 2

Basic Properties of Liquid Metal and Soft Matter



Abstract Many capabilities of the room temperature liquid metal are enabled due to its unique attributes such as high thermal and electrical conductivities, excellent fluidity, high surface tension, extremely low evaporation, chemical stability, and non-toxicity. Over the past few years, intensive research efforts based on these versatile features have led to the development of a group of newly emerging applications such as microfluidics, stretchable and soft electronics, energy management and storage, thermal management, biomedical technology, regulation of chemical reaction, actuators and soft robotics, as well as functional materials. This chapter is dedicated to present a basic introduction about the major properties of liquid metal materials in view its application in developing soft machine.

Keywords Soft matter · Composite · Physical property · Chemical property
Hydrodynamics

2.1 The Room Temperature Liquid Metals

Liquid metal discussed here refer to those metal elements or metal alloy, which maintain in liquid state at, or near, normal room temperature. Its melting temperature is generally lower than 100 °C, which means that the solid–liquid state transition is very facile and fast. There are four nonradioactive metal elements, mercury (−38.83 °C), caesium (28.65 °C), gallium (29.76 °C), and rubidium (38.89 °C), keep liquid state at near room temperature [1, 2]. Among these metal elements, gallium is the only one that is neither highly toxic (like mercury) nor highly reactive (such as rubidium and caesium), which is important for the practical applications, respectively, for making soft robotics in the biomedical engineering area. The most liquid metal with low melting temperature is in the form of alloy, which mainly includes gallium-based alloy and bismuth-based alloy. Gallium combined with other elemental metal such as indium, tin, and zinc could form a solid solution alloy with a lower melting temperature around even zero degree. The fusing temperature of most bismuth-based alloy arranges from 40 to 273 °C, which is often adopted as low-temperature weld-

ing materials. Table 2.1 lists several typical gallium-based and bismuth-based alloys with a low melting temperature. The room temperature gallium-based alloy is the major liquid metal candidate for making liquid machine, which is chemically stable and nontoxic. It is noteworthy that the alloys consisted of Bi–In–Sn with eutectic melting temperature around 60 °C also presents chemically stable property and non-toxicity. This eutectic alloy could be used as stiffness regulation material through the fast solid–liquid transition.

The element gallium is discovered in 1875, which is a soft, silvery blue metal at room temperature and standard pressure. Generally, the actual crystallization temperature T_n of a kind of metal is lower than the equilibrium crystallization temperature T_s . Such difference, i.e., $\Delta T = T_s - T_n$, is called degree of subcooling. The room temperature liquid metal usually has a high degree of subcooling. For example, gallium can be kept in a liquid state at a temperature much lower than room temperature. Related theory and experiments show that one can obtain a higher degree of subcooling by dispersing bulk samples into small droplets. Studies show that Ga remains in liquid even up to -80 °C when encapsulated in carbon nanotubes [6]. And the sub-micrometer gallium droplets can even be subcooled to 150 K when they are confined in epoxy resin [7]. The large temperature difference between the solidifying point and the melting point of Ga guarantees it a perfect coolant for convective cooling.

Elemental gallium is an important component of semiconductors for application in microelectronics and thin-film photovoltaic cells, such as GaAs, GaN, InGaN, and Cu(InGa)Se₂. These compounds are widely used in microwave integrated circuits, solar cells, laser diodes, and light-emitting diodes. Gallium (III) has a similar biological effect like ferric salt and has been used in some medical applications such as pharmaceuticals and radiopharmaceuticals. The primary gallium typically recovered at 99.9–99.99% as a by-product of processing bauxite and zinc ores, where about 90% of current primary gallium production is extracted from bauxite during the refining of alumina. China, Germany, Japan, and Ukraine were the leading producers of gallium, and China is current major producer of primary and refined gallium. In 2016, world low-grade primary gallium production was estimated to be 375 tons—a decrease of 20% from 470 tons in 2015. Low-grade primary gallium producers outside of China most likely restricted output owing to a large surplus of primary gallium (MCS-2017-Gallium [8]). Approximately, 70% of the gallium consumed in the United States was contained in GaAs and GaN wafers.

In fact, the alloys of K₇₈Na₂₂ (-11 °C) and Cs₇₇K₂₃ (-37.5 °C) have a much low melting temperature. These alloys own some properties (e.g., high thermal conductivity) which are good for use. But their most prominent drawback is that they are chemically active due to easy loss of the outermost electrons outside the nucleus. Unlike the alkali metal alloys, Ga–In alloys are the ideal materials on account of their operational safety, as well as their satisfactory physical and chemical properties. The disadvantage of this kind of materials is their market price. Both Ga and In are scarce. They are sparsely dispersed on the earth surface with a small content percentage. If certain cheap metals are added to Ga–In alloys to form new composite whose properties could fulfill people's need, the mole fractions of Ga and In will be

Table 2.1 Gallium-based and bismuth-based alloys [3–5]

Alloy	Melting temperature (°C)	Eutectic?	Gallium (%)	Bismuth (%)	Tin (%)	Indium (%)	Lead (%)	Cadmium (%)	Zinc (%)	Thallium (%)
GaInSnZn	7.6	Yes	61.0	–	1.0	25.0	–	–	13.0	–
GaInstan	10.5	Yes	67.0	–	12.5	20.5	–	–	–	–
GaIn	15.5	Yes	78.6	–	–	21.4	–	–	–	–
GaSn	20.5	Yes	86.2	–	13.8	–	–	–	–	–
GaZn	25.2	Yes	96.3	–	–	–	–	–	3.7	–
Ga	29.76	No	100.0	–	–	–	–	–	–	–
BiPb	41.5	Yes	–	40.3	10.7	17.7	22.2	8.1	–	1.1
Cerrolow 117	47.2	Yes	–	44.7	8.3	19.1	22.6	5.3	–	–
Cerrolow 136	58	Yes	–	49.0	12.0	21.0	18.0	–	–	–
InBiSn	60	Yes	–	33.1	15.6	51.3	–	–	–	–
Wood’s metal	70	Yes	–	50.0	13.3	–	26.7	10.0	–	–
BiIn	72	No	–	66.3	33.7	–	–	–	–	–
Cerrosafe	74	No	–	42.5	11.3	–	37.7	8.5	–	–
BiInSn	79	Yes	–	57.5	17.3	25.2	–	–	–	–
Rose’s metal	98	No	–	50.0	25.0	–	25.0	–	–	–

reduced. Many ways can then be figured out to modify as desired the existing liquid metal materials.

Taking the multicomponent liquid metals whose natures are already familiar to us as the center, a variety of multicomponent liquid alloys can be obtained by adding other kinds of metals. Galinstan, for example, is a set of eutectic alloys mainly composed of Ga, In, and Sn. This kind of material is liquid at room temperature, typically melting at much lower temperature [9]. Galinstan is significantly advantageous over mercury because of its nontoxicity. It is, therefore, a promising alternative to mercury on many occasions. The research on experimental and application for such liquid metal has thus been made [10]. And based on such material, some thermodynamic parameters (electrical conductivity, viscosity, melting point, etc.) can be altered through the addition of some other nanoparticles [11] or elements such as zinc, aluminum, and so on.

Full use can be made of the CALPHAD method to find out more optional liquid metal materials. Compared with the traditional alloy development method, the CALPHAD method can provide a clearer guideline for such selections and help avoid large-scale experiments with less promising alloys [12]. Thus, it is a powerful tool to cut down cost and time during the making of different metal alloys combined with key experiments. CALPHAD is based on the thermodynamic principle that the Gibbs free energy changes with the temperature, pressure, and compositions. In other words, the Gibbs free energy-composition diagram needs to be studied under constant temperature and pressure. According to the principle of minimum Gibbs free energy, to any system with a certain composition range, the phase with minimum free energy is the most stable phase. And there will be two phase coexistence regions between two stable phase regions. Therefore, the phase diagram can be obtained with the Gibbs free energy-composition diagrams of different composition ranges. If the thermodynamic model parameters of lower component (two-component and three-component) systems were known, the Gibbs free energy function of each phase of the multicomponent system can be obtained through the extrapolation method, and the phase diagram of the multicomponent system can thus be calculated. Figure 2.1 shows the phase diagrams of Ga–In–Sn [13] and Bi–In–Sn alloys [14], respectively.

2.2 The Physical and Chemical Properties of Liquid Metal Alloy

Here we focused on discussing the basic properties of gallium-based liquid metal due to its great potential applications in developing soft robotics. Solid gallium has a complex crystal structure. Its stable phase under standard temperature and pressure includes orthorhombic with eight atoms in the conventional unit cell. Many stable and metastable phases are found as function of temperature and pressure (see Fig. 2.2). Ga_2 dimers are the fundamental building blocks of the crystal due to the bonding between the two nearest neighbors covalent, which explains its lower melting point

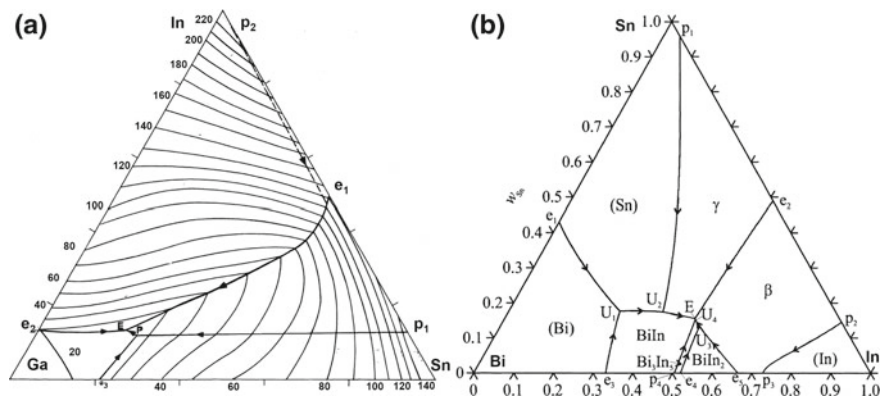


Fig. 2.1 **a** The phase diagrams of Ga–In–Sn and **b** Bi–In–Sn alloys [13, 14]. All pictures are reproduced with permission

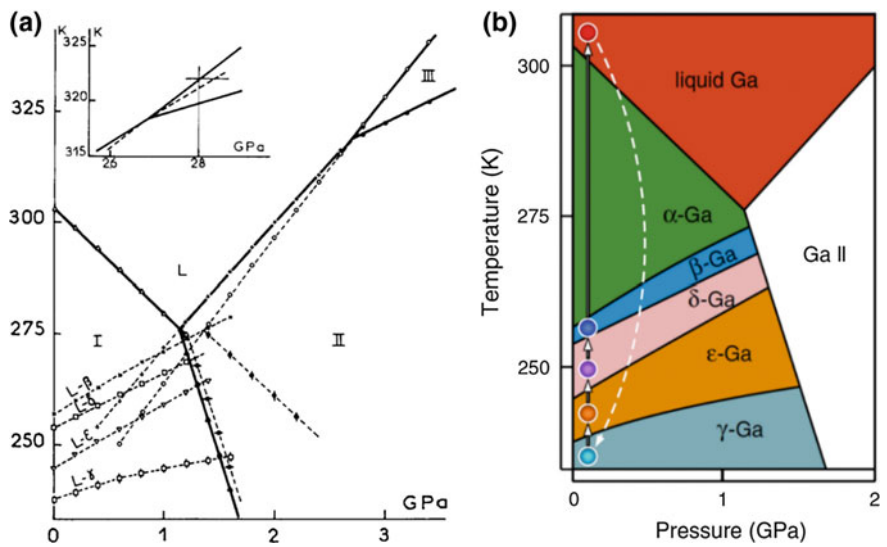


Fig. 2.2 **a** Equilibrium phase diagram of gallium: the inset shows the liquid–Ga(II)–Ga(III) triple point, and the dotted lines represent the metastable equilibrium phase boundaries [15]; **b** gallium phase diagram [16]. All pictures are reproduced with permission

relative to the neighbor elements of aluminum and indium. The physical properties of solid gallium are highly anisotropic due to its crystal structure of the trapezoid body.

Table 2.2 lists a comparison of the physical properties of several typical liquid metals and water. It can be seen that the liquid metals have a similar fluidity compared with water, while the thermal conductivities of liquid metals are generally dozens

Table 2.2 Comparison of physical properties of Ga-based liquid metal with those of other liquids [17]

Composition	Ga	Ga _{75.5} In _{24.5}	Ga ₆₇ In _{20.5} Sn _{12.5}	Ga ₆₁ In ₂₅ Sn ₁₃ Zn ₁	Hg	Water
Melting point (°C)	29.8	15.5	10.5	7.6	−38.8	0
Boiling point (°C)	2204	2000	>1300	>900	883	100
Density (kg/m ³)	6080	6280	6360	6500	13,530	1000
Conductivity (Ω/m)	3.7×10^6	3.4×10^6	3.1×10^6	2.8×10^6	1.0×10^6	–
Thermal conductivity (W/m/K)	29.4	26	16.5	–	8.34	0.6
Viscosity (m ² /s)	3.24×10^{-7}	2.7×10^{-7}	2.98×10^{-7}	7.11×10^{-8}	13.5×10^{-7}	1.0×10^{-6}
Surface tension (N/m)	0.7	0.624	0.533	0.5	0.5	0.072
Sound speed (m/s)	2860	2740	2730	2700	1450	1497
Water compatibility	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	–

of times higher than that of water. In addition, the excellent electric conductivity of liquid metal makes it become an ideal candidate of conductive ink.

Density of Liquid Metal The temperature dependence of density for room temperature liquid metals and alloys is linear, given by

$$\rho_T = \rho_m + \frac{\partial \rho}{\partial T}(T - T_m) \quad (2.1)$$

where ρ_T is the liquid density at temperature T , T_m is the melting temperature, ρ_m is the liquid density at the melting point, and the temperature coefficient of the density $\partial \rho / \partial T < 0$. For liquid gallium, $T_m = 303$ K, $\rho_m = 6.09$ g/cm³, and $\partial \rho / \partial T = -1.187 \times 10^{-4}$ g/cm³/K; for liquid indium, $T_m = 430$ K, $\rho_m = 7.01$ g/cm³, and $\partial \rho / \partial T = -6.978 \times 10^{-4}$ g/cm³/K; for liquid tin, $T_m = 505$ K, $\rho_m = 6.99$ g/cm³, and $\partial \rho / \partial T = -6.765 \times 10^{-4}$ g/cm³/K and for Galinstan, $T_m = 284$ K, $\rho_m = 6.58$ g/cm³, and $\partial \rho / \partial T = -7.76 \times 10^{-4}$ g/cm³/K [18–20]. The alloy density could be calculated from Vegard's law, which predicts a linear relationship between molar volume and the molar fraction of constituent elements [21], i.e.,

$$\rho^L = \sum_i x_i M_i / \left(\sum_i x_i \sqrt[3]{M_i \rho_i^L} \right)^3 \quad (2.2)$$

where M_i , ρ_i^L , and x_i are the molar mass, liquid density, and the molar fraction of the i th component in the liquid, respectively.

Electrical and Thermal Conductivities of Liquid Metal The thermal conductivity of the metal caused by the electron motion is much higher than that of the general liquid contributed by molecular movement, such as water, oil, and many organic fluids. The relationship between the electrical conductivity and the thermal conductivity of liquid metal is [1]

$$\frac{k}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} \quad (2.3)$$

where k is the thermal conductivity, σ is the electrical conductivity, k_B is the Boltzmann constant, T is the temperature, and e is the electron charge which is equal to -1.6×10^{-19} °C. This is the Wiedemann–Franz–Lorenz relation from which it can be inferred that the thermal conductivity is proportional to the electrical conductivity of the liquid metal. For liquid gallium, the thermal conductivity could be given as [22]

$$k_{\text{Ga}} = 30.2 + 0.041(T - 303) \quad (2.4)$$

For the $303\text{ K} < T < 700\text{ K}$, and for liquid indium [23], one has

$$k_{\text{In}} = -1.805 + 29.116 \frac{T}{273.15} - 4.030 \left(\frac{T}{273.15} \right)^2 \quad (2.5)$$

For $450\text{ K} < T < 750\text{ K}$, the thermal conductivity of GaInSn eutectic alloy has been carried out in the temperature range from its melting point up to 600 K [19], i.e.,

$$k_{\text{GaInSn}} = 23.4 + 0.0614(T - 283.5) + 4.9 \times 10^{-5}(T - 283.5)^2 \quad (2.6)$$

Heat Capacity and Latent Heat of Liquid Metal Heat capacity is the amount of heat required to change the temperature of a substance. If the heat capacity is larger, more heat per unit mass of the material will be absorbed. The specific heat capacity of the liquid metal is much smaller than that of other liquid nonmetals. However, the heat capacities per unit volume of these two types of materials are similar. For example, it is $4200\text{ kJ/m}^3/\text{K}$ for water and $2158\text{ kJ/m}^3/\text{K}$ for liquid gallium [1]. Metals have giant atomic structures held together by metallic bonds. Former researchers have found that in addition to the rearrangement of sodium atoms in liquid under pressure, electrons are transformed as well. The electronic cloud gets modified, and the electrons sometimes get trapped in interstitial voids of the liquid, and atomic bonds adopt pacific directions. As is well known, the metallic bonds between metal atoms were the strongest. Thus, the energy needed to destroy the metallic bonds and finally lead to phase transition from solid to liquid was larger than other nonmetallic materials. Ge and Liu [24] had ever proposed to adopt low melting point metals, typically gallium with latent heat of 480 MJ/m^3 and its alloys and bismuth-based with latent heat of $100\text{--}300\text{ MJ/m}^3$ alloys, as a new kind of phase change materials and successfully introduced it into the thermal management of smartphone which exhibited good performance. The main advantages of liquid metals lie in their high thermal conductivity and large volumetric latent heat. Since the thermophysical properties of liquid metals are much different from that of conventional paraffin phase change materials, some distinguishing features exist during their phase change process.

Some physical means could also help to prepare low melting point liquid metals. In the cooling process of liquid metal, the actual crystallization temperature is usually lower than the melting point. Some liquid metals can be subcooled to a large degree by changing the cooling rate or the diameter of the droplet. The heating and cooling rates and the holding time of the metal melt may evidently affect the material properties such as electrical conductivity, viscosity, and degree of subcooling [1]. The nucleation undercooling of these liquid metal materials becomes larger with the increase in heating and cooling rates. Therefore, according to the effect of heating and cooling rates on the nucleation undercooling of liquid metals, the ideal material with the actual crystallization temperature as required can be obtained. In addition, ion implantation is another effective physical method to innovate the liquid metal material. Ion implantation is a material engineering process by which the ions of a material are accelerated in an electrical field and impacted into solid, which is used

to change the physical, chemical, or electrical properties of the material. The science and technology of ion implantation have been well described [25]. Its various applications in material science [26], as well as in semiconductor device fabrication, have been illustrated. According to metallurgical principles, the melting point of the alloy may be lower than the melting point of each component. Thus, the melting point of the liquid metal can possibly be changed by using the ion implantation approach. But future efforts are urgently needed.

Viscosity of Liquid Metal There exist a large number of methods to measure the viscosity of liquids, but those suitable for liquid metals are limited by the low viscosities of metals (of the order of 1–10 mPa s), large density and the effect of oxidation. The existing measurement methods include capillary, oscillating cup, rotational bob, oscillating plate, draining vessel, levitated drop, and acoustic methods. For the viscosity of liquid gallium, the measurements from Tippelskirch performed in an absolute oscillating cup with an uncertainty of 0.5% are probably the best measurements, where they covered a range from 307 to 1806 K. The following equations were obtained for the viscosity μ (mPa s) of gallium and indium, as a function of the temperature [20], i.e.,

$$\log_{10}(\mu/\mu^0) = -a_1 + a_2/T \quad (2.7)$$

where $\mu^0 = 1$ mPa s, and the coefficients a_1 and a_2 should be determined through the experiment. For gallium, $a_1 = 0.4465$ and $a_2 = 204.03$ K; for indium, $a_1 = 0.3621$ and $a_2 = 272.06$ K; for mercury, $a_1 = 0.2561$ and $a_2 = 132.29$ K. Generally, liquid gallium and its alloys are Newtonian fluid at room temperature. The temperature dependence of GaInSn viscosity can be described by an Arrhenius-type empirical equation [19], which reads as

$$\mu/\mu^0 = \exp(E/RT) \quad (2.8)$$

where $R = 8.3144$ J/mol/K is the gas constant, T is the absolute temperature (K), and $\mu^0 = 0.4352$ mPa s, and $E = 3904$ J/mol are the fit parameters. Oxidation of liquid metals exposed to air leads to an increase in the shear stress and also produces a large yield stress, which could be eliminated by surrounding the metal with acid, and prevents further oxidation from contact with air and reduces existing oxidation from the surface. Usually, high shear rates enhance the oxidation and reduction process [27].

Surface Tension of Liquid Metal Surface tension is an inherent characteristic of surfaces and interfaces of materials. The interfacial motion of fluid induced by surface tension plays a fundamental role in many natural and industrial phenomena [28]. The surface and interfacial properties of liquid metals are of great importance in metallurgical industry for controlling the processes of casting, welding, and solidification. For example, the interfacial properties are key parameters to understand slag entrainment and determine the complexity to separate impurities from liquid steel.

To optimize these processes, a deep understanding of surface properties is crucial, especially surface tension which dominates the mass transport procedure of fluids. Surface tension is an energy source required to change the surface area of a material [8]. It decides the shape and other characters of the liquid steel on a free surface or an interface where the liquid phase is in contact with the atmosphere or other condensed phases such as inclusion, slag, and refractory. Consequently, it is practically essential to probe into the behaviors of surface tension of liquid metals [28].

Surface tension indicates the force acting on the liquid surface vertically by unit length, causing the surface area to shrink. In terms of mechanics, for the molecules located on the gas–liquid interface, the acting force from the gas phase is much weaker than that from the liquid phase. Such unbalance is counterbalanced by surface tension. Until now, several respectable models have been proposed to calculate interface tension, where the interface is simplified as a plane without thickness or a monomolecular layer, which is not corresponding to the reality that the thickness of interface is one or several times the molecular diameter. The tendency of the system to minimize its free energy leads to the concept of the surface tension. Many classical and quantum statistical models and theories have been proposed in the last century. Functional expansion becomes an effective tool to determine the interface tension. Based on the density functional theory (DFT), the systemic space density is a fundamental variable, and grand thermodynamic potential can be obtained via variation principle. Sequentially, other systemic properties can be approached.

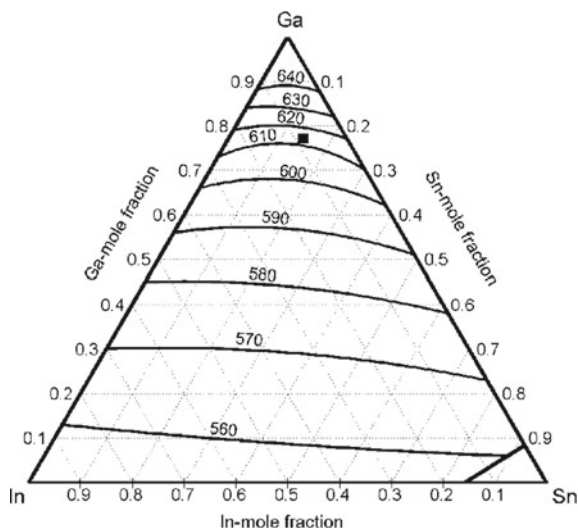
The surface tension of liquid decreases with increasing temperature [19], i.e.,

$$\gamma_T = \gamma_m + \frac{\partial \gamma}{\partial T}(T - T_m) \quad (2.9)$$

where γ_T is the surface tension at temperature T , T_m is the melting temperature, γ_m is the surface tension at the melting point, and the temperature coefficient of the surface tension $\partial \gamma / \partial T < 0$. For liquid gallium, $T_m = 303$ K, $\gamma_m = 712$ mN/m, and $\partial \gamma / \partial T = -0.0712$ mN/m/K; for liquid indium, $T_m = 430$ K, $\gamma_m = 559$ mN/m, and $\partial \gamma / \partial T = -0.115$ mN/m/K; for liquid tin, $T_m = 505$ K, $\gamma_m = 556$ mN/m, and $\partial \gamma / \partial T = -0.064$ mN/m/K; and for Galinstan, $T_m = 284$ K, $\gamma_m = 587$ mN/m, and $\partial \gamma / \partial T = -0.0109$ mN/m/K. The surface tension of Ga–In–Sn alloy could be estimated through the Butler model (see Fig. 2.3), which is in agreement with the experimental data. This indicates that one could estimate the surface tension of liquid alloy based on the experiment data of its constituent elements [19].

Surface tension is hard to be measured accurately because even a small quantity of surfactants or impurities can significantly reduce the value. Oxygen pressure is one of these surface-active factors which can lead to oxidation of pure metals and then make the surface tension data unreliable. Moreover, the temperature coefficient also changes at different oxygen pressures. Measurements of some pure liquid metals' surface tension as a function of oxygen content show an anomalous trend of the temperature coefficient that surface tension increases with temperature. This effect is attributed to the different actual availabilities of oxygen near the surface as a function of temperature [28]. Additionally, the gas flow rate is also an influencing

Fig. 2.3 Iso-surface tension line for liquid Ga–In–Sn alloys calculated by using the Butler model for $T = 480$ K. The square symbol (black square) represents the GaInSn eutectic alloy [19]. Picture is reproduced with permission



factor. It is understood that the wettability and adhesion are influenced by the affinity of the liquid phase metal to the reactive gaseous species [28]. Many researchers have proven that oxygen can strongly affect the surface tension of pure metals.

Electrochemistry of Liquid Metal For many applications, the behavior of system consisted of room temperature liquid metal (gallium-based alloy) and electrolyte, is very sensitive to its electrochemistry. Here we discussed the electrochemistry of liquid gallium, which may have an important reference value for the gallium-based alloy system. Recently, intensive research efforts have shown that the electrochemical behaviors of gallium vary widely [29, 30]. At room temperature, gallium metal is not reactive with air and water because it forms a passive, protective oxide layer. Gallium is found primarily in the Ga^{+3} oxidation state, and Ga^{+1} oxidation state is also found in some compounds. The various trivalent gallium ions such as Ga^{3+} , $\text{Ga}(\text{OH})^{2+}$, GaO^+ , GaO^{2-} , $\text{H}_2\text{GaO}_3^{3-}$, $\text{Ga}(\text{OH})^{4-}$, HGao_3^{2-} , and GaO_3^{3-} could be found in aqueous solution, which is mainly depending on the pH value. Figure 2.4 shows the Pourbaix diagrams, indicating the equilibrium states between possible gallium species including Ga(III) in aqueous systems and the theoretical conditions of corrosion and passivation of Ga [30]. It is noteworthy that Ga^{+3} is the stable oxidation state of gallium, which is corresponding to solvated Ga^{3+} in acidic solution and gallate in alkaline solution. Alkaline hydroxide solutions dissolve gallium, forming gallate salts containing the $\text{Ga}(\text{OH})^{4-}$ anion. Electrochemistry of liquid gallium is often depending on its double-layer structure in aqueous solutions, which has been studied via analysis of electrocapillary curves. In addition, the research has shown that the oxide film presumably consisted of Ga_2O_3 has marked impact on the electrochemical behavior of gallium for solid and liquid state. For the anodic dissolution of gallium in acid solutions, an oxide film of constant thickness formation benefits to permit penetration of Ga^{3+} . It is interesting that the passivation of solid gallium

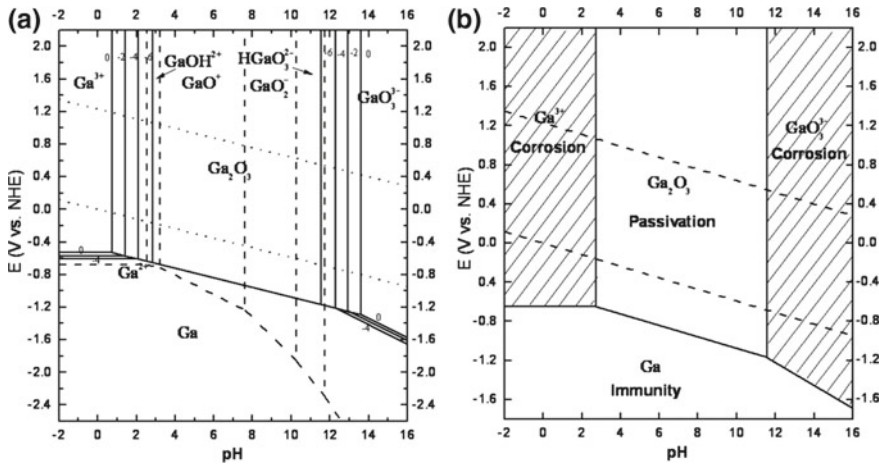


Fig. 2.4 Potential versus pH equilibrium diagram at 25 °C a for the gallium–water system and b theoretical conditions for corrosion, immunity, and passivation of gallium [30]. All pictures are reproduced with permission

apparently occurs more easily than for the liquid metal, which is further depending as well upon temperature and pH in neutral salt solutions [30]. For acid concentration of HCl higher than 1.0 M, solid gallium was not passivated, but at lesser acid concentrations both the solid and liquid metal were affected. The liquid gallium was less inhibited than for the solid. There is a difference between the formation of Ga_2O_3 on solid and liquid gallium, where the oxidation is easily formed on liquid gallium surface without overpotential, while a 70 mV of polarization on solid gallium surface was observed [30].

2.3 The Hydrodynamics of Liquid Metal Droplets

With pretty high surface tension, the room temperature liquid metal may inherit with unexpected behaviors that conventional fluids could not own. The Ohnesorge number $\text{Oh} = \mu / \sqrt{\rho \sigma R}$ relates the viscous forces to inertial and surface tension forces, where μ is the viscosity, ρ denotes the density, σ is the surface tension, and R is the droplet radius. Larger Oh numbers indicate a greater influence of the viscosity. For R lower than 1.7 mm, Oh for liquid metal is smaller than the critical value 0.1, which indicates that the viscous dissipation inside the liquid metal droplets is negligible to the inertial force and the surface tension force. Compared with water droplets of the same size, whose Oh number is larger than 0.1, the dominant factor is quite different. It was experimentally found that, when gently contacting (rather than colliding) two metal droplets with identical size together in NaOH solution, oscillating coalescence would happen which runs just like a spring after the interface

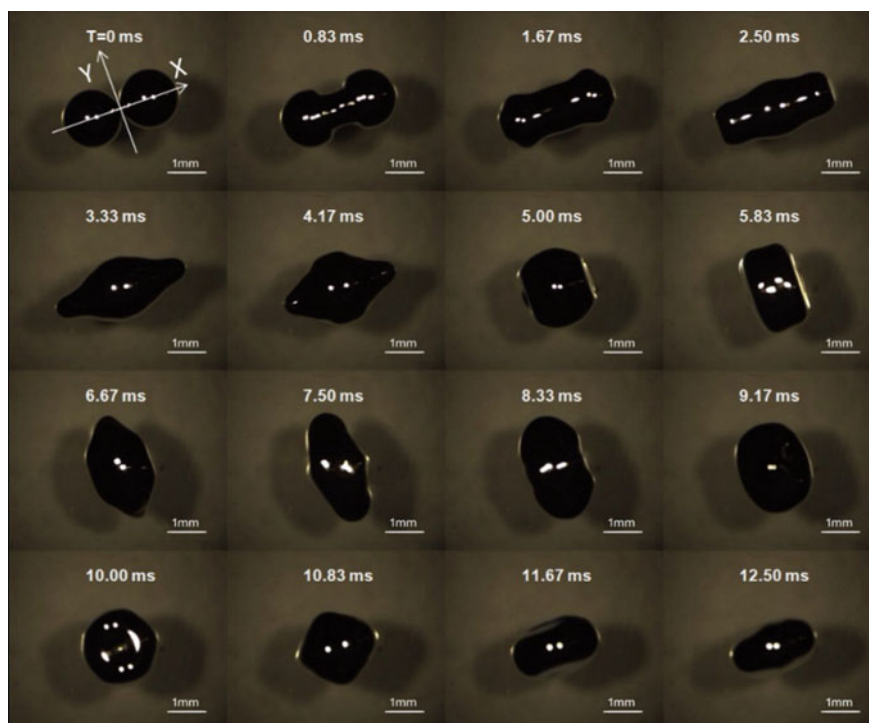


Fig. 2.5 Vertical view of oscillating coalescences of two contacting liquid metal droplets with identical diameter in NaOH solution [31]. Picture is reproduced with permission

ruptures and forms capillary waves [31]. Actually, when placing the two droplets next to each other, coalescence happened after several seconds rather than immediately. This can be explained by the drainage of the continuous film between the two droplets. When the distance between the two droplets approximated the atom size, the film ruptured and coalescence commenced rapidly with the growth of the liquid bridge between the two droplets. The two droplets became a unity with the connection of the liquid bridge. For two metal droplets with evidently different diameters, the coalescence induces rather unusual ejection phenomena. The large droplet would swallow part of the small one, and then eject another much smaller droplet. Such phenomenon provides a direct evidence for the existence of electrical double layer on metal droplets (Fig. 2.5).

The outcome of liquid metal droplet with oxides impacting onto a surface (dry, wet, liquid pools, etc.) is especially a fundamental fluid dynamic problem, which is not only of scientific interest but also significant for quite a few coming practices, such as ink-jet printed electronics [5], spray cooling, interface material painting and coating, enhancing boiling, metallurgy, and 3D packages. In fact, the impact of droplets has been an important topic for many years, and some typical trends

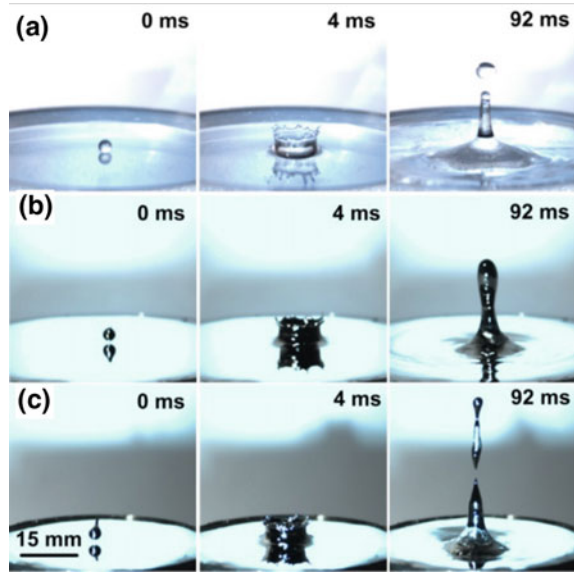
have been identified for water and aqueous solutions in preceding papers. However, up to now, only very few studies were ever performed on the impact dynamics of gallium-based liquid metal droplets. As is noticed, most of the previous literatures were based on the assumption that the droplets were spherical, although the shape of droplets moving through a fluid will always be rendered slightly as ellipsoidal by aerodynamic forces. However, this is not the case for liquid metal droplet due to its oxide skin.

Figure 2.6 shows the comparison of the representative droplets and splashing shapes over the process for both $\text{GaIn}_{24.5}$ and deionized water with the same inner diameter of needle of 1 mm and falling height of 900 mm. In water's case (Fig. 2.6a), spherical droplet and secondary droplet are observed no surprisingly, which is consistent with former work. However, the dynamic viscosity ($1.7 \times 10^{-3} \text{ m}^2/\text{s}$) of $\text{GaIn}_{24.5}$ is higher than that of water ($1.002 \times 10^{-3} \text{ Pa s}$) and even much higher when subjected to surface oxidation; thus, secondary droplet is hard to form under the effect of elevated viscous force, as shown in Fig. 2.6b. With the increase of the temperature of the pool, as illustrated in Fig. 2.6c, the viscosity of $\text{GaIn}_{24.5}$ droplet decreases after coalescence, and the viscous force dragging the liquid weakens, thus the secondary droplet forms. Yet, the most dramatic difference from the water's case is that the tip detached is not spherical, but fusiform. This is believed to be caused by the serious surface oxidation of $\text{GaIn}_{24.5}$ at high temperature. It was found that the droplet size and the impact velocity displayed similar proportional trends with respect to the splashing height, but did not accompany with the secondary droplet separation, while the increase of the pool temperature dramatically intensified the splashing effect, with the fusiform secondary droplet detached from a central jet. The reason for the differences can be attributed to the oxide skin of the liquid metal droplets which would significantly affect the appearance of the droplets and the splashing morphology [32].

In order to prevent the liquid metal from attaching to its surroundings and maintain the flexible reconfiguration, researchers had ever created liquid metal marbles through encapsulating liquid metal droplets inside the coating of nanoscale powder [33]. Compared with the conventional liquid marbles, such marbles possess many extraordinary physical and electronic features with their high surface tension, native oxide layer, high density and electrical conductivity. However, the liquid metal marble behaves like a soft solid due to its coating with nanoparticles. This may lose deformability and liquidity of a fluid which is however critical for some practical situations such as liquid metal jet cooling, printed electronics, 3D printing, metal droplet, or particle fabrication. Ding and Liu [34] proposed an alternative way of making new entirely liquid marble: the composite liquid metal marble, through coating liquid metal droplets with water film or more liquid candidates. In a composite liquid metal marble, the liquid metal preponderates over the water in volume and mass since the density of liquid metal is about six times that of the water. Therefore, the dynamic characteristics of composite liquid metal marbles are dominated by the liquid metal core.

Figure 2.7 shows sequential images of liquid metal droplets and composite liquid metal marbles with smaller diameters impacting at the speed of 1.27 m/s (Fig. 2.7b),

Fig. 2.6 Comparison of droplet and splashing shapes during the splashing process at the same moment [32]. **a** Deionized water (25 °C); **b** GaIn_{24.5} (25 °C); **c** GaIn_{24.5} (200 °C). All pictures are reproduced with permission



1.90 m/s (Fig. 2.7a, c), and 2.95 m/s (Fig. 2.7d), respectively. Figure 2.7a illustrates the deformation process of liquid metal droplet with velocity of 1.90 m/s. Compared with Fig. 2.7c, one can find that the differences between the experimental results of liquid metal droplets and composite liquid metal marbles are much more clearly. Without increase in the surface tension resulted from oxidization, the liquid metal marble recoiled off the surface and leaped into the air after being pulled back together by surface tension. Figure 2.7b–d shows the evolution of composite liquid metal marbles configurations with the increase of impact velocity. At a low speed of $V_0 = 1.27$ m/s (Fig. 2.7b), the droplet reached its maximum wetting area after $t^* = 1.69$. Then, the lamella was pulled back by surface tension and produced a jet, which achieved its maximum height at $t^* = 14.72$. With the jet rising, the neck became narrow due to the inward pull of the surface tension. Eventually, a small droplet was ejected from the tip of the jet. Increasing the impact velocity led to increases in the spreading area and decrease in lamella thickness. The recoil of the droplet was also distinctly enhanced so that the entire droplet lifted completely off the surface. At the highest speed in the experiments of Ding et al. [34], 2.95 m/s (Fig. 2.7d), the droplet spreads much quicker and the fingers could be seen very early. More fingers detached as satellite droplets because of higher kinetic energy. Increasing velocity resulted in the increase in the work done by the viscous force and decrease in the droplet recoil. The water coating was dragged by the liquid metal when it was pulled back toward the center and ejected under the effect of the great inertia of the liquid metal. Compared with the existing liquid marbles, the current composite liquid marbles consisting of two kinds of fluid present distinctive characteristics, such as

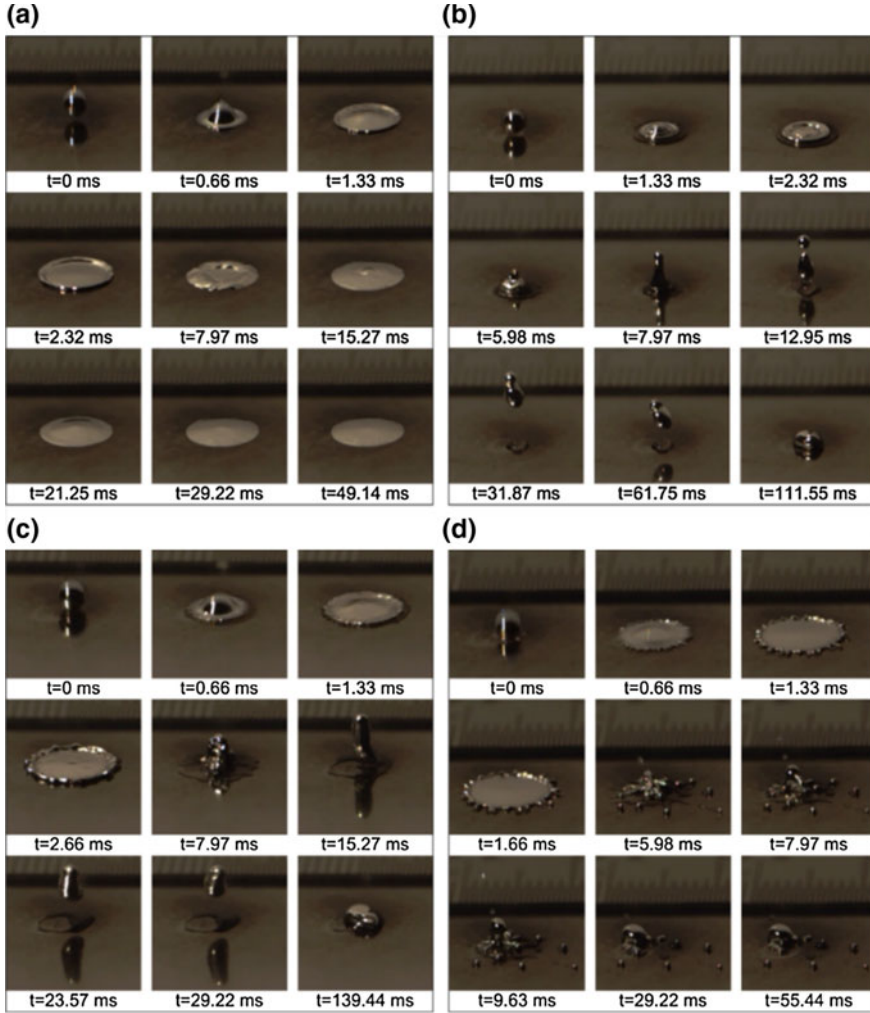


Fig. 2.7 Dynamic impacting processes of metal droplets for various impacting velocities [34]. **a** Case of 1.90 m/s and diameter 2.61 mm; **b** case of 1.27 m/s and diameter 2.75 mm; **c** case of 1.90 m/s and diameter 2.75 mm; **d** case of 2.95 m/s and diameter 2.75 mm. All pictures are reproduced with permission

non-oxide layer, deformability and complete liquidity of fluid, easy to prepare, and low cost.

Liquid metal surface is also used to provide a new method to generate Leidenfrost effect [35]. It is a particular case of the film boiling and has been of interest for centuries for its no-wetting properties, similar to the situation of superhydrophobicity, and its high locomotivity due to lubrication of the thin vapor film. Besides the solid surface, Leidenfrost effect on liquid surface was investigated, such as the film boiling

of a small liquid or solid sphere on the surface of liquid nitrogen, and the drop of liquid nitrogen levitating on the surface of viscous liquids. Sessile droplet evaporation experiments were conducted with different liquids on a liquid gallium surface to assess existing models. Unlike conventional rigid metal, such highly conductive and deformable liquid metal surface enables the levitating droplets to demonstrate rather abundant and complex dynamics. The difference between the Leidenfrost droplets on solid and liquid substrates originated from the deformation of liquid metal surface [35].

A meniscus was formed beneath a floating droplet on liquid metal surface due to its weight [35], as depicted in Fig. 2.8a, b. But the bottom of the Leidenfrost droplet on a stainless steel surface was flat and no meniscus appeared since the solid metal did not deform (Fig. 2.8c). Figure 2.8e shows the contact radius R_0 on the surfaces of liquid metal and stainless steel, respectively. It is worth noting that the fitting curves approximately follow the linear relationships predicted by the scaling analysis. The slope of the fitting line obtained on solid surface is evidently bigger than the result on liquid metal. This distinct difference can be interpreted as the effect of the substrate flexibility on the shape of the Leidenfrost drop. When the heating surface has good flexibility, for example, a liquid metal surface, the deformation of the levitating drop is offset by the deformation of the supporting surface. Leidenfrost droplets at different diameters present rather diverse morphologies and behaviors like rotation and oscillation. Depending on the distance between the evaporating droplets, they attract and repulse each other through the curved surfaces beneath them and their vapor flows. With high boiling point up to 2000 °C, liquid metal offers a unique platform for testing evaporating properties of a wide variety of liquids even solids.

Due to the deformability of the liquid substrate, the levitating drops demonstrated complex shapes and behaviors. Floating mechanism of such a small droplet is similar to that of a marble on liquid surface. Scaling analysis of such a drop leads to the conclusion that the meniscus angle approximately scales with the square root of Bond number, while the contact radius is proportional to the Bond number. The interactions between multiple droplets were investigated which behave like long-range attraction, short-range repulsion, and dynamic bound states, respectively. Experiments indicate the role of meniscus and droplet size in the formation of bound states. The nontrivial twin-star-like orbiting motion was similar to that of bouncing droplets on mechanically vibrated liquid surface, which was a valuable model to study the relation between droplets' orbiting motion and the surface wave in the supporting liquid.

2.4 Liquid Metal-Based Composite Materials

Adding metallic ingredients to a liquid metal base is contrary to incorporating the liquid metal into less conductive elastomers and organic bases [36, 37]. Both the electrical conductivity and the thermal conductivity of the latter are much smaller than the liquid metal base, although these combinations produce other benefits. The history

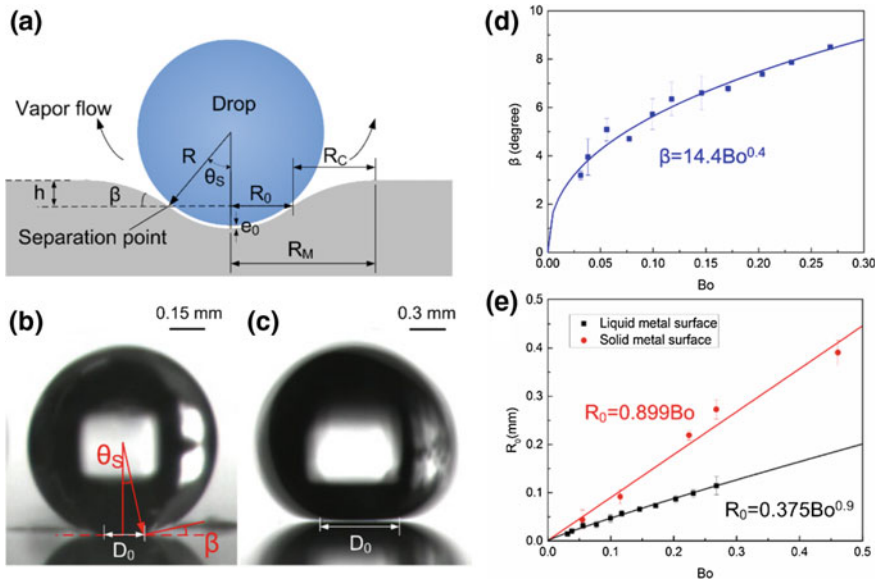


Fig. 2.8 **a** Schematic model of an evaporating droplet on liquid metal surface [35]. **b** Side view of a stationary drop with 0.68 mm diameter on liquid metal surface. **c** Side view of a stationary droplet with 2.04 mm diameter on stainless steel surface. **d** Meniscus angle β versus Bond number Bo . **e** Contact radius R_0 versus Bond number Bo on the surfaces of liquid metal and stainless steel. All pictures are reproduced with permission

of clinical dentistry has witnessed the rise and fall of mercury amalgams as restorative dental materials. However, the specific application of mercury amalgams inevitably directs the focus of previous practice to problems such as durability and safety. In pursuing of controllable improvements of nontoxic gallium-based liquid metals, it has been shown that highly conductive liquid metal paste and magnetic liquid metal can be prepared through directly mixing copper particles and nickel particles, respectively, with the liquid metal base [38]. However, such direct-mixing methods, successfully applied in making mercury amalgams, are unsatisfactory when it comes to gallium-based liquid metals due to their easily passivated surface, so despite the apparent practical significance, effective methods to disperse metal particles into gallium-based liquid metals have not been proposed until recently. There still remains a major challenge to prepare stable liquid metal/particle mixtures.

Tang et al. [39] proposed and demonstrated a two-stage route to prepare stable gallium-based liquid metal amalgams, a series of transitional-state metallic mixtures (denoted as TransM2ixes) with enhanced electrical conductivity, thermal conductivity, as well as appealing semiliquid/semisolid mechanical behaviors such as excellent adhesion, tunable formability, and self-healing ability. They also showed that the method of dispersing a large number of particles in the liquid metal base in a solution environment with the assistance of an electrical polarization is robust, while to obtain

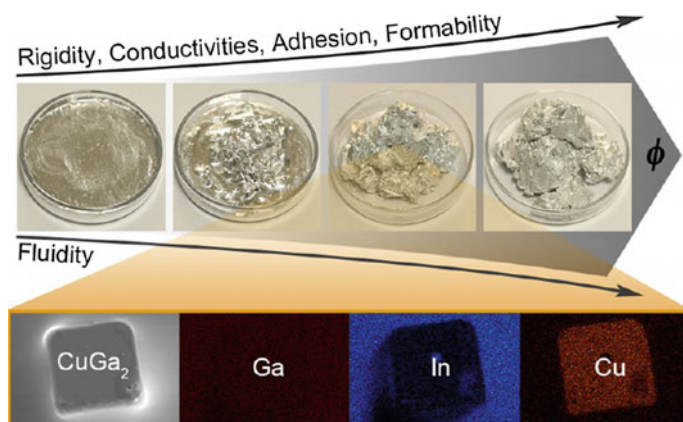


Fig. 2.9 The physical properties of TransM2ixes with different concentration of copper particle [39]. Picture is reproduced with permission

durable products, a follow-up vacuum-drying process is crucial. Compared to pure gallium-based liquid metals, the TransM2ixes show a remarkable increase in electrical conductivity, thermal conductivity, and more favorable adhesion and formability (see Fig. 2.9). Such easy-handling TransM2ixes are excellent choices for fabricating highly conductive patterns and structures that are at the same time flexible and conformable. This class of material represents a liquid metal/particle framework for the improvement of the functionalities of gallium-based liquid metals.

For more densely packed TransM2ixes ($\phi = 0.15$ and 0.20) which exhibit high stiffness and good formability, other methods such as stamping and molding can also be applied to create engineered patterns and large-scale freestanding structures (see Fig. 2.10), which cannot be created with pure liquid metal. Moreover, different from real sand castles, the structures made with the TransM2ixes are highly conductive [39]. As can be seen from these demonstrations, multiple simple yet reliable methods can be used to process the TransM2ixes owing to their transitional-state mechanical behaviors. Given their enhanced electrical and thermal properties, more diverse potentials of the materials in real applications are predictable.

Unlike conventional material category, Wang et al. [40] disclosed a new conceptual porous liquid metal enabled ubiquitous soft material (PLUS-M) through loading Ga–In alloy with a large number of iron particles along with heating and chemical reaction. Such PLUS-M could expand to a surprisingly large magnitude, say seven times of its original volume in a short time, and generate much more adjustable closed cell foams inside. This liquid metal composite (PLUS-M) offers the important capability of being able to float up and down inside the water even pull up underwater heavy object to be above the surface via remote control. Besides, the PLUS-M can transform between liquid and solid states with repeatable life span phase change cycles for more than 100 times without obvious performance degradation. This suggests the outstanding reusable features and wide potential applications

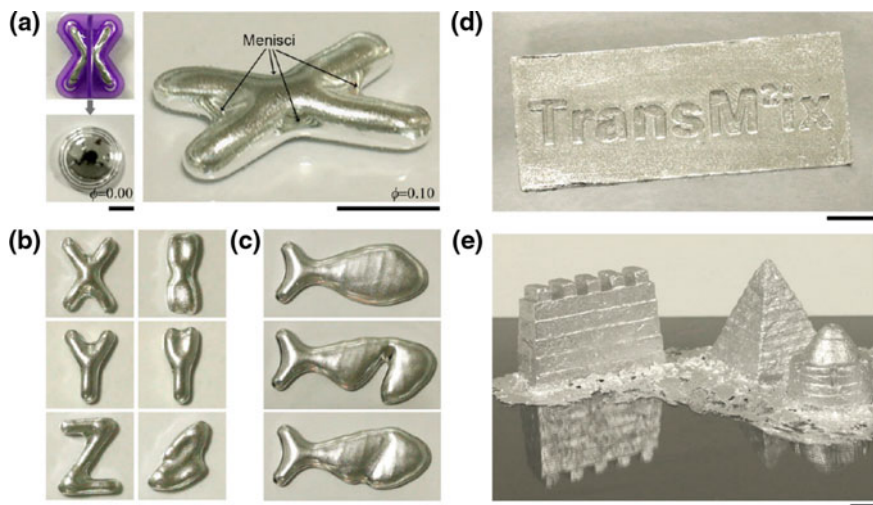


Fig. 2.10 Composite liquid metal materials [39]. **a** After geometrical constraints are removed, pure liquid metal ($\phi = 0.00$) instantly adapts a round shape, while the TransM2ix ($\phi = 0.10$) can maintain predefined structures. Liquid metal menisci, which are responsible for the reshaping and self-healing behaviors to be shown in **b** and **c**, are found between the “arms”. **b** Molded TransM2ix letters (left column) reshaping (right column) in HCl solution ($\phi = 0.10$). **c** Fish-shaped TransM2ix self-heals when cut ($\phi = 0.10$). **d** Concave letters made by stamping ($\phi = 0.15$). **e** Freestanding TransM2ix “sandcastles” made by molding (left: $\phi = 0.15$; middle and right: $\phi = 0.20$). Scale bars: 10 mm. All pictures are reproduced with permission

of the material. Based on the self-growth (expansion) properties and good conductivity of the PLUS-M, its switching on and off function in remotely controlling the lights timely was also demonstrated. This study suggests the way to fabricate and utilize functional soft conductive porous floating objects based on the room temperature liquid metal (Fig. 2.11).

The capacity of materials to tune stiffness was of great interest to many areas such as robotics, exoskeleton [41] and medicine. This material could transform between liquid and solid (paste-like) states. Besides, soft PLUS-M was also capable of becoming a stiff, rigid state when requiring a very hard structure. If treated with NaOH solution for more than 24 h, soft PLUS-M presented a stiff body. This is the first ever investigation into rigid porous materials state based on the liquid metal (EGaIn). The experiments had disclosed a group of very unconventional behaviors of such PLUS-M. The mechanism of such expansion in two parts: gas generation and reversible phase transformation between liquid and solid (paste-like) states. During the expansion process, tremendous small bubbles were produced on the surface of the iron nanoparticles as soon as liquid metal contacted with the HCl solution. It is a known fact that iron can be chemically dissolved in HCl solution spontaneously, generating hydrogen bubbles. Besides, the ferric ions were detected in the solution. The

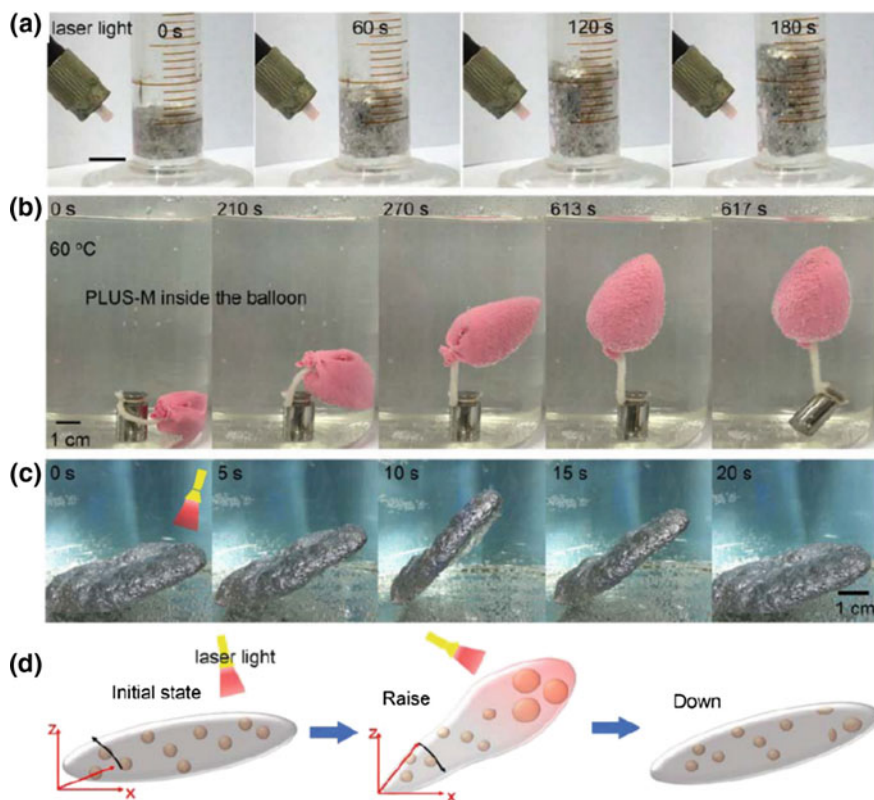


Fig. 2.11 PLUS-M went up and down in the water (3% NaCl) [40]. **a** The volume changes with laser light irradiation. The Fe particles raised the temperature with heating by the infrared light and increased the volume of the liquid metal. **b** Liquid metal balloon drove the weight (20 g) away from the bottom. At 60 °C, the liquid metal inside the balloon generated much hydrogen, which extended its volume and induced the transformation of liquid to solid foam. The inflated balloon drove the weight to move. **c** Liquid metal saucer went up and down with the laser light irradiation. When the laser light acted on the head of the liquid metal saucer, the temperature rose and induced the closed pores to become larger, which declined the density of the head region and drove the head rise **d**. When the infrared light was withdrawn, the closed pores became smaller and the head of liquid metal saucer swam down to the bottom. All pictures are reproduced with permission

gas produced from the PLUS-M was confirmed as hydrogen by flame test and gas chromatography.

The PLUS-M owned a surprising capability to significantly extend its volume in a short time with the outside stimulation, which could drive the heavy devices underwater from the bottom to the water surface. The expansion mechanism was disclosed and interpreted by a group of basic processes happened inside the PLUS-M. Based on the self-growth properties of the PLUS-M, they also demonstrated its switch function on controlling the lights sequential. This multifunctional material offered

many potential application ways in a wide variety of practical situations including driving mass in seawater and electric timer switch, etc. This work represented a step toward the fabrication and the use of the functional soft porous floating objects using the room temperature liquid metal.

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Chapter 3

Injectable Transformation of Liquid Metal



Abstract The room temperature liquid metal (RTLM) is emerging as an ideal material for fabricating microdroplets owing to its strong surface tension and easy phase switching property. In this sense, a bottle of liquid metal can be easily transformed into a large amount of tiny liquid metal droplets. Given specific control via external fields such as mechanical, electrical, chemical, boiling, or acoustic, different sized droplets can be quickly obtained in large amount. Such transition mechanism between large pool of liquid metal and its small-sized objects can be applied for making discrete soft machine which will also be illustrated in later chapters. Along this direction, Yu et al. [1] found out a low-cost and technically simple way for preparing metal droplets. They demonstrated a channelless fabrication method based on stream jetting and self breaking up mechanisms of the RTLM when injected into and interact with the matching solution. The role of such method in the fabrication is rather diverse. For example, the injected assembly of liquid metal droplets can be directly applied to construct a three-dimensional porous metal block with foam structures inside. Apart from the above mechanical injection, electrical field was also disclosed for the automatic generation of liquid metal droplets. Overall, the injection strategy provides an extremely simple way for large-scale fabrication of liquid metal microdroplets and particles which have rather important practical values. It also suggests a highly efficient approach for visualizing and investigating the fundamental mechanisms of fluids interactions between RTLM and general solution. This chapter is dedicated to present the basic strategy to realize the injectable transformation of liquid metal when subject to various external forces and discuss their potential applications.

Keywords Liquid metal droplet · Injectable fabrication · Porous metal Solution interaction

The room temperature liquid metal (RTLM) is emerging as an ideal material for fabricating microdroplets owing to its strong surface tension and easy phase switching property. In this sense, a bottle of liquid metal can be easily transformed into a large amount of tiny liquid metal droplets. Given specific control via external fields such as mechanical, electrical, chemical, boiling, or acoustic, different sized droplets can be quickly obtained in large amount. Such transition mechanism between large pool

of liquid metal and its small-sized objects can be applied for making discrete soft machine which will also be illustrated in later chapters. Along this direction, Yu et al. [1] found out a low-cost and technically simple way for preparing metal droplets. They demonstrated a channelless fabrication method based on stream jetting and self breaking up mechanisms of the RTLM when injected into and interact with the matching solution. The role of such method in the fabrication is rather diverse. For example, the injected assembly of liquid metal droplets can be directly applied to construct a three-dimensional porous metal block with foam structures inside. Apart from the above mechanical injection, electrical field was also disclosed for the automatic generation of liquid metal droplets. Overall, the injection strategy provides an extremely simple way for large-scale fabrication of liquid metal microdroplets and particles which have rather important practical values. It also suggests a highly efficient approach for visualizing and investigating the fundamental mechanisms of fluids interactions between RTLM and general solution. This chapter is dedicated to present the basic strategy to realize the injectable transformation of liquid metal when subject to various external forces and discuss their potential applications.

3.1 About Generation of Liquid Metal Droplets

As a flowing metal with high density and strong surface tension, liquid metal can be driven to agglomerate into some spherical droplets when separated into tiny parts, which exhibit a number of unique properties and attract wide applications such as MEMS devices for optical and electrical switches [2–4], and even metal components manufacturing based on microdroplet deposition [5–7]. Unlike the mercury with toxicity and the classical melting metals at high temperature such as Al or Pb/Sn alloy, the RTLM of gallium and the like are safe and far from being fully explored and exploited. Having the nature of metal and the phase of liquid around room temperature, such liquid metal perfectly combines the features from both sides. It thus offers an important way of fabricating microdroplets, and the droplets can be even made as drug carriers to achieve biomedical functions [8].

The way of fabricating microdroplets has been an important area either from academics or industries. In recent years, many methods have been developed to fabricate microdroplets, yet most researches were originally focused on emulsions, encapsulation, and other micro-fluidic analyses, which significantly stimulated the advances of the microdroplets science and art [9–12]. Among these trials, the micro-fluidic channel is the most common means in many reports, and the room temperature liquid metal has attracted more and more attention as a new fluid. In these studies, droplets take shapes by flow focusing, and the key factors for controlling the fabrication include fluid velocity, viscosity, and surfactant properties. With various micro-channels and fluids, it has been possible to produce liquid metal microdroplets with multiple sizes, even including nonspherical one which is also called micro-rice [13, 14].

Despite a few desirable merits, it is still expensive and technically complex in the manufacture of the micro-fluidic channels. Other than the micro-channels, there is another way to produce microdroplets. A liquid stream would break into droplets due to the surface tension when it jets from small aperture into a different fluid, which provides an alternative and simpler way of producing microdroplets [15–17]. These important contributions refreshed people's basic understandings of the fundamental issues of fluids interactions. So far, such method has mainly been applied to the conventional model of water in oil. Since the surface tension of liquid metal is much stronger, this feature may lead to an easier liquid metal droplets fabrication under appropriate conditions. Through a number of lab tests and manipulations with such metal fluid, it was disclosed that [1] simply injecting RTLM into the water would generate a large quantity of micro-metal droplets. Having very different physical properties with conventional fluids, the RTLM offers many opportunities for fundamental research as well as practical applications, for example, making the metallic foam. The metallic foam is a metal structure with a very high porosity, which has been applied in many fields, such as lightweight construction, energy absorption, filtration materials, battery materials, and thermal control. Nowadays, there are various methods to produce metallic foams, including molten powders and some state from the molten or deposited metal. The fabrication of RTLM microdroplets would provide a novel and simple alternative to produce metallic foam. The following section illustrates the method based on channelless fluidic jetting to fabricate liquid metal microdroplets at room temperature. Some interesting flow interaction phenomena between RTLM and matching liquid were presented. The fundamental mechanism for the droplets fabrication was interpreted. The influencing factors that are closely correlated with the channelless droplets fabrication process were discussed. Further, as an illustration for practical use of the method, construction of a porous metal block with micro-foam structures inside with the new material was provided as well.

3.2 Mechanical Approach for Liquid Metal Injection

To test the mechanical approach for liquid metal injection and transformation, pure gallium was adopted with 99.999% purity. The metal was placed in a plastic bottle and should be heated with water bath before use. Meanwhile, surfactant sodiumdodecylsulfate solution (SDS) was prepared with 99.0% purity and deionized water by mixing and shaking, heated to dissolve completely, and then cooled in the refrigerator. The requested medical alcohol was prepared with concentration of 75% v/v.

The fabrication process of the droplets is as follows [1]. Through pushing the syringe piston forward quickly, the liquid metal in the syringe would jet into the solution from the pinhead aperture, and the disturbance to the solution and the surface tension of the metal will reversely break the material into droplets soon later. Once the droplets were formed, the petri dish with these marbles would be put in the fridge to cool down, so that the phase of the droplets could be turned into solid quickly. For the jetting flow velocity of the liquid metal, through recording the dynamic

Fig. 3.1 Basic device for large-scale fabrication of liquid metal droplets [1]. Picture is reproduced with permission

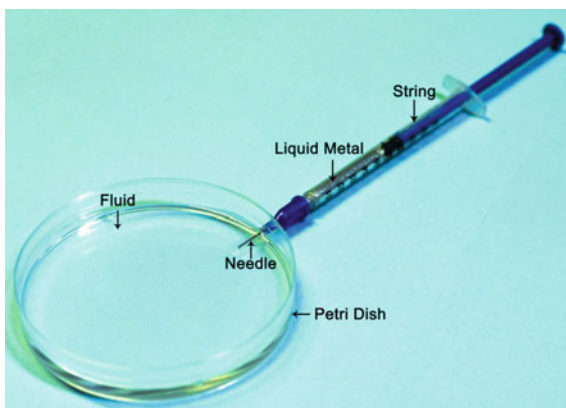


image of the syringe piston via high-speed camera and by calculating the injected volume of the liquid metal within a prescribed period, an average flow velocity at the syringe outlet can be estimated, which was about $70 \mu\text{L/s}$. Such fabrication method has been subjected to many repetitive experiments. For all the cases as tested, the injection velocity of the liquid metal is high and consistent enough to guarantee the fabrication of the droplets. As for the comparative experiments, the experimental platform should assure that the liquid metal in both fluids flow at the same initial velocity when leaving the syringes by pushing both syringes synchronously.

Figure 3.1 illustrates the basic droplets fabrication devices [1]. In the following example, the gallium was chosen as the liquid metal microdroplet material because of its nontoxicity and the suitable melting point (29.78°C) near the room temperature. The liquid metal is filled in a 1 mL syringe with a dispersing needle fitted to it. The fluid in the petri dish is the water solution added with the surfactant sodium-dodecylsulfate (SDS), aiming at preventing large-scale coalescence of the produced droplets when extruding them into the storage petri dish. The needle penetrates the wall of the petri dish and is placed under the water solution surface. The temperature of the fluid is flexibly changeable, but the range needs to be above the melting point of the metal.

3.3 Large-Scale Fabrication of Liquid Metal Droplets

With the abovementioned method [1], a large number of liquid metal droplets can be quickly fabricated (Fig. 3.2a). When observed under the microscope (Fig. 3.2b–d), these droplets were found to be stable and shiny. Overall, the present fabrications were under an average flow velocity as estimated about $70 \mu\text{L/s}$ for the jetting liquid metal at the syringe outlet. Details for such measurement can be found in later experimental section. For different jetting situations, similar procedure can be followed to estimate the flow velocity. However, it should be pointed out that, the

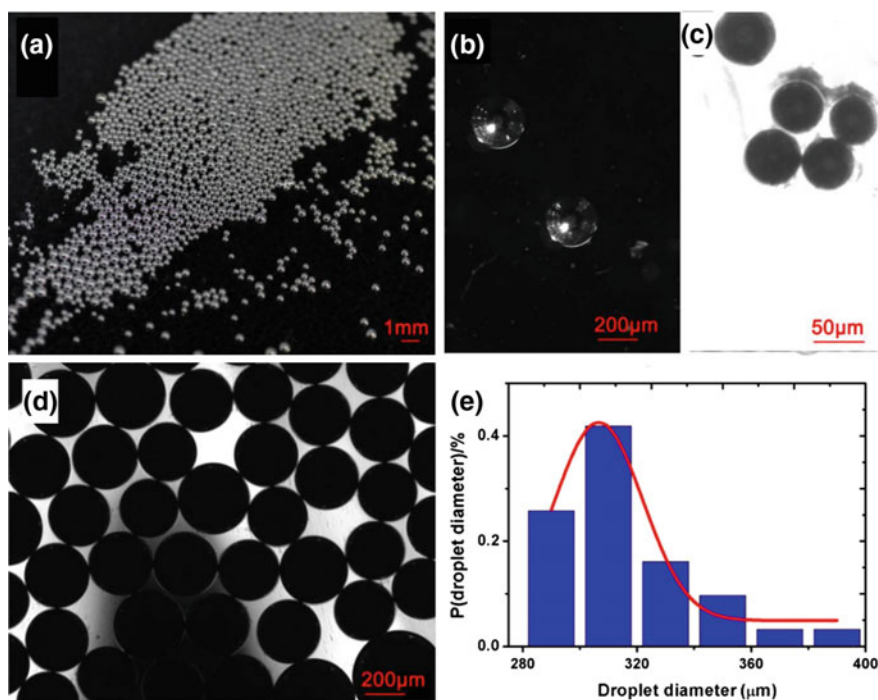
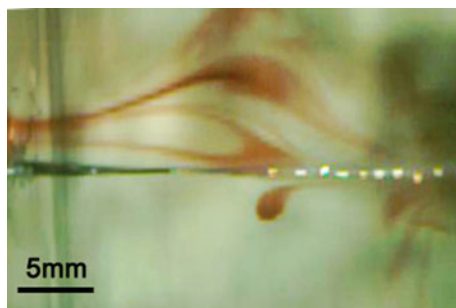


Fig. 3.2 Fabricated liquid metal droplets in microscale [1]. **a** Optical image for poly-dispersed liquid metal droplets before filtration. **b** Single droplet under microscope. **c** Droplets with a diameter of about 50 μm . **d** Microscopic image showing a single layer of liquid metal microdroplets contacting together. **e** Histogram of droplet diameter distribution in the sample. All pictures are reproduced with permission

process of acceleration at the beginning of piston pushing and deceleration at the end is unavoidable. Therefore, the liquid metal may leave the pinhead aperture with different velocities. Such an uncertainty brings on the nonuniform breaking up of the stream, which causes further unevenness in the diameters of the droplets. For quantifying such behavior, a histogram displaying the diameter distribution of the droplets in Fig. 3.2d is shown in Fig. 3.2e. The average droplet diameter was found to be $312 (\pm 24) \mu\text{m}$. Here, a needle with a diameter of 0.21 mm (27G) was adopted. With finer needle and faster jetting velocity, even smaller droplets can be produced. As is shown in Fig. 3.2c, the droplet diameter is about 50 μm . Here, adding the SDS was to assure that the droplets can be well dispersed and keep stable, which last for at least 24 h after being fabricated and kept at room temperature. For the further process, one could cool down these liquid metal droplets in water (or other solvents) to a temperature around 4 $^{\circ}\text{C}$, so as for the droplets to become completely frozen into solid particles due to their room temperature melting point. Under such situation, the “frozen” droplets would maintain dispersed and stable for a rather long time.

Fig. 3.3 Visualizing the fluid flow behavior surrounding the liquid metal jetting stream [1]. Picture is reproduced with permission



Besides the syringe needle, any thin tube, such as a capillary, can be used to produce liquid metal droplets as well, and their role is to jet the liquid metal into a thin stream at first. SDS is not the only surfactant, and Yu et al. [1] had also tried other solutions, for instance, sodium dodecylbenzenesulfonate, oil, and so on, which have also achieved excellent similar effects. Such fabrication method is mainly based on the fundamental phenomenon of self breaking up of the liquid metal jetting into another fluid. One of the possible reasons may be attributed to the fluidic turbulence which cuts off the ejected stream. However, such an assumption was denied by the experimental observation as displayed in Fig. 3.3. A drop of red ink was dripped into the solution surrounding the pinhead in order to observe the fluidic flow when the liquid metal stream was ejected. It could be clearly seen that the fluid around the stream of liquid metal flew in parallel with no obvious turbulence. Thus it can be thought that there lie in some other influential factors.

Figure 3.4 revealed the liquid metal jetting and droplets fabrication process under the high-speed video (via NR4-S3 Camera) [1]. As was shown in Fig. 3.4a, with a certain velocity (which can be quantified through image processing) the liquid metal formed a continuous thin stream that broke into droplets at a certain distance away from the pinhead. The stream flew into the aqueous solution, and then decelerated slowly due to the viscosity resistance. As the speed slowed down, a neck appeared at the front end, and then broke apart from the main jetting stream. After that, it continued to go ahead and reshaped into spherical microdroplets by the liquid metal surface tension. In the formation of each independent droplet, five stages (stream, neck appearing, shuttle shape when breaking apart from the stream, irregular shape, spherical droplet) could be observed according to Fig. 3.4b.

Though the platform is relatively straightforward, there still exist a few complex factors that affect the outputs of the droplet fabrication, including the pinhead aperture diameter, the velocities of liquid metal jetting, the viscosities and densities of fluid and the surfactant. The size of the microdroplet is definitely influenced by the flow velocity of liquid metal and the diameter of the syringe needle [1]. The former affects the distance where break up flow happens and the latter determines the diameter of the stream. Both the increase of the liquid metal flow velocity and the decrease of the syringe needle inner diameter will lead to smaller droplets. The inner diameters of the two needles as chosen for a comparison are 0.41 mm (22G) and 0.06 mm (34G),

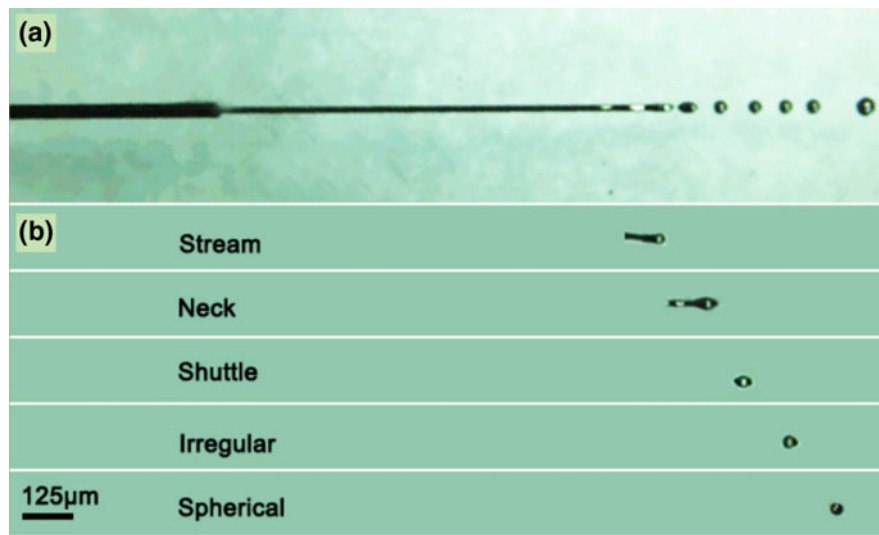


Fig. 3.4 The detailed processes of droplets fabrication detected by a high-speed video camera [1]. **a** A continuous thin stream that broke into droplets at a certain distance away from the pinhead. **b** Five stages of shape change for one droplet during fabrication. All pictures are reproduced with permission

respectively. Through observing and counting the fabricated liquid metal droplets using either needle with the stereomicroscope (Figs. 3.5a, c), the histograms of the droplet diameter distribution are given in Fig. 3.5b, d, respectively. It can be found that the average droplet diameters are $590(\pm 71) \mu\text{m}$ and $172(\pm 18) \mu\text{m}$ in both experimental results, respectively. Clearly, with modification of the needle in the near future, making metal particles with much smaller size than the present ones can still be very possible along this way.

3.4 Fabrication of Liquid Metal Droplets Inside Different Fluids

Yu et al. [1] further tested two fluids that evidently differ in density and viscosity—the water and medical alcohol (75% v/v) to disclose the influence of both parameters. Under the same jetting velocity, the liquid metal broke into droplets after a short distance in the water (Fig. 3.6b), while the stream in the alcohol still looks like a wire with some waves appearing at the front (Fig. 3.6a). Clearly, droplets were successfully formed in the water (Fig. 3.6b), while liquid metal turned into a wire in the alcohol after being jetted from the needle (Fig. 3.6c). At the temperature of $22\text{ }^{\circ}\text{C} (\pm 0.3)$ for both fluids, the densities of water and medical alcohol (75% v/v) were measured as 0.975 and 0.870 g/cm^3 , and viscosities 0.9579 and $2.341\text{ mm}^2/\text{s}$, respectively. For

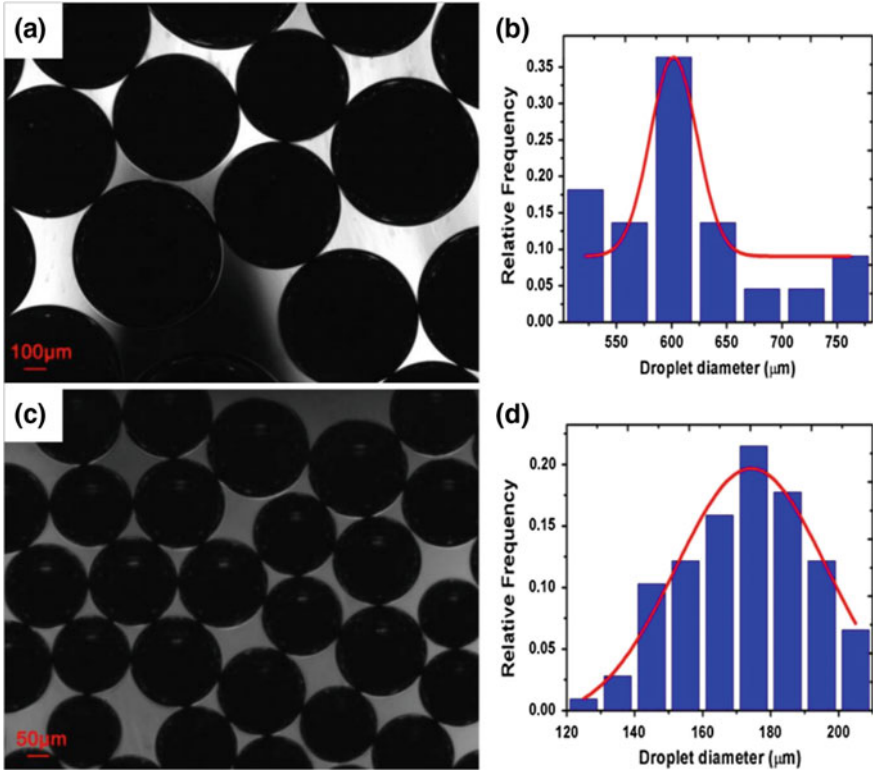


Fig. 3.5 Comparison on the liquid metal droplets fabricated using pinheads with 0.06 mm and 0.41 mm inner diameter, respectively [1]. **a** Microscopic image showing a sample of liquid metal droplets produced by pinhead with 0.06 mm. **b** Droplet diameter distribution of the sample produced by pinhead with 0.06 mm. **c** Microscopic image showing a sample of liquid metal droplets produced by pinhead with 0.41 mm. **d** Droplet diameter distribution of the sample produced by pinhead with 0.41 mm. All pictures are reproduced with permission

the apparently different results, the value of the parameters would give out a clear answer. According to the fluidic rules [15, 16], one of the major factors that influence the jetting liquid is the balance between the viscous shear stress and surface tension. When the shear stress is strong enough to overcome the surface tension, the liquid metal keeps jetting, or otherwise, it would break into droplets. Since the viscosity of alcohol is higher than that of the water, the viscous shear stress in the alcohol is stronger. Thus, the jetting length of the liquid metal in the alcohol is longer than that in the water. And the flow resistance at the front end of the jetting liquid metal is proportional to the surrounding liquid such as water or alcohol's density. In this sense, the deceleration effect of the liquid metal jetting flow in the water is relatively larger than that in alcohol. However, since the density difference between water and alcohol is not large enough, the density resistance effect of the liquid to the metal

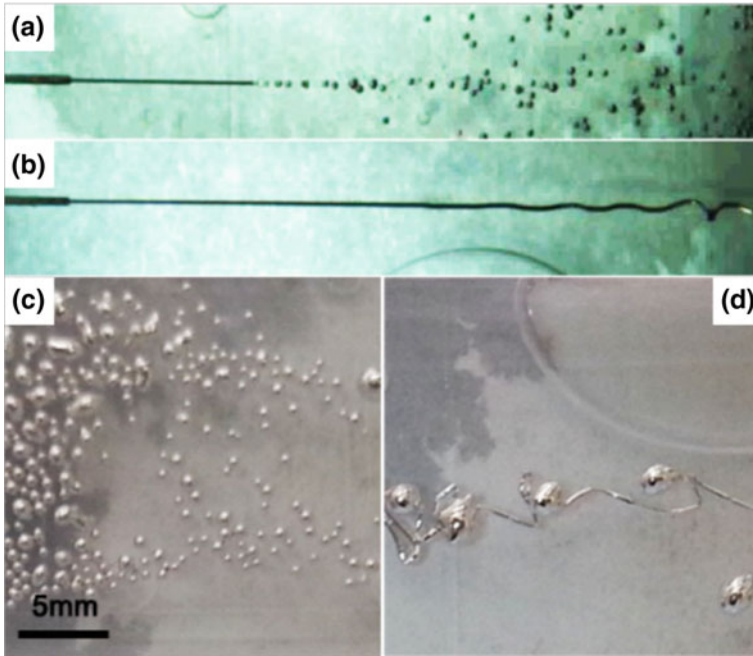


Fig. 3.6 Liquid metal droplets fabricated in water and alcohol [1]. **a** The process of liquid metal jetted from pinhead in water with a high-speed video camera. **b** The process of liquid metal jetted from pinhead in alcohol with a high-speed video camera. **c** Droplets produced in water. **d** Liquid metal wires produced in alcohol. All pictures are reproduced with permission

flow will not be the major reason compared to the influence of the viscosity in the present case.

In order to compare the different effects of water and alcohol, no SDS was not added in the experiments in Fig. 3.6. It was found that these metal droplets quickly coalesced after the jetting compared to the images in Fig. 3.2. This result also revealed and proved the interesting effect of using SDS to prevent the droplets coalescence phenomena. However, the next experiment showed that the influence of the surfactant on the droplet fabrication is more than that.

Choosing the SDS as the surfactant, two fluids with different concentrations have been tested for droplet fabrication [1]. The solutions in the two petri dishes were 10 g/L SDS solution and 20 g/L SDS solution at a temperature of 22 °C (± 0.3). The liquid metal droplets fabricating process were observed with the high-speed video camera (Fig. 3.7) in both fluids. With the same velocity and pinhead inner diameter, the continuous stream in the 10 g/L SDS solution was found to be almost double the length than that in the 20 g/L SDS solution ($L_1 \approx 2L_2$). Correspondingly, the course that the droplets reached in the 10 g/L SDS solution was also twice as long ($S_1 \approx 2S_2$). The densities of 10 g/L SDS solution and 20 g/L SDS solution were 0.985 g/cm³ and 0.995 g/cm³, with viscosity measured as 0.957 and 0.958 mm²/s,

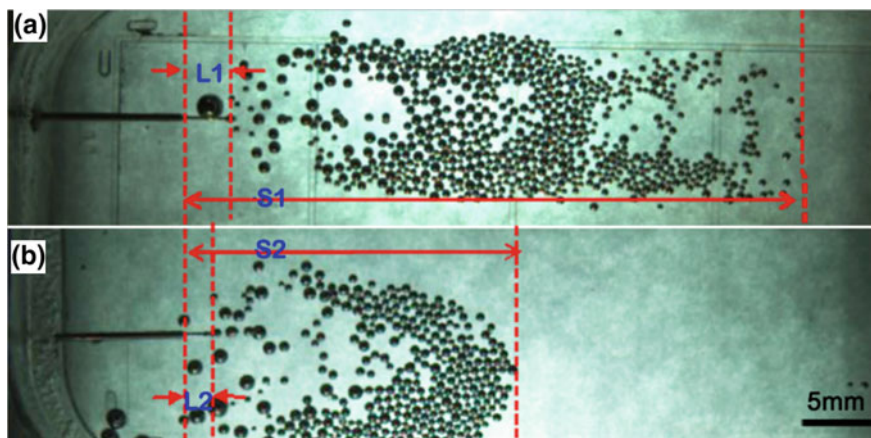


Fig. 3.7 Liquid metal droplets fabricated in 10 g/L SDS solution (a) and 20 g/L SDS solution (b), respectively, with a high-speed video camera [1]. All pictures are reproduced with permission

respectively. Since the density and viscosity of both solutions are almost identical, they differ only in the surface tension due to the distinct SDS concentration. As the surface tension of the solution decreases with the increase of SDS concentration, the interfacial tension between the liquid metal and the 20 g/L SDS must be stronger than that for the 10 g/L SDS case. In the course of jetting the liquid metal flow, the inertial force decreases with the velocity reduction, and interfacial tension dominates the formation of the droplets. The balance between the inertial force and the interfacial tension maintains the jetting. And it is easier to break when the interfacial tension becomes stronger, which means that the jet length will be shorter. Thus the stream length and the course of the droplets in 10 g/L SDS are much longer than in 20 g/L SDS because of a stronger interfacial tension.

The present method has generalized purpose in making RTLM droplets. It can be extended for more fabrication situations. For examples, this approach also provides a way to quickly make porous metal structures based on the construction and assembly of the formed microdroplets. These droplets could be interconnected arbitrarily or assembled as desired after being created in free space. Figure 3.8 presented some typical porous microstructure composed of stacked liquid metal droplets. Figure 3.8a showed the connection among these droplets. Improving the air pressure above these droplets would make them connected more closely. Figure 3.8b, c shows the images of 2D and 3D liquid metal droplets structures, respectively. With the accumulation of these metal droplets, one could produce a metallic foam structure Fig. 3.8d. This provided a simple way to produce metallic foams based on droplets fabrication and assembly method. Further extension of the production process and detailed properties of these metallic foams can still be investigated in future works.

It should be mentioned that, for the above work, gallium was mainly adopted as the test RTLM. In fact, other galinstan alloys such as the gallium–indium alloy or more

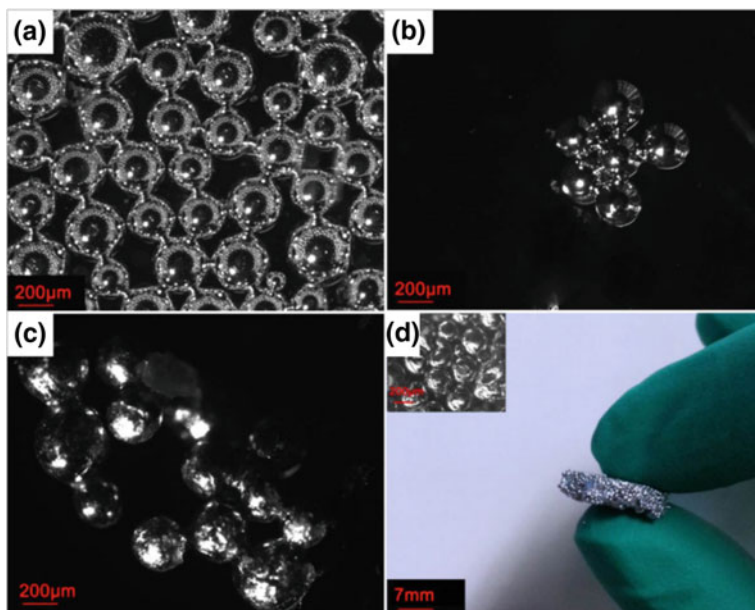


Fig. 3.8 Jet liquid metal to form porous structures [1]. **a** Arbitrarily interconnected droplets. **b** A 2D structure of six droplets. **c** A 3D structure of metal droplet. **d** A metallic foam produced by continuous deposition of liquid metal droplets. The amplified structure is presented as the upper left image. All pictures are reproduced with permission

low melting point metal candidates will also work for the same droplet fabrication [1]. Further researches along this direction are worth of performing in the coming time. Clearly, a channelless RTLM droplet fabrication method was established which is highly efficient in generating stable particles at microscale. In principle, the fluids interaction and the balance between the fluid resistance and liquid metal surface tension contribute to the channelless droplets fabrication. SDS solution prevents these produced droplets from coalescing. Compared with the conventional micro-channels droplets fabrication, such method owns the advantages of low-cost, high efficiency, and simple operation. Yu et al. [1] have managed to produce droplets that are smaller than $50\text{ }\mu\text{m}$ diameter expeditiously, and can possibly reduce such scale by using pinheads with finer inner diameters and increasing jetting velocity. Besides, it has also been demonstrated the possible application of the method in constructing porous foam structures using these liquid metal droplets. It is expected that the channelless droplets fabrication method would have big potential values in future research and practical applications in related areas.

3.5 Electro-Hydrodynamic Shooting Phenomenon to Generate Liquid Metal Droplets

Except for the mechanical approach as investigated above, Fang et al. [18] found an electro-hydrodynamic shooting phenomenon of liquid metal stream which displays the transformation behaviors between large liquid metal pool and its small droplet. A small voltage direct current electric field would induce ejection of liquid metal inside capillary tube and then shoot into sodium hydroxide solution to form discrete droplets. The shooting velocity has positive relationship with the applied voltage while the droplet size is dominated by the aperture diameter of the capillary nozzle. Further, the motion of the liquid metal droplets can be flexibly manipulated by the electrodes. This effect suggests an easy going way to automatically generate metal droplets in large quantity, which is important for both fundamental and practical aspects.

A test platform from Fang et al. [18] can be depicted in Fig. 3.9a with working mechanisms illustrated in Fig. 3.9b, c, respectively. Here, the capillary tube serves as the channel connecting the liquid metal and the sodium hydroxide (NaOH) solution container, where the cathode and anode are arranged as depicted in the figure. It is well known that a conductive object with induced charge in liquid phase would cause the formation of electrical double layer on its surface, i.e., bipolarization of the liquid metal. Therefore, an external nonuniform electric field will break up the symmetrical surface tension of the liquid metal. It is this effect that leads to the unconventional ejection phenomena as will be disclosed later. For comparative purpose, two diameters of the capillary tube as 1 and 0.7 mm were comparatively tested. The cathode and anode made of stainless steel are both linked with the direct current (DC) voltage controller. Regarding the test liquid metal, it was chosen as galinstan (made of 67%Ga, 20.5%In, and 12.5%Sn by volume), which has a broad temperature range of liquid phase with a melting point at 10.5 °C [18]. Such alloy might have undercooling point to be around -19 °C under certain measurement circumstances.

First, one could adjust the height of liquid metal level of the container so that the liquid metal can be infused into the capillary tube which however cannot flow out of the nozzle due to its pretty large surface tension. The practical distance of the two electrodes from the capillary nozzle to the anode is about 82 mm because of the conductive characteristics of the liquid metal. The voltage controller is turned on to apply the DC electric field on the electrolyte solution. Then, an unconventional phenomenon was discovered that the liquid metal would automatically eject from the capillary nozzle [18], which then shoots into the electrolyte solution, and forms droplets until finally move to the anode. The whole process is recorded by a high-speed camera (IDT, NR4.S3). The velocity of droplets can thus be calculated from the videos via image processing. Through altering the voltage, concentration of solution, and aperture size of capillary tube, one could systematically evaluate the effects of various typical factors on the droplets generation behavior.

When electric field is applied to the electrolyte solution, the force balance between pressure and surface tension on the interface of liquid metal and NaOH solution at

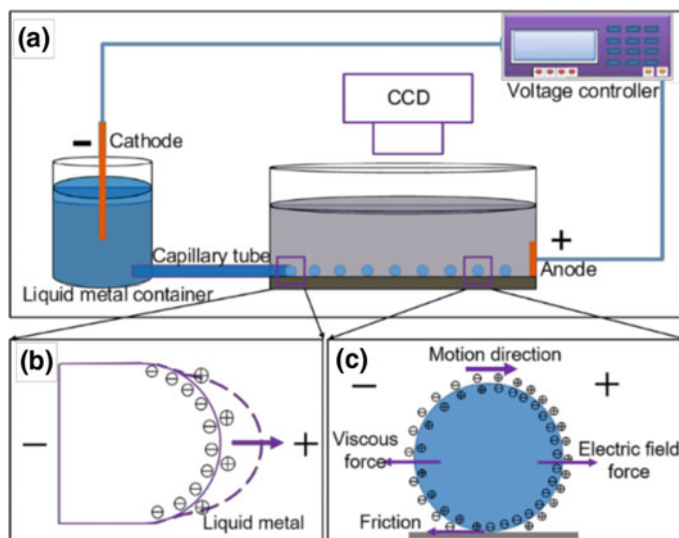


Fig. 3.9 a The schematic diagram of the experimental setup [18]. Both of the liquid metal injection **b** and droplet motion **c** are driven by electro-hydrodynamic force. All pictures are reproduced with permission

the capillary nozzle is broken immediately. The traction force induced by the external electric field would then promote the liquid metal to eject from the capillary nozzle and shoot into the electrolyte solution. Due to large surface tension of the liquid metal, the stream then splits to form a large amount of the droplets continuously [18]. Figure 3.10 shows the snapshots of typical ejections in NaOH solution of 0.25 mol/L under voltages from 2.5 V to 20 V. The intensity of the electric field can be considered as linear dependence on the applied voltage. For the too much low voltages (below 2.5 V), it will not happen for the liquid metal droplet generation due to its high surface tension. When raising the voltage strength, the injection velocity of the liquid metal increases evidently. Overall, the ejection direction of the liquid metal is along the central axis of the nozzle for the voltages below 5 V (Fig. 3.10a–b). However, it is interesting to notice that such ejection direction becomes unstable, which is affected by the high voltage (Fig. 3.10c–e). Turbidity around the cathode was seen when the voltage strength increases to about 5 V. According to comparative experiments, these dark-gray matters might be composed mainly of compounds containing In and Sn ions due to the electrochemical reaction at the interface between liquid alloy and NaOH solution. If only using the liquid gallium to perform the same actuation experiments, no such dark-gray matters were observed. It therefore can be inferred that the varied activity between the GaInSn alloy and the gallium (Ga) may lead to the different electrochemical reaction. It should be mentioned that, since the liquid metal is connected to the cathode, the reaction occurring here is a kind of electrochemistry reduction one. Further, from Fig. 3.10, it is also observed that the droplets are attracted

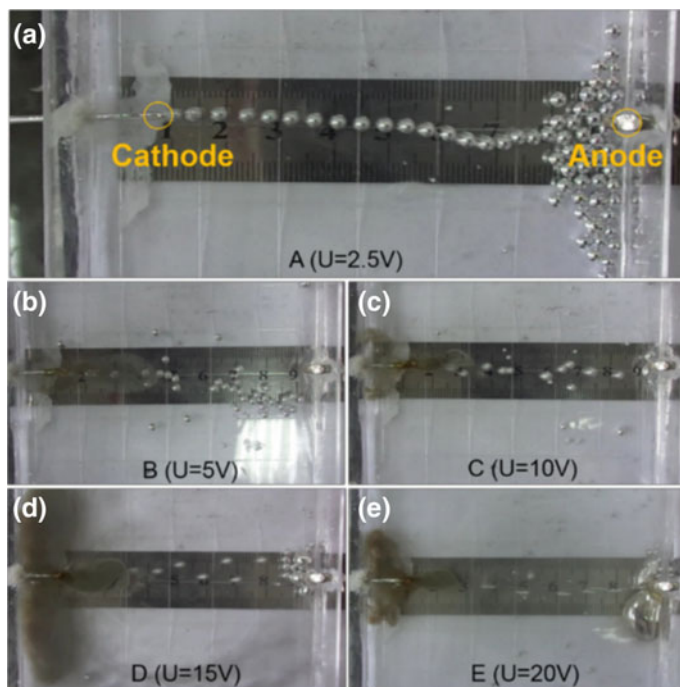


Fig. 3.10 The snapshots of liquid metal shooting in NaOH solution of 0.25 mol/L under different voltages [18]. **a** $U = 2.5$ V; **b** $U = 5$ V; **c** $U = 10$ V; **d** $U = 15$ V; **e** $U = 20$ V. All pictures are reproduced with permission

to the anode under external electric field. One particularly important discovery here lies in that it disclosed that a large pool of liquid metal in the container could be continuously ejected from the capillary tube into the surrounding solution which is quite useful for future large-scale fabrication of metal particles with controlled sizes.

The liquid metal droplets' generation behavior is mainly dominated by the size of the capillary nozzle, the voltage and the concentration of the NaOH solution [18]. Figure 3.11 depicts the relation between the applied voltage and liquid metal droplet velocity for different aperture sizes of capillary nozzle and positions in 0.125 mol/L NaOH solution, where the position is denoted by the distance from the capillary nozzle. From the measurements, one can conclude that the ejection speed of the droplets goes up rapidly with the increment of the voltage. The velocity of the droplet decreases due to viscous resistance effect applied to it during traveling along the solution. Figure 3.11 also indicates that the dependence of the droplet velocity on the voltage is less affected by the aperture size of the capillary nozzle considered here.

Figure 3.12 presents the relationship between velocity and concentration of NaOH solution under applied voltage from 5 to 20 V at the position (2 cm away from the capillary nozzle) [18]. The concentration of NaOH solution has no significant effect

Fig. 3.11 The relationship between applied voltage and liquid metal droplet velocity for different aperture sizes of capillary nozzle (D) and positions (L denotes the distance from the capillary nozzle) in 0.125 mol/L NaOH solution [18]. All pictures are reproduced with permission

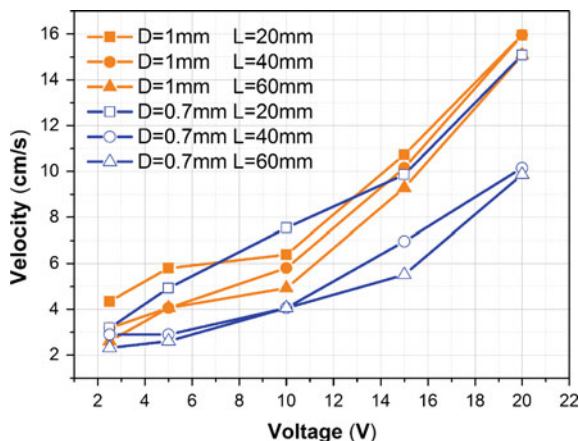
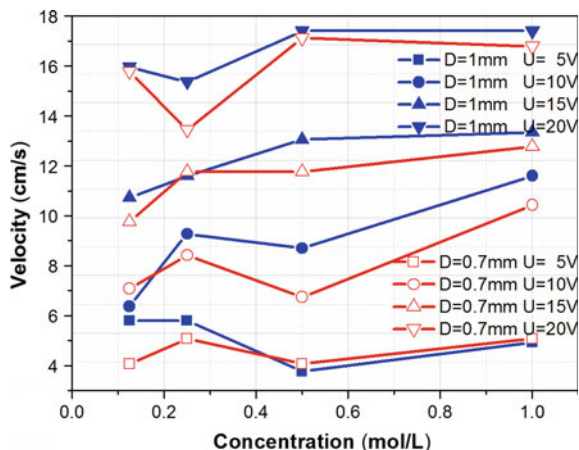


Fig. 3.12 The relationship between velocity and concentration of NaOH solution under different applied voltages at the position 2 cm away from the capillary nozzle [18]. All pictures are reproduced with permission



on the velocity of the droplets. In fact, increasing the concentration of NaOH would lead to the decrease of the electric permittivity of the electrolyte solution [19], and weaken the electro-hydrodynamic driving force. However, this effect is not evident in the present experiments. Besides, the relationship between voltage and velocity does not generate prominent difference with different capillary nozzles. According to the experiments, the size of the liquid metal droplets is mainly determined by the capillary nozzle diameter. When using capillary of diameter 1 mm, the average size of liquid metal droplet is about 2 mm. And for the case of diameter 0.7 mm, the average size of droplet is about 1.6 mm. Given micrometer or even nanometer capillary tube, much smaller droplets can still be obtained. Further, it was also observed that increasing the voltages can slightly lead to smaller droplets. In addition, the inner surface roughness of the nozzle also affects the droplet size.

Theoretically speaking, the above finding regarding the metal droplet generation and manipulation can be attributed to the fundamental electro-hydrodynamic mech-

anism of the interaction between liquid metal and electrolyte solution. Overall, the whole process can be divided into three phases: liquid metal ejection induced by electric field, the liquid metal stream breaking into droplets and the droplets locomotion in the base solution [18].

The first phase provides the initial momentum of the ejection in analogy to external mechanical force [18]. Without losing any generality, the Young–Laplace equation $\Delta p = 2\gamma/R$ can be used to characterize the force balance on the interface of liquid metal at initial stage, where Δp is the pressure difference between liquid metal and base solution and determined by the both liquids level, γ is the surface tension of liquid metal (around 0.7 N/m [20]), and R the radius of liquid metal sphere. For $R = 1$ mm, the liquid metal sphere can sustain a large pressure difference 1436 Pa. When the electric field is applied, an electrical double layer (EDL) is formed at the interface of the liquid metal (Fig. 3.9b). The induced electric force can be denoted by εE^2 , where ε is the electric permittivity of NaOH solution and E the electric field strength, acted on the liquid metal interface along its normal direction. As a result, the equilibrium of surface tension and pressure is broken. Then the interface deforms and tends to move toward the side of base solution. After this acceleration process, the liquid metal ejects out from the nozzle. Obviously, increasing the applied voltage will result in a larger electric force.

In the second phase, a liquid metal stream breaks into droplets due to Plateau–Rayleigh instability [18]. It should be mentioned that one did not observe here the continuous thin stream traveling phenomenon as found in the mechanical force controlled liquid metal injection. The reason lies in that the electrohydrodynamic force has much stronger effect on the flow instability, which thus enhances the liquid metal droplet generation and leads to the disorder of the injection direction. For the third phase, the liquid metal droplet is driven by electrohydrodynamic force to move along the proposed direction through the electrodes layout, which can be adopted for precise manipulation of the droplets. The basic phenomenon can be understood from Fig. 3.9c. Immediately after external electric field is applied, the current then drives positive (Na^+) and negative ions (OH^-) to move toward the corresponding side of the liquid metal droplet, which induces an equal and opposite surface charge on the conducting surface. The tangential electrical stress exerted within the electric double layer (shown in Fig. 3.9c leads to the imposed shear stress on the liquid metal surface, which can induce the flow inside droplet and drive its motion. Besides, droplets carrying negative charges when ejecting out of the capillary at cathode further contribute to the electric field force. Based on the electro-hydrodynamic theory [21], the velocity of the liquid metal droplet can be deduced as:

$$U = \frac{9kD}{40(1 + \mu_L / \mu_W)} \frac{\varepsilon DE^2}{\mu_W} \quad (3.1)$$

where k^{-1} is the Debye length (about 5.0×10^{-9} m), D is the diameter of the liquid metal (about 2×10^{-3} m), μ_L is the viscosity of galinstan (2.4×10^{-3} Pa s at 20 °C

[22]) and μ_w for NaOH aqueous solution (about 1.0×10^{-3} Pa s at 20 °C), ε is the electric permittivity of NaOH aqueous solution (about 6.75×10^{-10} Fm $^{-1}$ for 0.125 mol/L [19]). E denotes the electric field strength chosen as 61 V/m for voltage 5 V.

Thus the velocity of the liquid metal droplet estimated from Eq. 3.1 is about 13.3 cm/s, which is higher than the experimental results about 3 cm/s. The reason for this deviation lies in that the Eq. (3.1) is derived from the balance between viscous force and electric field force in free space [18]. However, the friction from the current substrate impedes the droplet motion. In addition, the electrochemical reaction on the liquid metal droplet surface could induce the surrounding flow disorder and thus weaken its directional motion. According to Eq. (3.1), the velocity of the droplet depends linearly on the electric permittivity. For 1 mol/L NaOH solution, its electric permittivity is [19]: 5.70×10^{-10} Fm $^{-1}$, which does not have too much difference with that of concentration 0.125 mol/L. Thus, droplet velocity depends less on the concentration of the NaOH solution as considered here.

The velocity of metal solid particle induced by the external electric field in electrolyte solution is given by $U = \varepsilon D E^2 / \mu_w$, and estimated as 5.0 mm/s according to the above parameters, which is much smaller than that for liquid metal droplet [18]. The reason lies in that the tangential electric field vanishes at free surface of liquid metal droplet. The viscous stress associated with Debye-scale shear within the electrolyte must be balanced by the electric stresses, which leads to amplified velocity scaling about kD compared with the metal solid particle. It is noteworthy that the NaOH solution plays a key role for droplet motion with high velocity. The liquid metal surface tends to come into being Ga₂O₃ due to electrochemical reaction under electric field, which decreases the surface tension and liquidity and weakens the electro-hydrodynamic effect. However, NaOH solution can effectively deoxidize Ga₂O₃. For NaCl solution, the velocity of the liquid metal appears smaller than that for NaOH solution.

Overall, the discovery of Fang et al. [18] on the electro-hydrodynamic phenomenon indicated that low magnitude electric field would easily induce liquid metal ejection from a capillary tube. The subsequent shooting of the metal stream into the solution would generate a large amount of discrete droplets. The experiments disclosed the major factors to dominate the events. Several important conclusions can be drawn as follows. Firstly, the ejection velocity of galinstan droplets has positive correlation with the applied voltage. Secondly, the concentration of NaOH solution has no significant effect on the ejection velocity. Thirdly, the size of the galinstan droplets depends mainly on the aperture diameter of the capillary nozzle. The finding opens an efficient strategy to flexibly fabricate liquid metal droplets in large amount and with controlled size via a rather rapid, easy, and low-cost way. It also raised important scientific issues worth of investigation in the coming time.

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Chapter 4

Electrically Induced Transformations of Liquid Metal Among Different Morphologies



Abstract As an emerging multifunctional material, the room temperature liquid metals own many intriguing properties that had never been anticipated before. Over the long year's exploration of liquid metal as a soft machine, the present lab (Sheng et al. in *Adv Mater* 26: 6036–6042, 2014 [1]) found for the first time that through applying an external electrical field on the liquid metals sprayed with or immersed in water, a group of very unusual transformation phenomena of liquid metal among different morphologies and configurations can be induced. These basic machine effects and roles include transformation from a large-sized liquid metal film into a tiny sphere (over one thousand times variation in specific surface area), quick mergence of separate metal droplets, controlled self-rotation, and planar locomotion under different conditions. Further, a series of novel phenomena were observed, such as the self-rotating liquid metal sphere induced accompanying water vortexes nearby, and liquid metal droplet moving across the channel bridge under programmable external electrical fields, etc. In addition, the shape, size, voltage, orientation, and geometry of the electrodes would play important roles in controlling the liquid metal morphologies and transformations. Such soft machine capabilities were hard to achieve on rigid metal or conventional liquid objects otherwise. These findings have both fundamental and practical significances which suggest a generalized way of making smart soft machine in the coming time, collecting discrete metal fluids, as well as flexibly manipulating liquid metal objects or machines. This chapter is dedicated to illustrate the basics about driving the liquid metal soft machine among different configurations.

Keywords Diverse transformation · Liquid metal transformers
Electrical actuation · Programmable material · Electrical double layer

4.1 About Transformable Soft Machines

Designing devices that can flexibly transform among different morphologies and freely move via a controllable way to perform desired tasks has long been a dream

across diverse scientific and technological areas ranging from mechanics, biology to physics. Tremendous efforts have therefore been invested to explore promising strategies to induce the motion of artificial swimmers [2] or to grow random [3] or directional [4] structures of conducting material between two electrodes by electrodeposition [5] or electropolymerization. To avoid the use of chemical fuel, various driving strategies were also developed, including light [6], ultrasonic propulsion [7], magnetic force [8], biomimetic propulsion [9], as well as electricity [10]. Among these typical methods, electric field is especially convenient for practical utility purpose since its magnitudes, phases, and frequencies can be easily adjusted. In this regard, electrokinetic effects of particles have been found when exposed to electric field which has also been adopted to manipulate the target objects [11]. Theoretically, with the administration of an electric field on the surface of two immiscible liquids, it would undergo a jump due to transition of physical properties from one medium to another. One consequence of such discontinuity was the presence of an electric stress at the interface. In the case that a droplet with a very high conductivity was placed in a nonuniform electric field and water, electric double layer would form and its charge repulsion behavior will induce surface tension gradients that would likely to deform the droplet. However, so far, most of the conductive droplets ever tested mainly fall into the category of a conventional liquid, and therefore, only very limited mechanisms were disclosed.

The room temperature liquid metals have been found to own unique virtues in a wide variety of important areas including chip cooling, 3D printing or printed electronics due to their outstanding diverse physical capabilities, such as high conductivity as well as favorable flexibility, etc. Though mercury is a well-known room temperature liquid metal, unfortunately, its toxicity poses a serious safety concern for the widespread applications. As an alternative, a class of room temperature liquid metal or its alloys has been explored to display very interesting properties that make them advantageous as multifunctional materials since they can be manipulated in a controllable way [12]. Particularly, the liquid metal GaInSn eutectic alloy (made of 67% Ga, 20.5% In, and 12.5% Sn by volume) has a broad temperature range of liquid phase with a melting point at 10.35 °C. In addition, it is generally chemically stable and does not react with water at around room temperature, and a series of previous studies have proven that such alloy is safe for humans in many normal occasions. Besides, the high conductivity of such alloy is up to $3.1 \times 10^6 \text{ Sm}^{-1}$ [13], which is several orders higher in magnitude than that of nonmetallic materials and comparable with many other common metallic materials. Therefore, with such intrinsically conductive liquid metal immersed in water, various electrically controllable behaviors can be achieved which had never been anticipated before [1]. Through years of continuous works on liquid metals, the present lab occasionally observed a group of very unconventional phenomena which will have generalized importance for both fundamental science and practical utility purpose.

4.2 Electrical Approach to Control Liquid Metal in Aqueous Environment

As is now clarified [1], liquid metal in aqueous environment can be flexibly controlled via electrical field. For illustration purpose, the following experiments on droplets of $\text{Ga}_{67}\text{In}_{20.5}\text{Sn}_{12.5}$ under different arrangements of the electrodes were taken as examples. In order to provide a relatively comprehensive evaluation of the basic effects, a series of conceptual experiments ever carried out were explained. The observed transformations mainly varied accordingly with the position, arrangement and the shape of the two electrodes, the intensity of the applied electrical field, and the coverage of water. For example, in the water accommodating with a large-sized sheet of liquid metal film, when the anode was placed in the water and the cathode was contacted with the liquid metal film, the shape of the metal formed into a sphere, and several formed metal spheres were merged into a larger one in electric field, which were both beneficial for collecting scattered liquid metals and flexibly manipulating liquid metal objects. Additionally, when the spherical liquid metal was exposed to the electrical field after the electrodes were rearranged, self-rotation of the metal accompanying with two vertexes of water was observed. Meanwhile, planar locomotion of the sphere occurred by the driving forces applied by the electrical field. Both the self-rotation and the planar locomotion were available for controlling the movement of liquid objects. All these reliable liquid metal-based transformations under designed electrical fields suggest a very practical approach to make a programmable smart soft machine in the near future. In the following, the aforementioned liquid metal-based transformations were illustrated with the experimental setup as shown in Fig. 4.1,

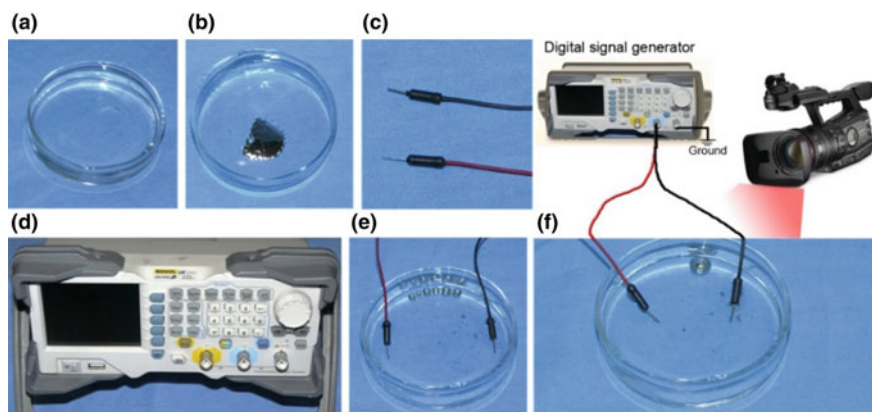


Fig. 4.1 Equipment and experimental diagram on investigating liquid metal transformations [1]: **a** water and petri dish. **b** A sheet of liquid metal splashed in water. **c** Electric cords with copper wire. **d** Power supply. **e** Liquid metal spheres in water with electric cords. **f** Close-up of the apparatus with camera. All pictures are reproduced with permission

and the major testing cases and main findings were summarized in Table 4.1 with a brief summary.

The experiments of the electrically controlled liquid metal transformations were carried out on the eutectic liquid metal GaInSn alloy (67% Ga, 20.5% In, and 12.5% Sn by volume) immersed in tap water. This kind of alloy has a low melting point (10.35 °C) which is beneficial for implementing the experiments. GaInSn alloy was prepared from gallium, indium, and tin metals with purity of 99.99%. Such raw materials with a volume ratio of 67: 20.5: 12.5 were added into the beaker and heated at 100 °C. Then a magnetic stirrer was utilized to stir the mixture after they were all melted to achieve uniformity. Subsequently, a series of designed experiments as listed in Table 4.1 were performed with a setup consisting of petri dish, GaInSn alloy, electric cords with copper wire, and power supply. All equipment was presented in Fig. 4.1 (a–e) and the apparatus was assembled as shown in Fig. 4.1f. Additionally, a high-speed camera Canon XF305 was adopted for shooting the experimental phenomena.

4.3 Transformation and Mergence of Liquid Metal Objects

Following the procedures as outlined in Fig. 4.2a, a drop of liquid metal $\text{Ga}_{67}\text{In}_{20.5}\text{Sn}_{12.5}$ was spread onto the surface of the plastic substrate to form a flat oval which was about 2 cm along its long axis (Fig. 4.2b). Then the same amount of water was sprayed on the liquid metal to contain it inside. The anode of the copper wire was immersed in water, and the cathode of the copper wire was attached to the liquid metal (Case 1 in Table 4.1). When switching on the electricity, it was found that the shape of the liquid metal quickly transformed from its original flattened shape into a spherical one (Fig. 4.2b), indicating significant variations of the interfacial tension effects on the liquid metal [1]. Here direct current was supplied by a 12 V voltage. For a much larger sheet of liquid metal film covering the whole dish (Case 2 in Table 4.1), similar phenomena were also observed. Typical snapshots for this kind of liquid metal transformation were presented in Fig. 4.2c. During the experiments, it was observed that the anode generated a repulsion effect on the liquid metal, while the cathode had an attraction on liquid metal. A wavy liquid metal flow occurred between the anode and the cathode. Such flow emerged around the anode at the beginning, and then moved toward the cathode, tending to encompass the cathode. As a result, a liquid metal sphere formed by the original liquid metal film was generated eventually at the cathode. To further investigate such transformation effect, two separate sheets of liquid metal films, which was deposited on the bottom of the petri dish and connected by liquid metal bridges (Case 3 in Table 4.1), were also prepared in advance. When placing the anode in the water over the right-hand side film and the cathode on the left film, the transformation of the right side occurred prior to that of the left. At last, the liquid metal assembled across the bridge and transformed into a sphere at the left side. Regarding the transient change of the liquid metal morphology, quantitative analysis was also performed in Fig. 4.2c, where the original area

Table 4.1 Investigation cases on liquid metal transformations based on $\text{Ga}_{67}\text{In}_{20.5}\text{Sn}_{12.5}$ [1]

Case	Waveform and voltage	Test subject	Main phenomena
1	DC-12 V (anode not fixed)	A pool of liquid metal	The liquid metal pool transformed from its original large flattened shape into a small spherical one
2	DC-12 V (anode fixed)	A sheet of liquid metal film deposited on the bottom of petri dish	The sheet of liquid metal film with large size quickly transformed from its original flattened shape into a spherical one
3	DC-20 V (anode fixed)	Two sheets of liquid metal film deposited on petri dish bottom and separated by a bridge	The large sheet of liquid metal film transformed from its original flattened shape into spherical one. The sheet of liquid metal film on the one side began to transform after the other side completed transformation
4	DC-12 V (anode not fixed)	Transformation and mergence with three scattered liquid metal droplets	Three separate droplets merged into a united sphere which was relatively large and appeared quite spherical in shape
5	DC-12 V (anode fixed)	Combination of five separate liquid metal droplets	Five separate droplets merged into a united sphere which was relatively large and appeared quite spherical in shape
6	DC-12 V (anode not fixed)	Rotation of liquid metal sphere accompanying with vortexes in the surrounding water	The rotation of the liquid metal sphere and the water vortexes were observed. The motion of the water vortexes near the liquid metal electrode was visualized by using black suspended particles
7	DC-12 V (two electric cords separated by 10 cm)	Planar locomotion of liquid metal sphere object (with diameter about 0.8 cm)	The liquid metal sphere moved in an accelerated way toward the anode with an average speed of approximately 6 body lengths per second
8	DC-12 V (same as in case 7)	Planar locomotion of liquid metal sphere object (with diameter about 1 cm)	The liquid metal sphere moved in an accelerated way toward the anode with an average speed of approximately 6 body lengths per second

(continued)

Table 4.1 (continued)

Case	Waveform and voltage	Test subject	Main phenomena
9	DC-12 V (same as in case 7)	Liquid metal sphere (with diameter about 1 cm) climbing up toward the right side which was slightly higher than the left-hand side	The liquid metal sphere moved in an accelerated way toward the anode with an average speed of approximately 6 body lengths per second. Back and forth movement of liquid metal sphere was produced due to gravity and driving forces induced by the electric field

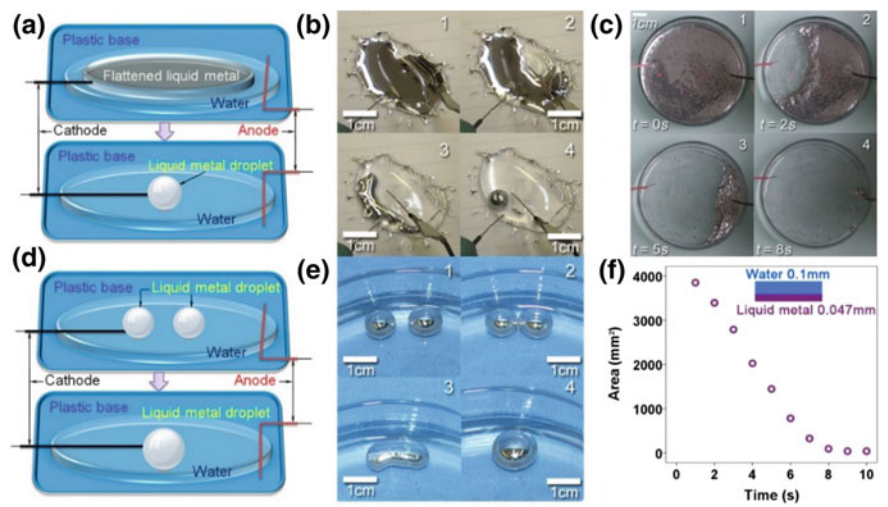


Fig. 4.2 The electric field-induced transformations of liquid metal objects in water [1]. **a** Schematic for electric field-induced transformation from a pool of liquid metal into a sphere. **b** Snapshots of liquid metal transformation from original flattened state 1 to intermediate states 2 and 3 until finally spherical shape 4. **c** Sequential transformation for a circular sheet of liquid metal film to change from its initial flattened state 1 to intermediate states 2 and 3 until finally spherical shape 4. **d** Schematic for electric field-induced mergence from two separate spheres into a single one. **e** Snapshots of the process that two separate droplets combined into a fused sphere from states 1 to 4. **f** The transient area variation curve from the original liquid metal film to a sphere in (c). All pictures are reproduced with permission

of liquid metal shape was 3848 mm^2 , and the thickness for the liquid metal or water layers was 0.047 mm and 0.1 mm , respectively. The result was depicted in Fig. 4.2f. It was surprising to find that tremendous surface area variation from originally flattened circular liquid metal film to the final tiny sphere was over one thousand times, while the total time to finish this morphology transformation in Fig. 4.2c was only 10 s. Clearly, few existing materials could possibly own such capability.

When assembling discrete liquid metal films, several separate spheres were formed. It was discovered that electrical field was rather useful for merging these separate metal spheres into a larger sphere instantly in the water [1]. Additional experiments were further conducted to confirm the coalescence by simply applying electricity (Fig. 4.2d). To test the performance of collecting the discrete liquid metal objects with different morphologies by forming a united sphere in the glass dish, several dispersed liquid metal objects with different shapes were placed in close proximity (Cases 4 and 5 in Table 4.1). Then the discrete liquid metal films formed into several spheres and a quick mergence between the metal spheres happened in sequence. During the experiments, it was observed that a larger liquid metal droplet generally tended to engulf a smaller one inside. Two liquid metal droplets with similar sizes attracted each other to merge ultimately as a single larger droplet. Figure 4.2e presented the original separate droplets, the application of a spatula to make them approximate each other, and the final merged sphere.

According to several former theoretical predictions [14, 15], the structural form of liquid metal object in water is mainly dominated by the surface tension. And the surface tension significantly depends on the intrinsic properties of the liquids and the external electric field. Thus, the above transformation and mergence were mainly governed by the application of the voltage. The high and controlled surface tension allows the liquid metal to display a number of unique properties, including very small contact area with surrounding surfaces leading to low friction rolling, superhydrophobic interactions with other fluids and the ability to be split or fused together with self-healing encapsulation layers. These revealed mechanisms suggest that the liquid metal offers an extremely useful material toward fabricating soft devices and recycling liquid metal in the future.

With the operation of experiments to merge several metal spheres, the distance between the two spheres determined the performance of the mergence [1]. Only a short enough distance could allow for the mergence, while it was unsatisfactory that after disposing of discrete liquid metal films by forming several spheres, additional force was required to keep the spheres close to each other. Fortunately, it was discovered that slightly changing the arrangement of the electrodes would be able to actuate these scattered spheres toward the assigned destination, which was very convenient for collecting the discrete spheres. The behavior of actuation included the self-rotation accompanying with water vortexes and planar locomotion, as illustrated in the following.

4.4 Rotation of Liquid Metal Sphere and Its Induced Water Vortexes

Except for the transformations of the liquid metal itself, additional effects on the surrounding water were also discovered by Sheng et al. [1]. It was observed that the self-rotation of the liquid metal sphere would induce water vortexes nearby on

the platform of the present two-fluid system consisted of liquid metal object and water. Here, the liquid metal droplet was immersed in the water and two electrodes were placed at the relative positions as shown in Fig. 4.3a. When switching on the electricity, an automatic rotation of the liquid metal sphere was observed (Fig. 4.3b). Simultaneously, two accompanying vortices appeared in the nearby water, which kept swirling at the cathode side (Case 6 in Table 4.1). Here, the arrows on the picture indicated the direction of the vortex motion in the water. The water vortices near the liquid metal sphere were clearly visualized by the participation of black suspended particles (Fig. 4.3c). The motion of both liquid metal sphere rotation and water vortices ran rather reliably. During the experiments, the observation was explicit that the metal on the two sides of the liquid metal sphere kept rolling up, resulting in the water around the two rolling sides taken away. Such water loss was complemented constantly by the nearby water, which attributed to the formation of two water vortices. Confirmed by comparative experiments, these behaviors were hard to achieve with a rigid metal or conventional conductive sphere only through the involvement of electricity. When changing the relative orientations of the two electrodes, similar phenomena were also observed. Plots of gray scale along the horizontal lines in the middle height of water vortices labeled as a1 and b1 in Fig. 4.3c were presented in Fig. 4.3d. The symmetrical curves in gray scale plots indicated the existence of the two swirls at a1 and b1.

The main reasons for these unusual fluidic behaviors were relevant to the diverse performances of liquid metal such as high conductivity and flowable features [1]. Essentially, the convective motions were driven by the electrically induced interfacial tension gradients of the liquid metal sphere. The rotation was meaningful when the planar locomotion took place since in contrast with single planar locomotion, the friction decreased a lot, which facilitated the achievement of metal spheres moving toward the destination.

4.5 Planar Locomotion of Liquid Metal Objects

Through a series of conceptual experiments, an electrically controlled directional locomotion with the liquid metal sphere was realized (Cases 7, 8 and 9 in Table 4.1). A liquid metal sphere was immersed in a water channel prepared on the plastic plate. The electric field was generated by applying a 12 V DC between the two electrodes which were vertically placed and separated by about 8 cm (Fig. 4.4a). When the electricity was switched on, several forces were induced as depicted in Fig. 4.4b and their imbalance resulted in a directional locomotion, as sequentially shown in Fig. 4.4c. The driving forces included the surface tension gradient force induced by the electric field and the rotational force for water. To achieve a directional or reciprocal motion, these forces overcame the retardation effects including the viscous friction between the droplet and its surrounding electrolyte as well as the frictional force between the droplet and the surface of the substrate [1]. The liquid metal sphere moved in an accelerated way toward the anode with an average speed of approximately 6 body

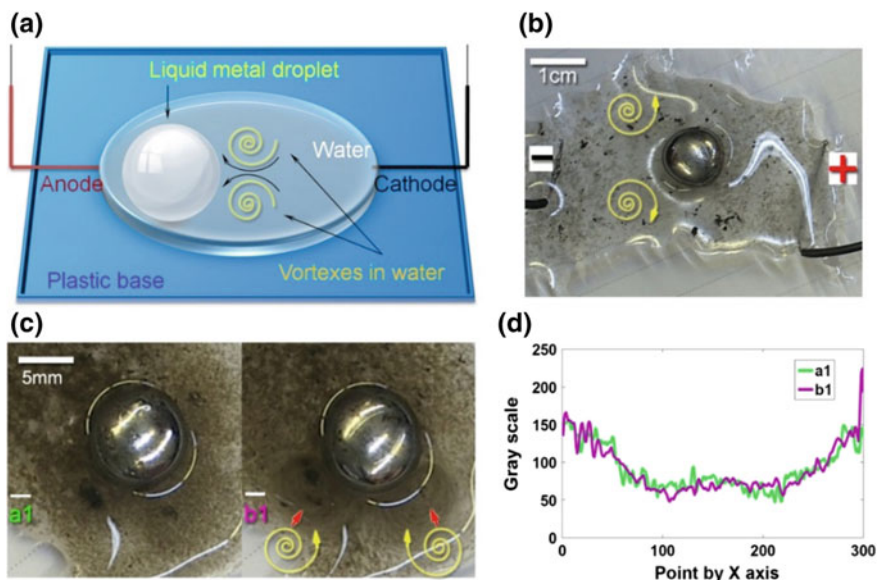


Fig. 4.3 The electric field-induced rotation of liquid metal sphere and accompanying vortices in water [1]. **a** Schematic for electric field-induced rotation. **b** Snapshots of liquid metal sphere rotation accompanying water vortices, where rolling arrows indicated direction of the vortices close to the cathode. **c** Another two cases of liquid metal sphere rotation and vortices in water, where the swirling of the water near the liquid metal electrode was visualized by using black suspended particles. **d** Plots of gray scale along the horizontal line in the middle height of the vortices labeled as a1 and b1 in Fig. 4.3c. All pictures are reproduced with permission

lengths. Quantification on the transient locomotion of two liquid metal droplets with different sizes was displayed in Fig. 4.4d. Clearly, the droplet with larger diameter moved quicker. It was worth to note that no movement was observed when the applied voltage was lower than 12 V under current experimental conditions. During the experiments, it was observed that the mode of movement of liquid metal spheres appeared like a kind of self-driven movement, rather than simple rolling. A tail was formed behind the liquid metal sphere toward the opposite direction of the movement. Referring to the two rolling sides on the metal as described in the above section, it was clearly seen that the metal flow at the two sides of the liquid metal sphere (along the moving direction) rotated in a high speed, acting like two wheels to drive the liquid metal sphere to move forward. Such mode of movement worked like that the local self-movement of the material led to a global movement. Previously, such planar locomotion phenomenon was observed mainly on conductive liquid marble coated with nanoparticles or liquid metal object driven by electrochemical reaction [16–19], and the material as well as the mechanism of planar locomotion was not as generalized as identified in the study of Sheng et al. [1].

Theoretically, charging a conductive surface in liquid phase caused the formation of electrical double layer on the surface. Such charge repulsion on liquid metal

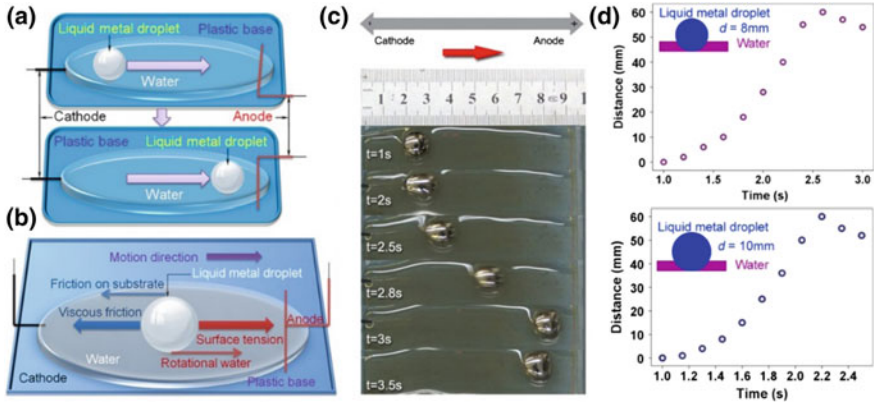


Fig. 4.4 Planar locomotion of liquid metal sphere induced by electric field [1]. **a** The diagram of electric field-induced planar locomotion. **b** Schematic of showing the forces affecting the motion of a liquid metal sphere in water under electric field. **c** Sequential snapshots for liquid metal sphere moving in water. **d** The transient locomotion distance by two different sized liquid metal droplets. All pictures are reproduced with permission

surface resulted in the shape change and coalesce [1]. In fact, the electricity of electrical double layer on the liquid metal surface can be regulated through changing the position of the electrodes. As clarified by existing researches, the surface tension of liquid metal and water are very different from each other. For example, the surface tension of liquid metal such as gallium alloy is about ten times larger than that of water, and the conductivity of such liquid metals is almost 3^{10} times larger than that of water [20]. Therefore, with the application of electric field, the oppositely charged ions will accumulate on the surface of the liquid metal to form an electric double layer, which just consists of the electric double layer capacitor. According to the Lippmann's equation

$$\gamma(V) = \gamma_0 - \frac{1}{2}cV^2 \quad (4.1)$$

where γ , c , and V are, respectively, the surface tension, the capacitance, and the potential difference across the electrical double layer; γ_0 is the maximum surface tension when $V = 0$ [16–19, 21], the surface tension between the liquid metal and the water depends heavily on the capacitance C and potential difference V . Further, as indicated by the Young–Laplace equation [21], the pressure jump p across the interface between the liquid metal and the water can be described by

$$p = \gamma \cdot (2/r) \quad (4.2)$$

Here, the surface tension for water has been omitted due to much smaller than that of the liquid metal γ ; r is apparent radius of the GaInSn sphere. Therefore, the surface tension γ will affect the final pressure difference between the water

and the liquid metal object. When an external nonuniform electric field is applied, the surface tension will become nonuniform, which induces imbalance of pressure difference [21–24]. As a result, the symmetry of the liquid metal system is broken up, and the change of the shape and transformations are thus generated. Furthermore, since the capacitance and the potential difference of electric double layer on the surface of liquid metal vary with the intensity of the electric field, which can be easily regulated through changing the position of the electrodes or the difference of potentials on the electrodes, the surface tension is controllable. As a consequence, a regulated movement or transformation can be achieved. In general, the foundation of the above discovered transformations lies in an imbalance of the giant surface tension of the liquid metal.

4.6 Programmable Liquid Metal Machines

A most noteworthy finding lying behind all the above phenomena was that such transformations were enabled by only relatively low voltage, say about 1–20 V. This was rather beneficial for making future programmable liquid metal machine with highly flexible controllability which would significantly expand the application ranges of the current discovery [1]. In principle, the speed of liquid metal transformation depended on the intensity of the applied electric field. As illustrated by the experiments, the higher the voltage, the faster the transformation would be induced. However, it should also be pointed out that, when the voltage was higher than a certain value (in different conditions such value varied), the obvious electrochemical reaction would happen, which restricted the described transformations. Clearly, the most important fundamental discovery achieved in the above work is that the desired transformation behaviors can be realized on the liquid metal objects with controlled electricity. It opens a generalized way to make software designed smart liquid machine in the near future. With easily controllable feature, such artificial transformer is expected to offer plenty of practical utility opportunities. Overall, liquid metal and water are two materials quite common and the liquid metal alloy is relatively safe for humans in normal occasions, owing to their excellent biological compatibility [22], which extensively enlarge the scope of practical value. Additionally, encapsulating the liquid metal with elastic materials is potential for fabricating artificial machine. A soft robot thus may be created with such liquid metal transformers. Besides, it is promising in designing the motion-assisted devices.

It should be mentioned that biological body often contains an electrolyte solution rather than pure water. Such solutions have evident effects on the experimental results. Actually, these phenomena were first observed on saline solution rather than the tap water [1]. According to experiments, with the electrolyte solution such as saline water, the higher the concentration (indicating higher conductivity) was, the faster the transformation could be realized. In this regard, more electrolyte solution effects will be tried in the near future to shorten the time of transformations. Here, the tap water was particularly chosen by considering that this might represent more generalized

discovery regarding the liquid metal transformations. The same phenomena were observed on pure gallium (99.99% with a melting point of 29.8 °C) while the required voltage was somewhat different, which also demonstrated that such discovery has generalized purpose. As the first trial along this direction, only the most typical experiments on $\text{Ga}_{67}\text{In}_{20.5}\text{Sn}_{12.5}$ were provided as above to present and discuss the main findings. For more other liquid metals, similar phenomena occurred under different conditions such as the intensity of the applied electric field, the surface tension of liquid metal, the conductivity of liquid metal, the ingredient of the water, and so on, as addressed in the present experiments.

Further, different forms of electronic signals regulate a variety of phenomena, which may generate more moving modalities of the liquid metal as desired and are worthy of pursuing [1]. The materials as tried are moldable and flexible, and the fabrication process is simple. In addition, they are compatible with water-based or high humidity environments. Since biological systems generally have flexible surfaces and tend to be operated under electronic current, the present soft, electronic current controlled mergence may be developed for potential applications in recycling the liquid metal residues which were previously injected into biological body as medical electronics [22], functional electronic 3D printing [23], bio-embeddable smart particles or biomimetic devices, etc. The mechanisms to cause such liquid metal transformations were attributed to the dynamic balance between the surface tension and the electronic force applied on the liquid metal surface. The present behaviors can be categorized as certain kind of self-organization on macroscopic scale. Whether such mechanism would realize expected transformation to cooperate with rolls or cells in microscale deserves further study.

Clearly, the scientific significances discovered on the electric field-induced transformations of liquid metal among different morphologies and configurations are rather profound [1]. In addition, along with rotation of the liquid metal sphere, accompanying water vortexes swirling reliably nearby were observed. With the diverse capabilities of the liquid metals under various electric fields, such material offers important opportunities for future practical applications like liquid metal recycling, soft machine manufacture, locomotion-assisted devices, moveable sensors, microfluidic valve, pump or artificial robots. Intriguingly, a smart programmable liquid metal machine could be extended to three dimensions when spatial electrode configurations are adopted. Further, the behaviors of those complex transformations behaviors without gravity effect are also worthy of pursuing in the near future which can possibly be applied to develop programmable space soft robot.

4.7 Alternating Electric Field to Control Liquid Metal

The motion control of liquid metal droplet could find its importance in a variety of areas such as microelectromechanical system (MEMS), microfluidics, and potential use in micromachine or reconfigurable soft robot. Yang et al. [24] explored the motion behavior of liquid metal droplet under AC electric field. The quickly induced

oscillation phenomena of liquid metal droplet and surrounding electrolyte solution were observed. Moreover, some typical features to distinguish AC field actuation with DC field are observed, such as intensive fluid waving induced by the resonance stimulation, and the efficient inhibition of solution electrolysis. For illustration purpose, two important applications of adopting AC induced surface oscillation of liquid metal droplet to develop solution mixer as well as fluidic pump were provided which successfully avoid gas generation inside electrolyte environment. The bulk oscillation effects of liquid metal as clarified here could be very useful in the situations such as solution disturbance and mixing, and fluid oscillator or pump, etc.

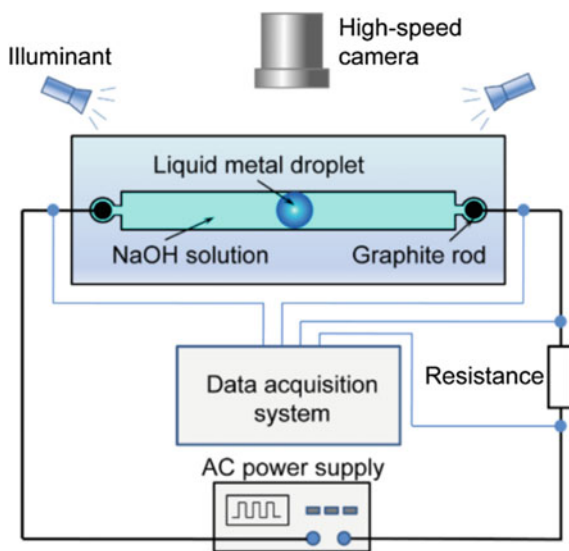
In the experiments of Yang et al. [24], the bulk motion and surface motion of gallium-based liquid metal droplet in milli/centimeter scale in aqueous sodium solution under AC signal is disclosed. Typical factors influencing the motion behavior are theoretically and experimentally investigated, including the size of liquid metal droplet, electrode voltage, electrolyte solution concentration, and signal frequency. Application of AC signal completely diminishes the electrolysis of the electrolyte solution, which is of unique significance for the use in situations where the continuously generated bubbles are undesirable. In addition, the power consumption of triggering all these liquid metals oscillation is quite small only about dozens of milli-watt. The fabrication process is straightforward and its oscillation performance can be easily controlled even programmable.

Figure 4.5 illustrates the schematic diagram of the experimental setup [24]. A drop of liquid metal (GaIn_{10} , 90% gallium and 10% indium by weight) is dropped into an open-top polymethylmethacrylate (PMMA) channel with dimension of 200 mm $\times$ 10 mm $\times$ 10 mm. The PMMA plate is placed on a horizontal desktop and the channel is filled with sodium hydroxide solution. A signal generator (Tektronix AFG 3051C, USA) is configured to supply an alternating electric field in the channel by two graphite rods inserted into the solution at both ends of the channel. A resistance of 56 Ω is cascaded into the circuit to measure the loop current indirectly. The voltage drop of the resistance and the voltage between two graphite rods are measured by Agilent Data Acquisition System (Agilent 34970A, USA). A high-speed camera (IDT NR4-S3, USA) is placed above the channel to capture the movement of both the liquid metal droplet and the electrolyte solution. Two cold light heads of a fiber optic illuminator system are set at both sides of the platform for illumination purpose.

4.8 Alternating Electric Field Actuated Oscillating Behavior of Liquid Metal

Figure 4.6a shows a typical oscillation process of liquid metal droplet in an alternating electric field [24]. In this case, a square wave voltage with amplitude of 5 V and frequency of 0.55 Hz (Fig. 4.6c) is exerted on the graphite electrodes. The original diameter of the liquid metal droplet is 10 mm, and the concentration of the NaOH solution is 0.5 mol/L. When the circuit is switched on, the liquid metal droplet is

Fig. 4.5 Schematic diagram of the experimental setup [24]. Picture is reproduced with permission



initiated to move toward the anode graphite rod on the left-hand side of Fig. 4.6a. After 0.88 s later, the polarity of two electrodes is exchanged. The liquid metal then decelerates immediately and moves backward to the current anode, namely, the right-hand side. The whole deceleration process takes about 0.12 s, and the distance of deceleration is about 0.7 cm, which occupies 6% of the oscillation distance. The reverse acceleration during the turnaround process is about 67 cm/s^2 , which shows a great response sensitivity. With the electrode alternating periodically, the liquid metal droplet moves back and forth between two electrodes at the same frequency as the AC signal. After one period, the oscillation reaches a steady state. Figure 4.6b depicts the displacement and velocity curve of the liquid metal droplet. It can be seen that under the current condition, the oscillation amplitude is about 5.5 cm and the velocity magnitude of the droplet is 8–12 cm/s. According to Fig. 4.6c, the current of the circuit is about 6.5 mA. Thus, the power consumption of the liquid metal oscillator is extremely small, say only about 33 mW.

The movement of the liquid metal droplet in NaOH solution is driven by the surface tension gradient of the droplet induced by external electric field. When a droplet of GaIn_{10} is placed in NaOH solution, electrical double layer (EDL) uniformly forms on the surface of the droplet [25], as shown in Fig. 4.7a. The EDL can be considered as a capacitor, thus the voltage drop of the capacitor is $V = q_0/c$, where q_0 and c are the initial surface charge density and capacitance per unit area of the EDL, respectively. When an external electric field exists, the surface charge of the liquid metal droplet will redistribute to reach an electrical equilibrium state (Fig. 4.7b), due to its intrinsic high electrical conductivity. The surface tension between the liquid metal and the solution can be described by Lippmann's equation: $\gamma = \gamma_0 - cV^2/2$, where γ is the surface tension, γ_0 is the maximum surface tension at $V = 0$ [26]. It is obvious

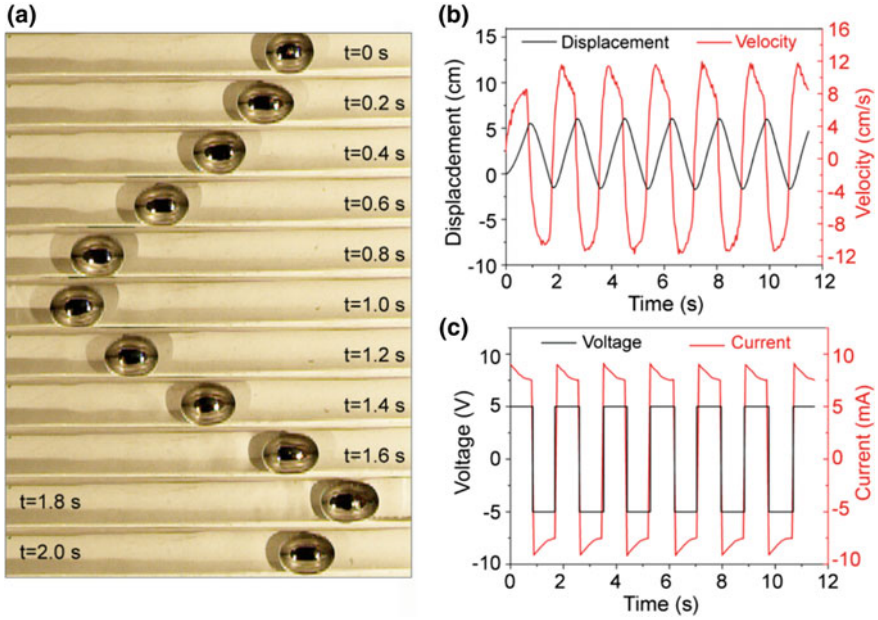


Fig. 4.6 A typical oscillation movement of liquid metal droplet in aqueous sodium solution under AC signal [24]. **a** Sequential snapshots of the oscillation movement; **b** displacement and velocity curve of the droplet; and **c** the AC voltage signal and corresponding current curve. All pictures are reproduced with permission

that the surface tension on the left side of the liquid metal droplet is larger than that on the right side, thus the droplet tends to move right. To quantitatively evaluate the surface tension induced driving force, one can assume that the droplet is a sphere and the electric charge is uniformly distributed on both hemispheres.

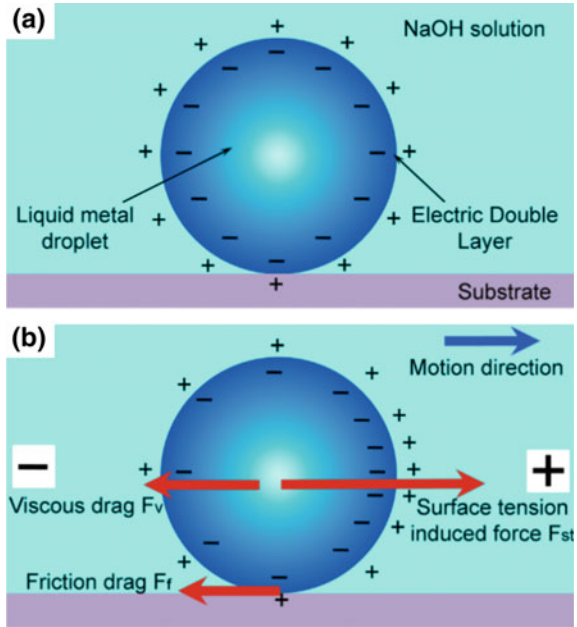
Thus, the EDL voltage on the left hemisphere can be given by $V_L = V - \Delta\phi/2$, and the right hemisphere $V_R = V + \Delta\phi/2$, where $\Delta\phi$ is the potential difference of the external electric field across the liquid metal droplet. The difference of the pressure of liquid metal P_{LM} and the pressure of NaOH solution $P_{solution}$ can be described by Young–Laplace’s equation [27]: $P_{LM} - P_{solution} = 2\gamma/r$, where r is the curvature radius of the droplet surface. Here, it is equal to the radius of the droplet.

It can be deduced that the pressure on the left semisphere of the droplet P_L is larger than that of the right semisphere P_R , and its difference can be given by Ref. [28]:

$$\Delta P = P_L - P_R = 2\Delta\gamma/r = 2q_0\Delta\phi/r \quad (4.3)$$

Since the size of the liquid metal droplet is quite small compared with the whole channel, thus the total electric resistance of the circuit R_{total} can be regarded constant with/without a liquid metal droplet and the potential drop across the droplet can be

Fig. 4.7 Electric double layer (EDL) distribution state on the liquid metal–electrolyte interface [24]: **a** without external electric field; **b** under external electric field. All pictures are reproduced with permission



evaluated as: $\Delta\varphi = V_{\text{electrode}} R_{\text{LM}} / R_{\text{total}}$, where $V_{\text{electrode}}$ is the voltage between the two graphite rods, R_{LM} is the resistance of the electrolyte solution between the liquid metal and the channel wall and bottom, and it can be estimated as

$$R_{\text{LM}} = \rho \frac{2r}{S} = \rho \frac{2r}{h_1 h_2 - 2\pi r^2 / 3} \quad (4.4)$$

where, ρ is the resistivity of the electrolyte solution; S indicates the equivalent cross section area of the electrolyte solution across the liquid metal, and it can be calculated as

$$S \approx \frac{2rh_1 h_2 - 4\pi r^3 / 3}{2r} = h_1 h_2 - 2\pi r^2 / 3 \quad (4.5)$$

where h_1 and h_2 are the width and depth of the channel, respectively. The driving force induced by the surface tension gradient of the droplet can be derived from Eqs. 4.3–4.5 as follows:

$$F_{st} = \Delta P \pi r^2 = \frac{V_{\text{electrode}}}{R_{\text{total}}} \frac{4\pi q_0 \rho r^2}{h_1 h_2 - 2\pi r^2 / 3} \quad (4.6)$$

It can be seen from Eq. (4.6) that the surface tension induced driving force of the liquid metal droplet is dependent on the voltage exerted, the initial EDL charge density, its diameter, resistance of the electrolyte solution, and the geometry structure

of the channel. It is worthy to note that Eq. 4.6 is an approximate evaluation of the surface tension driving force, since it is based on the assumption that the liquid metal droplet is a sphere. In fact, when the diameter of a GaIn₁₀ droplet is larger than 5 mm, it will deform to be an ellipsoid. Furthermore, when the diameter of the droplet is larger than the width of the channel, it will be compressed to the shape of a bar along the channel. Besides, when the droplet is moving in the electrolyte solution, it will deform, as shown in Fig. 4.6b. Thus, Eq. 4.6 can only be applied to the start-up condition of a small liquid metal droplet (with a diameter less than 5 mm). Nonetheless, the correlation reflected by Eq. 4.6 is suitable for large size droplet, which will be experimentally certified later.

Figure 4.8a shows the oscillation amplitude curve of liquid metal droplet with different diameters [24]. It can be seen that when the diameter of liquid metal is less than 1 mm, nearly no bulk oscillation is observed. With the increase of the diameter, the oscillation amplitude increases rapidly. When the diameter reaches about 10 mm (equal to the width of the channel), the oscillation amplitude reaches its maximum magnitude. Increasing the size of the droplet further, the oscillation amplitude diminishes. When the diameter of the droplet is larger than the width of the channel, the droplet will deform and shape to a flat bar. Here, we regard the length of the liquid metal bar as its size dimension. When the length of the liquid metal bar is larger than 30 mm, nearly no bulk oscillation can be observed, but the surface flow of the liquid metal is notable, and two vortexes will be formed at each side above the liquid metal.

When a drop of liquid metal is moving in the electrolyte solution along the channel under external electric field, three forces are exerted on the droplet in horizontal direction [24], namely, the surface tension induced driving force F_{st} , the viscous drag F_v on the interface of liquid metal and electrolyte solution, and the friction drag F_f on the bottom and sidewalls of the channel, as shown in Fig. 4.7b. Equation 4.6 indicates that the surface tension driving force has a positive correlation with the radius of the droplet, F_{st} increases with more than two power of the radius of liquid metal droplet. As for the viscous drag F_v , regarding the liquid metal droplet as a rigid ball for simplification, the Reynolds number of the movement of the liquid metal droplet in NaOH solution is $Re = 2\rho ur/\mu = 1 \sim 10$, where u and r are the velocity and radius of the liquid metal droplet, and μ and ρ are the viscosity and density of the electrolyte solution. Here, μ is approximately equal to that of water, thus the viscous drag F_v increases nearly linearly with the radius of the droplet, namely, $F_v = 6\pi\mu ur$ [29]. When the size of the liquid metal droplet is small, there is nearly no direct contact between the droplet and the bottom of the channel, the friction drag F_f is negligible. However, when the size of the droplet increases, a liquid metal bar is formed, the contact area between the droplet and the bottom and sidewalls of the channel increases dramatically and thus the friction drag F_f increases rapidly.

When the size of the liquid metal droplet is small, the surface tension driving force F_t is weak and not powerful enough to pull the droplet forward [24]. Increasing the size, the driving force mushrooms, it overcomes the viscous and frictional drags and drives the droplet to move back and forth. However, the friction drag increases

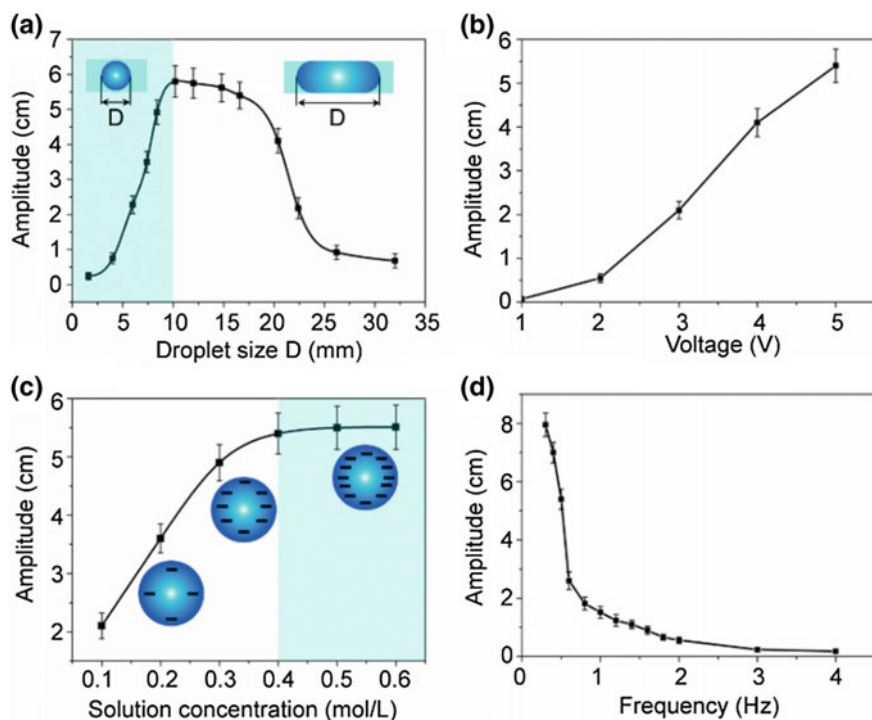


Fig. 4.8 The oscillation amplitude of liquid metal droplet under different situations [24]. **a** Frequency: 0.5 Hz, concentration: 0.5 mol/L, voltage: 5 V; **b** droplet size: 10.4 mm, frequency: 0.5 Hz, concentration: 0.5 mol/L; **c** droplet size: 10 mm, frequency: 0.5 Hz, voltage: 5 V; and **d** droplet size: 9.8 mm, concentration: 0.5 mol/L, voltage: 5 V. All pictures are reproduced with permission

rapidly with the increase of the droplet size, especially when the liquid metal is at a flat bar state, this drag force hinders the droplet movement and thus leads to the decrease of the liquid metal oscillation amplitude, as shown in Fig. 4.8a. Figure 4.8b shows the oscillation amplitude curve of a liquid metal droplet with diameter of 10.4 mm under different voltages. The frequency of the square wave signal is 0.5 Hz and the concentration of the electrolyte solution is 0.5 mol/L. It can be seen that increasing the voltage exerted on the two graphite rods, the liquid metal oscillation is enhanced, in accordance with Eq. 4.6. However, high voltage means large power consumption and intensive electrolysis of the solution, so a compromise should be made when selecting the voltage amplitude. Changing the solution concentration can also influence the oscillation behavior, as shown in Fig. 4.8c. The oscillation amplitude goes up with the increase of the concentration of NaOH solution when the concentration is lower than 0.4 mol/L, and the amplitude will keep constant when the concentration is higher than 0.4 mol/L. The reason behind is that increasing the solution concentration leads to the increase of the initial EDL charge density q_0 and thus increasing the surface tension driving force F_t as Eq. 4.6 indicates. When the

concentration is higher than 0.4 mol/L, the EDL charge density saturates and thus the oscillation amplitude keeps constant. High electrolyte solution concentration leads to low solution resistance and thus high current and high power consumption. So a concentration of 0.4–0.5 mol/L is recommended.

The influence induced by voltage signal frequency is also investigated in Fig. 4.8d. Increasing the frequency decreases the oscillation amplitude [24]. This is mainly because that the time for the liquid metal droplet to move toward one direction is shortened when the frequency goes up. It is observed that when the frequency is at 22 Hz, resonance happens. The liquid metal vibrates intensely and leads to a notable fluctuation of the electrolyte solution.

Figure 4.9a, b shows the surface flow of liquid metal under external electric field. The surface flow is induced by surface tension gradient across the droplet under an external electric field [24]. Areas with lower surface tension are pulled to flow toward the areas with larger surface tension, which is analogous to the Marangoni effect. It is worthy to note that, the direction of the surface flow is along the electric field direction, which is contrary to the bulk motion direction of the liquid metal droplet. As the external electric field alternates its direction periodically, the surface flow direction of liquid metal follows concomitantly. Increasing the alternating frequency, the surface flow switches direction intensively. To some extent, resonance happens, and intense solution waving is actuated. At resonance frequency, the liquid metal droplet has no bulk motion. Such resonance is caused by the reciprocating surface flow of the droplet. It is observed that droplet with larger size has lower resonance frequency, in Fig. 4.9c. This is because, with the increase of the droplet size, the distance the surface flows along one direction increases, and thus the time for the surface flow increases, which will lead to the decrease of the resonance frequency.

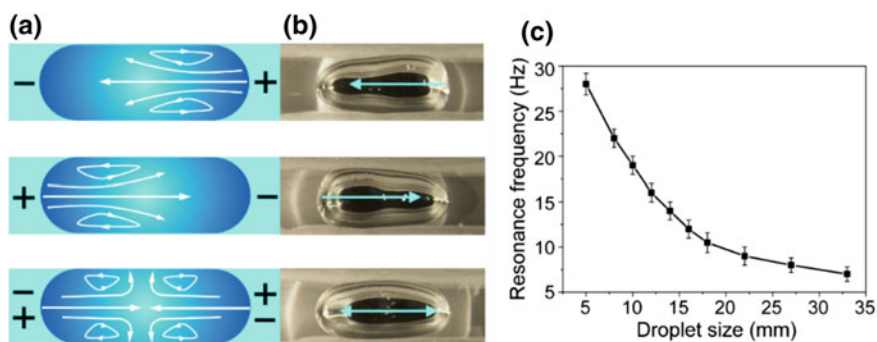


Fig. 4.9 Resonant oscillation phenomenon of liquid metal droplet under matching AC field [24]. **a** Surface flow of liquid metal under DC and AC field; **b** high-speed photos of the surface flow; and **c** variation curve of the resonance frequency with the size of liquid metal droplet. All pictures are reproduced with permission

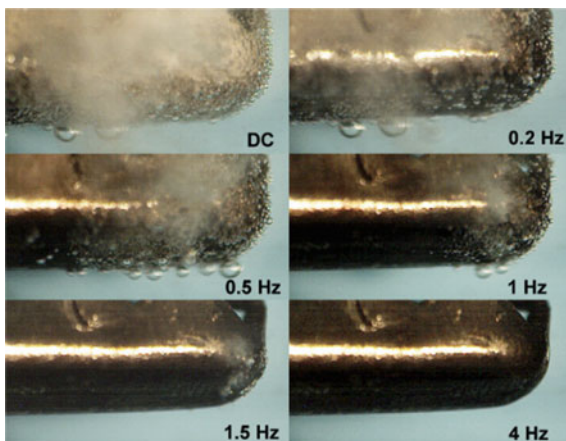
4.9 Practical Value of Alternating Electric Field Actuated Liquid Metal

A practically very useful phenomenon of liquid metal under alternating signal is that the electrolysis of the solution is dramatically diminished [24]. The higher the AC signal frequency is, the weaker the solution electrolysis. To provide quantitative data for practical reference, a demonstrative experiment is particularly illustrated. A pair of stainless steel electrodes is selected and their distance is shortened to 5 cm, which contributes to increasing the electrolysis rate. The voltage exerted on the electrodes is 5 V. As shown in Fig. 4.10, when the AC signal frequency is less than 0.5 Hz, the electrolysis rate of the solution is comparable to the DC situation. Increasing the frequency, the electrolysis is significantly inhibited. When the frequency is larger than 4 Hz, the electrolysis becomes very weak, and the bubble generation is negligible or just completely disappears.

The electrolysis of aqueous sodium solution is essentially water electrolysis [24]. When a DC electric field is supplied, hydrogen and oxygen are generated in cathode and anode, respectively. When an AC electric is supplied, both hydrogen and oxygen are continuously generated in each electrode. In this situation, the absorption of atom H and atom O on the electrodes surface is reduced due to the atomic vibration accompanying with the field oscillation, thus the generation of hydrogen and oxygen is inhibited [30, 31]. Apart from signal frequency, many other factors will influence the electrolysis rate, such as the signal amplitude, the electrolyte concentration, the material of electrode, and the distance between two electrodes.

As depicted by Eq. 4.6, the liquid metal oscillation behavior is positively related to the surface EDL charge density q_0 . Thus, increasing the concentration of electrolyte solution can increase the magnitude of q_0 . However, when the EDL reaches a saturation state, no further enhancement of the surface charge can be achieved by increasing the solution concentration. A small piece of aluminum foil can further increase the

Fig. 4.10 Electrolysis of the solution under different AC signal frequencies [24]. The electrode is made of stainless steel, the electrolyte solution is 0.5 mol/L NaOH, the distance between two electrodes is 5 cm, and the voltage exerted on the electrodes is 5 V. All pictures are reproduced with permission



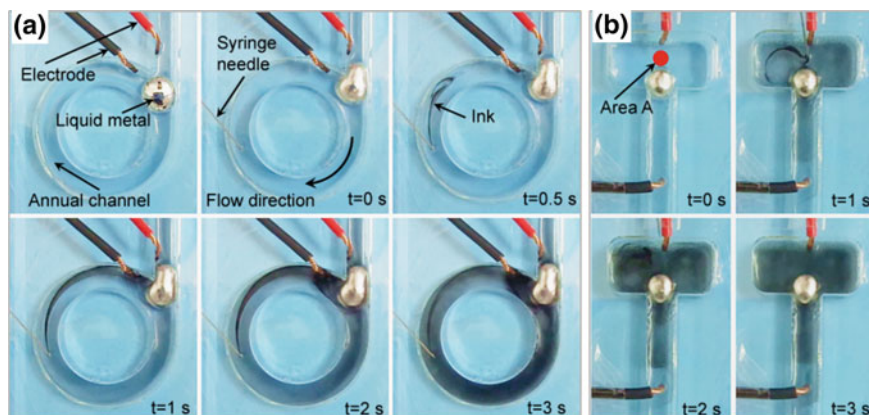


Fig. 4.11 AC signal actuated liquid metal mixer and pump [24]. The open-top channel with depth of 10 mm and width of 8 mm is fabricated with PMMA by laser cutting, and a glass plate is pasted as the bottom of the channel. The concentration of NaOH solution is 0.5 mol/L and the AC signal exerted is 5 V, 25 Hz. **a** Liquid metal enabled fluidic pump; **b** liquid metal enabled solution mixer. All pictures are reproduced with permission

surface charge of liquid metal, thus the liquid metal oscillation performance would be improved, and more details can refer to the later section [32].

Apart from the aqueous sodium solution, some other basic or saline solution, such as KOH, NaCl, etc., can also be used in the liquid metal oscillation system as electrolyte solution, and likewise, results can be observed [24]. When a liquid metal droplet is immersed in an acid solution, such as HCl, the oscillation behavior aforementioned will not occur. This is because that gallium-based gallate, such as $[\text{Ga}(\text{OH})_4]^-$, is formed on the surface of liquid metal droplet when the droplet is placed in the base solution, and this gallate is crucial for the formation of EDL and thus the generation of surface tension driving force. However, when the droplet is placed in the acid solution, no such negative charged gallate is formed and thus no movement of the droplet can be actuated [17].

Two important typical applications making use of the surface flow of liquid metal droplet under alternating electric field can be explained as follows [24]. Figure 4.11a is an AC signal induced liquid metal pump. When an AC signal is applied, the electrolyte solution in the annual channel is actuated to flow in clockwise direction, which can be visualized by the flow trajectory of the black ink slowly injected by a syringe. The ink is injected near the surface of the electrolyte solution, and its velocity is about 4 cm/s, which is calculated by a series of optical photos with constant time interval. Assuming that the flow velocity of the solution is linearly distributed from 0 at the bottom of the channel to the maximum 4 cm/s at the surface, the flow rate in the present channel can be estimated as about 17 mL/min.

Figure 4.11b shows a liquid metal enabled solution mixer. It can be seen that two vortices are actuated near the two sides of the liquid metal droplet, thus the solution is mixed [24]. The mixer as proposed and revealed here can also be used for heat

spreading, which would help take the heat away from the hot spot, such as area A in Fig. 4.11b, to the whole rectangular chamber, and then reject the heat to the outside with a much reduced flux.

Different from the electrowetting pump [33], which realized pumping function by elegant structure design and reciprocating bulk motion of the liquid metal droplet, the pump illustrated here is actuated by the surface motion of the liquid metal droplet with much simple structure. Unlike the pump proposed in Ref. [28], which is essentially actuated by a unidirectional intermittent DC voltage, otherwise it will not work, the current pump works well under strict AC signal, which benefits from the special channel design and the liquid metal mounting location, namely half part of the liquid metal is in the channel and the other half is outside the channel. The significant feature of AC induced pumping effect lies in that, both the electrolysis of electrolyte solution and the electrochemical oxidation of liquid metal near the cathode are dramatically inhibited, which is rather beneficial for the long lasting and high efficient work of the pump. Moreover, the pump can be easily fabricated and there is no mechanical revolving part, thus the operational failure is greatly reduced and much less maintenance is needed. The power consumption of the pump is quite low, in the magnitude of dozens of milli-watt, while providing a flow rate at about 17 mL/min in the channel shown in Fig. 4.11a. The performance of the AC signal induced liquid metal mixer and pump is dependent on many factors, such as the geometry of the channel, the arrangement of electrodes, the size of liquid metal droplet, and the magnitude and frequency of the AC signal.

Overall, the oscillation phenomena of liquid metal droplet in AC electric field include the bulk oscillation motion at low frequency and intensive surface indicate at high frequency [24]. The theoretical analysis and experimental results show that increasing the diameter of liquid metal droplet (less than the channel width), or the electrode voltage, or the concentration of electrolyte solution, is conducive to enhancing the oscillation. High signal frequency leads to small oscillation amplitude. At a specific frequency, resonance happens on the surface of the droplet and intensive solution waving is actuated. The oscillation behavior of liquid metal droplet under alternating voltage could be applied for solution disturbance and mixing, smart flexible sensors, fluid oscillation, and even future micromachine or soft robot. What is more, the AC signal enabled liquid metal fluidic mixer and pump and the special channel structure and electrodes arrangement can be extended to different fields, such as electronics cooling, mass delivery, and solution mixing whether in micro- or macroscales.

4.10 Capability Demonstration on Liquid Metal Worm Squeezing Across Narrow Gap

The deformation capability of robot has been a long-term research interest in robotic fields along with developing its controllability and adaptability. So far, many dif-

ferent structural design and materials had been carried out to build up a flexible and compliant robot. To illustrate the surprisingly large transformable capability of liquid metal machine, in the following, we present a series of highly deformable machine locomotion behavior overcoming sharp corner or small gap via EGaIn liquid metal materials [34]. Such “liquid metal worm” can be controlled by exterior voltages and veer in a loop channel. Besides, it can narrow through a highly confined gap fifth times slimmer of its own size and restore to its original shape and movability. The size of the worm could also be adjusted with different volume of liquid metal, which varies from ~ 0.1 mL to ~ 1 mL. In addition, other solid functional structures or modified particles can be mounted according to previous researches. Several phenomena regarding reconfigurational reversing of moving direction due to metal droplet morphology were presented with mechanism interpreted. Overall, the worm displays its biomimetic deformative characteristic and may have profound implication in other fields such as vascular robots and microfluidics. It is expected that such machine capability could contribute to the development of soft robots and their miniaturization in the coming future.

4.10.1 Test Situations for Running the Liquid Metal Worm

In the following experiments, 76% Ga, 14% In EGaIn is exclusively implemented to form the worm robot. Channels and reservoirs with several different sizes and depths are implemented. Three straight channels with widths of 6, 8, 10 mm, a length of 150 mm and a depth of 6 mm are machined on a PMMA (Polymethylmethacrylate) transparent plate. These straight channels are utilized to verify the decisive factors of the dual-directional locomotion demonstrated by the worm. Another machined PMMA pool is used to display how the head and the tail of the worm perform differently when linked by a 0.5 mm thin copper rod. The size of the pool is 25 mm $\times$ 100 mm, with a depth of 8 mm.

Several curved channels with angles of 30°, 60°, 90°, 120°, and 150° are fused deposition modeling (FDM) 3D printed. The width of the channels is 8 mm while the depth is 6.5 mm. And the printer is a Dobot Magician robotic arm, which owns a precision of 0.1 mm.

A loop channel and obstructive channels are stereolithography (SLA) 3D printed because of their irregular shapes. One of the obstructive channels has a 2 mm wide slit at the middle, while the other obstructive channel has a convergent and divergent joint section that connected two reservoirs. All the obstructive channels have a width of 11 mm and a length of 58 mm. The loop channel is a 4 mm deep rectangular groove with rounded corners. The width of the rectangular is 20 mm while the length is 75 mm. A deeper reservoir is designed in the loop to store liquid metal bulk and solution.

The electrolyte is 0.5 mol/L NaOH alkaline solution which is filled in all the channels and reservoirs aforementioned. Then different volumes of liquid metal

materials are injected into the channels or reservoirs within different experiments. Both the solution and liquid metal can be drawn out with a syringe.

After setup preparation, electrodes are administrated to apply consistent voltage stimuli. Copper wires are implemented as electrodes, which is connected to a constant voltage source (ZhaoXin KXN3030D). The range of the applied voltage is from 7 to 23 V. The tips of electrodes are placed at opposite extremities of the grooves and dipped in alkaline solutions. After the voltage implement, the locomotion of the worm would initiate.

4.10.2 Liquid Metal Worm as Case of Transformable Machine

In former sections, electric field would drive a sphere liquid metal droplet moving toward anode electrode in alkaline or acid solution. The locomotion speed is positively relative to the voltage amplitude which means droplet would move faster under a higher voltage. The appropriate interpretation of the phenomenon is that the driving force is induced by the surface tension gradient while the gradient is induced by electric field implementation and electric double layer (EDL). The liquid metal on the droplet skin flows from low surface tension area to high surface tension area according to Marangoni effect, which means from cathodic pole to the anodic pole. When the driving force overcomes retardation force, the liquid metal droplet is propelled to moving toward anodic electrode.

The present lab found that [34] liquid metal can also be controlled to move toward cathodic electrode by an exterior electric potential. The essential factor of the phenomenon differing from the previous research is the shape of liquid metal droplet. When a droplet of liquid metal is injected into a thin long channel, due to the confinement of the channel, liquid metal would form a cigar or a worm shape rather than a round sphere in free space. After voltage implementation, the liquid metal would locomote toward cathode with a much slower speed compared with moving toward the anode. As liquid metal bulk is slender, smooth, and moving slowly, to some extent, it resembles an earthworm crawling on the soil. So we named it “liquid metal worm” [34], fitting to its locomotive pattern. To clarify the relationship between the shape of liquid metal worm and the direction of locomotion, channels with different widths of 6, 8 and 10 mm were implemented (Fig. 4.12). First, a bulk of 0.4 mL EGaIn alloy is injected into the 10 mm open-top channel, along with 0.5 mol/L NaOH solution. The channel is wide enough to contain the liquid metal without squeezing it. Thus, the liquid metal bulk gets rounded like a ball. Two copper electrodes are placed at two extremities of the channel and connected to the constant voltage power supply. Adjusting the output of the power source to 13 V, one can find that the liquid metal ball would dash toward the anode at a speed of 30 mm/s, approximately. As is shown in Fig. 4.12b, the blue graph illustrates the locomotion, while the navy top and right axis represent the coordinate of the blue line. Then switch the liquid metal ball into

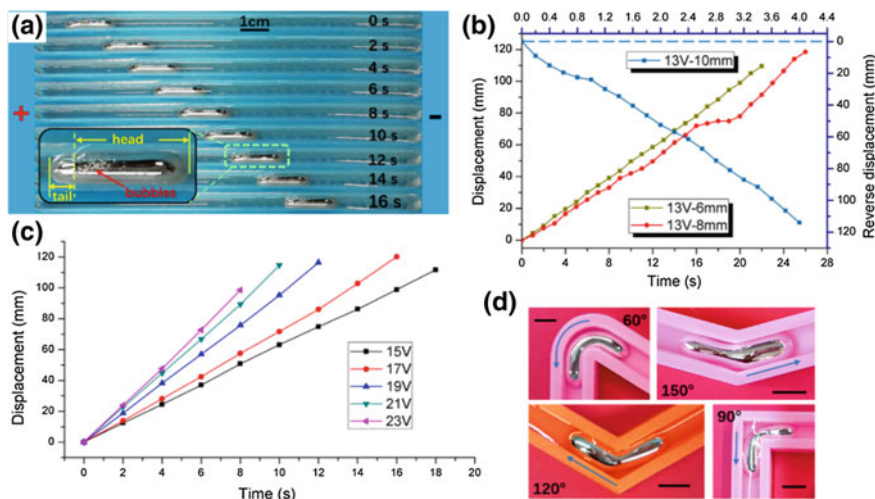


Fig. 4.12 Crawling locomotion of liquid metal worm analogizing an earthworm [34]. **a** Liquid metal worm crawling toward the cathode. **b** Displacement diagram of liquid metal movement in the channels with different widths. **c** Displacement diagram of liquid metal locomotion under incremental voltages. **d** Liquid metal worms crossing corners with different angles. The blue arrows represent motion directions. The scale bars are 1 cm. All pictures are reproduced with permission

another parallel channel with width of 6 mm, due to constraints of the channel wall, the sphere would form into a much longer and slenderer shape. This makes it look like a worm. Still, filling the channel with 0.5 mol/L NaOH solution and applying a 13 V voltage at both sides of the channel, consistent as previous setup, then the worm would start to crawl forward toward the cathode copper wire electrode, though the speed of crawling is much slower, which is about 5 mm/s (Fig. 4.12a).

According to a supplementary experiment with a channel of 8 mm width, it was observed that the liquid metal worm also moved toward the cathode at a speed of ~ 4.6 mm/s [34]. Of all three experiments, their displacement–time diagrams are plotted in Fig. 4.12b, in which the blue descending line represents liquid metal ball moving toward anode in 10 mm channel, while the red and brown ascending lines represent liquid metal worm moving toward cathode in 6 and 8 mm channel, separately.

Further, the relationship between magnitude of applied voltage and locomotive velocity is also unveiled by a series of experiments [34]. With the same environmental parameters as the previous experiments (6 mm channel and 0.5 mol/L NaOH solution), the magnitude of the voltage varies to examine the relevance. The voltages start from 15 V and ascend to 23 V with an interval of two volts. The volume of liquid metal is 0.4 mL thus one can illustrate displacement–time graphs utilizing the experimental data, from which it can be noticed that with a higher applied voltage, the liquid metal worm would crawl faster toward cathodic electrode, shown in Fig. 4.12c. Zoom into the snapshot of liquid metal droplet in motion, it can be noticed

that there exists an obvious separation between the two sides of liquid metal worm, the head of the worm is bigger and longer than its rear parts, which owns a smaller diameter along with a shorter length. This appearance also resembles an earthworm that has a big head and slim tail (Fig. 4.12a and d). Meantime some tiny bubbles attached to the joint section between the worm head and tail. Bubbles floating in the NaOH solution can be regarded as indicators of the vortex flow, which shows that the head and the tail of the liquid metal worm have different locomotive tendencies toward opposite direction within the open-top channel. It looks more likely that the two ends of the liquid metal worm are competing with each other to drag the whole body into its own direction. Nevertheless, the worm was driven toward the cathode in this condition, which means that the head of the liquid metal worm has a higher dragging force compared with its counterpart.

The liquid metal worm is also tested in several curved channels with angles of 30°, 60°, 90°, 120° and 150°. While the volume of metal is about 1 mL and the applied voltage is 15 V (Figure 4.12d). The results showed that the worm could cross all the corners but 30°, in which the worm would be cut in half by the sharp of the corner. The time costs of passing through the corner are 5.2, 4.4, 7.8, and 5.4 s with angles of 60°, 90°, 120°, and 150°, respectively. The shape of the worm also implies that the worm head and tail may have different motion characteristics [34].

To prove the conjecture, one can increase the volume of the liquid metal bulk to about 1 mL, and increase the voltage to a relatively higher value of 19 V in the straight channel. The head and the tail of the worm would move in different directions and the middle body would be stretched into a long slim waist [34]. At this time the shape of the worm is more like a dumbbell, shown in Fig. 4.13a. If the exterior voltage endured for a second, the joint of the two ends would break and the body of the worm would be tearing into two individual parts, which move in opposite directions. At the same time, the slim waist shifted onto the longer part. This phenomenon is quite similar to the regeneration of planarian flatworm, which belongs to a separate phylum from earthworms. When a planarian flatworm is cut into several segments, every piece is able to reform its entire body. In these experiments, although the separate parts of the liquid metal worm would not grow larger, still they keep functionality and could be driven by exterior voltage to crawl.

Decrease the volume of the liquid metal to 0.2 mL in the open-top channel with width of 6 mm, thus the longitudinal length of the droplet would get shorter, which makes the shape more round [34]. Filled the channel with alkaline solution and after a 23 V voltage implementation, the shorter and rounder liquid metal worm would oscillate forward and backward in the channel. In this specific condition, the driving force toward anode and cathode is almost equivalent, which makes the worm to stay in an unstable state. But the tugging force is not strong enough to tear the worm apart. In other words, this state is a turning point between cathode-oriented and anode-oriented locomotion, and it furtherly supported our former observation.

Yao et al. [34] also placed the worm in an SLA 3D printed loop channel to inspect whether it can steer direction along the 4 mm wide ditch as a real earthworm. One milliliter EGaIn alloy is injected into the open-top channel along with NaOH solution. Two copper electrodes are immersed into the solution at neighboring corners, as is

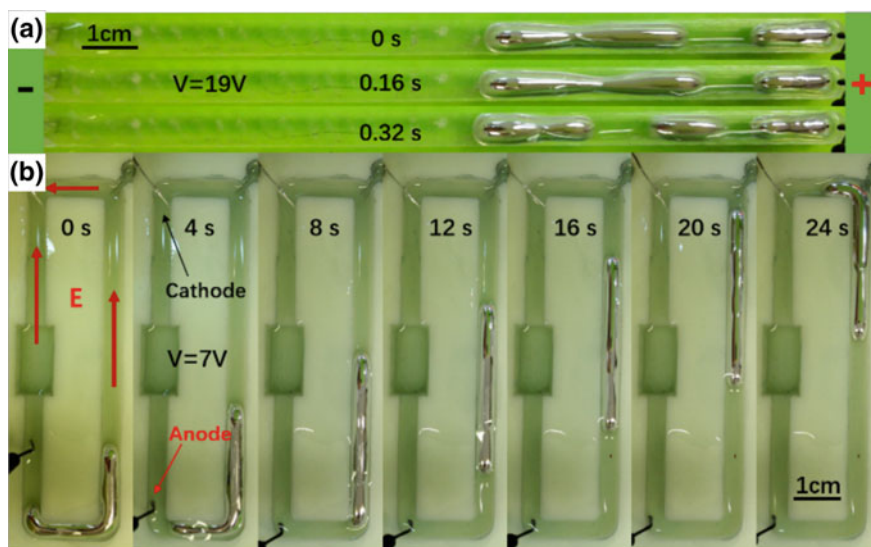


Fig. 4.13 Splitting and deflected crawling of liquid metal worm [34]. **a** The liquid metal worm was torn apart under a 19 V applied voltage. **b** The worm wriggled in a loop open-top channel with an applied voltage of 7 V. Red arrows represent electric field directions in the electrolyte. All pictures are reproduced with permission

shown in Fig. 4.13b, while the output of the electrodes reduced 7 V in case of splitting. When the power is switched on, the liquid metal worm would gradually accelerate and wriggle along the channel. The entire length of the worm, which is about 35 mm, is much longer than the short side of the channel, thus the worm head needs to swirl its direction at the corners, as well as other parts of the body. With a closer observation, it can be found that the worm shivers as it crawling forward and the solution at proximity is stirred, generating small vortex and ripples. It takes about 24 s to travel half the entire loop. Figure 4.13b displayed the snapshots of the locomotion process every 4 seconds. The upper surface of the liquid metal worm is not completely covered by aqueous solution but it seems that the movement is not evidently affected.

4.10.3 Transformable Capability of Liquid Metal Worm

Considering that this metal worm is thoroughly composed of liquid material, intuitively, one would have a strong interest in whether it can deform freely at twisted spatial condition. Such attribute would be very attractive and pragmatic in many fields, especially in robots and biomedical engineering. For instance, if a vascular robot can narrow through a vascular valve and restore its original shape and func-

tion, then the region of the movement could be extended and more works could be accomplished such as drug delivery or thrombus removal.

To inspect whether the worm could cross a slit or a thin channel, Yao et al. [34] designed two open-top channels with narrow joints at the midst, as is shown in the right side of Fig. 4.14a and b. The bright green represents 3D printed channel walls while the pale yellow indicates the bottom of the channel. The cathode electrode is placed at the upper end and the anode at the lower extremity. There are fences structures at the two ends of the channel to isolate the electrodes, for the electrolysis generated bubbles may diffuse among the solution surface and disturb the observation. The liquid metal worm is set in lower reservoir initially. For the worm is more stout, a higher voltage is needed, here the power source output was set to 17 V to drive the worm.

The first channel has a gradually contracted middle section, which is formed by two arcs with the narrowest position has a width of 3 mm. The convergent curve would help the worm to deform without making too much retardation force. When power is on, the cigar shape liquid metal worm starts staggering to the neck, which looks like a De Laval nozzle. The head of the worm would squeeze to an extrusive point and distort to adapt the shape of the neck. In less than 0.2 s, the front of the worm had crossed the neck and the tail shrinks to a tiny long droplet. Sometimes the tail may break apart from the worm as is shown in the seventh snapshot [34]. During the crossing, a ring of dim gray stripe appeared at the waist of the worm, which is labeled by short black arrows, and it also moves along the body and stops at the narrowest position. It can be noticed that when the worm tail departs from the

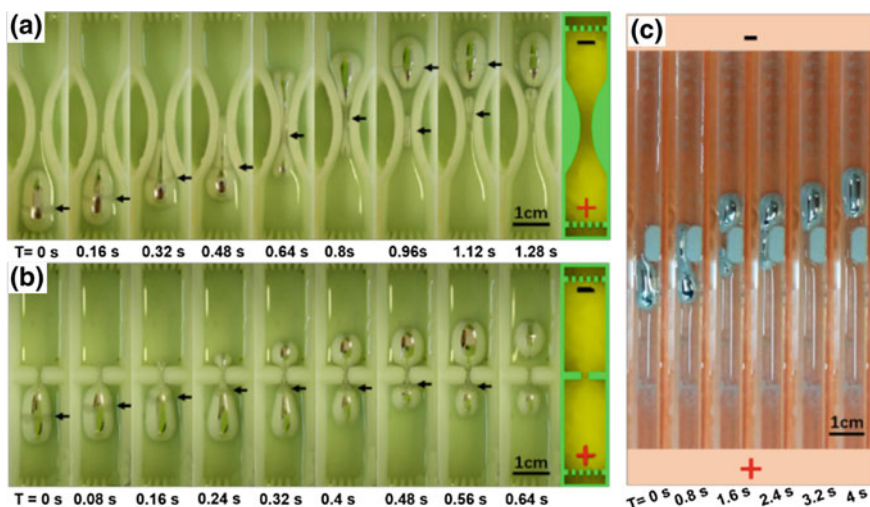


Fig. 4.14 Liquid metal worm crossing different types of obtrusive channels [34]. **a** The worm crossed a contractile–expanded channel. **b** The worm crossed a 2 mm wide slit. **c** The worm bypassed an asymmetric obstacle within a straight channel. All pictures are reproduced with permission

body, the break point is right upon the stripe. In the end, both the head and the tail of liquid metal worm would run cross the contractile channel and recover to its original morphology.

To further test the crossing capability of the worm, a more difficult obstructive channel is designed to evaluate its deformability [34]. Two reservoirs at upper and lower parts are connected by a small slit (Fig. 4.14b), while the width and the length of the channel are consistent, which is 11 and 58 mm, respectively. In the experiment, after the voltage activation, the worm would wriggle and moving toward the cathode electrode as well as the gap. At the time when the worm contacts the middle wall, a tiny bud generated and strode into the slit. The bud grew longer inside the gap as the worm moving forward. When the bud bumped out the gap, it grows to a sphere pattern and increases its volume. At the same time, the gray stripe at the waist of the worm would move toward the slit and be stuck at the barrier, which can be seen from the first four snapshots. The size of the worm reaching into the upper channel keeps increasing while the stayed lower part keeps decreasing until more than half of the worm transferred to the upper reservoir. When the two liquid metal parts are connected by a thin liquid metal line, this connection might break by the disturbance of peristalsis, shown in the last snapshot. Thus, the worm would split with the head and tail staying in upper and lower channel, respectively.

Both experiments above are implemented with symmetrical obtrusive gaps. Another experiment with an asymmetrical is also conducted in the 8 mm width straight channel. A rubber cube with 4 mm thickness and 10 mm length is adhered to one side of the PMMA channel wall. Thus, an asymmetrical barrier is formed. When applied a 13 V voltage at the two extremities, the worm with a volume of 0.5 ml could deform to bypass the rubber cube, as is shown in Fig. 4.14c.

Yao et al. [34] used an HD camera to better observe the dim gray stripe on the waist of the worm, which is placed in a small reservoir, as is shown in Fig. 4.15b and c. The edge shapes of the stripes are different at two sides, which are labeled by cyan dashed line. The border close to the cathode is a straight line while the edge close to the anode is a crescent curved line. At two extremities of the bulk droplet that are not covered by thin stripe, the flow at the liquid metal surface and adjacent solution vortex can be observed by the floating of generated bubbles.

When a liquid metal worm is placed within the absence of an external electric field, an asymmetric reactivity would be generated on the surface of the conductive liquid metal, according to bipolar electrochemistry. Setting E_a and E_c as the potential of the anode and the cathode, D being the distance between the two electrodes, thus the electric field value δ is given by

$$\delta = (E_a - E_c)/D \quad (4.7)$$

The imposed potential drops linearly across the solution in a first-order approximation. The polarization potential difference occurs between the two extremities of the worm could be calculated as

$$\Delta V = \delta l \quad (4.8)$$

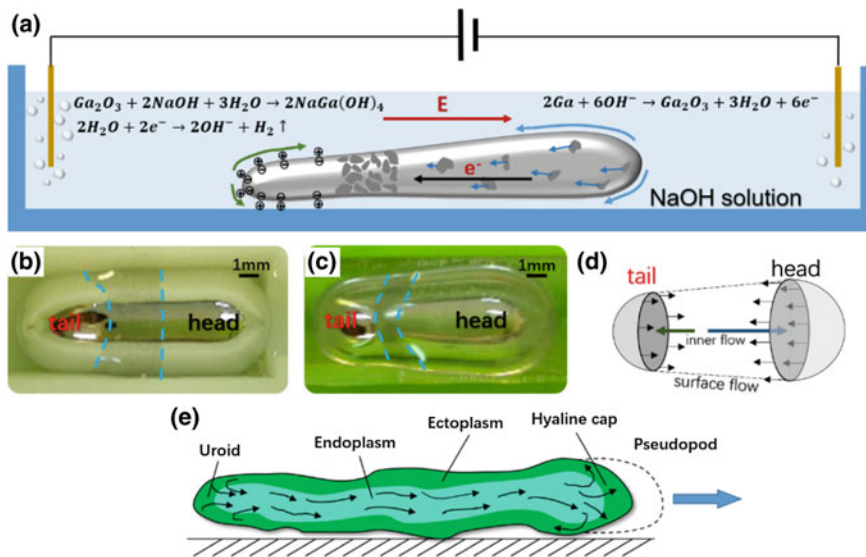
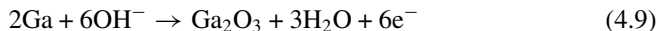
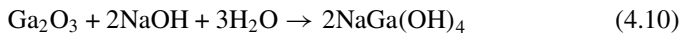


Fig. 4.15 Schematic diagram of the liquid metal worm locomotion and the way for analogizing an amoeba [34]. **a** Schematic diagram of the liquid metal worm locomotion. Green and blue curved arrows represent the surface flow among the worm skin. Red straight arrow represents the direction of electric field while the black straight arrow represents migration of electrons within the body. Deep gray fragments represent gallium oxide generated upon the skin. **b** and **c** Zoomed in view of liquid metal worm and its dim stripe that separates the head and the tail. **d** Flow directions of the bulk liquid metal corresponding to (b) and (c). **e** Schematic diagram of amoeba locomotive pattern. Endoplasm transformed to ectoplasm at hyaline cap and restored at uroid. Pseudopod is elongated by the endoplasm flow. All pictures are reproduced with permission

with l being the length of the conducting worm. This value is related to the reactivity at the polarized interface, which is



and



The extremity closer to the cathode, which is anodic pole, would impose the first reaction. While along the worm skin, the generated oxide layer would be consumed by the second reaction. When a bulk of liquid metal is confined in a slim channel, the characteristic length l would increase thereby raise the ΔV , which consolidates the polarization effect.

Inside the liquid metal worm, electrons flow from anodic pole to the cathodic pole. With the formation of solid-state oxide Ga_2O_3 thin layer, the distal anodic pole would have the lowest surface tension. According to Marangoni effect, the liquid

would flow from low surface tension area to high surface tension area. Due to the less oxide formation away from distal anodic pole, the skin of the liquid metal worm would flow from anodic pole toward the waist of the worm (Fig. 4.15d).

The solid-state oxide Ga_2O_3 would float among the skin and be carried to the middle section of the worm by the surface fluxion [34]. With the accumulation of oxide, there would generate a dim stripe at the waist. Against the one that flows from anodic pole to the middle position, the stripe would face a reverses fluxion, which stops its advance toward the cathodic pole. When approaching the posterior part of the worm, the oxide would reduce to liquid state gallium by migrated electrons. Thus, the amount of gallium oxide reaches a dynamic balance. NaOH in circumstance also contributes to the consumption of gallium oxide, which slightly dissolves in alkaline solution.

When the worm skin moves, it would propel the solution in vicinity as well as interior channel surface [34]. The propulsion would give the worm a reaction force to drive it moving forward. This locomotion pattern analogizes the movement of amoeba, which has a convertible exterior ectoplasm and interior endoplasm. Endoplasm converts to ectoplasm at the hyaline cap and ectoplasm transforms back to endoplasm at the uroid. Inside endoplasm flows from the tail to the cap and elongates the pseudopod. With ectoplasm adhesively fixed with the plate beneath the amoeba, an amoeboid movement could be achieved (Fig. 4.15e). Here one could regard the oxide of gallium as “ectoplasm” and liquid state alloy as “endoplasm”, then these two movements would be quite similar to each other.

This mechanism can also be utilized to explain the capability of narrowing through a contractile channel [34]. As the anodic pole at the worm head contacted with the convergent channel wall, the surface tension lowered by oxide would allow the head to deform to the confinement of the channel. With the existence of surface tension gradient, the skin movement would drive the tip point of the head to bump out the slit, just like pseudopod of amoeba. Inside the body, liquid metal flows from the waist to the head to enlarge the bulge. When crossed the obstacle, the anterior body would pull the other part out through the slit. The movement in the loop channel suits the same interpretation as well.

Gallium oxide accumulated at the waist limited the mobility of skin herein [34], thus when the bulk inside liquid metal had crossed the barrier, the dim stripe would stay in front of the gap, as is shown in Fig. 4.14 (a and b). As the tail shrinks, the waist of the worm also contracted to a thin line, since the tail and the head own different kinetic trends. In most cases, the worm would break when the waist got too thin to bridge the two parts. Although sometimes If the worm is smaller and the gap is a little wider, the worm could cross the gap without any interruption.

While if one sets sight on the other side of the worm, the tail skin also flows but in an opposite direction [34]. When the liquid metal is immersed in NaOH alkaline solution, there would generate an electric double layer among the interface, in which the liquid metal side is negatively charged while the solution is positively charged. The phenomenon could be interpreted by the Lippmann's equation, which is also mentioned in previous work. After implementing an exterior electric field, the outermost point at the cathodic pole would have a higher electric charge density, so

the potential difference V would increase. According to Lippmann's equation, the surface tension γ would decrease at this position. Considering the Marangoni effect, the skin would flow from the tip point to the middle joint of the worm, which would generate a resistance to drag the worm backward. Because the tail has an opposite locomotive tendency, the worm would crawl quite slowly compared with liquid metal locomotion in previous research.

If this opposite locomotive tendency is strong enough, the worm might be torn apart at the joint section, as is shown in aforementioned experiment, after which the initial tail would rush to the anode electrode while a new tail formed at the end of the head [34]. Or if the worm is too stout to split, meantime the dragging resistance equals the pulling force, it may oscillate in the channel with disturbance of surface roughness and vortex.

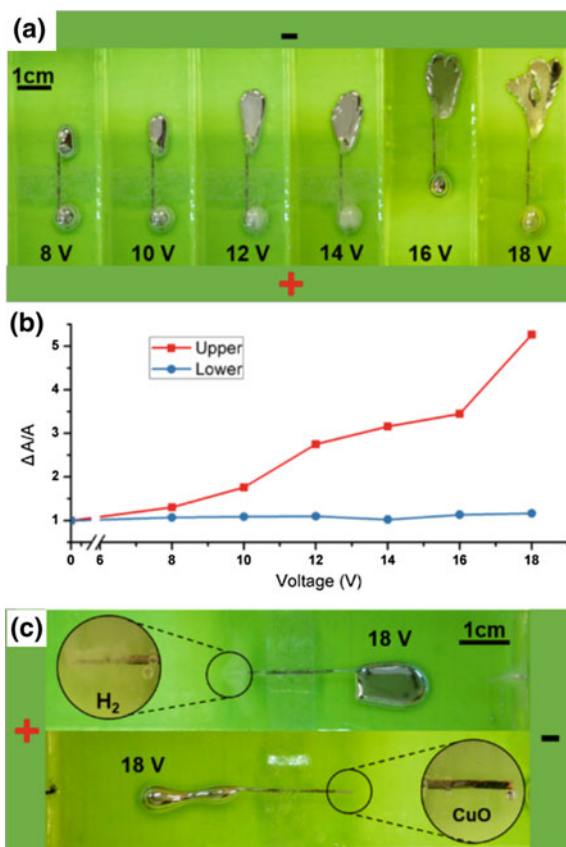
To prove this explanation, Yao et al. [34] conducted another experiment in which two liquid metal droplets with the same volume of 0.15 ml are connected by a fixed copper rod with a diameter of 0.5 mm. Both the rod and two droplets are immersed in 0.5 mol/L NaOH solution contained within a 25 mm $\times$ 100 mm transparent pool, shown in Fig. 4.16a. The copper rod had a solid surface thus liquid metal cannot flow from one droplet to the other. Still, applying incremental voltages to the solution, starting from 8 V to 18 V with an interval of 2 V, the droplet closer to the anode would flatten while its counterpart would struggle to get rid of the rod connection. The flattened deformation at upper droplet is highly analogic to the experiment that anode contacted with liquid metal droplet. As was elucidated before, this is caused by accumulation of gallium oxide. Without any reduction or surface transportation, the oxide would stay where they are and can only be consumed by NaOH chemical reaction, of which the speed is far below the oxide generation. At the very beginning, surface tension gradient would still exist and made the flattened puddle expand outward. With the surface area increasing and the oxide covering the entire surface, the oxidation would balance with the consumption process. In the end, the puddle would stop expansion and become steady. The thick oxide layer had limited the mobility of liquid metal.

The other droplet is supplied with electrons conducted by the copper rod, so oxide cannot exist and H_2 bubbles generated because of reduction [34]. At this end, the EDL is stable as well as the surface tension gradient. The droplet shook to depart from the rod and was adhered by metal wetting.

When the external voltage increased, the oxide layer upon upper droplet would be thicker and caused a more deplanate shape [34]. Here the relatively occupied area ($\Delta A/A$) was taken as an indicator of how much the shape had changed. In Fig. 4.16b, it can be seen that the upper droplet occupied area increased about five times compared with its original state (red line), while the area change of the lower droplet is negligible. If removing one droplet and observing the copper end with a digital microscope, it would find that the copper tip is oxidized to black CuO or generated massive gas, when the tip is close to cathode or anode accordingly.

In another experiment, a liquid metal worm crawled forward in a straight channel [34]. When contacting the cathode wire electrode, it bounced back instantaneously with a high speed and restored to its original state in ~ 0.5 s. This "crawling

Fig. 4.16 Liquid metal droplet connected by a copper rod [34]. **a** The droplet closer to the cathode (upper) would expand under different voltages, while the other one (lower) would generate gases. **b** Area changes of the two droplet under incremental voltages. **c** The tip of the copper rod would generate H_2 bubbles (top) or be oxidized to black CuO (bottom) according to the positions of electrodes. All pictures are reproduced with permission



forward-contact-bounce back” process could repeat periodically as long as the voltage is implemented. Several cycles are recorded by the displacement–time diagram (Fig. 4.17), from which one can calculate that the period is about 2.5 s. The right-hand side figures are snapshots of one period with a time interval of 0.4 s. The red and the black dashed lines represent anode and cathode, respectively.

This phenomenon can also be interpreted by the formation and reduction of the gallium oxide layer [34]. When the worm contacted with the cathode, the oxide layer is reduced and removed to expose the inner EGaIn alloy. Thus, the only surface tension gradient is caused by potential difference across the EDL, which makes the worm rush back and separate with the cathode. Afterward, the oxide layer regenerated by the polarization effect and the worm would crawl back in the original direction. Both the velocity and the periodicity are embodied in the graph, where the dashed black line marked the position of the cathode.

Overall, the above characteristic of EGaIn liquid metal displayed a “worm-like locomotion” behavior of the transformable machine [34]. The speed of the locomotion is much lower compared with anode-oriented movement as discovered before.

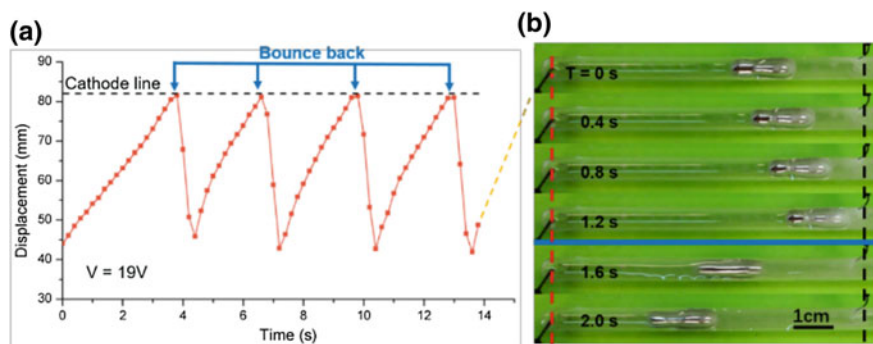


Fig. 4.17 Bouncing back locomotion of the liquid metal worm [34]. **a** Displacement of the locomotion. The yellow dashed line represents the continuous periods. **b** Snapshots of the locomotion. The red and black dashed lines represent the anode and cathode, respectively. The worm moved rightward above the blue line but leftward below the line. Applied voltage is 19 V. All pictures are reproduced with permission

The reason for low speed is endowed by surface oxide layer generation and Janus locomotion. The oxide layer also reduced the surface tension significantly thus made the liquid metal worm can squeeze and narrow across a highly confined gap. This characteristic endows the liquid metal worm the capability to overcome varied obstacles such as vascular flap or thrombus.

Such a liquid metal worm can be utilized in many pragmatic fields such as microfluidics, miniaturized vehicle, flexible micro-bot, and so on. If attaching other solid structures or modified pharmaceutical molecules, then the worm could be regarded as a functional transporter or delivery system. The velocity can be controlled by external or mounted voltage supply while the size of the worm could be adjusted according to specific application. It is expected that such worm like soft machine could inspire more researches in related areas and advance the development of smart, biomimetic, and flexible robots in the coming future.

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Chapter 5

Reversible Transformation of Liquid Metal Machine



Abstract Reversible transformation of a liquid metal machine holds enormous promise across many scientific areas ranging from mechanical engineering to applied physics. So far, such capabilities are still hard to achieve through conventional rigid materials or depending mainly on elastomeric materials, which however imply somewhat limited performances and require complicated manipulations. The present lab (Zhang et al. in Synthetically chemical–electrical mechanism for controlling large-scale reversible deformation of liquid metal objects, 4:7116, 2014, [1]) established a basic strategy which is fundamentally different from the existing ones to realize large-scale reversible deformation through controlling the working materials of liquid metal. The method is termed as synthetically chemical–electrical mechanism and abbreviated as SCHEME. Such activity incorporates an object of liquid metal whose surface area could spread up to five times of its original size and vice versa under low energy consumption. Particularly, the alterable surface tension based on combination of chemical dissolution and electrochemical oxidation is ascribed to the reversible shape transformation, which works much more flexible than many former deformation principles through converting electrical energy into mechanical movement. A series of very unusual phenomena regarding the reversible configurational shifts are disclosed with dominant factors clarified. Such finding suggests a generalized way to combine the liquid metal serving as shape-variable element with the SCHEME to compose functional soft machines or devices, which implies the big potential for developing future smart robots to fulfill various complicated tasks. This chapter illustrates the basic SCHEME to realize the reversible transformation of liquid metal machine.

Keywords Liquid metal machine · Reversible transformation · SCHEME
Shape control

5.1 Basics of Reversible Transformation

Conventionally, most of the modern machines are fabricated with rigid materials, which however may encounter many restricted applications in certain specific requirements, such as owning capability of diverse flexible deformations, adaptability to unconventional environment, particularly passing through a narrow channel or uneven terrain. Based on the unique merit varying among different configurations and controllable locomotion, soft machines are competent for addressing many such tough issues which are hard to achieve otherwise through conventional rigid machines, especially when tackling some high-risk tasks. In order to obtain a desired reversible deformation or locomotion, tremendous efforts have been concentrated on developing various driving strategies, including pneumatic actuation [2], electric field-induced locomotion [3, 4], magnetic force [5], biomimetic propulsion [6], light-driven rotation [7], materials-based actuation [8], temperature or pH actuation [9], surface tension-driven self-folding [10], to name just a few. Among these methods, electric field is a rather versatile tool as its magnitudes, phases, and frequencies are often easy to regulate.

Meanwhile, various materials such as hydrogels [9, 11], photo-crosslinked polymers [12], acrylonitrile butadiene styrene (ABS) [2], and nanoliquids [13] to compose soft devices have also been extensively investigated. Recently, a mountain of energy has especially been invested into the multifunctional material liquid metal, so as to exploit its potentials in various newly emerging areas, such as liquid metal enabled pump [14], energy system [13], health care [15, 16], antennas [17, 18], and printable ECG electrode [19]. The room temperature liquid metals such as gallium, eutectic GaIn (75% gallium and 25% indium), and galinstan (68.5% gallium, 21.5% indium, and 10% tin) are quite appealing since they own a group of remarkable merits including super-compliance in liquid phase, high surface tension [20], favorable electrical conductivity [20], extremely low vapor pressure and low toxicity [21]. With an unusually large variation on surface area-to-volume ratio and surface tension, the liquid metal was found to display outstanding performance of shape transformation [22]. Due to its inherent scalability, such material could easily transform among diverse morphological states under the exposure to the external electricity. These behaviors are rather unique and extremely hard to achieve otherwise through conventional rigid materials and thus opened many opportunities to make soft machine. However, an only pity in aforementioned efforts lies in that, the realized deformations of the liquid metal machine are overall mono-directional, which means that the liquid metal can transform from an extremely large sheet of thin film into a small sphere, but not vice versa. That is to say, reversible deformation of liquid metal among different configurations, which is the key to make a soft machine, is still yet to realize.

Through continuous trials, this lab got to envision that if additional control mechanisms could be incorporated on the liquid metal, reversible deformation of machine thus made should be possible [1]. Among the many potential effects, it is conceivable that the chemical dissolution on the surface of the liquid metal object would help realize strong deformation reversibly, since such configurational transformation

was governed mainly by the surface tension. The key reason lies in that chemical dissolution can easily recover the surface tension through removing the oxide skin on the surface of the liquid metal, which is produced during the electrochemical oxidation process, and inversely reduces the surface tension. Such synthetically chemical–electrical mechanism (SCHEME) approach is liable to achieve the reversible deformation of the liquid metal which thus enables it as a smart material to manufacture soft machines in the near future. Zhang et al. [1] clarified the main control issue of SCHEME. Thereinto, an object made of liquid metal gallium is adopted as the working machine to reconfigure itself into an arbitrary shape and reversibly deform between sphere and non-sphere states. Through altering the voltage, electrode spacing, electrolyte solution type, or volume of the gallium machine, different performances of the material shape deformation are revealed. Overall, such reversible configurational transformation is achieved via the combination of electrochemical oxidation and chemical dissolution processes of oxide gallium, which can easily tune the surface tension of the liquid metal ranging from 700 mN/m [20] to near zero, upon application of the external electric field and alkaline or acidic electrolyte solution. To clarify the critical factors dominating the shape transformation of the working object, a series of comparative experiments were implemented and theoretical interpretations of the phenomena and mechanisms were carried out by the present lab.

5.2 Working SCHEME of Reversible Liquid Metal Deformation

As is shown in Fig. 5.1a, a square insulated vessel with a cross section of 12 cm × 12 cm is adopted to accommodate the gallium droplet and electrolyte solution. Two inert platinum electrodes with a diameter of 0.5 mm are employed, one of which is inserted into the metal droplet, while the other is placed in the surrounding electrolyte solution. To investigate the effect of the voltage between the two electrodes on the deformation, the applied voltage varies from 0 to 30 V. In addition, different electrode spacings are prescribed since the distance between the two electrodes directly affects the intensity of the electrical field [1]. On account that under the same electricity, the performance of the deformation is also related to the dosage of the liquid gallium, different volumes of gallium droplet are tested. In order to clarify the chemical events and thus evaluate the influence of electrolytes on the deformability and reversibility, the electrolytes including sodium hydroxide (NaOH), sodium sulfate (Na₂SO₄), sodium chloride (NaCl), and hydrogen chloride (HCl) solutions are adopted and comparatively investigated. The presented results are mainly obtained with NaOH solution, as the phenomena of the system operated with HCl solution are similar to those with NaOH solution. However, the deformation is significantly restricted when operating with Na₂SO₄ or NaCl solution, and the reversibility does not occur.

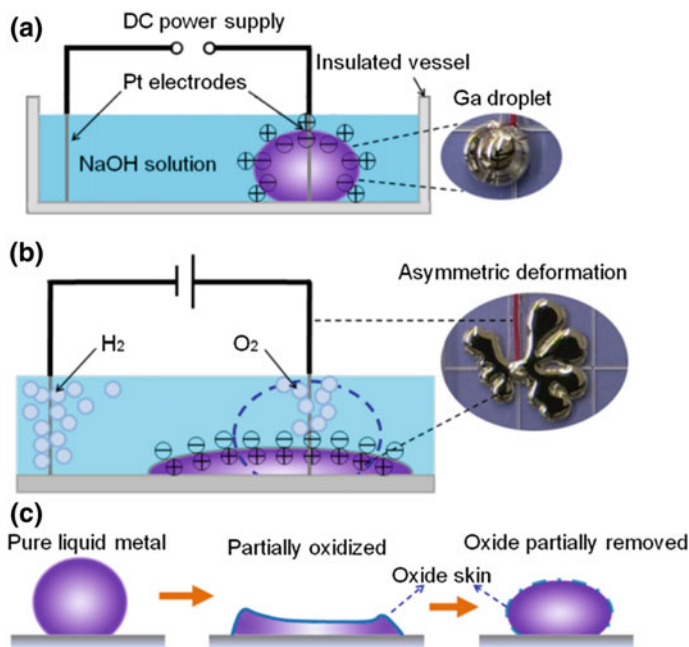


Fig. 5.1 Working mechanism of the reversible liquid metal deformation [1]. **a** Schematic of the experimental setup without external power supply when the gallium droplet is placed in the NaOH solution. **b** Schematic of the gallium droplet surface charge redistribution when the direct power is applied. **c** The surface tension dominates deformation of liquid metal object along with the accumulation and dissolution of the oxide layer. All pictures are reproduced with permission

Generally, the liquid gallium forms into a spheroid in the aqueous solution through injection due to its high surface tension (~ 700 mN/m), and the hydrostatic pressure resulted from the gravity slightly distorts the shape [1], as seen in Fig. 5.1a. In the NaOH solution, gallium can react with the alkali solution slowly, producing gallates like $[\text{Ga}(\text{OH})_4]^-$, which makes the surface of gallium negatively charged and cations accumulated nearby (Fig. 5.1a). Therefore, the electrically charged interface forms into a diffuse electrical double layer (EDL), which can be modeled as a charged capacitor. When an external power with the anode inserted into the gallium droplet and the cathode in the electrolyte solution is supplied, the previous equilibrium state will be broken up. Due to the high conductivity of the liquid metal gallium, the liquid metal droplet can be regarded as part of the anode. As a consequence, the ions on the surface of the droplet are altered, as shown in Fig. 5.1b. Conversely, anions accumulate near the droplet. As such, the EDL changes accordingly. The introduction of the external power supply reduces the initial surface tension of the liquid metal in a modest range when the applied power is not sufficient to produce electrochemical reaction. Under this circumstance, the relationship between the surface tension and the potential drop across the EDL has been thermodynamically analyzed, which is

known as electrocapillary for an ideal model [23]. Such relationship can be described by the integrated Lippmann's equation [14, 24, 25], which has been verified through a large number of experiments with many different setups and various electrolytes [24], i.e.,

$$\gamma = \gamma_0 - \frac{1}{2} c V^2 \quad (5.1)$$

where γ is the surface tension, c is the capacitance of electric double layer per unit area, V is the potential difference across the EDL, and γ_0 is the maximum surface tension when $V=0$ [24].

Following the Young–Laplace equation, the pressure difference p across the electrolyte and the liquid metal droplet can be given as follows:¹⁴

$$p = \gamma \cdot \frac{2}{r} \quad (5.2)$$

where $1/r$ is the curvature of the droplet surface. From Eq. (5.2), with a slight decrease of the surface tension, the pressure difference p across the electrolyte reduces modestly. Thus, the deformation of the liquid metal droplet is not obvious, and the liquid metal behaves in a manner similar to the classic electrocapillary effect.

5.3 Realization of Large-Scale Reversible Deformation

With the application of the external electrical potential above a critical value, redox reaction between the two electrodes proceeds [1]. Since platinum is inert metal and the electrolyte is NaOH, the reduction reaction on the cathode produces hydrogen, while the oxidation reaction on the anode is divided into two parts: oxygen is electrochemically formed on the platinum electrode, of which part contacts with the electrolyte solution, while a thin layer of gallium oxide is produced on the surface of the liquid metal gallium. The surface tension of the liquid metal drops substantially with the formation of the solid oxide layer, which induces the droplet into a pronounced nonspherical shape [26], as seen in Fig. 5.1b and c. The mass of the products on the anode, including oxygen and the oxide gallium, can be calculated according to the Faraday's law of electrolysis as follows:

$$m = k I t \quad (5.3)$$

$$k = \frac{Mq}{Fn} \quad (5.4)$$

where m is the mass of the products on the anode, I and t are the intensity of the electric current and power-on time, respectively, k is the electrochemical equivalent, M is the molar mass of the products on the anode, n is the valency of the products, and $F = 9.65 \times 10^4$ C/mol is the Faraday's constant. Though the products on the

anode consist of oxygen and the oxide gallium, the amount of the oxide layer still depends on the intensity of the electric current and the power-on time. As the oxide gallium can react with NaOH solution, the oxide layer is dissolved in the solution at the same time of its formation, and the dissolution of the gallium oxide recovers the surface tension of the liquid metal, which renders the metal back into a spheroid, as shown in Fig. 5.1c. Additionally, the dissolution rate depends on the concentration and temperature of NaOH solution. In fact, with fixed electrode spacing and fixed concentration of NaOH solution under a constant temperature, the voltage affects the current intensity directly. Thus, the external voltage can be applied to adjust the electrochemical reaction and the consequent liquid metal deformation. In general, the gallium droplet spreads along with the production of the oxide layer. Since the solid oxide layer hinders the flow of the liquid metal, the dissolution also affects the deformability. Moreover, the reversible reconfiguration is governed by the dissolution of the oxide layer.

5.4 Major Factors to Dominate the Reversible Deformation

Obtained by Faraday's law of electrolysis Eqs. (5.3) and (5.4), the formation rate of the oxide gallium F_{rate} can be calculated as follows:

$$F_{\text{rate}} = \frac{dm}{dt} = kI = \frac{Mq}{Fn} \cdot \frac{U}{R} \quad (5.5)$$

where U is the external voltage and R is the electrical resistance along with the electric current path. Here, U/R is used to approximate the electric current for simplification. The deformability depends on the accumulation of the solid oxide gallium to some extent, which renders the surface tension to drop suddenly.

Obviously, the electrical resistance R is the function of both the electrode spacing and electrolyte concentration. The relationship is expressed with the introduction of the abstraction function f as follows:

$$R = f(c, d) \quad (5.6)$$

where c and d denote the concentration of the electrolyte and the electrode spacing, respectively. Though the variables c and d are not exactly linear to the electrical resistance R , the change of R by c and d is clear: larger concentration reduces the electrical resistance, while larger electrode spacing increases it.

As aforementioned above, the deformability and reversibility rely on the dissolution of the oxide gallium [1]. The dissolution rate D_{rate} is related to the acid–base property of the electrolyte solution, the concentration of the electrolyte solution, the contact area between the electrolyte solution and the oxide skin, and the temperature of the solution. Here, another abstraction function g is introduced to describe the relation between the dissolution rate and these variables:

$$D_{\text{rate}} = g(c, s, T) \quad (5.7)$$

where c , s , and T are concentration of the electrolyte solution, contact area, and temperature of the solution, respectively. Equation (5.7) is only applicable under the condition that the electrolyte is acidic or alkaline. Both higher concentration c and larger contact area s can accelerate the dissolution rate. Thereinto, the contact area s depends on the gallium volume and the deformation, and thus, it dynamically changes during the extension and contraction process. The temperature should be higher above the melting point of gallium to maintain the fluidity of the liquid metal, and the dissolution rate increases along with the rise of the temperature.

It is noteworthy that the reversible deformation mainly depends on the formation rate of the oxide gallium F_{rate} and dissolution rate D_{rate} , but is not limited thereto. Theoretically, both the size and material of the working electrode affect the deformation, as the electrode size affects the initial contact area c slightly and the anode material has an impact on the oxidation reaction. Furthermore, the hydrogen produced on the cathode provides an opposite force to push the gallium away, which is quite obvious when the liquid metal approaches the cathode and the production of hydrogen is evident.

5.5 Effect of the Applied Voltage and Electrode Spacing

Figure 5.2a, b and c illustrates the reversible deformation of liquid metal object in response to the voltage of 10, 20, and 30 V, respectively [1]. As the power-on time progresses, the metal extends gradually. As the drop of electric current across the EDL is less on the side toward the cathode, the formation of the oxide gallium becomes faster on this side, and thus the deformation near the cathode is prior to that far away from the cathode. Consequently, the deformation turns out to be asymmetric and extends to the cathode in advance of the other location away from the cathode. Interestingly, when the surface spreads to a certain degree, the metal forms an irregular shape like petals (Fig. 5.2b). The speed of extension, which is faster in the first 2 s than that in the last 3 s (Fig. 5.2d), especially in the condition of 10 and 30 V, depends heavily on the voltage. However, the main reasons of such speed difference in the last 3 s are not the same: upon the 10 V voltage, along with the deformation, the area contacting with the solution increases, which accelerates the dissolution process, and thus the formation of the oxide layer basically keeps up with the dissolution process. With the application of 30 V voltage, the formation of oxide gallium appears much faster than the dissolution all the time, which causes oxide layer to accumulate continuously. And in the first 2 s, the surface of the metal has not yet been totally coated with the oxide layer, which induces the deformation, while in the last 3 s, the totally coated oxide layer is only thickened, which hampers the further deformation (Fig. 5.2c). After 5 s, the direct voltage is removed, and the metal reconfigures itself into a sphere reversibly. With the increase of the voltage,

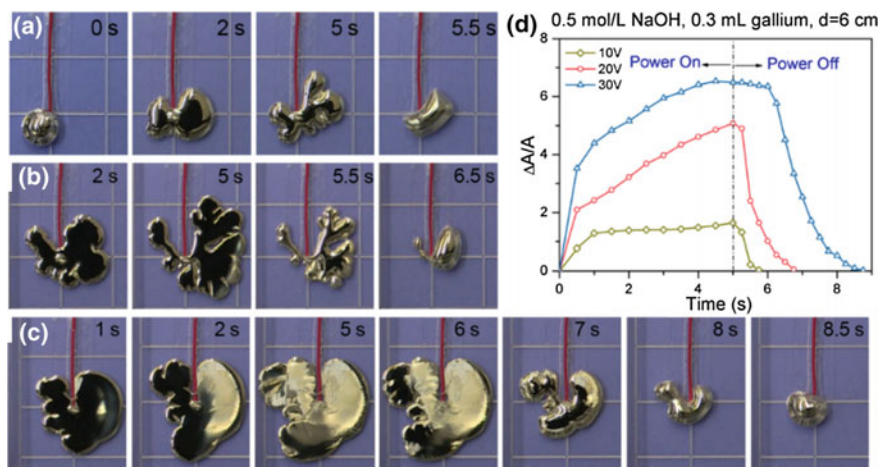


Fig. 5.2 The reversible deformation with 6 cm electrode spacing and 5 s power-on time under the condition of 0.3 mL liquid gallium and 0.5 mol/L NaOH solution at 32 °C [1]. **a**, **b** and **c** Sequential snapshots when 10, 20, and 30 V direct voltages are applied, respectively. **d** The relative change of the cross-sectional area along with the time. The symbol ΔA and A , respectively, refer to the change of the cross-sectional area and the original cross-sectional area upon 0.3 mL liquid gallium. All pictures are reproduced with permission

more gallium oxide is accumulated, and thus the recovery rate decreases, as shown in Fig. 5.2d.

To further explore the representative characteristics of the reversible deformation, a series of comparative experiments are conducted [1]. First of all, in the absence of NaOH electrolyte, i.e., in the deionized water, no deformation occurs, demonstrating that the deformation does not simply rely on the potential difference. Second, when adding NaOH electrolyte in the deionized water, obvious change of the droplet morphology is observed, confirming that it is the electric current that results in the deformation. With the application of the external direct power, the electric current depends on the voltage as well as the concentration of the electrolyte solution, as indicated in Fig. 5.3a. Whether increasing the voltage or raising the solution concentration can improve the electric current, and the electric current is not constant during the deformation since the deformation disturbs the current circuit. As for voltage, at the beginning, the performance of the deformation is enhanced along with the increase of the voltage, while it decreases when the voltage is above a critical value, as shown in Fig. 5.3b. This is mainly due to that the continuous accumulation of the solid oxide layer hampers the further deformation (Fig. 5.2c). Besides, in response to the same applied voltage, enlarging the distance between the two electrodes renders the electric current path with larger electrical resistance, and consequently, the relative electric current is reduced, which weakens the electrochemical reaction, as expressed in Eq. (5.2). As a result, with the exposure to the same low voltage and larger distance, smaller deformability is obtained (Fig. 5.3b). However,

as the voltage continuously increases, the deformation performance is improved with larger distance since the evident oxidation is relatively weaker than that with shorter distance, as shown in Fig. 5.3b.

5.6 Effect of Concentration and Acid–Base Property

The concentration of the NaOH solution affects the intensity of the electric current (Fig. 5.4), which is closely related to the formation of the oxide gallium [1]. On the other side, the concentration of the NaOH solution determines the rate of the oxide layer dissolution. The two roles are opposite, and thus it is not easy to control the deformation via the solution concentration accurately. However, the concentration of the NaOH solution is very important to the rate of both extension and contraction. As shown in Fig. 5.4b, under the condition of high external voltage and high concentration of NaOH solution, both the formation and the dissolution are so fast that the accumulation of the oxide gallium appears less accordingly. As a result, the surface tension drops a little slower, and the gallium reversibly contracts faster. Meanwhile, along with the fast dissolution, the oxide gallium is not sufficient enough to hinder the deformation, and thus under high voltages, the deformability is improved, as shown in Fig. 5.4a. In the high concentration of NaOH solution, once the voltage is removed, the gallium reconfigures itself immediately due to the not much accumulation and fast dissolution (Fig. 5.4b). Additionally, since the gallium deforms into a petaloid shape, the over quick deformation can lead to the rupture of the petals. In addition, several separate smaller spheres can be formed when the rate of the contraction becomes too fast as the gallium petals near the center of the flower become much thinner, as shown in Fig. 5.4b.

Figure 5.4 shows the reversible deformation of the liquid gallium under different concentrations of NaOH solution [1]. In contrast to the experiment operated in the 0.5 mol/L NaOH solution (Fig. 5.4a), regarding the 1 mol/L NaOH solution, the production of the hydrogen appears much more since the higher concentration reduces the electrical resistance along the current path and thus increases the electrical current. Theoretically, the larger electrical current also facilitates the generation of the oxide skin. However, no obvious oxide layer is observed as the higher concentration of NaOH solution also accelerates the oxide dissolution. In addition, the final reconfiguration is the formation of several smaller separate spheres rather than a single one. The main reason for the different reconfigurations is that in the higher concentration of NaOH solution, more petals are likely to be formed, as displayed in Fig. 5.4b.

Though under the same voltage and electrode spacing, raising the concentration of the NaOH solution can reduce the electrical resistance of the current path and thus increase the electric current [1], as shown in Fig. 5.3a, the performance of the liquid metal deformation is not improved in the high concentration of NaOH solution as the concentration affects the dissolution of the oxide layer as well (Fig. 5.3c). At this stage, it is challenging to quantify the exact relation between the

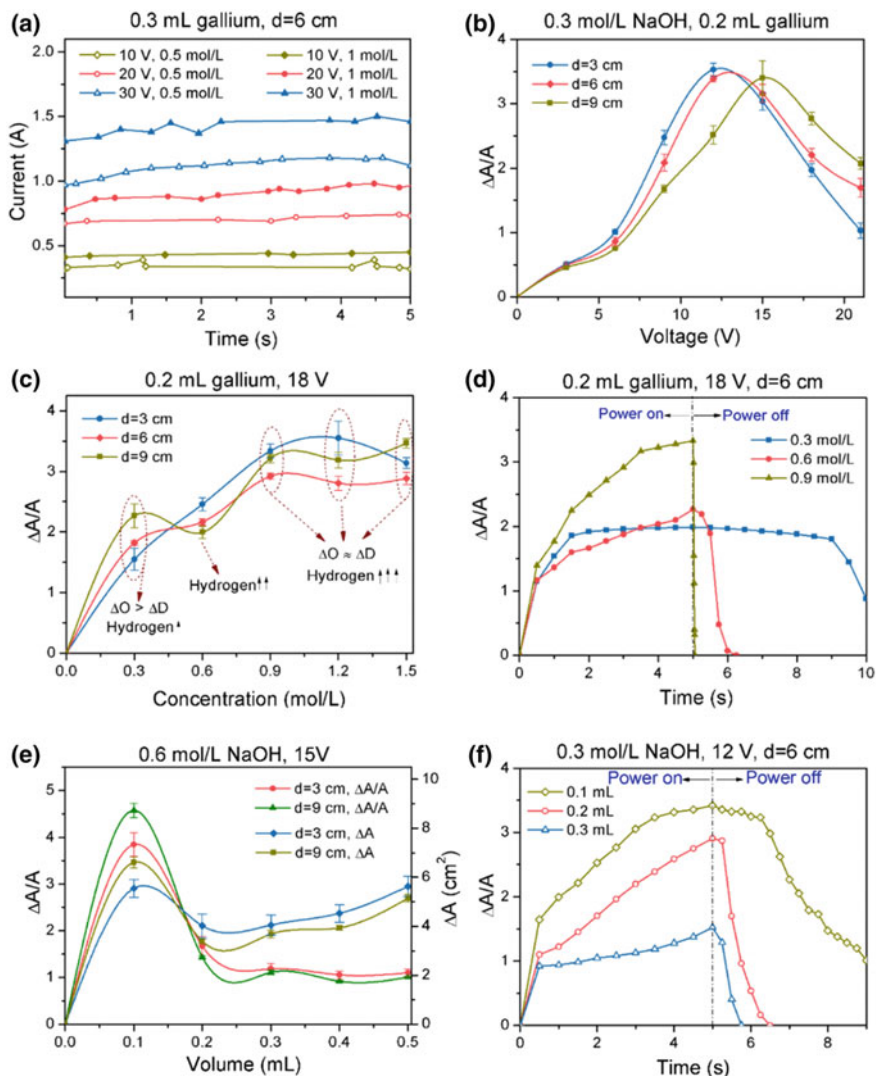


Fig. 5.3 The exploration of the main factors affecting the reversible deformation [1]. The left vertical coordinate of **b–f** all refers to the relative change of cross-sectional area, where the symbol ΔA and A denote the change of the cross-sectional area and the original cross-sectional area, respectively. The power-on time lasts for 5 s. **a** The electric current in response to different voltages. **b** The relative change of cross-sectional area at the fifth second under different electrode spacings and voltages. **c** The relative change of cross-sectional area at the fifth second with different concentrations of NaOH solution and electrode spacings. The symbols ΔO and ΔD denote the rate change of oxidation and dissolution, respectively. **d** The relative change of cross-sectional area along with the time under different concentrations of NaOH solution. **e** The relative change of the cross-sectional area (the left vertical axis) and change of cross-sectional area (the right vertical axis) at the fifth second with different volumes of liquid gallium and electrode spacings. **f** The relative change of cross-sectional area along with the time under different volumes of the liquid droplet. All pictures are reproduced with permission

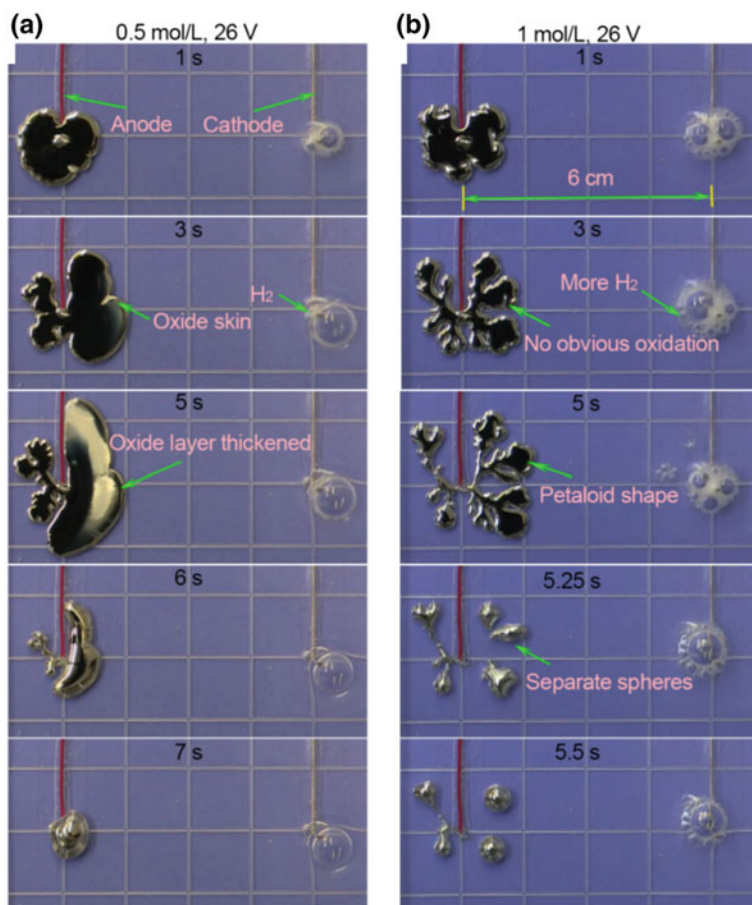


Fig. 5.4 Sequential snapshots for reversible deformation of liquid metal upon two typical concentrations of NaOH solution [1]. The applied voltage and electrode spacing are 26 V and 6 cm, respectively. **a** The concentration of the NaOH solution is 0.5 mol/L. **b** The concentration of the NaOH solution is 1 mol/L. All pictures are reproduced with permission

deformability and concentration of the NaOH solution since the increase of the concentration accelerates both oxidation and dissolution, as demonstrated in Eqs. (5.5), (5.6) and (5.7), respectively. As displayed in Fig. 5.3c, upon the exposure of 18 V voltage, the increment of the oxide accumulation becomes much larger than that of the oxide dissolution in 0.3 mol/L NaOH solution. As a result, the deformation is improved along with longer electrode spacing. In contrast to the 0.3 mol/L NaOH solution, the result is inverse in 0.6 mol/L NaOH solution since the oxidation does not obviously hinder the deformation. However, there is no significant difference when the experiment is operated in 0.9, 1.2 or 1.5 mol/L NaOH solutions, respectively (Fig. 5.3c) since the increments of both oxide accumulation and dissolution

are approximately the same. In the high concentration solution, the opposite force acting on the liquid metal from the production of the hydrogen cannot be neglected as such force impedes the deformation toward the cathode, especially when operating with shorter electrode spacings (Fig. 5.3c). Therefore, it is reasonable to explain the fluctuation phenomenon in the relatively high concentration case of NaOH solution (Fig. 5.3c). Assuming an ideal situation that when the voltage and electrode spacing are determined, a certain concentration of NaOH solution makes the oxidation speed approximate to that of the oxide dissolution, the deformation is minimized. It is noteworthy that in the high concentration of the NaOH solution, a shorter electrode spacing may cause the change of the metal morphology smaller since the deformation is so fast that the petals are ruptured and reversibly form into several spheres instantly, such as in the 1.5 mol/L NaOH solution with 3 cm electrode spacing as shown in Fig. 5.3c. The newly formed spheres either scatter or recombine with the rest petals and deform again until the direct power is switched off. As shown in Fig. 5.3d, upon the 18 V voltage and 0.3 mol/L NaOH solution, the deformability is extremely limited as the oxide layer is coated on the surface of the liquid metal very fast and hampers the deformation, which can be observed that from the 2 s to the 5 s the deformation is barely unchanged and when the power is turned off, it takes about 4 s when the morphology of the liquid gallium starts to recover. However, in the 0.9 mol/L NaOH solution, the deformation performance increases, and the speed of the extension becomes much faster. Meanwhile, the reversibility accelerates and takes less than 0.1 s to retract back into a sphere or several smaller spheres (Fig. 5.3d), which is mainly caused by that the high concentration induces less accumulation of oxidation and dissolves the oxide skin much faster. To demonstrate that it is the dissolution of the oxide layer that regulates the reversibility, a series of control experiments are conducted. Instead of NaOH electrolyte, Na_2SO_4 solution has also been studied with the reason that it cannot dissolve the oxide gallium. As a result, though the electrochemical reaction renders the neutral solution to alkalinity, the deformation is still rather limited, and the metal cannot reconfigure itself into a sphere. After the deformation of the gallium in the Na_2SO_4 solution, when adding appropriate NaOH or HCl solution on the liquid metal surface, the deformed droplet recovers back into a sphere slowly, confirming that the key mechanism of the reversibility is really based on the dissolution of the oxide layer. Clearly, the concentration of NaOH solution is the main factor to regulate the reversibility.

5.7 Effect of Liquid Metal Volume on Its Deformability

To investigate the operation of the reversible deformation under different amounts of the gallium, several typical volumes of the droplet from 0.1 to 0.5 mL have been studied [1]. The relative change of the cross-sectional area is not simply reduced with the increase of the metal, as shown in Fig. 5.3e. With 15 V voltage and in 0.6 mol/L NaOH solution, the relative change of the morphology is the largest upon 0.1 mL gallium, while it reduces when increasing the volume of gallium droplet (Fig. 5.3e).

From 0.3 to 0.5 mL of liquid gallium, the relative change of the cross-sectional area is not obvious, and the change of the total morphology slightly increases, though the production of the oxide gallium cannot cover the whole droplet and the larger original surface of the gallium is conducive to dissolve the thin oxide layer. It mainly results from that larger droplet is closer to the cathode at the initial time, and thus the formation of the oxide gallium is a little bit more than that with smaller droplet. In contrast to the experiment in 0.6 mol/L NaOH solution with 15 V voltage, the deformation in the 0.3 mol/L with 12 V voltage is quite different (Fig. 5.3f): the relative change of the cross-sectional area declines upon with 0.1 mL gallium, while it rises upon 0.2 mL gallium since the aggravated oxide accumulation restricts the deformation of 0.1 mL liquid gallium and contributes to the extension of 0.2 mL gallium inversely. In response to 0.3 mL gallium, the relative change does not differ evidently since the larger initial surface of the liquid gallium accelerates the dissolution of the oxidation since the area contacting with the alkali solution is also larger. Moreover, the average thickness of the oxide layer becomes thinner as the oxide gallium should be distributed on the whole surface of the droplet, which results in that the oxidation is not sufficient to contend against the dissolution. According to the Faraday's law in Eqs. (5.3) and (5.4), under the same condition except for the amount of gallium, the output of the oxidation obtained from different volumes of gallium varies slightly if ignoring the effects of volume and the deformation on the electric current. Theoretically, though the output of the oxidation is almost the same, the original surface affects the dissolution. Therefore, compared with larger droplet, the retraction speed with smaller droplet is lower as the contacting area with the solution is less (Fig. 5.3f), which slows down the dissolution.

At the beginning of applying the voltage, when ignoring the influence of the gallium volume on the electric field, the stronger initial surface tension by the larger gallium volume can accelerate the dissolution of the oxide layer since the oxide skin covers a larger surface, which makes the oxide layer thinner [1]. When the concentration of the applied NaOH solution becomes appropriate, the deformability of different sized gallium droplets varies from voltage to voltage. Under the exposure of high external voltage, it is favorable for a larger droplet to deform as the rate difference between the formation and dissolution is relatively reduced. On the contrary, under the low external voltage, the deformability of smaller gallium droplet becomes better since the rate of the oxide gallium formation is slow. Therefore, in order to improve the performance of the deformation, it is necessary to slow down the dissolution process.

As shown in Fig. 5.5, for the same voltage and concentration of the NaOH solution, the deformability and the reversibility are different when cooperating with different volumes of the gallium droplet [1]: the surface of the 0.1 mL deformed metal is obviously coated with a thick oxide skin, which significantly restricts the deformability (Fig. 5.5a). In contrast to the 0.1 mL gallium droplet, the formation of the oxide layer on the surface of 0.3 mL liquid metal is obviously observed only in the narrow region close to the cathode (Fig. 5.5b). Across the whole liquid metal with 0.5 mL, no obvious oxide gallium is visible, and the deformation performance would become weak (Fig. 5.5c). As previously mentioned, the rate of the reconfiguration depends

on the net accumulation of the oxide gallium, and thus it is imaginable that the rate is decreased along with the increase of the gallium volumes (Fig. 5.5).

5.8 Deformation of Liquid Metal Induced by Low and Periodic Voltage

When a 10 Vp-p square wave signal connecting with a $50\ \Omega$ in series is applied, the low voltage loading on the liquid metal makes its morphology regular and circularly symmetric. In addition, the change of the morphology is periodic along with the power supply [1]. Figure 5.6a and b, respectively, shows the relative change of the cross-sectional area with frequency of 1 and 0.5 Hz. Under such low frequency and periodic voltage, the behavior of the droplet is similar to heartbeat, rhythmically relaxing and contracting. When the gallium extends to some degree, prolonging the power-on time will not increase the relative change since the oxidation reaches its equilibrium state with dissolution dynamically. In contrast to the square wave, the periodic voltage with sine wave can slow down the rate of extension and contraction.

5.9 Deformation Induced by Larger Size Electrodes or Unfixed Cathode

Taking the size of the electrodes into account, graphite electrodes with 2 mm diameter are adopted. The oxygen generated on the anodal graphite electrode is much more than that on the anodal platinum electrode as the contacting area with the alkali solution on the anodal graphite electrode is much larger. Actually, the change of liquid metal morphology induced by the graphite electrodes cannot be neglected, especially when the dosage of the gallium is only a small amount. In addition, the size of the graphite electrodes affects the distribution of the electric field in the solution and consequently affects the oxidation. Interestingly, when moving the cathodic graphite electrode, the liquid metal locomotes following the cathodic graphite electrode, as revealed in Fig. 5.6c and d. The deformation tends to spread toward the cathode, while the hydrogen produced on the cathode pushes the metal aside.

5.10 Conclusion

In summary, it was discovered that the liquid metal-based reversible shape transformation phenomenon can be enabled by the SCHEME. The main mechanism for such large-scale material deformation comes from the combined electrolytic oxidation and the dissolution effect, as demonstrated by a series of comparative experiments [1].

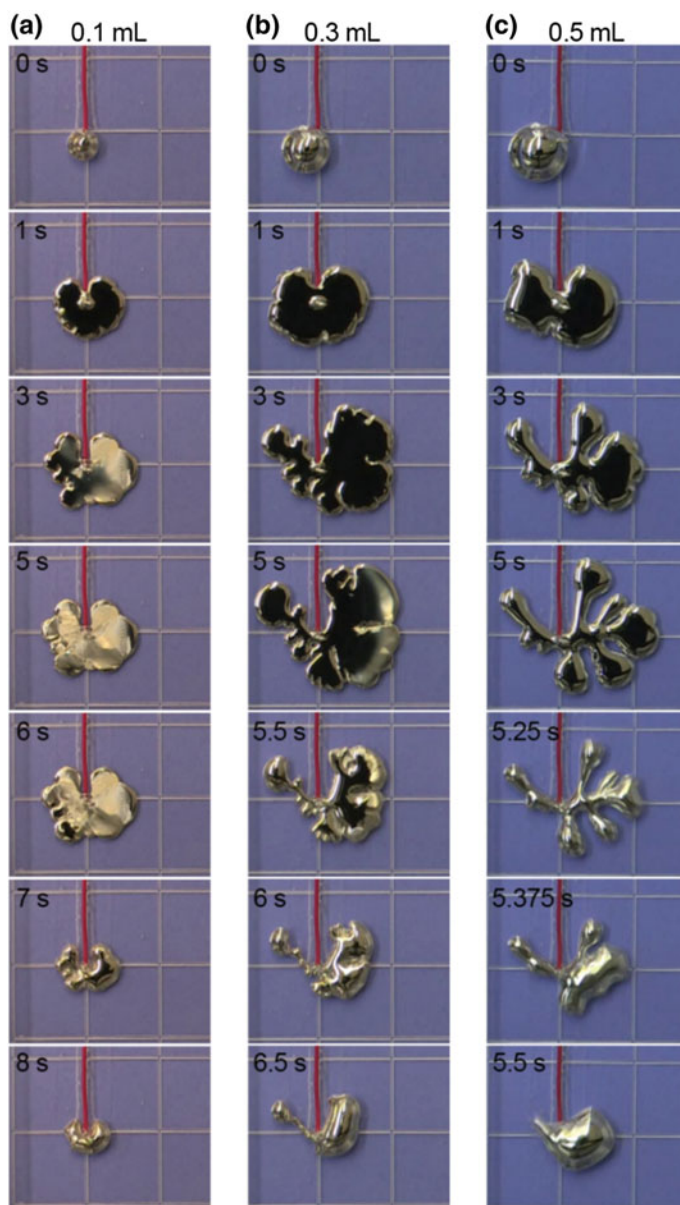


Fig. 5.5 Sequential snapshots for reversible deformation of liquid metal upon different volumes of gallium droplet [1]. The applied voltage and electrode spacing are 22 V and 6 cm, respectively. The concentration of the NaOH solution is 0.5 mol/L. **a** The volume of the gallium droplet is 0.1 mL. **b** The volume of the gallium droplet is 0.3 mL. **c** The volume of the gallium droplet is 0.5 mL. All pictures are reproduced with permission

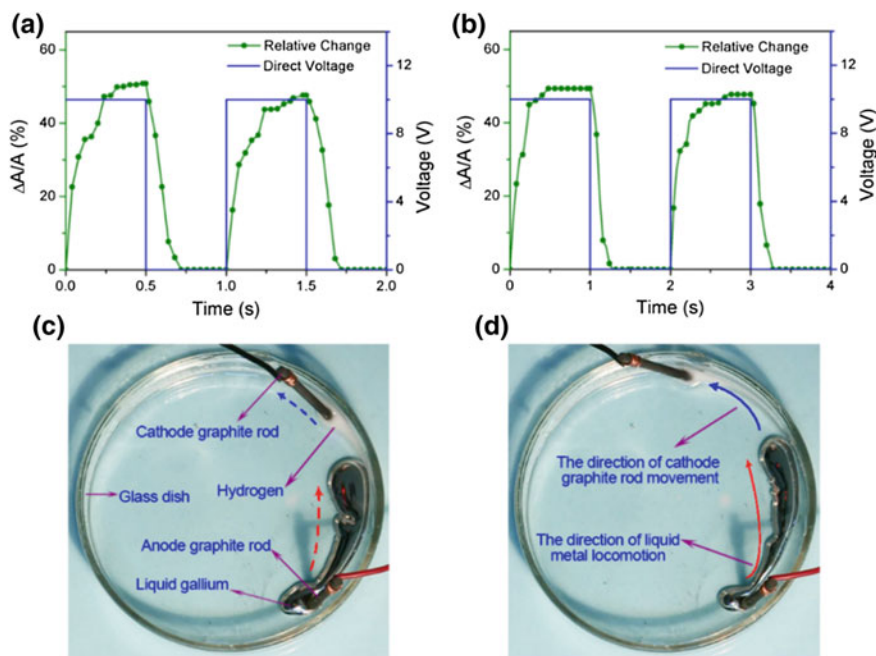


Fig. 5.6 The periodic deformation and the locomotion following the movement of the cathode [1]. The concentration of the applied NaOH solution is 1.0 mol/L. The left vertical coordinate of **a** and **b** both refer to the relative change of cross-sectional area, where the symbol ΔA and A denote the change of the cross-sectional area and the original cross-sectional area, respectively, while the left coordinate refers to the applied voltage. In **a** and **b**, the electrode spacing and the volume of the gallium are, respectively, 3 cm and 0.2 mL. **a** The frequency of the square wave voltage is 1 Hz. **b** The frequency of the square wave voltage is 0.5 Hz. In **c** and **d**, the volume of the gallium is 0.4 mL, and the electrodes are graphite rods with diameter of 2 mm. All pictures are reproduced with permission

A series of typical conditions including the concentration and acid–base property of the solutions, the external electrical voltage, the electrode spacing, the size of the electrode, and the volume of the gallium objects all affect the deformability of liquid metal. It is important to notice that the material extension rate is under control of the electrical voltage and the concentration of the acidic or alkaline solution, while the retraction rate immensely depends on previous oxide accumulation and concentration of the acidic or alkaline solution. Since the reversibility relies heavily on the chemical dissolution, the primary task for controlling such reversible deformation is to identify the appropriate electrolyte solution and its optimum concentration. As a result, the applied voltage and the electrode spacing can be designated to realize the expected deformation. Overall, it can be seen that the SCHEME principle has generalized adaptability. For example, the liquid metal material with strong shape changeable capabilities is not only restricted to the gallium. More candidate materials can in fact be easily found among quite a few room temperature liquid metals. For

example, if simply adopting the metal fluids such as eutectic gallium–indium alloy GaIn₂₅ (75% gallium and 25% indium) or Galinstan (68.5% gallium, 21.5% indium, and 10% tin) as the testing machine, similar phenomena can be observed. Further, such shape transformational behavior can also naturally be extended to various pre-designed device structures or patterns to realize desired tasks according to specific needs. In general, the SCHEME opens a basic strategy of utilizing liquid metal as smart material to manufacture soft machines. Meanwhile, the disclosed reversible deformation phenomenon also offers an exciting platform for developing diverse applications that cannot easily be achieved through rigid materials, such as functioning as flexible components, assembling electronic devices, and eventually realizing a dynamically programmable and reconfigurable soft robot in the near future.

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Chapter 6

Electromagnetic Field Induced Transformation of Liquid Metal



Abstract Unlike using a single external electric field, simultaneous administration of both electrical and magnetic fields would induce rather complex transformation behaviors of liquid metal. Along this direction, the present lab (Wang and Liu in *Electromagnetic rotation of a liquid metal sphere or pool within a solution*, 471:20150177, 2015, [1]) demonstrated a group of transformational behaviors of liquid metal electric motors. The machine system is composed of a pair of concentric ring electrodes, permanent magnet, and electrolyte solution. A liquid metal galinstan sphere, along with NaOH solution, is stimulated to rotate centrifugally around the central electrode and the rotating speed increases with the voltage. The NaOH solution serves to remove the oxide on the liquid metal surface in time, reduce the motion friction, and provide impetus to the liquid metal. As the liquid metal is added to 12.16 g to form a kidney like body, its rotating speed appears more controllable and the effect of the electrolytic action in the NaOH solution becomes weak in the range of 0–1.82 V. As the liquid metal is increased to 18.20 g to form a circular ring-shaped body, the ideal voltage range for controlling the rotating motion of the liquid metal is 0–0.81 V. The metal fluid rotates at a speed of 1.9 rpm even at an extremely low voltage of 0.03 V. Further, with the administrated increased electrical field, a variety of surface folding patterns of rotational liquid metal like wheel shape, dual concentric ring shape, and so on were found to occur (Wang and Liu in *Liquid metal patterns induced by electric capillary force*, 108:161602–161605, 2016, [2]), which refreshes the basic understanding of classical fluid kinematics. The knowledge obtained and the liquid metal electric motor, thus, established can find important applications in realizing certain future rotating soft machine. This chapter presents the typical phenomena of the electromagnetic field induced transformation of liquid metal.

Keywords Liquid · Metal transformation · Electromagnetic control
Rotational machine · Flow patterns

6.1 Electromagnetic Rotation of Liquid Metal Sphere

Designing micro- or nanoscale motors which could convert diverse forms of energy into a specific motion has received a lot of attention in the science community. Generally, object actuation can be achieved by propulsions from light [3], bioelectrochemical [4], electric field [5, 6], magnetic field [7], acoustic action [8], and so on. The room-temperature liquid metal exhibits properties that are very different from solid metal due to its intrinsic fluid behavior. Activities of such fluidic materials are quite important in a variety of areas like electronics cooling [9, 10], lab on a chip [11, 12], flexible electronics [13], printed electronics [14, 15], to name only a few. The motion or transformational characteristics of liquid metal in an electrolyte solution under various configurations have become a focal point of recent researches [16]. As it was found [17], a liquid metal sphere immersed in an electrolyte solution could be manipulated to move between a pair of anode and cathode electrodes due to its asymmetrical surface tension. In addition, induced Marangoni flow at the surface of the liquid metal when activated by current signal was also found [17–19] and utilized to make a pump. Further, researches [20] disclosed that the liquid metal marbles, coated with nanoparticles, could be propelled by bubbles generated through a photochemical reaction. More behaviors like liquid metal actuations [19, 21] and ejection [22] were also found which can partially be attributed to the electrocapillarity phenomenon. From an alternative, Wang et al. [1] investigated the issues regarding the controllable centrifugal rotational motions of liquid metal especially a single sphere in solution which is critical for a group of important applications like chip cooling, fluid mixture, rotor machine construction, etc. Although magnetohydrodynamic (MHD) pump [23, 24] has been investigated to drive fluid by Lorentz force, the manipulated object was either liquid metal alone [25] or electrolytic solution only [26, 27]. Focusing on the manipulation of the global rotation of a two-phase fluid, Wang et al. [1] demonstrated a fundamental approach for propelling a liquid metal sphere or pool in an electrolyte solution under the specially designed electromagnetic force.

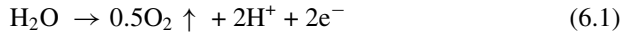
6.2 About the Test Liquid Metal Materials

Although quite a few different liquid metals or alloys can be adopted as the testing candidates, only galinstan (68.5% gallium, 21.5% indium, and 10% tin by weight), a kind of nontoxic liquid metal with melting point around 11 °C, is illustrated in the following as the manipulated object for brief. NaOH solution with a concentration of 1 mol/L is used as the electrolyte in all the experiments. The liquid metal adopted in the experiments is gallium, indium, and tin with the purity above 99.99% was weighed according to the ratio of 68.5: 21.5: 10 and were then added to a beaker.

The mixture was stirred in the beaker which was heated in a water bath at about 90 °C for 1 h to achieve uniformity. All the measured voltage and current values in the experiments were acquired via Agilent 34972A (USA). The velocity of the liquid metal was determined by analyzing the video frames.

6.3 Motion Characteristic of Electrolyte Solution in Electromagnetic Field

To investigate the motion characteristic of the electrolyte solution in an electromagnetic field, an experimental apparatus is designed with its schematic diagram as shown in Fig. 6.1a. A permanent magnet is set under the bottom of a Petri dish filled with NaOH electrolyte solution. A pair of graphite anode and cathode electrode bars is vertically immersed into the NaOH solution. When the electrodes are powered by a DC (direct current) source, quite a few bubbles are generated as shown in Fig. 6.1b. This is due to the electrolytic action on the anode and the cathode electrodes which can be, respectively, expressed as [28].



Clearly, the bubbles generated on the anode and the cathode electrodes are oxygen and hydrogen, respectively. Combining the above equations together, one has



It can be seen from Eq. (6.3) that the volume of hydrogen generated is twice larger than that of oxygen. Therefore, the amount of bubbles surrounding the cathode electrode is much larger than that around the anode electrode which is proven in Fig. 6.1b.

The electric potential distribution as depicted in Fig. 6.1c is simulated with software COMSOL Multiphysics, when the potentials of the anode and the cathode are set as 5 and −5 V, respectively. The red arrows represent the electric field direction from high potential to low. The Lorentz force exerted on the NaOH electrolyte fluid is expressed as [29]

$$\mathbf{F} = \mathbf{J} \times \mathbf{B} = \sigma(\mathbf{E} + \mathbf{u} \times \mathbf{B}) \times \mathbf{B} \quad (6.4)$$

where $\mathbf{J}$ is the electric current density. σ and $\mathbf{u}$ are the conductivity and the velocity of the electrolyte fluid, respectively. $\mathbf{E}$ is the electric field strength whose direction is shown as the red arrows. $\mathbf{B}$ is the magnetic induction strength. Assuming that the direction of $\mathbf{B}$ is outward the plane of paper, then the Lorentz force $\mathbf{F}$ indicated as black arrows in Fig. 6.1c is perpendicular to the plane of $\mathbf{E}$ and $\mathbf{B}$ and is on the

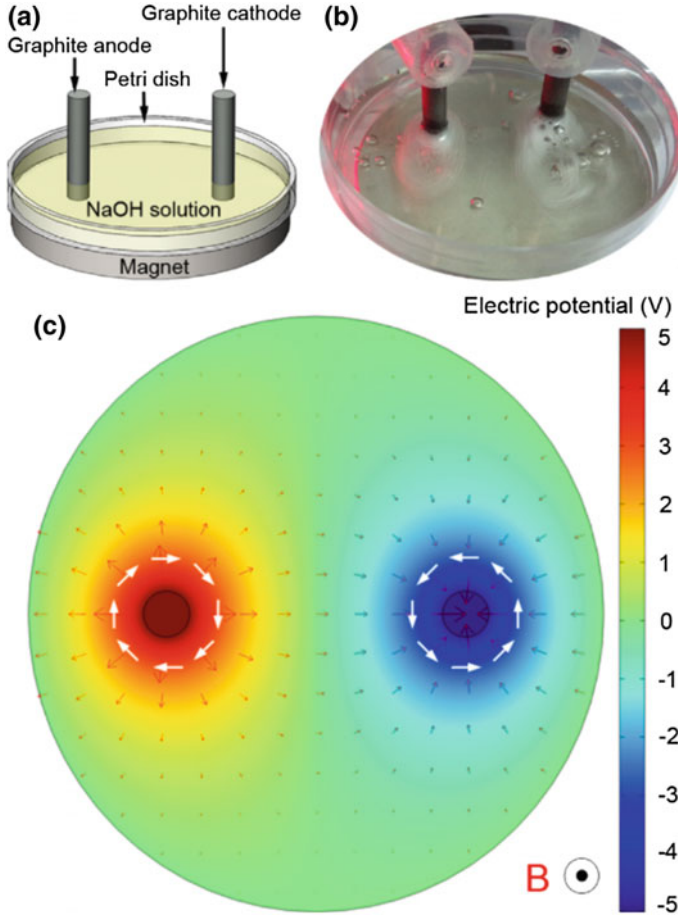


Fig. 6.1 The rotating motion of NaOH electrolyte in the electromagnetic field [1]. **a** The schematic diagram of the experimental apparatus. **b** The photo of the NaOH electrolyte in rotating motion. **c** The simulation results of the electric potential distribution between the anode and the cathode which are, respectively, set as 5 and -5 V with COMSOL Multiphysics software. The direction of induced magnetic field B is outward the plane of paper. The red arrows represent the direction of E , and the white arrows indicate the direction of the Lorentz force exerted on the electrolyte fluid which is around the anode and the cathode. All pictures are reproduced with permission

right-hand side of E . Therefore, the bubbles propelled by the surrounding solution which is subjected to the Lorentz force will rotate around the anode and the cathode electrodes in opposite direction which is verified in Fig. 6.1b.

6.4 Rotational Motion of Liquid Metal Sphere in Electromagnetic Field

In order to rotationally actuate the liquid metal sphere and control its motion speed, an experimental device is designed and the assembling drawing is shown in Fig. 6.2a. A pair of concentric ring graphite electrodes is placed in a Petri dish under which there is a disk-shaped permanent magnet [1]. The liquid metal immersed in NaOH solution is located between the two electrodes. There is a circular symmetric distribution for the magnetic induction strength $\mathbf{B}$ on the surface of the magnet and the direction of $\mathbf{B}$ is perpendicular to the upper surface of the annulus electrode. Here, it was assumed that D and d , respectively, represent the diameter of the inner round bar electrode and the inner diameter of the outer annulus electrode. The symmetrical distribution of $\mathbf{B}$ for the concentric ring electrodes with $D = 30$ mm, $d = 20$ mm and $D = 30$ mm, $d = 4$ mm are shown in Fig. 6.2B, C, respectively. The lower and upper limits of $\mathbf{B}$ in the shade region in Fig. 6.2B are, respectively, measured as 276.7 mT and 305.5 mT, while the lower and upper limits of $\mathbf{B}$ in the shaded region in Fig. 6.2C are, respectively, 258 and 305.5 mT. Here, the shade regions in Fig. 6.2b, c represent the motion radius range of the liquid metal and the NaOH solution.

Controlling the motion of a liquid metal sphere is investigated by using a pair of concentric electrodes with $D = 30$ mm and $d = 20$ mm. $\mathbf{B}$ is directed into the upper surface of the annulus electrode. A galinstan liquid metal sphere (84.28 mg) is immersed into 1 ml NaOH electrolyte solution which is filled between the two electrodes. As the electrodes are powered, the Lorentz force exerted on the galinstan sphere and the NaOH solution is generated and is along the counterclockwise direction as shown in Fig. 6.3a according to the right-hand rule [1]. The electrolyte solution rotates more rapidly than the galinstan sphere due to its low density (1.045 g/cm^3) and gives an impetus to the liquid metal sphere. The measured current–voltage, resistance–voltage, rotating speed–voltage and power–voltage relationship curves of the galinstan sphere are presented in Fig. 6.3b, c. It can be observed that with the increase of the voltage between the two electrodes, the current approximates to a linear increase while the resistance approximates to a linear decrease. The rotating speed increases with the increase of the voltage and the increasing speed reaches the maximum value of 1.114 rps/V (revolutions per second per voltage) in the range of 7.05–7.53 V. Such changing trends in the curves can be interpreted as follows: The conductive property of the electrolyte solution is dependent on the intensity of the ion motion which is determined by the electric field intensity $\mathbf{E}$ in the solution. As the voltage increases, the resistance decreases due to the increase of $\mathbf{E}$, and the current and the consumed power are, thus, increased. Therefore, the liquid metal sphere moves faster as a result of the increase of the Lorentz force imposed on both the liquid metal and the solution. As the voltage increases, the part of the galinstan sphere facing the anode will be coated with an oxide layer because of the oxidation potential [30] and the electrolyte solution will become turbid due to the increas-

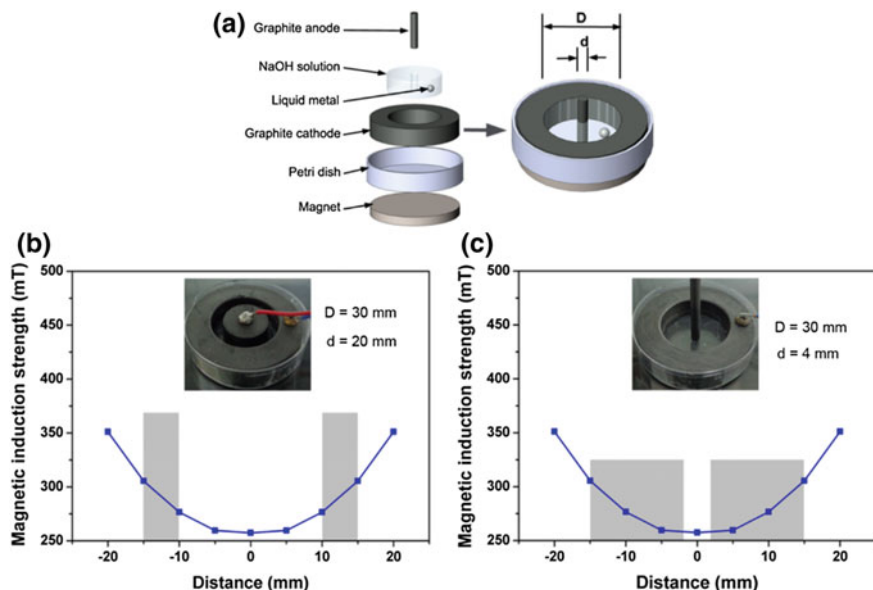


Fig. 6.2 a The explosive view (left) and the side view (right) of a pair of concentric ring electrodes with a permanent magnet underneath [1] b and c. The relationships between the magnetic induction strength B on the surface of the permanent magnet and the distance away from the center of the magnet. The curves in the shadows represent the symmetrical distribution of B on the region between the concentric ring electrodes with $D = 30$ mm, $d = 20$ mm and $D = 30$ mm, $d = 4$ mm, respectively. The insets in b and c are the photos of the concentric ring electrodes. All pictures are reproduced with permission

ingly generated oxide in the solution. Besides, the electrolytic degree of the NaOH solution becomes larger with the increase of the voltage. And, the movement of the galinstan sphere will, thus, be impeded by the increasing bubbles generated in the NaOH solution.

6.5 Controlling the Rotating Motion of a Liquid Metal Pool

When a pool of liquid metal is immersed between the anode and the cathode electrodes to contact the walls of the two electrodes simultaneously, a different motion characteristic can be observed [1]. The experimental device is shown in Fig. 6.4a. 1 ml NaOH solution is filled between the concentric ring electrodes with $D = 30$ mm and $d = 4$ mm, together with a pool of 12.16 g galinstan liquid metal whose shape looks like a kidney. Due to the existence of the NaOH aqueous solution, the oxide will be changed to gallium oxide monohydroxides (GaOOH) to weaken the oxide skin strength as the liquid metal is exposed to water, as well as an interfacial slip layer [31] will be formed between the liquid metal and the graphite electrodes and the

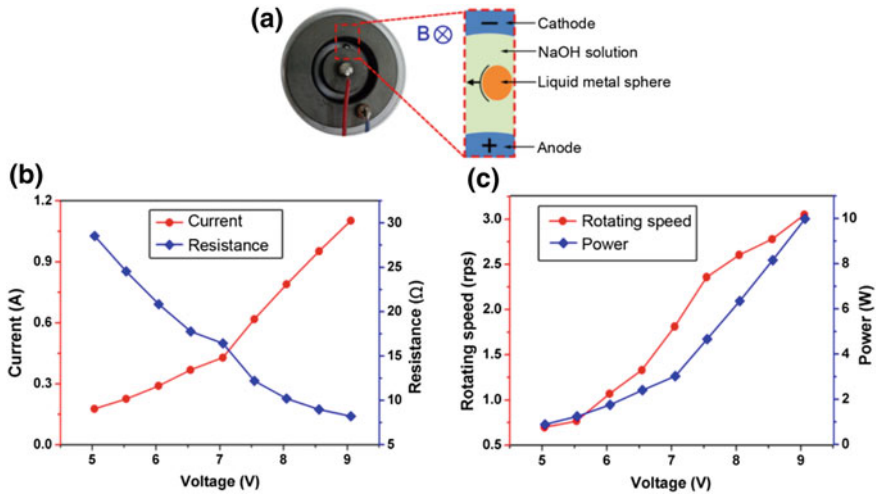


Fig. 6.3 **a** The structure diagram of a liquid metal sphere immersed in the NaOH solution between a pair of concentric ring electrodes with $D = 30$ mm and $d = 20$ mm [1]. The magnetic field B is directed into the paper. The black arrow represents the direction of the Lorentz force imposed on the liquid metal sphere. **b** The measured current–voltage and resistance–voltage relationships of a galinstan sphere (84.28 mg) located between the anode and the cathode. **c** The measured rotating speed–voltage and power–voltage relationships of the galinstan sphere. All pictures are reproduced with permission

bottom of the Petri dish. Such a slip layer will greatly reduce the frictional resistance of the liquid metal, as well as avoid shortcuts between the two electrodes. In addition, the NaOH solution can remove the oxide generated on the liquid metal surface in time and provide an impetus to the liquid metal. Further, when the electrodes are powered, the liquid metal is driven by the Lorentz force and rotates around the inner round bar electrode. The measured current–time and the voltage–time relationships are shown in Fig. 6.4b. It can be seen that the voltage between the anode and the cathode keeps almost constant (1.63 V), while the measured current values present sinusoidal periodic variation and the fitting expression is given as follows:

$$I = 0.2867 \times \sin(13.55 \times t + 6.8^\circ) + 0.7409 \quad (6.5)$$

where I and t represent current and time, respectively. The frequency (2.16 1/s) computed from the current–time relationship is consistent with the measured result (2.18 rps), which indicates that the current passing through the liquid metal changes periodically. The variations of current, resistance, consuming power, and rotating speed of the liquid metal with the change of voltage are shown in Fig. 6.4c, d. As the voltage becomes lower than 1.82 V, the liquid metal is in uniform circular motion and there are hardly any bubbles generated in the NaOH solution. This can be verified from Fig. 6.4e, which shows the snapshots of the liquid metal at 0,

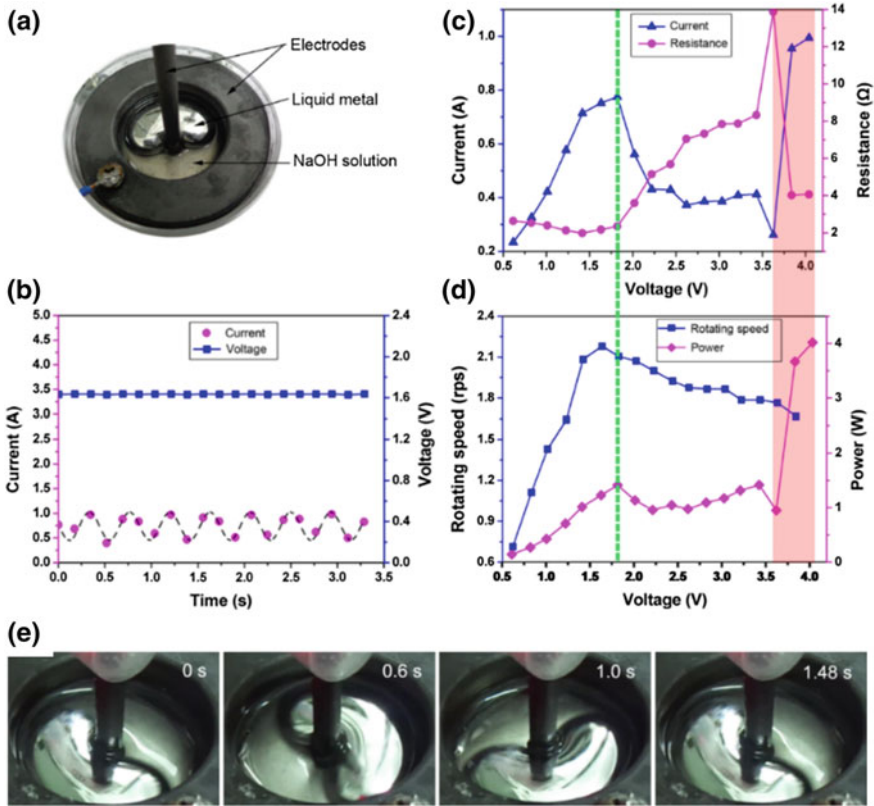
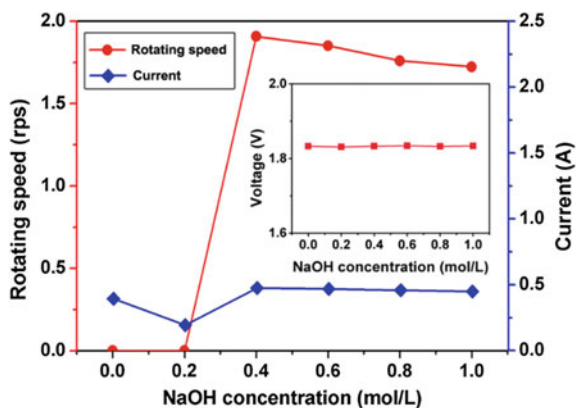


Fig. 6.4 **a** The photo of a body of kidney like galinstan (12.16 g) between a pair of concentric ring electrodes with $D = 30$ mm and $d = 4$ mm. **b** The measured voltage–time and the current–time relationships of the liquid metal in the uniform rotation. The dashed curve is fitted by the measured current values. **c** The average current–voltage and the average resistance–voltage relationships of the liquid metal in the uniform rotation. **d** The rotating speed–voltage and the average power–voltage relationships of the liquid metal in uniform rotation. The green dashed line represents the demarcation between the moving states of the liquid metal. The liquid metal deforms and beats the walls of the electrodes violently when the voltage is within the shadow region in **c** and **d**. **e** Snapshots of the liquid metal at 0, 0.6, 1.0, and 1.48 s when the voltage is set as 0.6 V [1]. All pictures are reproduced with permission

0.6, 1.0, and 1.48 s, when the voltage is regulated at 0.6 V. The current and the electric power consumed on the liquid metal increase with the increase of voltage, while the resistance which is mainly the contact resistance between the electrodes and the liquid metal is within the scale of 2–2.6 Ω . The rotating speed reaches the peak when the voltage is 1.63 V which is near 1.82 V. As the voltage is in the range of 1.82–3.63 V, the liquid metal rotates more and more slowly and the bubbles in NaOH solution are gradually increased. The resistance goes up quickly while the current displays a contrary tendency. The power fluctuates in the range of

Fig. 6.5 The rotating speed of a kidney-shaped liquid metal (9.8 g) immersed in NaOH solution with different concentrations, as well as the current between the two electrodes [1]. Inset is the relationship between the voltage and NaOH concentration. All pictures are reproduced with permission



0.95–1.41 W, and the rotating speed–voltage curve shows a descending trend. As the voltage becomes larger than 3.63 V, the NaOH solution gets increasingly turbid, and the liquid metal rotates more and more slowly with severe deforming and violent beating. The resistance goes down sharply due to the obvious spreading phenomenon of liquid metal, which shortens the distance between it and the electrodes, and the current gets larger accordingly. The power consumed on the liquid metal rises sharply. To the galinstan used in this experiment, the maximum rotating speed occurs when the voltage is about 1.63 V. Higher voltage between the electrodes will cause a higher electrolytic degree of NaOH solution which is not desirable. Therefore, the ideal voltage range for controlling the rotating speed of the liquid metal falls in 0–1.82 V and the electrolysis of the NaOH solution is rather weak within this range.

The influence of NaOH concentration on the rotating speed of liquid metal is investigated and the result is presented in Fig. 6.5. The mass of liquid metal is 9.8 g and the voltage is regulated at about 1.83 V. As the solution is deionized water (NaOH concentration is 0 mol/L) or low concentration (0.2 mol/L), the oxide on the liquid metal surface cannot be completely removed. And, the Lorentz force exerted on the liquid metal cannot overcome the friction due to the adhesion between the oxide and the substrate [1]. The liquid metal deforms and spreads once the electrodes are energized which is ascribed to the electrocapillary effect [32]. When NaOH solution concentration is a large value (larger than 0.4 mol/L), the liquid metal will rotate around the inner round bar electrode.

Figure 6.6a shows a pool of circular ring-shaped galinstan liquid metal (18.20 g) covered by 1 ml NaOH solution between the concentric ring electrodes with $D = 30$ mm and $d = 4$ mm. NaOH solution is spread over the surface of the liquid metal due to its lower density, and its main role is to remove the oxide and to reduce the motion resistance of the liquid metal [1]. The measured power–voltage and the rotating speed–voltage relationships are shown in Fig. 6.6b. As the voltage is lower than 0.81 V, the liquid metal rotates around the central electrode uniformly. Figure 6.6c shows the snapshots of the liquid metal at 0, 3, and 5 s when the voltage is regulated at 0.45 V. With the increase of the voltage, the rotating speed increases and the power

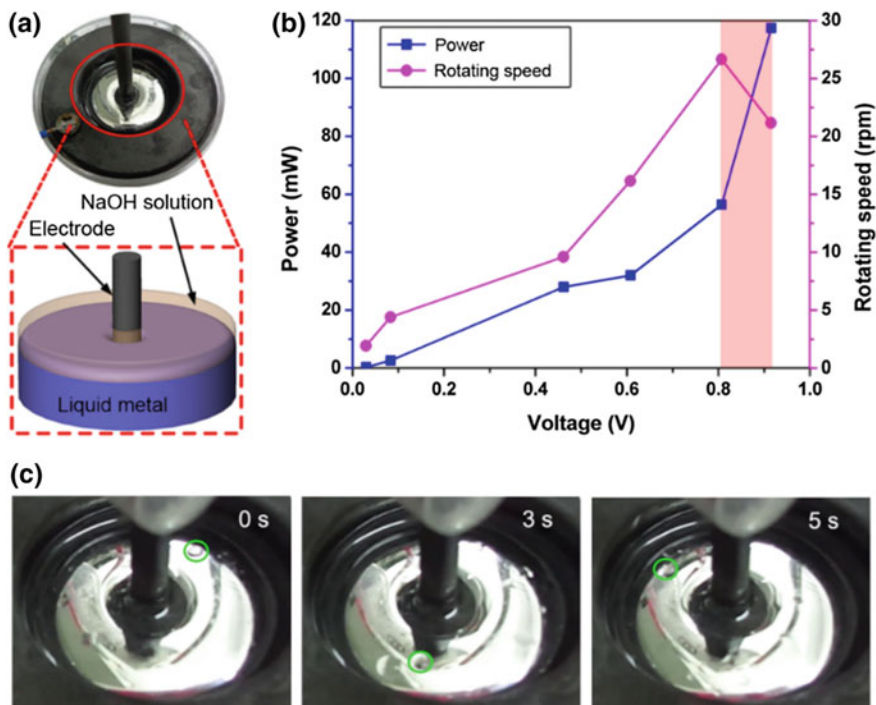


Fig. 6.6 **a** The photo and structure sketch of a circular ring-shaped galinstan (18.20 g) body between a pair of concentric ring electrodes with $D = 30$ mm and $d = 4$ mm. **b** The measured power–time and the rotating speed–time relationships of the liquid metal in uniform rotation. When the voltage is within the shadow region, the liquid metal either rotates rapidly or deforms severely. **c** Snapshots of the liquid metal at 0, 3 and 5 s when the voltage is set as 0.45 V. The green circle represents a marking point on the liquid metal surface [1]. All pictures are reproduced with permission

shows the same changing trend. As the voltage becomes larger than 0.81 V, the power increases faster while the rotating speed exhibits an opposite trend. The liquid metal either rotates rapidly or deforms severely accompanied by the turbid solution. Therefore, the ideal voltage for controlling the rotating speed of the liquid metal mentioned above is within the range of 0–0.81 V. Although the maximum rotation speed of the circular ring-shaped liquid metal (0.353 rps) is much lower than that of the kidney-shaped liquid metal (2.3 rps), the circular ring-shaped liquid metal can rotate slowly with a speed of 1.9 rpm (revolutions per minute) at the extremely low voltage of 0.03 V and the power of 0.25 mW.

As it is revealed, the NaOH solution is an important agent in controlling the rotational movement of the liquid metal sphere or pool [1]. Without it, such liquid metal objects can hardly be driven to move. Here, NaOH solution serves to remove the oxide on the liquid metal surface in time, and thus to reduce the friction and to give an impetus to the liquid metal. In fact, other alkaline or acid solutions such as KOH, HCl solutions are also good candidates for the electrolyte used in the experiments.

The rotational motion characteristics of the liquid metal under the electromagnetic force enable it to be a liquid metal electric motor (LMEM) which converts the electromagnetic energy into the kinetic energy. Manipulating the centrifugal motion of liquid metal via regulating the voltage between the electrodes has important practical value in a wide variety of engineering areas. For example, in addition to manufacturing liquid metal pump, the motion controlling method as introduced here can be adapted for making a compact cooling device in delivering heat away from the hot-end to the cold-side due to the excellent heat-conducting property of the liquid metal coolant. Further, such control strategy, combined with heating and/or ultrasonic devices, should also be very useful for mixing two or more kinds of liquid metals in the near future. Besides, with the controllable rotational behavior, the current running liquid metal sphere or pool, in fact, has already served as the certain soft rotor. Efforts made in this paper suggest a feasible way to address these potential needs in the coming time.

Overall, the above work demonstrated an approach to control the centrifugal rotating motion of liquid metal machine through incorporating the electromagnetic force and electrolyte solution together [1]. Galinstan and NaOH solution was selected as the manipulated liquid metal and the surrounding assistive fluid, respectively. As a liquid metal sphere was immersed in the NaOH solution between a pair of concentric ring electrodes in a magnetic field, it was induced to rotate around the central electrode along with the solution. The rotating speed of the liquid metal sphere increased with the increase of the voltage between the electrodes, but the bubbles and the oxide were also increasingly generated in the NaOH solution due to the electrolytic action which was not desirable however sometimes. As a pool of galinstan with weight of 12.16 g was filled between the anode and the cathode electrodes to form a kidney like body, the liquid metal runs in uniform circular motion and the electrolysis of the NaOH solution was weak when the voltage was regulated in the range of 0–1.82 V. As the liquid metal galinstan was added to 18.20 g to form a circular ring-shaped body, it could rotate even at a voltage of 0.03 V with the power of 0.25 mW. In all these experiments, the roles of NaOH solution were multiple, such as removing the oxide on the liquid metal surface, reducing the motion resistance, conducting the electricity and giving an impetus to the liquid metal. In addition, NaOH solution concentration was an important influence factor to the rotating speed of liquid metal. The rotational control strategy of the liquid metal can be found very useful in chip cooling, liquid metal pump, soft machine making, teaching props, and so on.

6.6 Liquid Metal Folding Patterns Induced by Electric Capillary Force

Starting from the above work, Wang and Liu [2] further discovered a fundamental phenomenon regarding the spontaneous formation of symmetrical folding patterns induced on rotating liquid metal free surface with circular shape features. According

to the experiments, the electric capillary force imposed on liquid metal due to surface tension gradient was found responsible for producing a variety of surface folding patterns like wheel shape, dual concentric ring shape, and so on. All the patterns display a property of axial symmetry and could be analog to the Rayleigh–Benard convection, which produces hexagonal patterns. Such finding on liquid metal flow folding refreshes knowledge of classical fluid kinematics and would help to design rotational liquid metal machine in the coming time.

Liquid metal can be controlled to deform or move with the electromagnetic way [33]. It was shown [34] that the surface charge had a rather limited effect on the surface waves in liquid metals. When a pool of liquid metal was placed in an electric field directed normal to the surface, it would become unstable and the surface relief would occur [35]. Although magnetic field had a stabilizing effect on the liquid metal which was in convective instability, the liquid metal surface would present drastic changes when subjected to a varying magnetic field according to theoretical research [36]. As the direction of the Lorentz force imposed on the liquid metal layer was against that of the gravity, the liquid metal surface became unstable due to the Rayleigh–Taylor instability [37]. However, there are still few researches on the regular folding pattern occurred on the liquid metal.

In Wang and Liu's experiments [2] on disclosing the liquid metal folding patterns, galinstan (68.5% gallium, 21.5% indium, and 10% tin by weight, 20.1 g) with a melting point about 11 °C is selected as the testing object. It is immersed in 1 mol/L NaOH electrolyte solution whose main role is to remove oxide on the liquid metal surface and reduce its kinetic friction. Both the liquid metal and the solution are located between a pair of concentric ring graphite electrodes which is described in the former section. All the liquid metal, NaOH solution, and the electrodes are placed in a Petri dish below which there is a permanent magnet to produce a vertical magnetic field. The schematic diagram of the vertical cross section of the experimental setup is presented in Fig. 6.7a.

As the liquid metal is placed in the NaOH electrolyte, an electrical double layer (EDL) which is equal to a parallel plate capacitor will be created at the metal–electrolyte interface [2]. Such layer isolates the liquid metal from the surrounding electrolyte, and the liquid metal is negatively charged while the electrolyte is positively charged [38]. The liquid metal can be regarded as an equipotential body due to its high electric conductivity [39]. And there is a uniform charge distribution of the potential difference across the EDL in the case of no external voltage. The relationship of the interfacial tension γ and the voltage difference V between both sides across the EDL can be expressed by Lippman's equation [40], i.e.,

$$\gamma = \gamma_0 - \frac{1}{2}cV^2 \quad (6.6)$$

where γ_0 is the maximum surface tension at $V = 0$, c capacitance of the EDL per unit area. The pressure difference Δp between the liquid metal and the electrolyte can be expressed by the Young–Laplace equation [40]:

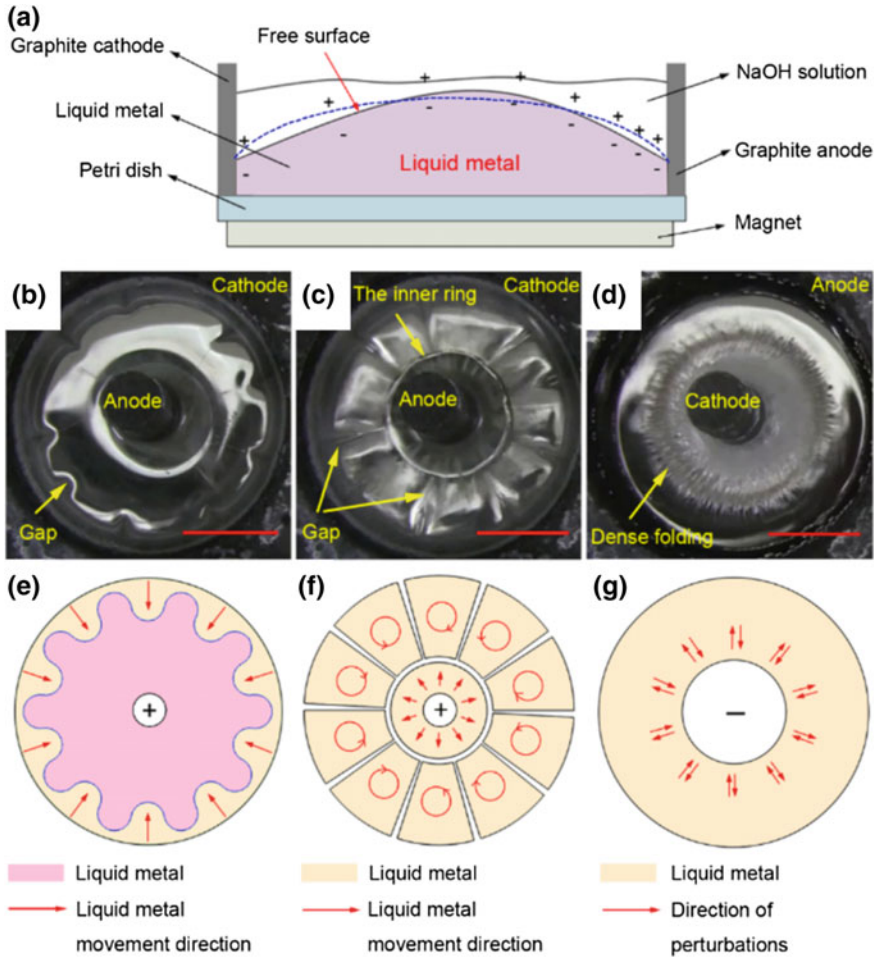


Fig. 6.7 **a** Schematic of experimental setup and surface charge distribution of the liquid metal when the electrodes are powered. The blue line represents outline of the liquid metal in un-electrified state; **b** and **c** are real object snapshots of the liquid metal, respectively, when $t = 0$ s and $t = 0.04$ s as the voltage between the inner and the outer electrodes is 1.7 V; **d** The real object snapshot of the liquid metal when the voltage between the inner and the outer electrodes is -18.78 V; **e**, **f**, and **g** are motion diagrams of the liquid metal corresponding to **b**, **c**, and **d**, respectively. The positive sign “+” and the negative sign “-” represent the graphite anode and the cathode, respectively. The scale bars in **b**, **c**, and **d** are all 10 cm [2]. All pictures are reproduced with permission

$$\Delta p = \gamma \frac{2}{R} \quad (6.7)$$

where R represents the curvature radius of the liquid metal with a spherical shape. In absence of an external electric field, the pressure difference is almost equal everywhere across the liquid metal surface. As the electrodes are electrified, a potential

gradient in the electrolyte along the anode–cathode direction is generated due to electrolyte’s finite conductivity [41]. The equal-potential-difference across the EDL is altered and the surface charge on the liquid metal is redistributed, which result in the formation of a liquid metal/electrolyte interfacial surface tension gradient according to Eq. (6.6). The surface tension of the liquid metal near the cathode is larger than that near the anode [17, 18], which results in the larger surface curvature radius according to Eq. (6.7). The Marangoni flow on the liquid metal/electrolyte interface and the electrocapillary motion of the liquid metal are thus generated [42], due to surface tension gradient. The driving force of the flow exerted upon the interface can be expressed as [41]

$$f \sim \frac{\varepsilon V E}{\lambda_D} \quad (6.8)$$

where E is the electric field intensity, ε and λ_D are electric permittivity and the Debye screening length of the electrolyte, respectively. Such electric capillary force is the reason causing various liquid metal patterns. The surface charge distribution and outline variation (from dotted line to solid line) of the liquid metal in an electric field are presented in Fig. 6.7a.

Figure 6.7b and c, respectively, display the gear pattern ($t = 0$ s) and the fan blade pattern ($t = 0.04$ s) induced on the free surface of the liquid metal when the voltage between the inner and the outer electrodes is 1.7 V. And Fig. 6.7d shows the glitch pattern on the liquid metal surface when the voltage between the inner and the outer electrodes is -18.78 V. The pattern-forming reasons can be interpreted as follows: The deformation of the liquid metal is mainly influenced by its physical properties such as gravity, viscosity, and surface tension [2]. On the basis of the related research results, the surface tension acts as the dominant factor in determining the deformation and breakup of the liquid metal in an electric field compared to gravity and viscosity [43, 44]. This is verified in Fig. 6.7b, d where the folding phenomenon first occurs on the liquid metal with higher surface tension near the graphite cathode. When the inner electrode is set as the anode, the edge of the circular ring-shaped liquid metal close to the outer cathode has a contracting trend due to its increased surface tension whose direction is tangential to the liquid metal surface. And there appear gaps with uniform symmetrical distribution on the edge of the ring-shaped liquid metal in the presence of external disturbances. It is due to the Rayleigh–Plateau fluid instability [45–47] that perturbations with a wavelength greater than a critical value (λ_c) will be amplified. Then the liquid metal is divided by the gaps into several equivoluminal parts with trapezium shape. As a liquid metal sphere located between the two electrodes is in a self-rotating state [17] due to its unbalanced internal pressure, it can be deduced that the divided parts are all in a state of self-circulation which is similar to that of Rayleigh–Benard convection cells [48–50]. Meanwhile, the liquid metal surrounding the inner anode has a spreading trend [21] due to the oxidative potential imposed on it [32]. And an inner ring is, thus, generated close to the trapezium-shaped parts. Figure 6.7e and f present motion diagrams of the liquid metal which correspond to Fig. 6.7b, c, respectively. As the inner electrode works as a cathode, however, the

surface tension of the liquid metal near the outer anode is too weak to form gaps on the liquid metal surface. And the generated dense folding pattern shown in Fig. 6.7d is quite different from that in Fig. 6.7c. Figure 6.7g presents clutter direction of the perturbations imposed on liquid metal corresponding to Fig. 6.7d.

As a magnetic field combined with the electric field is applied on the liquid metal, the latter will be subjected to a perturbative Lorentz force $\mathbf{F}$ which can be expressed as Eq. (6.4) [29]. Assuming the direction of $\mathbf{B}$ is normal to the substrate, then $\mathbf{F}$ is along the clockwise or counterclockwise direction viewed from the overlook to the circular ring-shaped liquid metal according to the right-hand rule [2]. Figure 6.8 shows the measured voltage–time and the current–time relationships of the liquid metal in the electromagnetic field and several typical patterns. It can be seen that there are two time periods in which the voltage is kept almost constant. In the first period (0.75–1.35 s), the voltage is 2.48 ± 0.01 V and the current is 0.74 ± 0.292 A. The liquid metal is in a state of rapid rotating with a bright surface which can be seen in Fig. 6.8b at time point 1 marked in Fig. 6.8a. It is due to that the Lorentz force imposed on the liquid metal is larger than the friction force which propels its rotation. In the second period (1.8–5.85 s), the voltage is 4.07 ± 0.059 V and the current is 1.56 ± 0.626 A. The electrolyte gets a bit turbid along with the emergence of many bubbles, which is attributed to the generation of oxide, oxygen, and hydrogen. The liquid metal deforms severely and presents a variety of different folding patterns. It should be pointed out that the patterns appear randomly, and the liquid metal suddenly stops its rapid rotating as the patterns appear. Figure 6.8c and d shows a high dense folding pattern and a dual concentric ring pattern which corresponds to time points 2 and 3, respectively. In addition, although the variation coefficients of the current in the two periods are similar (39.5 and 40.1%, respectively), the relative extreme difference in the second period (190.1%) is much larger than that in the first period (85.0%). It can be interpreted that with the increase of the voltage and the current between the two electrodes, the ever-increasing capillary force, oxide, and bubbles contribute to a larger friction force between the graphite electrodes and the liquid metal. When the friction force is greater than or equal to the Lorentz force, a variety of liquid metal patterns will appear due to the destabilizing effect. As the voltage drops below 2.5 V, the rapid rotating state of the liquid metal is regained. It reflects that the Lorentz force has an inhibition effect on the appearance of the patterns to the ring-shaped liquid metal.

To illustrate the formation and evolution processes of the liquid metal surface folding, Fig. 6.9 presented continuous snapshots of the pattern in about one second and the photographs [2]. At $t = 0$ s, the liquid metal rotates rapidly and even leaves the inner electrode due to strong centrifugal force. Then the folding pattern appears and gradually spreads over the top surface ($t = 0.24$ s) of the liquid metal. It becomes clear with the time ($t = 0.28$ s) due to the growth of the perturbations. Meanwhile, several small gaps appear at the outer edge of the liquid metal circular ring which is divided by these ones ($t = 0.24, 0.28$ and 0.32 s). The distance between the inner edge of the liquid metal circular ring and the inner electrode becomes larger ($t = 0.48$ s), and an inner thin ring appears between the outer liquid metal and the inner electrode ($t = 0.68$ s). The emerging ring becomes thicker and clearer with the time

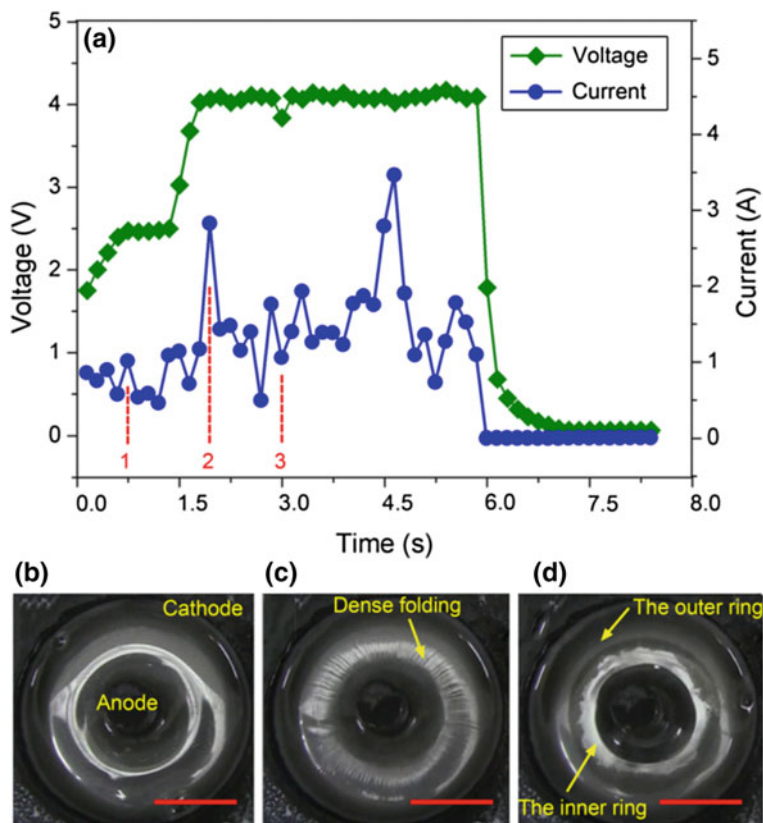


Fig. 6.8 **a** The voltage–time and current–time relationships of the circular ring-shaped liquid metal when the electrodes are electrified; Numbers 1, 2, and 3 represent $t = 0.75$, 1.9, and 3.0 s, respectively; **b–d** are three liquid metal patterns corresponding to the time point 1, 2 and 3 in **a**, respectively. The scale bars in **b**, **c**, and **d** are all 10 cm [2]. All pictures are reproduced with permission

($t = 0.72$ s), and it is gradually swallowed by the outer circular ring ($t = 0.76$ and 0.80 s). Subsequently, a new liquid metal ring reappears ($t = 0.88$ s) and is swallowed by the outer circular ring again ($t = 0.92$ s). Finally, the circular ring-shaped liquid metal returns to its fast-rotating state ($t = 1.04$ s). Here, the rheological behavior of the liquid metal is similar to that of the tide. It is the electrocapillary force that drives the liquid metal to flow toward the anode while it is the large surface tension to force the liquid metal to withdraw from the anode. The reason for the repeated emergence of the inner ring may lie in that the generated oxide on the surface of the liquid metal near the anode increases the friction force between it and the substrate. And this part of liquid metal is left behind to form the inner ring due to the large friction force when the whole metal fluid is withdrawn from the inner electrode. It is verified in the snapshot ($t = 0.88$ s) that there appear tearing traces on the outer edge of the inner ring.

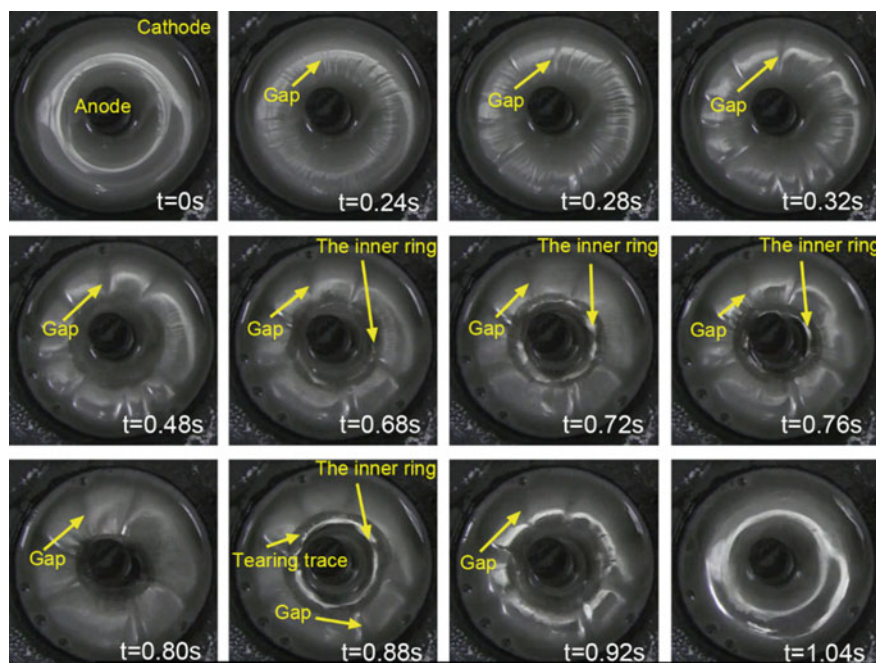


Fig. 6.9 The formation and evolution processes of the liquid metal surface folding patterns [2]. All pictures are reproduced with permission

Several different liquid metal patterns occurred in the experiments are recorded and presented in Fig. 6.10a where circular ring-shaped liquid metal with high-grade folding dense surface appears just like a folding fan [2]. It can also be divided into 20 parts (Fig. 6.10b), which look like the cross section of a corn, 5 parts (Fig. 6.10c), 4 parts (Fig. 6.10d), and 3 parts (Fig. 6.10e), respectively. Besides, the liquid metal can also be separated into two concentric circular rings such as a circular ring with a narrow ring inside (Fig. 6.10f), two circular rings both with high-grade folding dense surface (Fig. 6.10g), and a circular ring with a triangle inside (Fig. 6.10h). All these patterns take a property of axial symmetry, which is analogous to the hexagonal patterns presented in the Rayleigh–Benard convection which is induced by buoyancy-driven instability [51, 52]. Compared to the conventional fluid such as water, liquid metal owns much high conductivity and surface tension which are responsible for its unique behavior. The surface tension gradient on the liquid metal in an electric field plays the main role in the formation of various symmetric patterns of the liquid metal. Clearly, the present discovery would help to promote further investigation of the metal fluid mechanics.

Overall, a group of very unique liquid metal folding patterns can be induced by a pair of energizing graphite electrodes with concentric ring structure [2]. The driving force lies in the electrocapillary force thus involved. A wheel pattern with

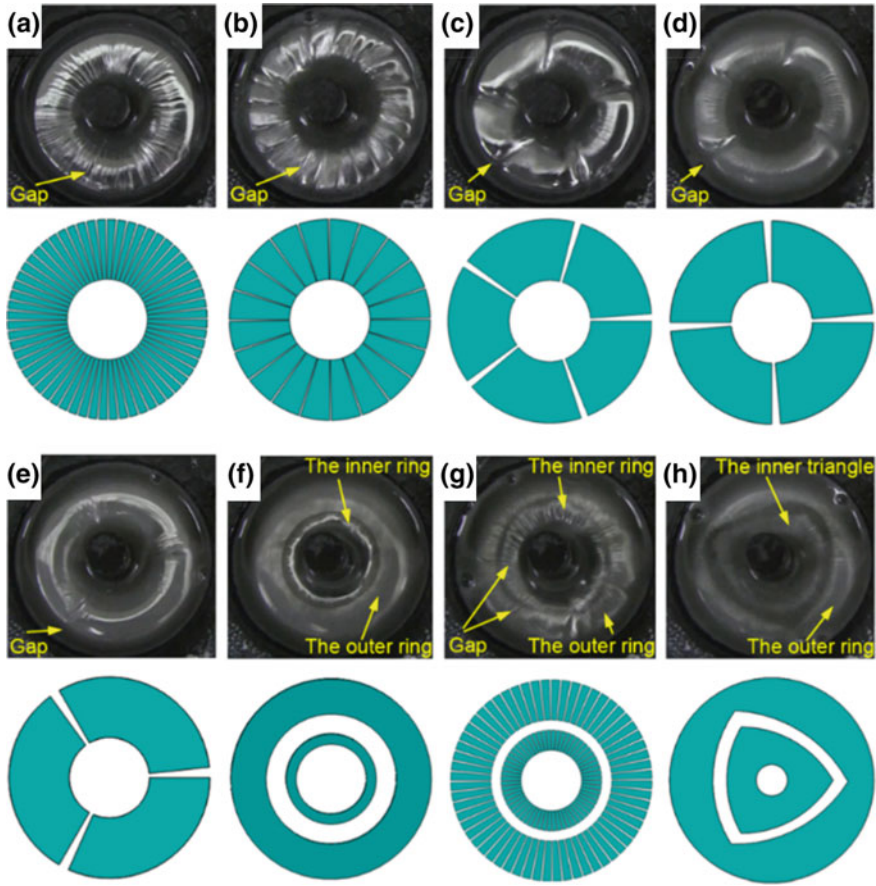


Fig. 6.10 Several typical types of approximate axisymmetric topographies of the liquid metal between the inner and the outer electrodes [2]. **a** A circular ring with high-grade folding dense; **b** A circular ring divided into 20 parts; **c** A circular ring divided into five parts; **d** A circular ring divided into four parts; **e** A circular ring divided into three parts; **f** A circular ring with a narrow ring inside; **g** Two circular rings with high-grade dense folding; **h** A circular ring with a triangle inside. The upper parts of **a–h** are real images of the liquid metal while the lower parts are schematic diagrams of the topography images in which the discrete parts represent the liquid metal. All pictures are reproduced with permission

surface folding can be observed when the inner electrode is used as the anode. As a magnetic field is added, the liquid metal will rotate around the inner electrode with changing patterns. Different types of approximate axisymmetric topographies appear randomly and the typical ones, however, can be classified. Such rheological property of the liquid metal is quite different from that of the conventional fluid. The mechanism can be attributed to the surface tension gradient on the liquid metal in

an electric field and the destabilizing effect. This finding on conductive liquid metal refreshes the basic understanding of classical fluid wave mechanics and will be of the important reference value for the design of future rotational liquid metal machines.

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Chapter 7

Self Fuelled Transformable Liquid Metal Machine



Abstract Synthetic self-fuelled motors, which can spontaneously convert chemical energy into mechanical activity to induce autonomous locomotion, are excellent candidates for making self-powered machines, detectors/sensors, and novel robots. The present lab (Zhang et al. in *Adv Mater* 27:2648–2655, 2004 [1]). discovered an extraordinary self-propulsion mechanism of synthetic motors based on liquid metal objects. Such motors could swim in a circular Petri dish or different structured channels containing aqueous solution with a pretty high velocity on the order of centimeters per second, and surprisingly long lifetime lasting for more than one hour without any assistance of external energy. The soft material liquid metal enables the motors to self-deform, which makes them highly adaptable for accomplishing tough missions in special environment. Interestingly, the motors work just like biomimetic mollusk since they closely resemble the nature by “eating” aluminum as “food”, and can change shape by closely conforming to the geometrical space it voyages in. From practical aspect, one can thus develop a self-powered pump based on the actuation of the liquid metal enabled motor. Further, such pump can also be conceived to work as a cooler. Apart from different geometrical channels, several dominating factors, including the volume of the motor, the amount of aluminum, the property of the solution and the material of the substrate etc., have been disclosed to influence the performance of the autonomous locomotion evidently. This artificial mollusk system suggests an exciting platform for molding the liquid metal science to fundamentally advance the field of self-driven soft machine design, microfluidic systems, and eventually lead to the envisioned dynamically reconfigurable intelligent soft robots in the near future. In this chapter, the typical behaviors and fundamental phenomena of the self fuelled transformable liquid metal machines were illustrated.

Keywords Liquid metal machine · Self fuelled robot · Biomimetic mollusk
Convergence · Divergence

7.1 About Self-fuelled Machine

As is well known, synthetic self-fuelled motors should move autonomously with an independent trajectory as if they have their own idea of a destination [2]. Potential technologies would pave the way for diverse applications ranging from targeted drug delivery [3, 4] to smart sensors [5–7]. Such motors are generally equipped with asymmetrical sensing and/or actuating elements, which can induce propulsion in liquid environment (e.g. water [8, 9], hydrogen peroxide [10–12], acids/bases [11, 13]). Nowadays, tremendous investigations on self-propelled motors have been performed with remarkable progress to achieve rather interesting artificial micro/nano-machines or large size robots. However, so far the macroscopic counterpart still remains a big mystery since it is generally difficult to obviate the requirement of external physical energy in order to generate sufficient mechanical momentum. Typically, to achieve controllable locomotion of a macroscopic object, external physical energies from the surrounding electromagnetic field [14–16], electric field [17, 18], or thermal gradients [19] should be employed to transform them into mechanical energy. This however may somewhat restrict the independence of the motors and make their actuation problematical once the external sources are inaccessible. In principle, the driving force must be increased by several orders approximately when scaling up the operational motors from nano-/micrometer to milli-/centimeter to overcome the resistance from the aqueous environment. It is noteworthy that the velocity, which usually refers to the velocity relative to the body length of the objects, is extremely sensitive to the size of the object [20]. Thus, for a macroscopic motor, it is often necessary to expedite the absolute velocity, and correspondingly, it requires a further stronger driving force. As such, it is challenging to actuate milli-/centimeter scaled objects with a velocity on the order of centimeters per second without any exposure of external stimuli.

The macroscopic motors which are external-energy independent have been perused over decades. Such motors can be classified into solid motors [21–23] and liquid motors [21, 24–26]. Under the macroscopic scale, the flexibility or rigidity influences the application of the material significantly. The macroscopic motors based on soft materials are capable of deformation, and thus they are competent for performing special missions under tough conditions. Most of the existing self-propelled liquid motors are organic droplets like 4-octylaniline [24], oleic anhydride [25], and aniline oil [26]. From an alternative, Zhang et al. [1] invented the room temperature liquid metals such as EGaIn (75% gallium and 25% indium) and Galinstan (68.5% gallium, 21.5% indium, and 10% tin) to fabricate radically different liquid motors. Regarding the perspective of materials, different materials own varied properties and merits, which render different performances and potential applications. The liquid metals own many favorable properties, including pretty large surface tension, desirable flexibility, high electrical conductivity and low toxicity in comparison with mercury [27], which make them promising for designing soft robot or microfluidic systems.

7.2 About Self-fuelled Liquid Metal Machine

In regard to the self-propulsion, it is ubiquitous for living organisms to move autonomously along with the consumption of their internally stored bioenergy. Inspired by these highly efficient living organisms, the currently exhibited self-fuelled motor based on liquid metal in milli-/centimeter scale successfully achieved the capability to “eat” a small aluminum (Al) flake as “food” and then move spontaneously in the aqueous solution without requesting any complex preparation or fabrication procedures [1]. When contacting Al with EGaIn or Galinstan in electrolyte solution for a while, Al is firmly stuck to the liquid metal since Al is vulnerable to be amalgamated by liquid metal. According to Rebinder’s effect, liquid metal alloy EGaIn or Galinstan would penetrate into aluminum, destroying the oxide skin on Al surface and leading to the activation of Al [28], which initiates redox reaction. Taking advantage of the chemical or electrochemical energy supplied by the reaction, the milli-/centimeter scaled liquid metal motor navigates itself in the aqueous solution for more than one hour with a pretty large and relatively constant velocity of 5 cm/s. More intriguingly, the shape of such motor is self-adaptive which can fully conform to the geometrical space it voyages in, closely resembling the behavior of a mollusk like living organism. For these reasons, we call the motor biomimetic liquid metal mollusk. Such artificial soft machine can swim not only in the free space like a Petri dish, but also can swim in different shaped channels. In addition, the liquid metal-based motor can work as a self-powered pump, which can be conceived to serve as a cooler to pump cold liquid. Overall, the performance of the motor is governed by several dominate factors, such as the volume of the motor, the amount of aluminum, the property of the solution and the material of the substrate. Apart from the surprising performance of such motor, what renders it different from the existing macroscopic motors is that the motor can be remedied by electric field due to controllability of the high surface tension and conductivity under the exposure of electric field when the self-propulsion is obstructed. Such versatile motor presents exciting possibilities for practical actuators and will significantly stimulate the way to design future biomimetic robot.

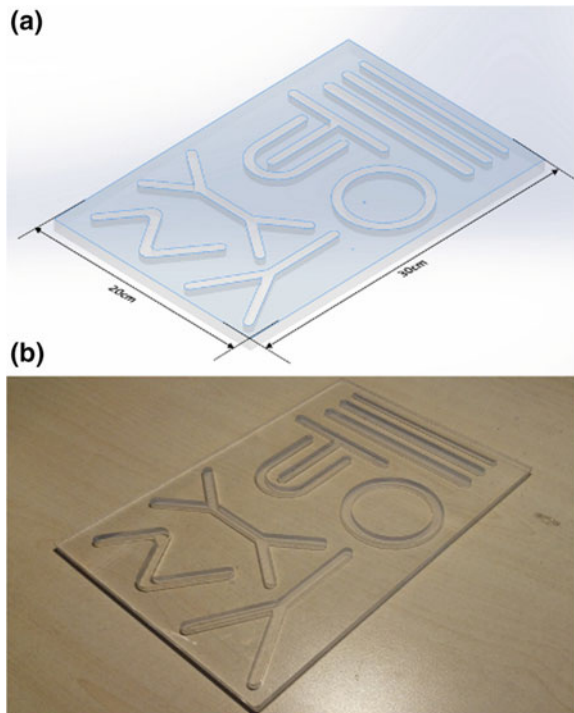
In the following, the presented results are mainly operated with sodium hydroxide (NaOH) solution since it provides the best performance. Some other chemical solutions such as sodium chloride (NaCl) solution, sodium carbonate (Na_2CO_3) solution could also work and have in fact been partially tried [29–31]. All the representative results are exhibited with EGaIn droplet, and similar results have already been demonstrated with Galinstan. The motor can swim in both free space like Petri dish and different geometrical channels.

7.3 Fabrication of Structures for Running Liquid Metal Machine

To illustrate the basic characteristics of the self-propelled locomotion of the liquid metal motor in different types of trajectories through feeding aluminum as fuels, Zhang et al. [1] designed and manufactured several channels with representative shapes elaborately, either straight or somewhat irregularly structured. There are totally four types of open-top channels adopted for the experiments: (1) Circular channel; (2) U-shaped channel; (3) Straight channel; and (4) Zigzag channel. Figure 7.1a depicts the designed shapes and sizes of these channels, and Fig. 7.1b shows the actually fabricated channels.

Figure 7.2 demonstrate the actual running of the liquid metal motor in such channels where it is found that the motor conforms well to the wall, no matter what its shape, structure or surface roughness is. This amazing behavior reveals the pretty high adaptability of the liquid metal mollusk when facing various situations.

Fig. 7.1 The size of the substrate and the shapes of several representative fabricated channels [1]. **a** The figure designed by the software SolidWorks 2012. **b** The manufactured entity by PMMA material. All pictures reproduced with permission



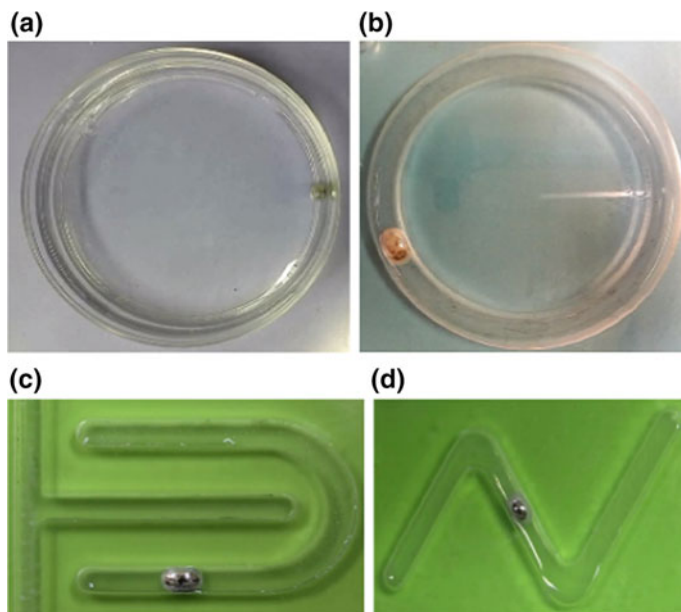


Fig. 7.2 Schematic for the running of a liquid metal motor in different channel structures [1]. **a** Free space in Petri dish. **b** Circular channel. **c** Hybrid channel with straight and semi-circular structures. **d** Zigzag channel. All pictures reproduced with permission

7.4 Locomotion of Liquid Metal Motor in Free Space of a Petri Dish

As has been clarified by our former work [1], the locomotion of the liquid metal motor is actuated in principle by the EGaIn-Al galvanic cell reaction. To perform the experimental tests, we adopted tweezers to pick up a small aluminum (Al) flake and attached it to the liquid metal EGaIn object, which looks just like feeding the mollusk. Both Al and liquid metal object are immersed in 0.25 mol/L NaOH solution in a Petri dish. After approximately one minutes, the contacting site between Al and EGaIn liquid metal starts galvanic cell reaction with bubbles generated under observation of a digital microscope. Al chemically reacts with NaOH solution which can be denoted by the following equation as:



This reaction can be observed that when Al is immersed in NaOH solution, small bubbles are slowly generated and depart from the surface of aluminum [1]. When Al starts to attach to the EGaIn droplet, the liquid metal droplet slightly flicks away due to its high surface tension. After several repeats of the attachment, Al and liquid metal droplet merge together and the reaction rate is accelerated with lots of bubbles

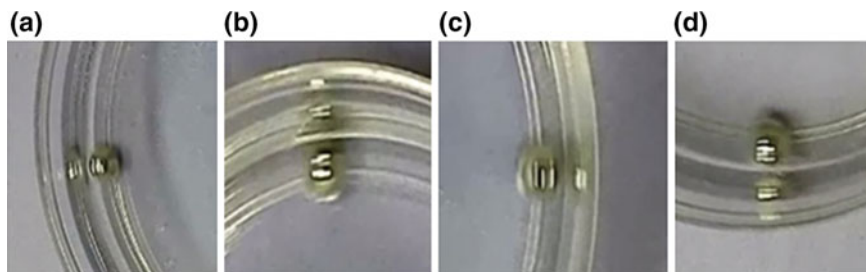


Fig. 7.3 Schematic for four positions of liquid metal motor running along the wall of the Petri dish [1]. **a** Left hand side wall. **b** Upper wall. **c** Right hand side wall. **d** Bottom wall. All pictures reproduced with permission

emerging from the solution. Simultaneously, the liquid metal motor starts to self-rotate on the lateral, which induces a flow field in the aqueous solution. The direction of the lateral motion is correlated to the position of Al-liquid metal reaction point, and such swirling behavior can be clearly indicated by the accompanied floating and moving bubbles. When the local self-rotation of the liquid metal droplet launches, the droplet starts to move along the wall of the Petri dish (Fig. 7.3), working similar to a mollusk. It looks the dish wall always serves as a supporting track for positioning the running metal (Fig. 7.3a–c). When stirred by glass capillary, such motor may change its locomotion direction temporarily but still keeps running along with the wall of the Petri dish autonomously after the removal of the disturbance. With different volumes of the liquid metal and aluminum fuel, various running speed and lasting time can be achieved. This can assist future design of a practical machine in the coming time.

7.5 Adaptability of Liquid Metal Mollusk to Various Surface Profiles

To observe the autonomous locomotion of the liquid metal-based motor in channels, experiments are conducted in different geometrical open-up channels, such as circular channel, U-shaped channel and zigzag channel [1]. The diameter of the droplet is a bit wider than the width of these channels, and thus the motor moves by squeezing itself into an ellipsoid shape, showing favorable flexibility, which indicates that such liquid motor achieves surprisingly strong adaptability to the environment.

Through repeated experiments, it could be found that the liquid metal motor owns rather outstanding adaptability to various channel profiles, either smooth or rough [1]. The capability of this soft machine appears much superior compared with rigid robots and deserves to be developed as practical machines in the near future. To characterize the surface property of the channels, the white-light interference profilometer is implemented to measure the surface roughness of the channels. The results were depicted in Fig. 7.4. It is found that the fabricated channel has in fact

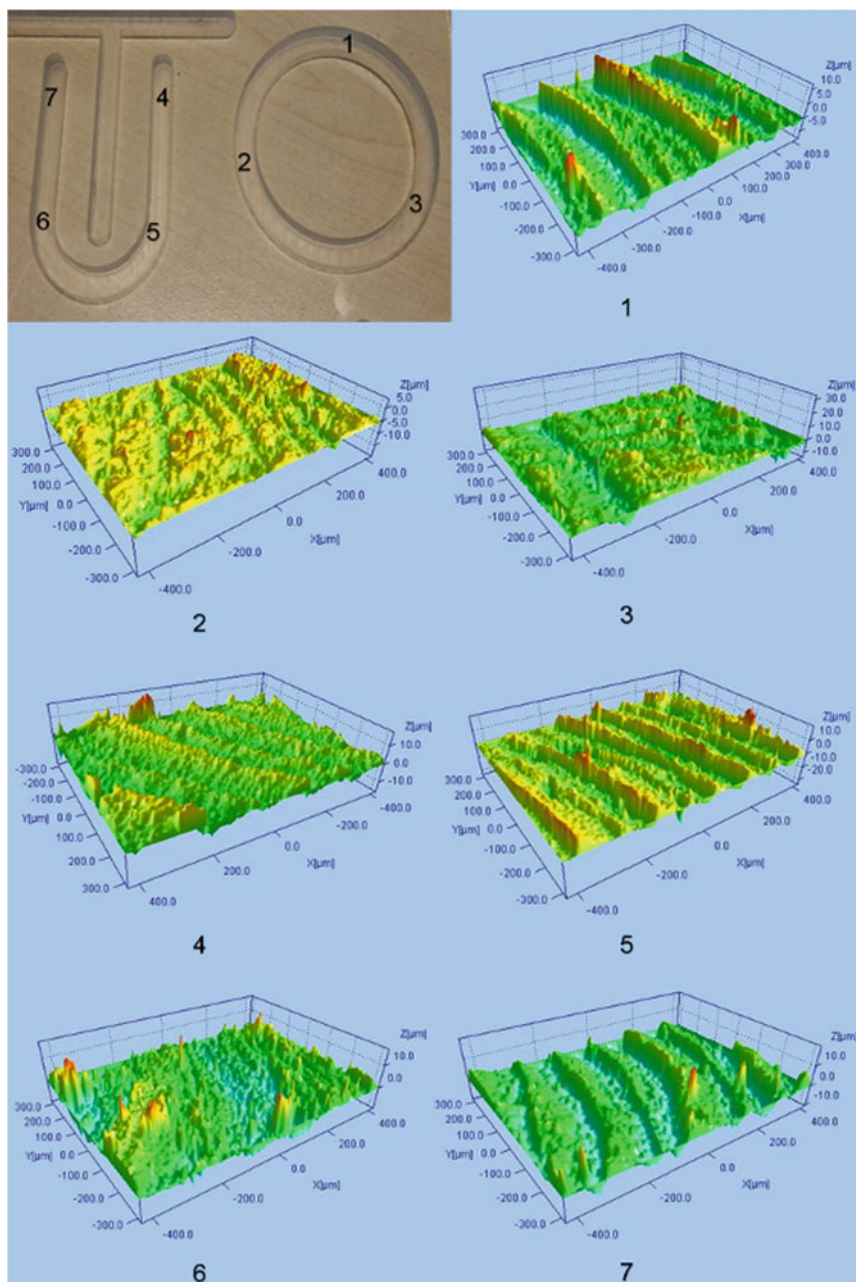


Fig. 7.4 The fabricated channel (upper left) and surface roughness of various sites along the PMMA channels [1]. Here, seven sites from 1 to 7 are marked to measure the surface characteristics. Pseudo-color is used to display surface topography more intuitively. All pictures reproduced with permission

intrinsically a relatively rough surface which is not as smooth as a Petri dish. For a rigid machine, it may be incapable of moving in such irregularly structured channel. But for the current liquid metal motor, it can easily overcome the barriers owing to its entirely soft property and extremely low rolling friction. As is measured, the average roughness of PMMA channel is about $S_a = 2 \text{ } \mu\text{m}$, and the straight section appears relatively smoother than that of the curved section of the channel. One surprising fact is that, the liquid metal motor runs smoothly throughout all these channels, even some surfaces of which are rather rough. Except for adapting to the surface property, the current liquid metal motor can also very well adapt to various structured channels, either straight or irregular. As is shown in the hybrid channel structure of Fig. 7.5 and zigzag channel in Fig. 7.6, when moving into different places with varied cross sectional channel, the liquid metal motor flexibly modifies its configuration so as to move smoothly across the corresponding site. The various ratios among these transient shapes or cross sectional areas can be rather large, which is hard to achieve otherwise by an ordinary rigid machine. This again demonstrates the unusual capability for the new biomimetic machine. Presented in Fig. 7.7, it depicts the transient motion velocity and displacement of the liquid metal mollusk when crawling within the zigzag channel. Clearly, due to the relatively large volume of the motor and the irregularly sized narrow channel, the moving speed here is much slower than that in the former case. Another reason of the slower velocity is that the trip is somewhat more challenging. Further, it is also very interesting to observe that, when the motor reaches the corner, it stays there for a short break without evident movement. Later soon, it resumes its motion activity again along the zigzag channel.

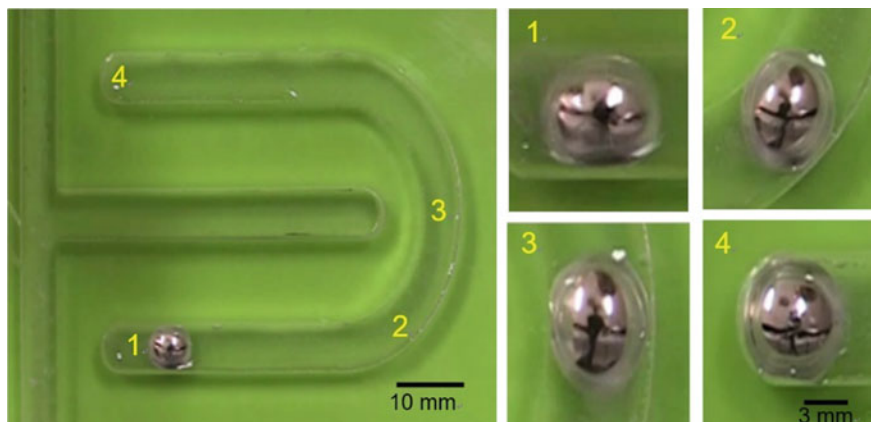


Fig. 7.5 Running of liquid metal motor and its respective configurations at four positions inside the hybrid structured channel [1]. Here, 1, 2, 3 and 4 refer to four positions that liquid metal motor is moving onto. All pictures reproduced with permission

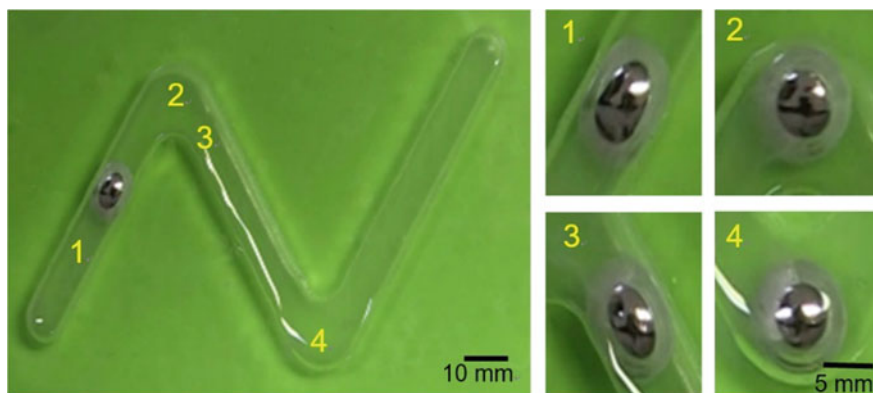


Fig. 7.6 Running of liquid metal motor and its respective configurations at four positions inside the zigzag channel [1]. Here, 1, 2, 3 and 4 refer to four positions that liquid metal motor moves into. All pictures reproduced with permission

Fig. 7.7 Moving velocity and displacement of liquid metal mollusk across the zigzag structured channel [1]. The sites where the velocity drops to zero are the corners for the motor to adapt itself to the changeable channel. Picture reproduced with permission

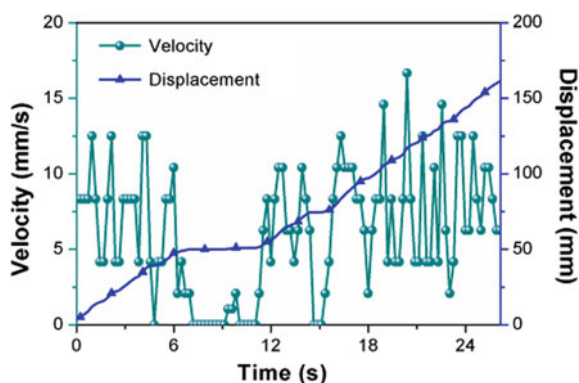


Figure 7.8a exemplifies a 60- μ L liquid metal droplet swimming autonomously in a circular Petri dish containing NaOH solution [1]. The wall of the dish attracts it apparently when placing the droplet in the dish. After attaching the liquid metal with an Al flake (measured about 0.012 g), the metal droplet starts to swim along with the wall continuously with an average speed of approximately 5 cm/s (about 10 body lengths per second), accompanied by the generation of bubbles. Theoretically, the velocity of the droplet motor is governed by the resistance f_v from the solution, the frictions from the substrate f_s and the wall f_w , the bubble thrust force f_b and electrochemical propulsion f_p (Fig. 7.8b). The velocity and displacement of this motor within 112 s (about 19 laps) are depicted in Fig. 7.8c, and the inset displays a velocity drop since there is a small upslope under the Petri dish. The lifetime of such self-propelled motor is more than one hour. The motor is capable of travelling stably and uni-directionally with a distance of over one hundred meters unless it is disturbed by a glass capillary, which is rare among the existing macroscopic motors.

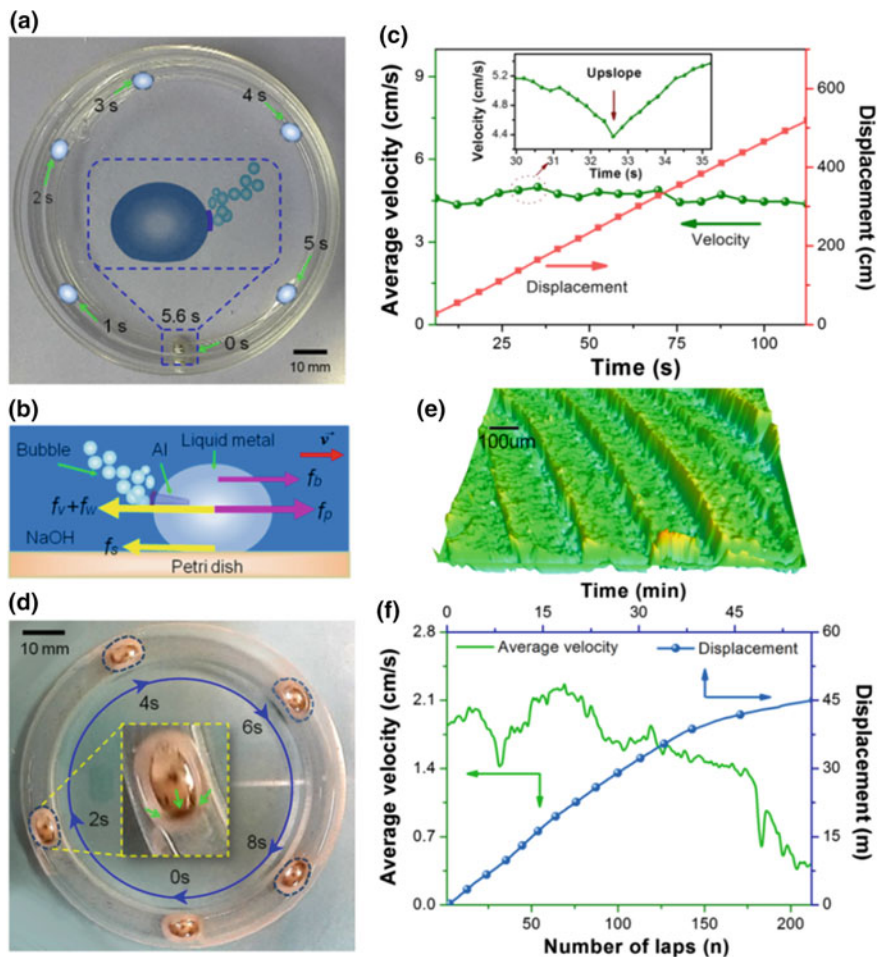


Fig. 7.8 Self-fuelled liquid metal motor running in a circular Petri dish and in a circular channel [1]. **a** Spatiotemporal evolution of the liquid metal EGaIn with 60- μ l volume in a Petri dish containing 0.25-mol/L NaOH solution. **b** Schematic of forces affecting the velocity of the motor. **c** Time-average velocity and time-displacement plots within 112 s for the liquid metal object in **a**. *Inset* is the velocity during one of the laps. **d** Spatiotemporal evolution of a 160- μ l EGaIn droplet in a circular open-top channel containing 0.25-mol/L NaOH solution. *Inset* shows the magnified image of the squeezed metal droplet, in which small bubbles are observed. **e** Surface topography of the circular channel measured by a white-light interference profilometer. **f** Lap-average velocity and time-displacement plots within an hour for the liquid metal in **d**. All pictures reproduced with permission

As is shown in Fig. 7.8d, a liquid metal-based motor swims in a circular channel [1]. Measured by the white-light interference profilometer, the surface of the channel is rather tough, as is indicated in Fig. 7.8e, which may lead to a larger friction and hinders the movement. However, the droplet exhibits exceptionally low rolling

friction due to the fluidity of the metal, and thus the motor still keeps running smoothly and continuously. In contrast to the motor in the Petri dish, the velocity of the motor in the channel appears somewhat slow due to larger volume, although the flow of the solution driven by the motor supplies as a positive feedback for the movement of the motor in turn. Figure 7.8f displays the average velocity per lap and the displacement of the larger motor in the circular channel within an hour. The motor swims for more than 212 laps (about 45 m) with an average velocity of 1.35 cm/s, while after about 50 min, the average velocity decreases obviously.

It looks the stop of the movement is not likely due to the depletion of Al. As was observed [1], after the motor stops moving, bubbles are still emerging from the surface of the liquid metal, and the reaction area takes up a larger surface, indicating the Al is not depleted. This mainly results from that the amalgamation of Al by the liquid metal renders the intact Al to form into lots of small fragments [1], and these fragments cover a larger surface of liquid metal, which breaks the asymmetry. Besides, as time goes on, bubbles accumulate on the surface of the metal and in the channel, which hinders the movement as well. The surface of the liquid metal at different times can be found as shown in Fig. 7.9.

7.6 Liquid Metal Motor Moving Autonomously in One-Way Channel

The behaviors of the liquid metal based-motor shown in Fig. 7.10 are observed in one-way open-top channels [1]. The diameter of the motor is a little larger than the width of these channels, which disconnects the aqueous solution. Therefore, the water level is higher on the side of the motion direction, which induces an unstable movement. Figure 7.10a depicts a metal droplet moving in a U-shaped channel. The U-shaped channel is divided into three sections (i.e. two straight pathways and one semicircular pathway) to evaluate the unstable velocity of the motor, as is shown in Fig. 7.10b. The velocity of the motor fluctuates as the liquid metal pauses to adjust the water level by its flexibility, especially in the section of the semicircular pathway where the direction of the spontaneous motion is also continuously adjusted. Compared with the average velocity in the circular channel, it is much slower in the one-way channel due to the difference of water level. When increasing the volume of the liquid metal to 170 μl , the much larger motor moves for about 40 mm and then turns round slowly, swimming back and forth in order to seek for balance.

A zigzag channel is elaborately fabricated with larger width around the corner to test the deformability of the motor according to different sizes in one channel (Fig. 7.10c). At first, the motor is squeezed and swims along with the straight pathway. When reaching the corner, it recovers to a sphere, pausing for a while as if it was thinking which way to choose. Meanwhile, the water level comes back to balance. Then the motor moves on again, willing to be squeezed to access the next narrow channel.

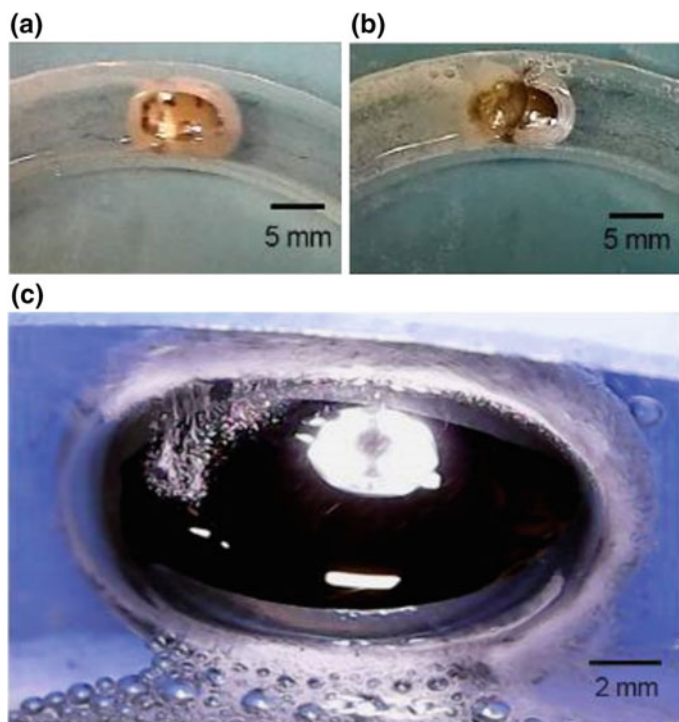


Fig. 7.9 The surface of the liquid metal at different times [1]. The 160- μ L EGaIn motor moves in a circular open-top channel containing 0.25 mol/L NaOH solution. **a** The motor moves at 10 min. **b** The motor moves at 52 min. **c** The motor stops moving at 70 min. All pictures reproduced with permission

7.7 Working Mechanism for Self-fuelled Liquid Metal Motor

For more details on the running mechanism of the mollusk machine, a digital microscope is employed to observe the nearby flow around the liquid metal induced by the lateral self-rotation of the motor and the bubble generation when the metal droplet is fixed at a certain site [1]. With the indication of the bubbles, the velocities and the flow direction of the aqueous solution in different area of flow field are clearly demonstrated, as is shown in Fig. 7.11. The solution along both the front (Fig. 7.11a) and rear (Fig. 7.11b) of the liquid metal motor flows anticlockwise. And at further distance away from the liquid metal, the flow rate slows down gradually. Additionally, some bubbles depart from the rear of the liquid metal motor where the Al is attached.

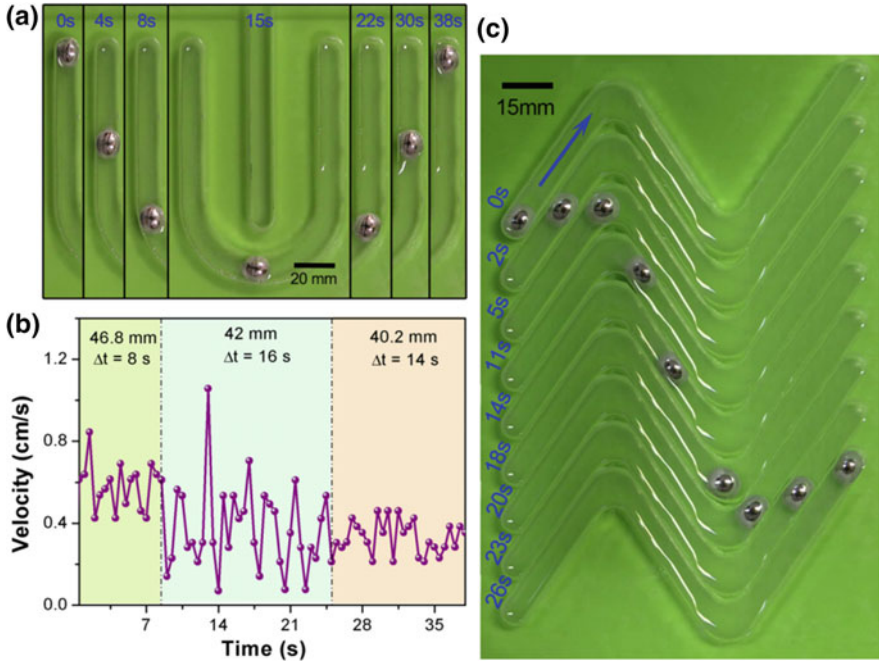


Fig. 7.10 Liquid metal motor moving autonomously in one-way channel containing 0.25-mol/L NaOH solution [1]. **a** Sequential snapshots of the motion of a 130- μ l EGaIn droplet in a U-shaped open-top channel. **b** Time-velocity plots for the liquid metal in **a**. The U-shaped channel is divided into three sections: two straight pathways and one semicircular pathway. **c** Sequential snapshots of the motion of a 150- μ l EGaIn motor in a zigzag open-top channel. All pictures reproduced with permission

7.7.1 The Resistance from the Solution to Overcome for the Actuation

It is inappropriate to use Stokes law to characterize the driving force for the droplet in the Pertri dish to move since the Reynolds number for the current flow ranges from 240 to 290. The real resistance is larger than the calculation based on Stokes law [1]. Theoretically, the resistance F for a sphere moving in fluid can be expressed as follows:

$$F = C_D \frac{1}{2} \rho v^2 A \quad (7.2)$$

where C_D is resistance factor, ρ is density of the fluid, v the velocity of the sphere relative to the distant fluid, and A is the meeting area of flowing, which equals to πr^2 (r is the radius of the sphere) for a sphere. From Eq. 7.2, one can get the resistance factor:

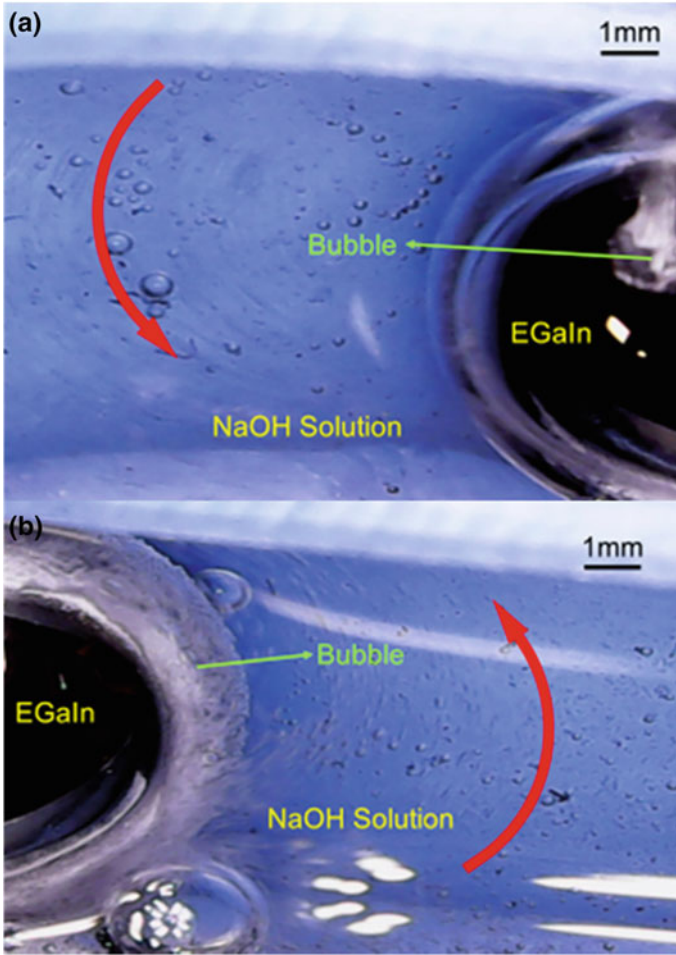


Fig. 7.11 The flow field of the solution around the liquid metal motor displayed by the trajectory of the bubble departure [1]. **a** The flow field on the left hand side of the liquid metal. **b** The flow field on the right hand side of the liquid metal. All pictures reproduced with permission

$$C_D = \frac{F}{(\rho v^2/2) \pi r^2} \quad (7.3)$$

For a sphere moving in the fluid, the Reynolds number Re is calculated as follows:

$$Re = \frac{2r\rho v}{\mu} \quad (7.4)$$

where r is the radius of the sphere, ρ is density of the fluid, v is the velocity of the sphere relative to the distant fluid, and μ is the viscosity of the fluid. Under the condition that $Re < 1$, according to the Stokes law, the resistance is:

$$F = 6\pi\mu rv \quad (7.5)$$

According to Eqs. 7.3–7.5, the resistance factor is expressed as follows:

$$C_D = \frac{24}{Re} \quad (7.6)$$

However, when $Re > 1$, the resistance obtained based on Eq. 7.5 is smaller than the real resistance. There is an empirical formula by fitting to experimental data to calculate the resistance factor [2], i.e.

$$C_D = \frac{24}{Re} + \frac{6}{1 + \sqrt{Re}} + 0.4, \quad 0 \leq Re \leq 2 \times 10^5 \quad (7.7)$$

The maximum error calculated by Eq. 7.7 is 10%. The Reynolds number is much less than 2×10^5 , thus Eq. 7.7 is applicable for the calculation of the resistance. Based on Eqs. 7.2, 7.4 and 7.7, which are all applicable when $Re > 1$, one can get that the resistance for a sphere is as follows:

$$F = 6\pi\mu rv + \rho\pi r^2 v^2 \left(\frac{3}{1 + \sqrt{\rho vr/\mu}} + 0.2 \right) \quad (7.8)$$

Comparing Eq. 7.8 with Eq. 7.5, one can get that when $Re > 1$, using Eq. 7.5 to estimate the resistance induces that the calculated result deviated from the fact, and the resistance calculated from Eq. 7.5 is smaller than that based on Eq. 7.8.

Therefore, from Eqs. 7.5 to 7.8, when the motor size scales from nano-/micrometers to milli-/centimeters, the resistance for the motor to overcome increases 3–6 orders under no consideration of velocity. However, as the reported velocity is generally relative to the body length, the absolute velocity for a macroscopic motor is larger than that for a microscopic motor. In conclusion, the driving force for a motor in milli-/centimeter is several orders larger than that for a motor in nano-/micrometer.

7.7.2 The Mechanism of the Autonomous Motion of Liquid Metal Motor

According to the experiments, there are some bubbles departing from the liquid metal, which can generate an opposite force to thrust the liquid metal forward [1]. The bubble recoil facilitates the motion. The addition of Al breaks up the symmetry of the liquid metal, which further facilitates the motion in two aspects. On the one hand, according

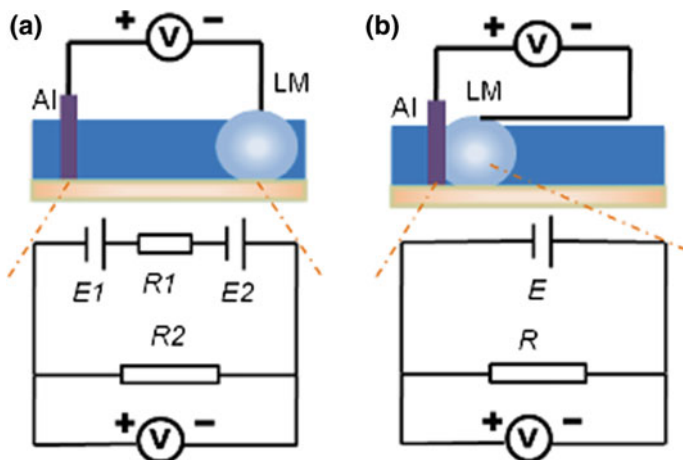


Fig. 7.12 Two different ways to actuate the liquid metal motor [1]. **a** The equivalent circuit when the liquid metal is separated from Al. The separation renders an extra resistance R between two metals. **b** The equivalent circuit when the liquid metal is contacted with Al. The contact renders the two metals to consist of a galvanic cell, which accelerates the electrochemical reaction. All pictures reproduced with permission

to Rebinder's effect, liquid metal EGaIn or Galinstan would penetrate into aluminum, destroying the oxide skin on Al surface and leading to the activation of Al [3]. The activation of Al makes it react with hydroxide ions more rapidly and efficiently. Such reaction results in the electro-migration of hydroxide ions in the electrical double layer and the electro-osmotic flow of water molecules [4], which generate a momentum equivalent to the water motion. On the other hand, the distribution of the charges across the EDL is altered and a potential gradient is generated along the liquid metal surface, which induces an imbalance of the surface tension on the liquid metal and actuates the metal droplet. Unlike the previously investigated case where external electricity is applied, the electricity in the present system is supplied by the electronegativity property of the Al-liquid metal, and the internal electricity driven motion is more efficient, since the voltage is almost entirely applied on the liquid metal itself (Fig. 7.12). But in former case, most of the voltage is in fact loaded on the electrolyte which is rather resistive thus the efficiency is not very high. Both the potential difference and electrical current are increased due to the contact between the Al and the liquid metal, which induces a higher efficiency for bipolar electrochemical reaction.

The Reynolds number of the motor in the dish is from 240 to 290, and thus the fluid flow in the rear is "Karman Vortex Street". In contrast to the Reynolds number of the motor in the dish, it is much smaller for the motor in the closed loop since solution flows along with the motor, which results in less relative velocity [1]. Therefore, it is observed that the flow field in the front and the rear of the motor in the circular channel is quite stable (Fig. 7.13a). During the autonomous movement, lateral motion

is evoked on the surface of the liquid metal due to convective flow (Fig. 7.13b), which renders the droplet to exhibit exceptionally low rolling friction from the substrate and facilitates the movement. However, the driving force for a milli-/centimeter motor to overcome the resistance from the solution is several orders larger than that for a micro-/nanomotor, while the above liquid metal droplets move autonomously only by the attachment of a small Al flake. Thus, it is of great importance to figure out the mechanism of the self-propulsion here. It is initially speculated that bubble recoil and the bipolar electrochemical reaction induce the movement synergistically. Therefore, the mechanism for the self-propulsion can be demonstrated from two aspects.

It is well-known that Al can be chemically dissolved in NaOH solution spontaneously, generating hydrogen bubbles. According to the observation, bubbles spiral and depart from the Al-covering site in the direction opposite to the motor motion, which seems like that the actuation is subject to the bubble recoil [1]. Comparative experiments were conducted to manifest the role of liquid metal for the bubble recoil, in which an Al bead with a diameter of 4 mm is partially coated with plastic adhesive tape and deposited in NaOH solution. However, bubbles are observed on the uncoated surface without occurrence of the motion. NaOH solution with higher concentration accelerates the bubble generation, but the sphere stays still, demonstrating that the force from the bubble recoil is insufficient to actuate the autonomous locomotion of a rigid bead. In contrast, when attaching Al flake to the liquid metal, the liquid metal embrittlement of Al shifts the charges on the Al surface to more negative values (Fig. 7.13c), and this biased condition dramatically promotes the spontaneous redox reaction between Al and the NaOH solution, producing much more hydrogen bubbles than the reaction without liquid metal. It is noteworthy that heat is released due to the exothermic Al ion hydrolysis reaction, which forms a positive feedback to accelerate the generation and release of bubbles in turn [32]. The acceleration of bubble generation and release by liquid metal renders the force from bubble recoil much more significant.

Apart from the increased bubble recoil force, the bipolar electrochemical reaction induced by the involvement of liquid metal may also play an important role for the actuation [1]. The Al/liquid metal system forms a galvanic cell: Al is the cathode and liquid metal works as the anode. In NaOH solution, Al reacts with hydroxide ions, inducing the electromigration of hydroxide ions in the electrical double layer and the electro-osmotic flow of water molecules (Fig. 7.13d), which generates a momentum equivalent to the water motion. Additionally, the dissolution of Al on the cathode renders Al to lose electrons, generating electrokinetic propulsion by the internal electron flow from Al to liquid metal. Under the equilibrium state, gallium reacts with the alkali solution slowly, producing gallates like $[\text{Ga}(\text{OH})_4]^-$, which makes the surface of gallium negatively charged and cations accumulated nearby, and thus the electrically charged interface forms into a uniform diffuse electrical double layer (EDL) (Fig. 7.13d). According to Lippmann's equation, the relationship between the surface tension and the potential difference across the EDL can be characterized as $\gamma = \gamma_0 - \frac{1}{2}cV^2$, where γ is the surface tension, c the capacitance of electric double layer per unit area, V the potential difference across the electrical double layer (EDL), γ_0 is the maximum surface tension when $V = 0$ [33]. Presumably, the

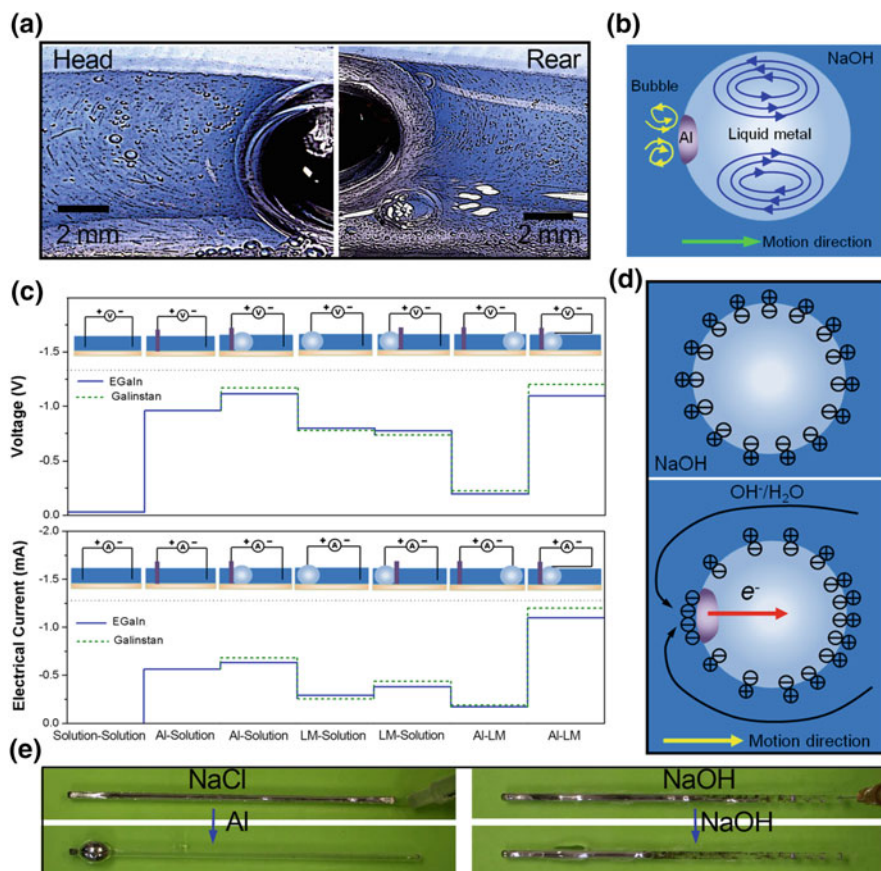


Fig. 7.13 Working mechanism for the self-fuelled liquid metal motor [1]. **a** The flow field of the solution in the channel induced by the motor. The snapshots are sharpened by the digital image processing to show more details. **b** Schematic of the lateral motion of the liquid metal and bubble departure. **c** Average voltage and electrical current measured by AVOMeter. The result is approximate as the value is not constant during the reaction. The symbol "LM" denotes liquid metal. **d** Schematic of the electromigration and EDL alteration. **e** The alteration of surface tension induced by NaCl solution, activated Al and NaOH solution. Both the concentrations of NaCl solution and NaOH solution are 0.2 mol/L. The Al flake is activated by liquid metal in advance. All pictures reproduced with permission

electrons flowing internally from Al to the liquid metal preferentially deoxidate the oxidized gallium near the Al, which alters the distribution of the charges across the EDL, leading to the generation of a potential gradient along the liquid metal surface. The alteration of the EDL induces an imbalance of the surface tension on the liquid metal. As is shown in Fig. 7.13c, the potential difference is smaller at the rear (near Al) than that at the head, and thus the surface tension is lower at the head of the droplet. Following the Young-Laplace equation, the pressure difference p across the

solution and the liquid metal droplet can be expressed as $p = \gamma \cdot \frac{2}{r}$, where $1/r$ is the curvature of the droplet surface. Therefore, the imbalance of the surface tension induces a pressure difference between the rear and the head, which produces a thrust to drive the droplet toward the head.

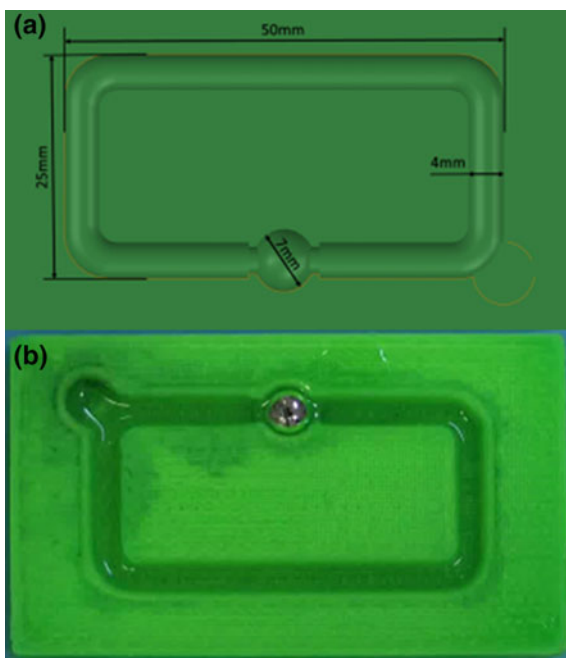
To demonstrate that the bipolar electrochemical reaction affects the surface tension and induces the locomotion, further comparative experiments were carried out [1]. The liquid metal is filled to a straight open-top channel at the half height in advance, and is exposed in ambient air to oxidize fully. The color of the metal is turned from metallic luster into dull gray. The formation of the solid oxide layer reduces the surface tension significantly. When adding some NaCl solution in the channel, the liquid metal stays still (Fig. 7.13d). As an activated Al flake is attached to one end of the metal, the liquid metal contracts swiftly from the Al-existing end to the other end, forming into a sphere and recovering metallic luster, which indicates that the oxide gallium is reduced by the activated Al and the reduction preferentially occurs near the Al site, recovering the surface tension in sequence. If the NaCl solution is replaced by the NaOH solution, the oxide layer is removed by NaOH solution directly. It is observed that the liquid metal contracts for half length, and it is much slower than that by the addition of activated Al. More NaOH solution is added to the channel, but the rest liquid metal does not continue to contract. With the attachment of the activated Al, the rest liquid metal forms into a sphere instantly, which illustrates that the bipolar electrochemical reaction changes the surface tension more evidently than chemical dissolution of the oxide layer.

7.8 Pumping Effect of EGaIn Motor

For a better demonstration of the pumping effect of the liquid metal motor in a practical device, Zhang et al. [1] further designed and fabricated a closed-loop open-top channel with Poly Lactic Acid (PLA) materials, as shown in Fig. 7.14. Such channel is designed by the software SolidWorks2012 and then printed by a 3D printer. The EGaIn mollusk is constrained by the wall of the droplet seat chamber, and the channel contains 0.2 mol/L NaOH solution for reaction. The sphere chamber connects with the channel on its two sides, which consists of the closed loop. Another semicircular chamber is designed to facilitate the addition of the ink. Droplets of ink are added to exhibit the pumping effect. It takes about 22 s to pump the ink for one lap. The sectional area of the solution is about 10.28 mm², and the overall length of the channel is about 125 mm. Therefore, it can be estimated that the flow rate of such self-powered pump is over 50 mL/s, which is quite high for pumping liquid. The pumping direction can be altered through stirring the liquid metal motor by a glass capillary, which mainly changes the relative position of the Al attachment.

The lateral motion behavior of the current liquid metal motor offers many opportunities for developing future robot machine. One of such typical applications is to directly develop the running sphere as a liquid pump [1], which should be the first ever self-powered one. A series of experiments were thus performed to demonstrate

Fig. 7.14 The size and the shape of the printed closed-loop channel [1]. **a** The picture is designed by the software SolidWorks 2012. **b** This picture refers to the manufactured entity. The 70- μ l EGaIn droplet seating in the chamber works as a pump. All pictures reproduced with permission



its role in the fluidic area. Exhibited in Fig. 7.15 are sequential snapshots for showing the pumping effect of an EGaIn motor with 8 mm width in the PMMA channel containing NaOH solution (0.2 mol/L) inside. It can be observed that, when a small bit of Al is fed to the liquid metal, the solution around the liquid metal mollusk flows rather quickly. In order to clearly display such fluidic behavior, a droplet of ink is added to demonstrate the pumping effect and flow field. As it works, the dark ink attenuates in just less than a half second. Depending on an actual need, various pumping velocity can be obtained through justifying the dosage enabled by the liquid metal, the Al and the surrounding solution etc.

Meanwhile, it is noteworthy that in contrast to the nearby flow, the far end flow runs somewhat different. Two vortexes spin around the liquid metal, while a distant stream flows anticlockwise, as is indicated in Fig. 7.16. This phenomenon may be resulted from the asymmetrical rotational direction of the two vortexes [1]. From the images, it can be found that the ink is dissolved into the solution very quickly. Such effect in fact serves rather well as a new way to induce chaotic advection, which can be utilized to fabricate novel micro-mixer in the near future.

Overall, as is shown in the above figures, there are two different parts on the surface of the liquid metal motor: One has a black and dim surface, which refers to the site Al attaching to the liquid metal, while the other part has a polished surface, through which the liquid metal flow can be observed. At the juncture of these two parts, there are some bubbles generated which are soon taken away by the rapid flow.

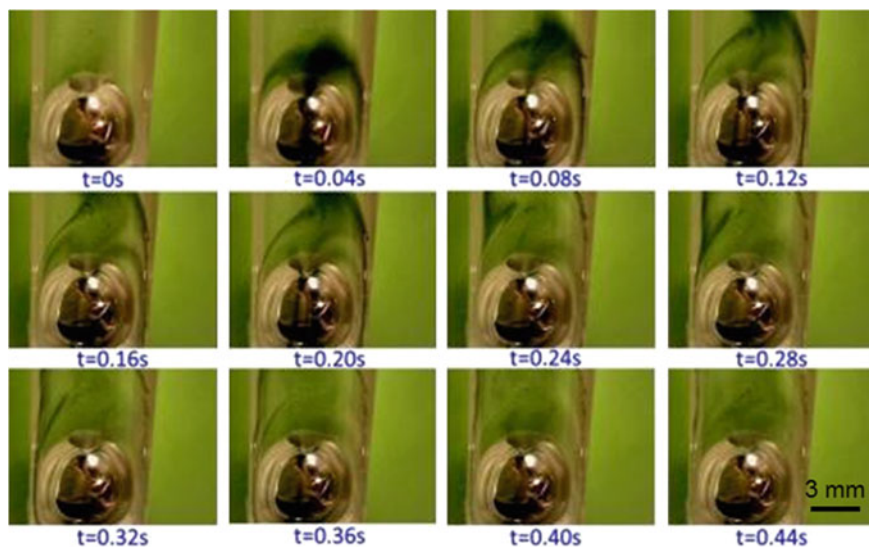
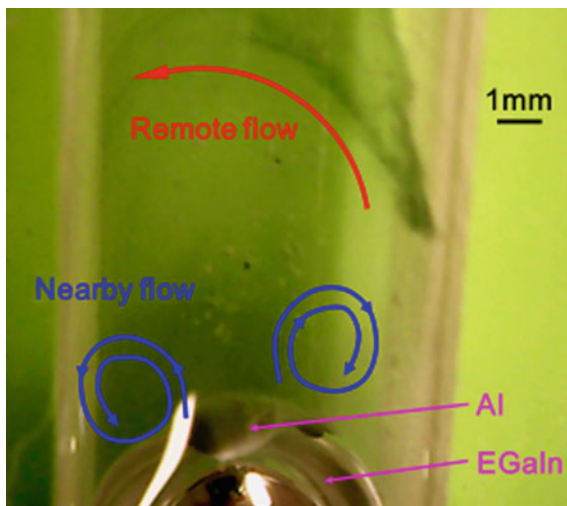


Fig. 7.15 Sequential snapshots for the pumping effect of an EGaIn motor [1]. The volume of the liquid metal is 120 μl , and the concentration of NaOH solution is 0.2 mol/L. All pictures reproduced with permission

Fig. 7.16 Snapshot for the flow direction of the solution induced by the motion of the liquid metal motor [1]. The volume of the EGaIn motor is 120 μl , and the concentration of NaOH solution is 0.2 mol/L. Picture reproduced with permission



The self-powered motors present exciting possibilities for sensors and actuators in practical applications [1]. Here, the self-powered pump is exhibited with the motor playing the core role as an actuator. As is well-known, the integration of small-scale pumps is hampered by rather complicated fabrication procedures or input power. For this purpose, the self-powered liquid metal motor is deposited in a closed-loop open-

top channel printed by a 3-D printer and containing NaOH solution (Fig. 7.17a). It is estimated that the flow rate of such self-powered pump is over 50 mL/s, which is quite high for pumping liquid. Additionally, the direction of the flow is dominated by the location of Al and the local self-rotation of liquid metal. Figure 7.17a, b respectively show that, the motor pumps the solution counterclockwise and clockwise as desired. The flow of the solution and bubbles around the liquid metal captured by a digital microscopic are exhibited in Fig. 7.17c. Switching on the light source equipped on the digital microscopic, the bubbles and rotation direction of the solution around the liquid metal are observed more obviously (Fig. 7.17c). With the removal of the light and addition of an ink droplet, it is observed that ink passes through the metal droplet from one side of the droplet seat (Fig. 7.17c), demonstrating that the solution is pumped to the other side rather than freely diffused. Further, the pump actuated by the self-powered motor can also be conceived to run as a cooler, as is shown in Fig. 7.17d, pumping cold solution to dissipate heat. Such self-fuelled pump without any trigger of external sources leads to a highly flexible self-supporting pump system, and no sophisticated fabrication is involved, which is almost the simplest structure and energy element ever developed so far. Therefore, more practical applications based on such self-fuelled motor are deserved to be explored.

The unusual capabilities and lifetime of the liquid metal-based motor are very surprising [1], which are hard to simulate otherwise by using conventional rigid materials. This finding opened an important way for making biologically like soft machine. Meanwhile, it also raised a series of intriguing fundamental or practical issues for further investigation in the area. Clearly, many critical sciences are still lying behind. To investigate influence of different factors on the performances of the motor, lots of experiments are worth of conducting. The volume of the metal droplet affects the velocity significantly, since velocity is extremely sensitive to the droplet for the autonomous locomotion. The optimal amount/ratio of Al is determined by the volume of the metal droplet, which affects the lifetime of the motor in some degree. As aforementioned, the cease of the movement results from the covering of Al fragments rather than the depletion of Al. On the one hand, larger amount of Al generates more fragments, covering more surface of the metal and breaking the asymmetry. On the other hand, if the reaction area is too large, the influence of the priority on electron reduction is not obvious, which may reduce the imbalance of the surface tension and is not beneficial to actuate the droplet. Therefore, more Al does not mean faster speed or longer life span of the motor. The aqueous solution has a great impact on the movement of the motor. In contrast to the running implemented in NaOH solution, experiments in NaCl or Na_2CO_3 solution exhibits a much shorter lifetime. In NaCl or Na_2CO_3 , the activation of Al enables Al to react with water, generating the sediment aluminum hydroxide ($\text{Al}(\text{OH})_3$), which is attached to the surface of the liquid metal and hinders the further reaction. However, it is doubtful in Na_2SO_4 solution as no successful experiment is achieved in such neutral solution. Therefore, the property of the solution is pending to be figured out to acquire the best efficiency and thus expand the survival condition range of the motor. Besides, the higher temperature of the solution facilitates the initiation of the motor, but the quantitative relationship between the temperature and the performance deserves

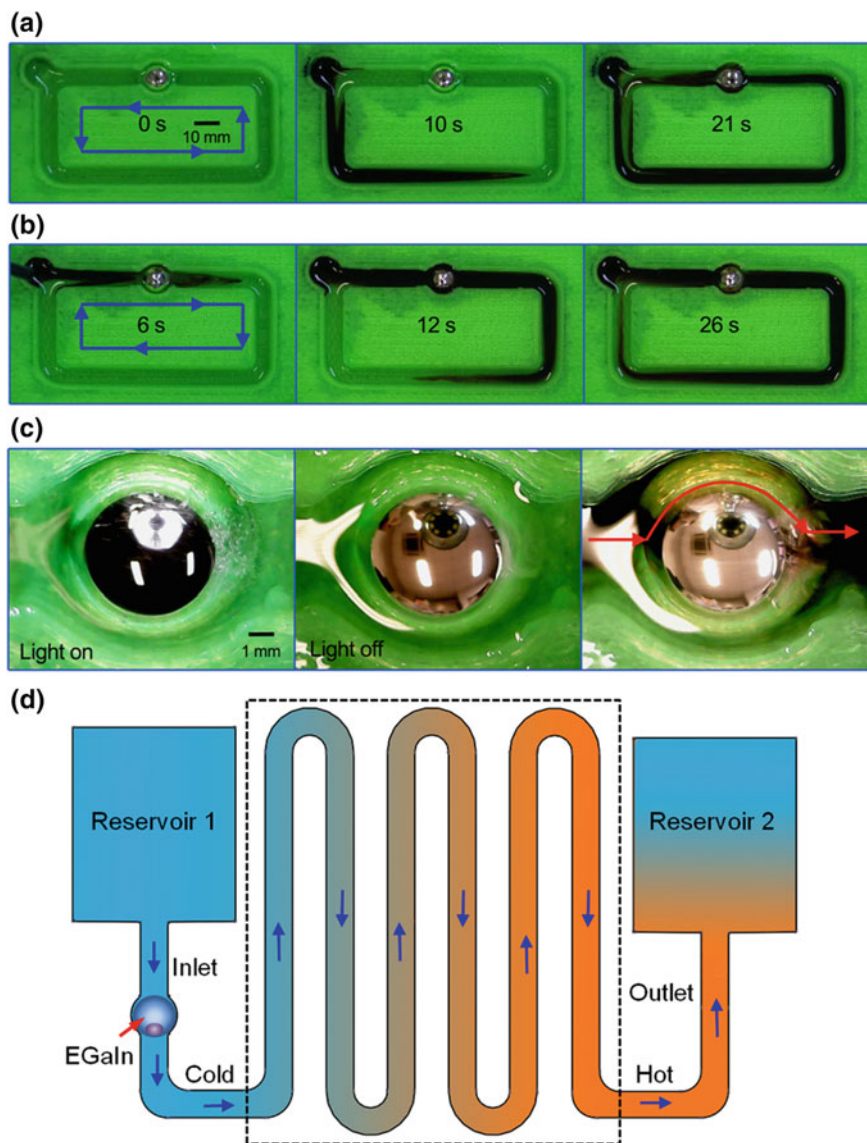


Fig. 7.17 A pump based on self-fuelled liquid metal motor in a closed-loop open-top channel [1]. An EGaln motor with 70- μ l volume is seated in the channel filled with 0.2 mol/L NaOH solution. A droplet of ink is added to indicate the direction of the flow. **a** Sequential snapshots for the counterclockwise flow of the solution. **b** Sequential snapshots for the clockwise flow of the solution. **c** Snapshots for the EGaln droplet by a digital microscope. The arrows denote the flow direction. **d** Schematic for the self-fuelled pump to work as a cooler. All pictures reproduced with permission

further study. Clearly, the performance of the motor is influenced by the container substrate evidently. In the above experiments, the Petri dish is made of polystyrene (PS), and the channels are made of polymethyl methacrylate (PMMA), which is easy to be fabricated by computer numerical control (CNC) machine. Experiments are also conducted in Petri dish made of high borosilicate glass (HBG) and polypropylene (PP). The PS substrate is vulnerable to be scraped, and the scrapes would hinder the movement obviously. In the PMMA channels, bubbles basically did not accumulate in the preliminary stage. However, after about 45 min, the movement starts to slow down and bubbles accumulate in the channel obviously. The observations in the dish made of HBG and PS are similar. In contrast to the PS substrate, the HBG substrate is much more durable, since it is not easy to leave scrapes. When carrying out the experiments on the PP substrates, a failure is encountered since the bubbles are accumulated on the surface. Furthermore, other species of the liquid metal as well as the fuel can also be sought to obtain more generalized motor. All these issues are worth of pursuing for a comprehensive understanding of the new soft machine in the coming time.

Overall, in the above demonstrated self-powered motor based on liquid metal cooperated with a small Al flake fuel, it could swim swiftly in Petri dish or different geometrical channels containing aqueous solution at a pretty high velocity, up to centimeters per second [1]. The motor sustains its unidirectional self-movement for more than one hour without the involvement of external energy. The soft material liquid metal enables the motor to self-deform according to different conditions, which makes it more adaptable for specific task. Combining the theory with experiments, the mechanism for the self-actuation has been illustrated. Overall, the force from the bubble recoil and the imbalance of surface tension induced by the bipolar electrochemical reaction serve as the driving force to overcome the resistance from the surrounding solution, propelling the liquid metal droplet to move autonomously. Additionally, a self-powered pump, which can be conceived to work as a cooler, is achieved based on the actuation of the liquid metal-based motor. Through a series of comprehensive experiments, several dominate factors including the volume of the motor, the amount of aluminum, the property of the solution and the material of the substrate, have been clarified to influence the performance of the autonomous locomotion evidently. The self-fuelled motor enables the soft material liquid metal to be rather promising to fundamentally advance the field of self-motion in robot design, microfluidic systems and reconfigurable intelligent machines in the near future.

7.9 Autonomous Convergence and Divergence of Liquid Metal Vehicles

Conventional rigid machines, even biological systems in nature, generally do not own the capabilities like autonomous convergence or divergence as required. Such extraordinary behavior can be realized by the liquid metal material machine generated

and fuelled by an aluminum flake to initiate its locomotion like a running vehicle in an open-top circular channel containing NaOH solution [34]. With varied velocities, the disperse liquid metal vehicle, chasing the one in front of them, is capable of entirely coalescing with the slower ones without leaving any gap while keeping wriggling forward. If breaking this assembled big machine into several separate smaller vehicles, each one of them still resumes its running state along the original track. This capability of liquid metal machine offers considerable opportunities for constructing self-reconfigurable soft robots in the near future.

Zhang et al. [34] managed to make several liquid metal vehicles swim in the open-up circular channel spontaneously and demonstrated a series of unusual self-assembly phenomena that such separately chasing vehicles can autonomously merge together. It was found that, the larger vehicle can swallow the smaller one during the voyage, which resembles the self-configurable soft robot. If needed, one can also apply the syringe to break up the composed machine into several smaller ones. Unexpectedly, the divergent liquid metal vehicle still resumes its running behavior along the original traveling track. Such high compliance is distinguished from the conventional modular robots, which usually generate a gap after self-assembling. The coalescent or divergent capability is hard to compete even by a biological system in nature. The most noteworthy point still lies in that a pretty large liquid metal vehicle requests extremely small amount of Al and basic solution to realize non-gap coalescence and dispersive locomotion. Additionally, no complex preparation or procedures are involved.

As shown in Fig. 7.18a, a 0.35-mL EGaIn liquid metal vehicle with the attachment of an Al flake is sub-immersed in 0.2 mol/L NaOH solution in an open-top circular channel made of polymethyl methacrylate (PMMA) through digital control machining [34]. The machine is running at an average velocity of 17 mm/s during one lap. As the surrounding solution is sucked out by a syringe, the movement slows down, which illustrates that the volume of the solution affects the motion of such soft metal machine. Additionally, the velocity is not uniform due to the coarse wall of the channel. To demonstrate the influence of the temperature on the locomotion, a comparative experiment was carried out. A thermostat water bath is employed to maintain the temperature of the electrolyte solution in the channel higher than the room temperature. At first, the liquid metal vehicle slows down to 2.77 mm/s with the removal of the solution. Then the substrate is mounted on a thermostat water bath, and the temperature of the water remains at 70 °C. The steam from the thermostat water bath is utilized to heat the substrate. The average velocity rises swiftly to 9.2 mm/s, which indicates that the rise of the temperature accelerates the autonomous motion.

The volume of the EGaIn droplet metal is increased to 1 mL to exhibit the locomotion of a larger machine. The vehicle appears to be cumbersome. A little NaOH solution is supplemented to the channel for acceleration. A syringe is utilized to divide the vehicle into three dispersive droplet vehicles with similar volumes. As a result, all the vehicles swim in the channel spontaneously as depicted in Fig. 7.18b. Each liquid metal vehicle chases the one in its front, and bubbles emerge at the tail of the vehicles where Al reacts with the solution. From Fig. 7.18c, it can be noticed

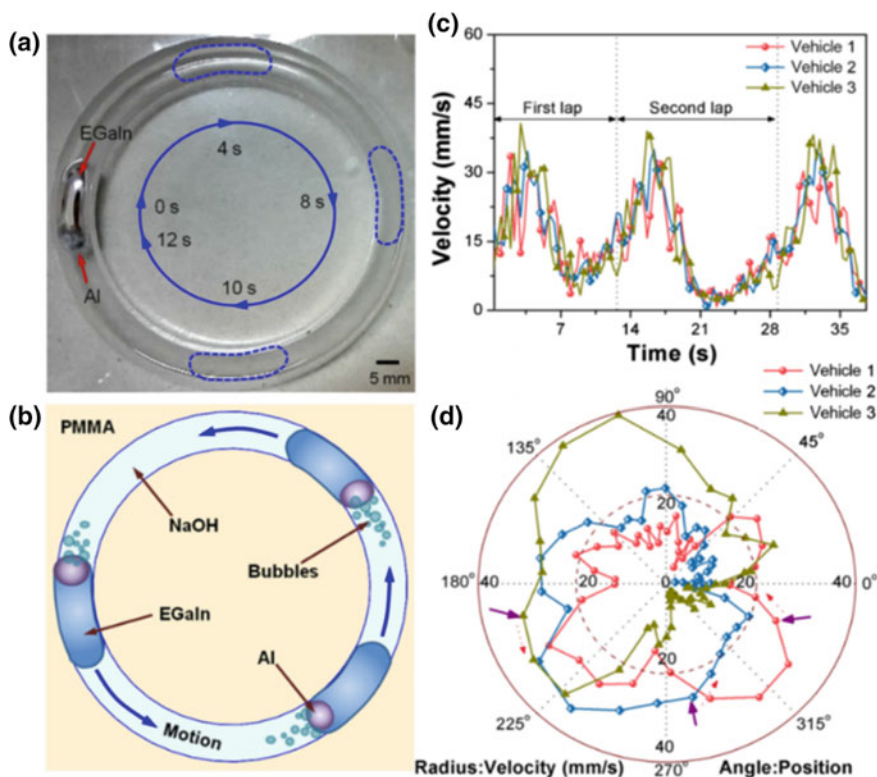


Fig. 7.18 **a** Spatiotemporal evolution of a 0.35-mL EGaln droplet in a circular open-top channel containing 0.2-mol/L NaOH solution. **b** Schematic of three 0.33-mL EGaln droplets chasing autonomously in an open-top circular channel which contains 0.2-mol/L NaOH solution. **c** Time-velocity plots within 37 s for the three vehicles in **b**. **d** Position-velocity plots during one lap for the three vehicles in **b**. The angle refers to the related position of the circular channel, and radius (the length between the center and the measured point) denotes the velocity at the related position. The maximum radius (i.e. the radius of the outer circle) represents velocity of 40 mm/s [34]. All pictures reproduced with permission

that the velocity tendencies of the three vehicles during each lap are basically synchronous, which fluctuate at the same time. It can be hypothesized that there exists certain feedback from the motion of the vehicles, which results in the phenomenon of synchronous oscillation [34]. However, at the same moment, the velocities of the vehicles are inconsistent, which implies that the propulsion of the vehicles does not only depend on feedback from the flow of NaOH solution apart from the effect of Al reaction. The distributions of the velocity for the three vehicles during one lap are measured to figure out the traveling course of the inconsistency, as illustrated in Fig. 7.18d. The angle refers to the corresponding position of the circular channel, and the radius to the center characterizes the magnitude of the velocity. Presumably, there is some obstruction at the position from 0° to 90° where it is observed that the vehi-

cles slow down. Meanwhile, the vehicles accelerate when they arrive at the diagonal position, which suggests that an upslope may exist at the position from 0° to 90° . The arrows in Fig. 7.18d denote the position and the velocity of the three vehicles at the same moment, while the adjacent point in clockwise corresponds to the position and the velocity at the next measured time point. The position for the minimum velocity of each vehicle shifts slightly, while the position for the maximum velocity of each vehicle varies evidently, which illustrates that the feedback from the solution affects the locomotion more obviously when the vehicle swims faster. Besides, the positions for three vehicles to reach the minimum or maximum velocity is sequential, which means that if Vehicle 1 is defined as the headmost machine, it reaches the minimum or maximum velocity first, and the middle Vehicle 2 reaches second, prior to Vehicle 3.

The velocities of the disperse vehicles change constantly along with the position and the flow of the solution, which induces that the faster vehicle is potential to overtake the slower one in its front. It has been disclosed that the velocity of the autonomous motion is extremely sensitive to the size of the droplet [34]. Therefore, when several smaller vehicles, the diameters of which are smaller than the width of the channel, are injected into the channel gently, their velocities vary from that of the initial larger vehicles. The locomotion stability of the smaller vehicles tends to be disturbed by the propulsion of the solution flow, since only one side of the vehicles is proximate to the wall of the channel. Additionally, though the reported velocity of small objects, which is often relative to their body length, are typically very fast, the actual velocity of the smaller object is often slower than that of the larger object. With slower velocity, the smaller vehicles are caught up and swallowed by the larger vehicle behind them very soon. As is shown in Fig. 7.19a, b, the faster the larger vehicle moves, the shorter distance it will be from this machine to the smaller vehicle. In the same interval time, the premise for the larger vehicle to catch up with the smaller one can be described as $\Delta t = \frac{s+\Delta s}{v_1} = \frac{s}{v_2}$, where, s refers to the displacement of the smaller vehicle during the interval time Δt . From this equation it can be deduced that velocity v_1 must be larger than v_2 , and Δs is proportional to the ratio v_1/v_2 , which is also reflected in Fig. 7.19b. It is noteworthy that after the two droplet vehicles coalesce, the velocity v_3 of the combined object is larger than both v_1 and v_2 . That is to say, the kinetic energy after coalescence is larger than that before. One can mainly ascribe the increase of the kinetic energy to the decrease of the surface free energy, which means partial surface free energy converts into kinetic energy automatically, similar to the conversion between gravitational potential energy and kinetic energy when an object falls down. To verify this hypothesis, a conceptual experiment was also carried out. In 0.2 mol/L NaOH solution, a liquid metal vehicle is deposited on a copper sheet, wetting the surface and forming a spherical cap. The copper sheet is 15° inclined, approaching another liquid metal vehicle, which is placed in the solution. A slight disturbance renders the liquid metal on the sheet to contact with the droplet in solution. As a result, the vehicle in solution climbs up very quickly to merge with the spherical metal cap. The precipitate kinetic energy derives from the decrease of the metal droplet surface energy.

Though after the coalescence, the velocity during the interval time Δt increases, after the next Δt time, the velocity (i.e. v_4) decreases again. The deformation of the

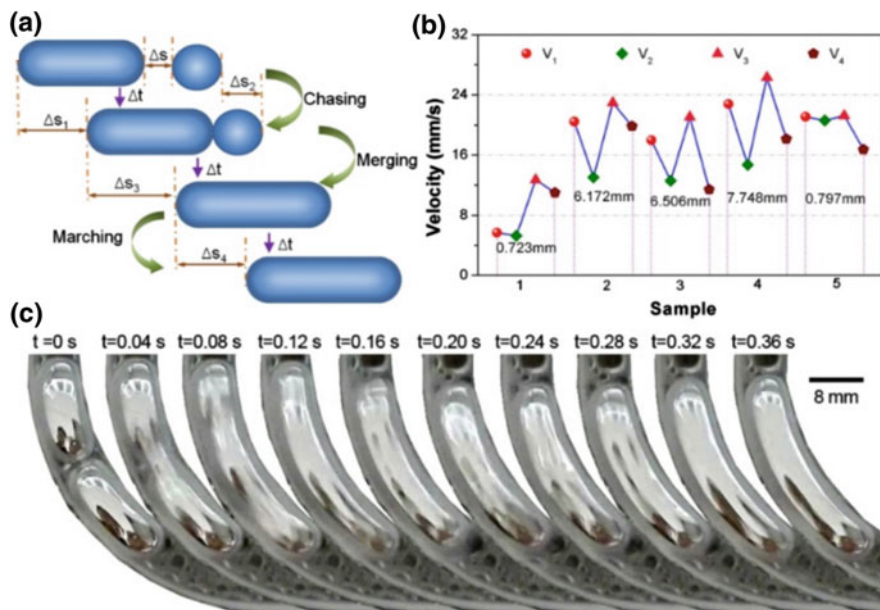


Fig. 7.19 **a** The schematic for two contacting vehicles before and after coalescence. The interval time Δt is 0.32 s. The larger vehicle chases and merges with the smaller one, both of which move forward with a displacement of Δs_n ($n = 1, 2, 3, 4$). The symbol Δs refers to the initial distance between the two droplet vehicles before coalescence. **b** The change of velocity corresponding to the process in **a**, where the symbol Δv_n is described as $\Delta v_n = \Delta s_n / \Delta t$ ($n = 1, 2, 3, 4$). Five samples are selected, and Δs is measured and marked under each plot. **c** Sequential snapshots of the coalescence process. The volumes of the two disperse vehicles are both about 0.33 mL [34]. All pictures reproduced with permission

liquid metal object occurs correspondingly [34]. Figure 7.19c exhibits the dynamic morphology of the vehicles during coalescence. Clearly, the self-assembling is seamless and instantaneous. The deformation is similar to the elongation and compression of a spring. From 0 to 0.12 s, the two droplets coalesce and the combined object elongates. In contrast, from 0.16 to 0.24 s, the body of the vehicle is obviously shortened, and the rear body rushes down, while the front body stays. Interestingly, from 0.28 to 0.36 s, the front body rushes down, while the rear body stays in turn. It is speculated that the flexibility of the soft droplet induces the deformation. As aforementioned, the velocity of the rear vehicle is larger than that of the front one before the two vehicles coalesce. Therefore, the rear part of the combined object moves faster than the front part when they coalesce, compressing the front body. The coalescence and compression thrust the front body, which accelerates the front body. In return, the acceleration of the front body rushes down and induces the elongation.

More solution is added in the circular channel to investigate the influences of the feedback by the solution. Meanwhile, two disperse vehicles with different sizes are deposited in the channel with an initial interval of 8.3 cm (the arc length). The

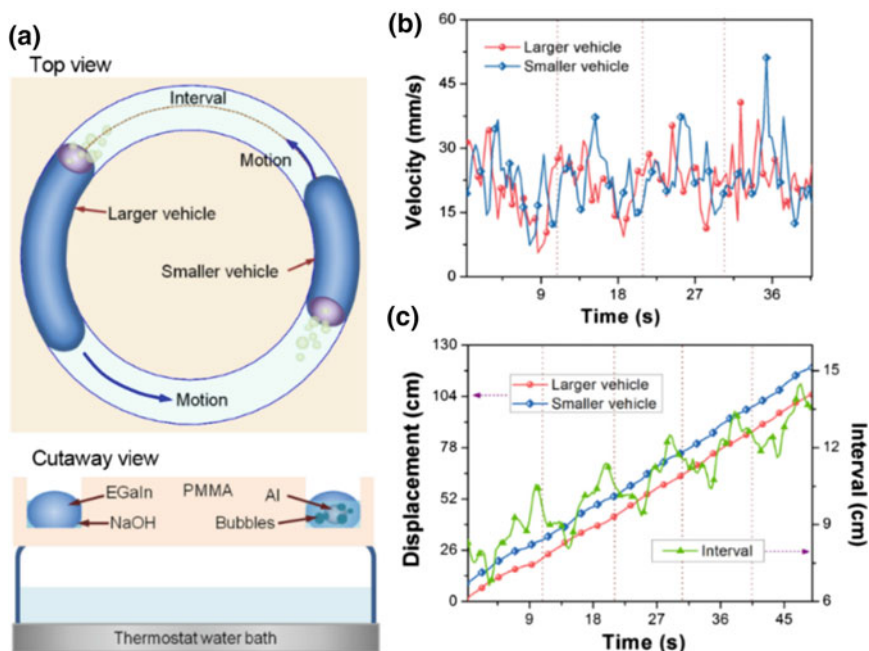


Fig. 7.20 **a** Schematic of the top view and cutaway view for two vehicles with in-equal sizes in the circular channel. The volumes of the larger and smaller vehicle are 0.5 and 0.3 mL, respectively. **b** The velocity of the two vehicles in **a**. Each lap is separated by a dashed line. **c** The displacement of the two vehicles and the interval between the two vehicles in **a**. Each lap is separated by a dashed line [34]. All pictures reproduced with permission

volumes of the two droplet vehicles are 0.5 and 0.3 mL, respectively, both of which occupy the most of the channel in width to reduce the circulation of the solution, as depicted in Fig. 7.20a. As a result, the tendency of the velocity varies from that in Fig. 7.20c obviously, and it becomes desynchronized. As mentioned before, adding solution appropriately induces acceleration and synchronization. However, the average velocity during one lap is larger than that in Fig. 7.20c, while it loses the synchronization, which demonstrates that the influence of the droplet volume is stronger than the solution volume. Figure 7.20c shows the displacement and the interval during four laps. The two vehicles voyage for 1 m in 50 s, which is pretty fast in contrast to micro-/nanomotors (it takes about 80 min to overcome a distance of 1 m for a typical micro-/nanomotors). Additionally, the interval between the two vehicles increases gradually, and during each lap, the fluctuation of the interval is similar, which implies that the variation of the velocity has a close relation with the position [34]. The increasing interval creates an opportunity for one droplet vehicle to overtake the other one. Furthermore, the amount of the solution between the two vehicles influences the assembling greatly, since the change of the interval affects the water level.

Theoretically, to actuate a cylindrical moving object, the driving force should at least be equal to the flow resistance which can be characterized by the classical Eq. (7.2). Clearly, the longer the vehicle, the larger driving force is needed [34]. For a very short vehicle, say a liquid metal machine with a diameter of 8 mm, the driving force can be over milli-Newton in magnitude, which is quite large and usually has to be supplied by external energy. It is estimated that if the droplet vehicle is propelled only by the bubbles the Al generates, the mass of the bubbles should be equal to the mass of the metal droplet when the velocity for the bubble departure equals to that of the metal. This is unreasonable. The droplets here move at a velocity of centimeters per second, and their diameters are over 8 mm. Thus, it is necessary to figure out the source of the main driving force.

To further confirm whether the force from the bubble recoil is sufficient to actuate such a metal droplet vehicle in centimeter, a rigid metal block with attachment of similar amount of Al is deposited in the same NaOH solution [34]. Bubbles emerge, while no movement is observed, which manifests that the actuation is not only attributed to the bubble evolution. This side-fact indicates that the interfacial or chemical property of the material may dominate the autonomous motion. The droplet is capable of moving in room temperature, and it has already been demonstrated that the temperature is a factor to accelerate the motion. Therefore, the temperature is doubted to supply the energy to actuate the droplet. To exclude the influence of the chemical reaction, the droplet is deposited in the channel without the involvement of Al. The solution is heated up by a thermostat water bath, while the droplets do not move, which suggests that the temperature does affect the motion velocity, however it is still not strong enough to initiate the motion.

Through these comparative evaluations, the mechanism of chemical Marangoni effect can be identified as the source to drive the autonomous traveling [34]. The addition of Al has double effects to initiate the motion. The departure of the bubbles, generated by the reaction between Al and NaOH solution, provides part of the driving force, but it does not play a decisive role, as the experiment already confirmed. The other effect is that the contact between Al and liquid metal in fact forms into a Galvanic cell, and Al works as cathode while liquid metal works as anode. The oxidation reaction renders Al to dissolve in the solution chemically. Since gallium reacts with the alkali solution and produces gallates like $[\text{Ga}(\text{OH})_4]^-$, which makes the surface of gallium negatively charged and cations accumulated nearby, forming into a uniform diffuse electrical double layer (EDL), the reduction reaction makes the gallium change from valence state to the original state. The relationship between the surface tension and the potential difference across the EDL can generally be described by Lippmann's equation. The reduction reaction deoxidates the gallates near the Al preferentially, which alters the distribution of the charges across the EDL and leads to the generation of a potential gradient along the liquid metal surface. Thus, electrochemical reaction induces an imbalance of the surface tension on the liquid metal. It is the imbalance of the surface tension that induces pressure differences to be inequable around the droplet, which incurs a force to push the vehicle forward.

The reaction renders Al to be amalgamated by liquid metal EGaIn, and it dissolves in the liquid metal [35, 36]. Through the experiments, it is observed that an intact

Al flake forms into many small pieces in the liquid metal droplet. When a larger vehicle is divided into several disperse smaller droplet vehicles, each one is able to move autonomously and individually. The difference of velocity induces the vehicles to meet and coalesce by the decrease of surface energy. Consequently, the velocity increases and facilitates the locomotion. Therefore, the dispersion and coalescence allow the self-assembling of the liquid metal machine.

Clearly, the aluminum fuelled liquid metal machine achieved autonomous convergence and divergence of macroscopic soft vehicle in a velocity of centimeters scale per second. The actuation is enabled by the chemical Marangoni effect [34]. During the driving process, the chasing vehicles can be self-assembled to swim individually or coalesce seamlessly without slowing down. If needed, the large vehicle can be cut into several separate running machines which still keep quick running state. Such unusual capability is hard to compete by a conventional rigid machine even biological system in nature. This finding opens the possibility for constructing future soft self-assembling machines or robots.

7.10 Dynamic Hydrogen Generation Phenomenon in Liquid Metal Machine

Reaction between aluminum and water offers a simple way for the propulsion of liquid metal machine fuelled. The passive oxide film subsequently formed on Al would become a major obstacle for its continuous reaction. Gallium was proven to be an effective way to remove the passive oxide film through penetrating into Al granules, which fosters the reaction between Al and water. Unlike the existing strategies of using solid state Al-rich alloys for the hydrogen generation system, the liquid phase alloy was introduced for making the self-running machine where the mass percentage of Al can be less than 1%. Such conceptual innovation would help maintain the alloy in liquid state which thus allows for rather convenient operation. To probe into the methodology, the dynamic hydrogen generation phenomenon of such Al-fed liquid phase GaIn alloy inside NaOH electrolyte was disclosed [37]. According to the experimental observations, the hydrogen was generated mainly at the interface between the liquid metal and the Petri dish rather than the liquid metal-electrolyte interface. Homogenous hydrogen generation only takes place at the liquid-solid interface while heterogeneous hydrogen generation from the moving accumulated Al granules happens on all surfaces. Such finding would help better understand the mechanisms lying behind as well as the dynamic traveling behaviors of the aluminum powered gallium alloy machine. It also opens a new way towards low cost and straightforward hydrogen generation.

As illustrated in former sections, aluminum fed gallium alloy demonstrates its unique self-actuation performance in the alkaline electrolyte. The surface tension gradient resulted from the Al-Ga bipolar electrochemical reaction and the H_2 bubble propulsion account for such driving force. When the aluminum foil was dissolved

into the gallium alloy, each tiny droplet made through injecting the mixed alloy into the alkaline electrolyte can also move swiftly [31]. It is found that the H_2 bubbles are generated from the bottom of the tiny droplets, where the droplet contacted with the Petri dish floor. The bubble propulsion accounts for the main driving force of such tiny droplets. Previously, we mainly focused on the self-actuation behavior of the droplets. However, the hydrogen generation happening there is also of large significance since hydrogen is among the most important clean and high quality energy sources which should be an ideal option for future design of soft robot.

As is well known, aluminum is the most abundant metal on earth with a low density and high energy storage capability. Its reaction with water is environmentally friendly and recyclable, i.e. $2Al + 6H_2O = 2Al(OH)_3 + 3H_2 \uparrow$. However, a thin film of Al oxide would easily adhere on the Al surface, which hinders the subsequent reaction. So far, the most typical ways of activating aluminum generally include [28]: alloying aluminum with other metals, milling aluminum alloy with salt and oxide powder, using alkaline electrolytes, lifting the reaction temperature, etc. Among the many methods ever tried, Ga was found to be an excellent activator in that it would penetrate into the Al grain and lead to the embrittlement of aluminum, which is also known as Rebinder's effect [38]. Besides, Ga would destroy the oxide film on Al surface, shifting the electrode potential of Al to more negative values. However, former studies mainly focus on Al rich solid phase alloys where the mass percentage of Al is often higher than 90%. Clearly, obtaining such reactants is a time, energy consuming process and the hydrogen generation process is often hard to control. So far, few attempts had ever been made on Ga rich liquid phase alloys which can in fact be realized through a rather straight forward way, as will be explained later.

Yuan et al.'s work [37] disclosed the dynamic hydrogen generation phenomenon of Al fed liquid GaIn alloy in alkaline electrolyte, where the mass percentage of Al is only 1% or even less. The small amount of Al ensures the liquid phase of the alloy. Due to the fluidity of the liquid phase alloy, the hydrogen generation appears quite different from that of the conventional solid aluminum rich alloy. Most of the hydrogen was generated at the interface between liquid metal and Petri dish floor rather than the interface between the liquid metal and NaOH electrolyte. All these unconventional phenomena and the mechanisms involved will be comparatively investigated and interpreted.

For the experiments, liquid metal $GaIn_{10}$ (10 wt% In) was injected onto a piece of Al foil in a 10 ml beaker. The mass ratio of Al and $GaIn_{10}$ was about 1:99. The $GaIn_{10}$ would gradually penetrate into Al grain boundaries. In order to accelerate the dissolving speed, NaOH aqueous electrolyte (0.5 mol/L) was added to the beaker and covered the Al foil and $GaIn_{10}$. It took about twenty minutes for the Al foil to be dissolved into the $GaIn_{10}$ and the left was floating on the surface of the liquid metal in the form of tiny Al granules. The prepared Al fed GaIn alloy was then moved into a glass Petri dish filled with NaOH aqueous electrolyte (0.5 mol/L). In order to investigate the hydrogen generation process in detail, we placed the transparent Petri dish on an optical platform with the tilt angle as 3° . In this way, the liquid metal droplet would stay at the lowest bottom of the Petri dish, which facilitated the observation. Two background lights were illuminated from up and down for better

visualization of the hydrogen generation process. Images were acquired from the bottom, side and upper positions, respectively.

Without losing any generality, the contact interface between the liquid metal and the surroundings can be divided into three parts [37]: the bottom interface between liquid metal and Petri dish base, the side interface between liquid metal and Petri dish flank, the upper interface between liquid metal and NaOH electrolyte. For illustration purpose, hydrogen generation dynamics on the three interfaces were depicted in Fig. 7.21. These three parts showed quite different behaviors during the whole process.

As the GaIn alloy destroyed the inter-granular bonds of the Al foil, Al was gradually broken into much smaller granules. Some of them were dispersed inside the liquid metal uniformly while others accumulated together into big granules [37]. The big granules mainly floated on the liquid metal interface. The invisible uniformly dispersed Al tiny granules inside the liquid metal and the visible accumulated granules floating on the liquid metal surface led to two different forms of hydrogen generation: nearly homogeneous hydrogen generation at the contacting area between liquid metal and Petri dish, and heterogeneous hydrogen generation from the accumulated Al granules floating and moving on all interfaces, respectively.

Homogeneous hydrogen generation can be seen on the bottom interface and the side interface rather than the upper interface (Fig. 7.21). Due to different reflectivity of liquid metal surface and the hydrogen bubbles [37], the homogeneously generated hydrogen bubbles appear brighter relative to the liquid metal area illuminated by the light source, as can be seen in Fig. 7.21a, b. They emerged uniformly on the bottom and side contacting interface. Because these tiny H_2 bubbles cannot escape from the bottom contacting interface into the solution directly, they will accumulate until coalesce into a big bubble generated by moving Al granules at the contacting surface. When the bubble moves to the edge of the contacting interface, the H_2 bubble will burst and become scattered in the solution. This process was taking place all the time on the bottom surface and the side surface. However, the homogenous hydrogen generation was not found on the upper interface between the liquid metal and the electrolyte. It might be explained by the difference of the interface roughness. The liquid metal-electrolyte interface was much smoother than the Petri dish surface. The rough sites on the Petri dish triggered the redox reaction between the homogeneously dispersed Al tiny granules in liquid metal and NaOH electrolyte. The constantly generated hydrogen bubbles also indicated that liquid phase allowed Al granules to diffuse freely to the reaction sites.

Heterogeneous hydrogen was generated from the visible Al granules on all the three interfaces [37]. The H_2 bubbles were generated in a larger size and larger quantity. This indicated a higher reaction rate because of the dense Al accumulation. At the same time, the accumulated Al granules were moving on the surface of liquid metal randomly. At most of the time, the Al granules moved at the bottom interface surrounded by the bubbles and electrolyte. These granules can separate and coalesce from time to time with the propulsion of H_2 bubbles. Sometimes, small amounts of Al granules can escape from the bottom to the upper interface, as can be seen in Fig. 7.21b. These Al granules quickly merged together on the upper interface

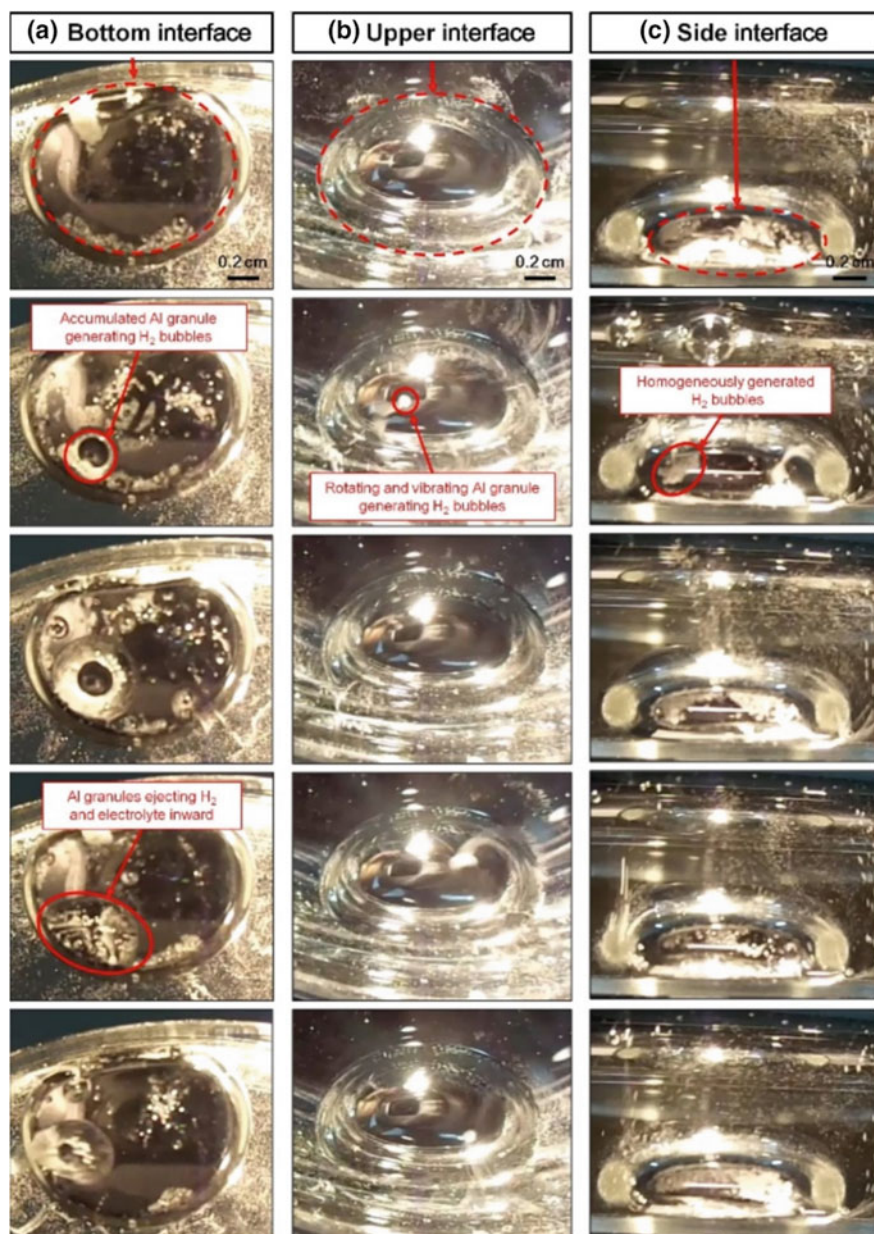


Fig. 7.21 Hydrogen generation dynamics at different sites [37]. **a** Case at the bottom interface between liquid metal and Petri dish base; **b** Case at the upper interface between liquid metal and NaOH electrolyte; **c** Case at the side interface between liquid metal and Petri dish flank. The time interval is 2 s. All pictures reproduced with permission

into a vibrating and rotating larger granule with H_2 generated fast. However, the vibrating Al granule on the upper interface was unstable. It would soon move to the bottom interface or side interface. Figure 7.22 depicts the dynamic process of an Al granule moving from the upper interface to the side interface within 0.5 s. The granule moved back and forth on the side interface at the speed between 0 and 7 cm/s. The larger Al granules at the bottom were also unstable. From time to time, it would move on the bottom interface, producing hydrogen and bringing electrolyte into the interface. Besides, new small Al granules would appear randomly on the bottom or side interface. They may also move randomly on the interfaces and coalesce into bigger granules. Clearly, the liquid phase reduced the moving friction of the Al granules.

Actually, the heterogeneous hydrogen generation behavior of the accumulated Al granules was much more complicated than expected [37]. First, the motion behavior of Al granules was different on different interfaces. On the upper interface, the small Al granules had the tendency of merging together with the increasing speed (from 0 to 7 cm/s). However, on the bottom and side interface, they seemed to be independent and move randomly until collided. This might be explained by the friction difference between liquid-liquid interface and the liquid-solid interface. The upper liquid-liquid interface was much smoother than the bottom and side liquid-solid interface. Besides, the homogeneous hydrogen bubbles on the bottom and side interface also hindered the movement of Al granules. The attraction force can be neglected compared to the friction force on the bottom and side interface. Secondly, the hydrogen generation behavior of Al granules on the upper interface was also different from that on the bottom and side interface. Hydrogen bubbles generated on the upper interface can be released to the surrounding electrolyte freely. However, there was limited space on the bottom and side interface. Thus, the hydrogen bubbles accumulated beside the Al granules until they reached the edge. They were then ejected to the surrounding electrolyte. The generation of hydrogen on the bottom and side interfaces provides big propulsion due to limited space.

Since the hydrogen generation dynamics on the side interface resembles that on the bottom interface [37], one can discuss the bottom interface in detail, as shown in Fig. 7.23. At initial stage, H_2 were generated homogeneously on the bottom interface (Fig. 7.23a). These H_2 bubbles were of similar size (less than $30\text{ }\mu\text{m}$) and adhered to the Petri dish. Later on, Al granules of different sizes would appear on the bottom and move swiftly and randomly (Fig. 7.23b). They swept out the homogenous H_2 bubbles on the interface, leaving a wide electrolyte band. Homogenous H_2 generation would take place soon on the electrolyte band before the next sweep. These running granules with the speed ranging from 0 to 8 cm/s would collide and coalesce and finally hit the large moving Al granule at bottom edge (Fig. 7.23c). The large Al granule at bottom edge was generating H_2 fiercely all the time. Part of the granule would separate from it and move into the bottom interface with mixed electrolyte and H_2 bubbles surrounding it. Usually, there would be a relatively large bubble in the center, surrounded by the middle bubbles generated constantly by Al granule. These middle bubbles would be coalesced into the large bubble. And still, the outer layer was the mixture of tiny bubbles and electrolyte. These tiny bubbles were the homogeneously

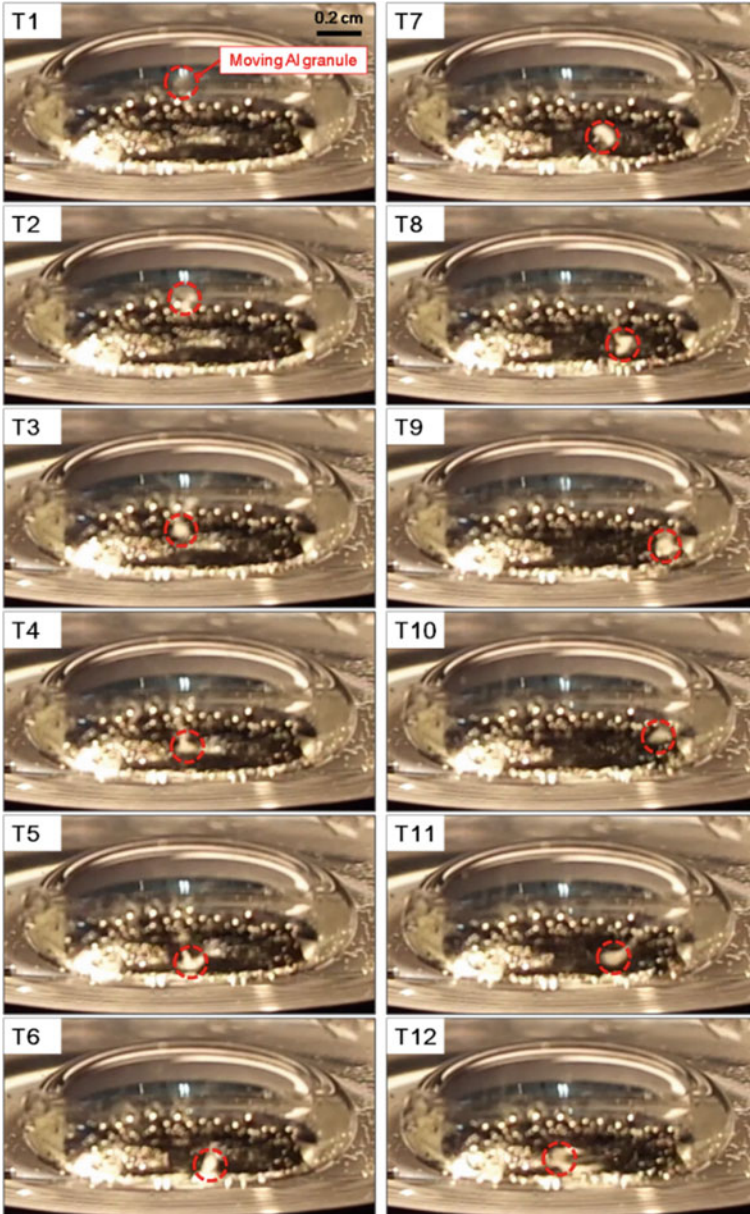


Fig. 7.22 Images of an Al granule running from the upper interface to the side interface [37]. The scale bar is 0.2 cm. T1–T12 denotes the time sequence with the time interval to be 1/29 s. The Al granule moves from upper interface to the side interface (T1–T6) and then moves back and forth on the side interface (T7–T12). All pictures reproduced with permission

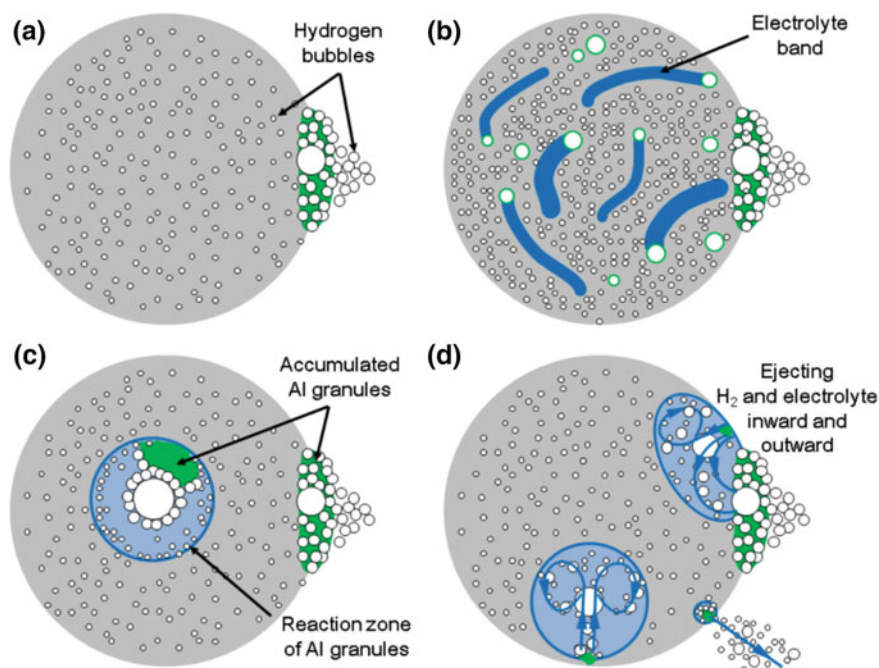


Fig. 7.23 Hydrogen generation dynamics on the bottom interface between liquid metal and Petri dish base [37]. The blue parts denotes electrolyte. The green part denotes Al granules. **a** The homogeneous hydrogen generation on the bottom interface. **b** Electrolyte bands behind the moving tiny Al granules. **c** Reaction zone of moving accumulated Al granules. **d** Al granules at the bottom edge, ejecting electrolyte and H_2 inward and outward the bottom interface. All pictures reproduced with permission

generated H_2 bubbles on the bottom interface. The whole circular structure shifted the liquid metal and prohibited the homogenous H_2 generation. Besides, due to the H_2 propulsion inside the structure, the bubble was unstable and moved randomly. Once it reached the edge of the bottom, H_2 would be let out and the Al granule will move into the bottom interface again with new H_2 generation. Apart from the above events, another unique phenomenon was observed at the bottom edge. Contrary to the common H_2 ejection into the surrounding electrolyte, some Al granules at the bottom edge ejected the H_2 into the bottom interface (Fig. 7.23d). These Al granules came from liquid metal sedimentation, rather than being transported from the large Al granule. Some of them would eject H_2 into the surrounding electrolyte while others ejected in the opposite direction and brought both H_2 bubbles and electrolyte into the bottom interface. When the inward ejection reached a certain extent, the electrolyte and bubbles would again be ejected outside the bottom interface into the surrounding electrolyte. This process repeated from time to time. Besides, adjacent Al granules ejection areas would combine together. If the ejection area reached the large Al granule, the H_2 and electrolyte would be transported from the small granule to the large one.

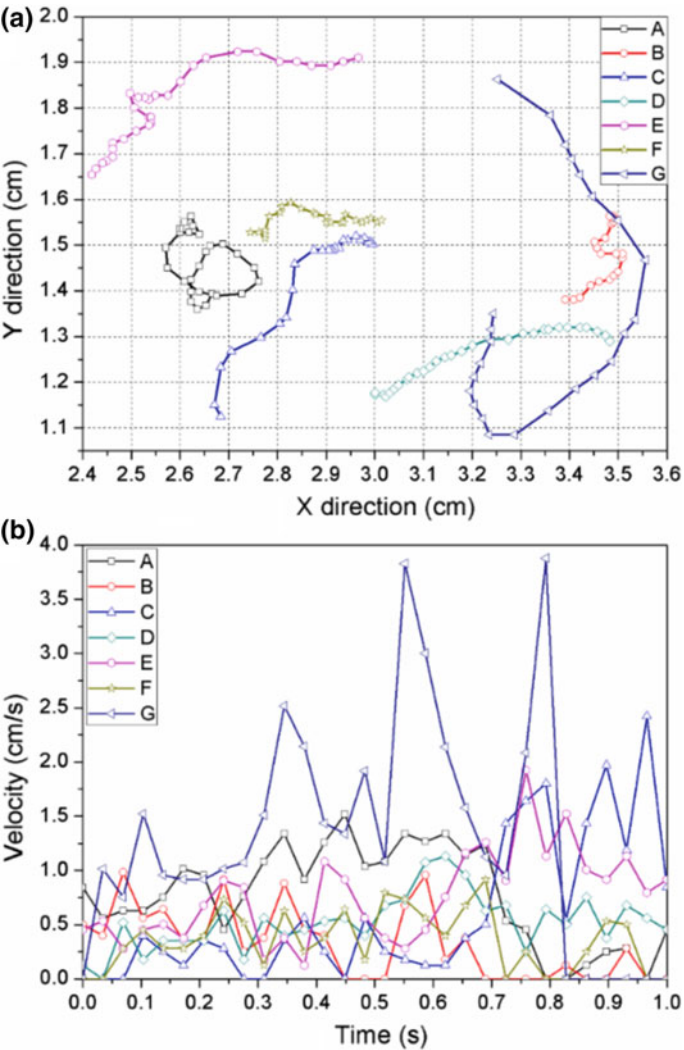


Fig. 7.24 Motion trajectory and transient velocity of 7 randomly chosen tiny Al granules (namely, A, B, C, D, E, F, G) on the bottom interface during 1 s [37]. **a** The motion trajectory of 7 tiny Al granules during the same time interval. **b** The transient velocity of the granules. All pictures reproduced with permission

In order to investigate the motion behavior of Al tiny granules on the bottom interface (Fig. 7.23b) in detail, one can process the images to obtain the quantitative motion trajectory and transient velocity of 7 randomly chosen Al tiny granules on the bottom interface as shown in Fig. 7.24. The images were taken at the speed of 29 frames per second. Assume that the displacement during each time interval was linear, one can then calculate the transient velocity at each location. As can be seen,

the motion trajectory of any granule was different [37]. It might turn left or right, speed up or slow down. They might even stay still for a period before initiating motion again. The transient velocity also fluctuated with time, mostly ranging from 0 to 4 cm/s. The highest transient velocity monitored can be 7 cm/s. The speed of the granules has no relation with location or time. The large moving speed of Al granules indicates that the liquid phase alloy facilitated the transportation of Al to reaction sites.

Overall, the above work disclosed the hydrogen bubble generation dynamics of Al fed GaIn alloy (mass percentage of Al is less than 1%) in NaOH electrolyte in an inclined glass Petri dish [37]. Al foil was dissolved into the liquid metal GaIn10 and broken into many smaller granules. Some of the granules were dispersed inside liquid metal uniformly and others accumulated into big granules floating on the liquid metal surface. Two forms of hydrogen generation can be observed: homogeneous hydrogen generation on the bottom interface and side interface by uniformly dispersed tiny Al granules, heterogeneous hydrogen generation on all interfaces by the moving accumulated Al granules. On the upper interface, small Al granules appear occasionally and quickly merge into a bigger one. The large granule is vibrating and rotating with hydrogen generated constantly till it moves to the bottom or side interface. On the bottom interface, homogenous hydrogen generation takes place all the time. Small Al granules would appear randomly and then move on the interface. Overall, they are dynamically driven by the hydrogen propulsion. Big Al granules on the liquid metal surface would also move to the bottom interface surrounded with hydrogen bubbles and electrolyte. The hydrogen generation behavior on the side interface is similar to that on the bottom interface. All these properties will help understand the self-fuelled liquid metal machine and thus aid for designing potential soft robot in the coming time.

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Chapter 8

Self-Powered Tiny Liquid Metal Motors



Abstract Liquid metal machine can also be made as tiny motors. In fact, the micro- or even nanomotors that could run in a liquid environment is very important for a variety of practices such as serving as pipeline robot, soft machine, drug delivery, microfluidics system, etc. However, fabrication of such tiny motors is generally rather time and cost consumptive and has been a tough issue due to the involvement of too many complicated procedures and tools. This lab had discovered a straightforward injectable way for spontaneously generating autonomously running soft motors in large quantity Yao et al (Injectable spontaneous generation of tremendous self-fuelled liquid metal droplet motors in a moment, 2015 [1]). It was demonstrated that injecting the GaIn alloy pre-fuelled with aluminum into electrolyte would automatically split in seconds into tremendous droplet motors swiftly running here and there. The driving force originated from the galvanic cell reaction among alloy, aluminum, and surrounding electrolyte, which offers interior electricity and hydrogen gas as motion power. This finding opens the possibility to develop injectable tiny-robots, droplet machines, or microfluidic elements. It also raised important scientific issues regarding characterizing the complicated fluid mechanics stimulated by the quick running of the soft metal droplet and the gases it generated during the traveling. Our lab Yuan et al (Sci Bull 60:1203–1210, 2014 [2]) made further efforts to disclose that the self-powered liquid metal motors takes interiorly driven macroscopic Brownian motion behavior. Such tiny motors in millimeter-scale move randomly at a velocity magnitude of centimeters per second in aqueous alkaline solution, well resembling the classical Brownian motion. However, unlike the existing phenomena where the particle motions were caused by collisions from the surrounding molecules, the random liquid metal motions are internally enabled and self-powered, along with the colliding among neighboring motors, the substrate, and the surrounding electrolyte molecules. This chapter illustrates the typical behaviors of the self-powered tiny liquid metal motors.

Keywords Self-powered machine · Soft-robot · Autonomous running
Tiny motor · Hydrogen generation · Magnetic trap effect

8.1 Size Issue of Self-Fuelled Liquid Metal Machines

With outstanding merits, the liquid metal alloy, consisting mainly of Ga, In, Sn, would display unusual behaviors when subject to electric force [3, 4], magnetic field [5], or laser lamination [6]. Actuation of liquid metal could be applied to dissipate heat [7], produce advection [8], or even deliver drugs [9]. A very unique fundamental effect of liquid metal objects lies in that it could realize self-actuation behavior with the help of Al fuel [10]. The size of the metal machine can in fact span from the order of centimeter to either larger or smaller. Additional discoveries were thus continuously made in the present lab. For example, different vehicles self-running in the same channel can lead to autonomous convergence and divergence during traveling [11]. This leads to the assembly of the further larger reconfigurational machine with sizes in five or six centimeters. According to the magnitude evaluation, the driving forces there for such soft motor came mainly from the electrochemical propulsion while the only minor part is from the bubble thrust force. Clearly, many important scientific mechanisms lying behind remained unclear. Particularly, a big fundamental issue could be raised as that when the liquid metal motors reach a much smaller size, say in millimeter scale or even smaller, what kind of the driving mechanisms will dominate their motions and which moving behavior they would take. Such works can be further clarified through making tiny liquid metal motors [1].

8.2 Injectable Generation of Self-Fuelled Liquid Metal Droplet Motors

To fabricate the liquid metal tiny motors [1], one can first prepare eutectic GaIn (EGaIn) alloy with 74.5% Ga, 25.5% In in weight. Although different liquid alloy and matching metals can be adopted as the candidate materials, only EGaIn and aluminum was focused for the brief. An aluminum piece 0.27 g was added to 3 mL EGaIn to make a functional solution. To guarantee the fabrication quality, the whole process was performed in the 0.2 mol/L NaOH solution which can help remove the oxidation film on both aluminum and EGaIn and thus enhance their fusion. Then through the mixture, an alloy of Al–EGaIn alloy with different configurations can be formed (Fig. 8.1a). In principle, there may form different mixtures for the final functional solution such as total, partial, discrete, or zero immersing of aluminum into EGaIn, as illustrated in Fig. 8.1b. This would affect the specific running of the tiny motors thus generated. For the case that no Al–electrolyte contact exists, the electric double layer on liquid metal droplet would remain stable. And no movement will be induced. While for the case the fuel is exposed to the electrolyte, the electric double layer of the liquid metal droplets would become unbalanced and motor locomotion will be induced. In this case, we called such alloy as a pre-activated functional solution [1]. It was then sucked into a syringe for later use (Fig. 8.1c).

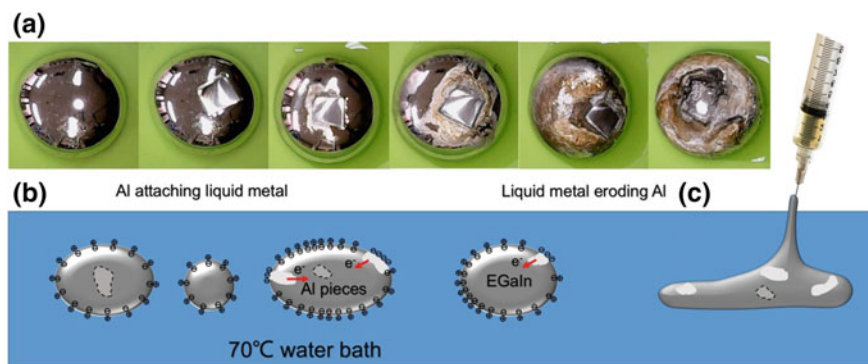


Fig. 8.1 Preparation of pre-activated liquid metal solutions [1]. **a** Eroding fuel aluminum pieces into EGaln alloy. **b** Electrical double layer charges distribution on the surface of the liquid metal sphere immersed in the electrolyte. **c** Suction of liquid metal functional solution into a syringe for subsequent injection fabrication. All pictures are reproduced with permission

8.3 Basic Behaviors of Liquid Metal Droplet Motors Running Inside Channel

The above functional solution can be injected into 0.2 mol/L NaOH alkaline solution to make tiny motors [1]. By pushing the syringe piston forward, the liquid metal would jet into the electrolyte and break up into a large number of droplets (Fig. 8.2a) in 1 or 2 s. Such droplet formation mechanism is due to the high surface tension of the liquid metal stream, as revealed before. Interesting enough, a surprising phenomenon is that such droplets just keep running here and there, representing tremendous tiny motors. According to specific needs, various quantities of liquid metal motors can be generated. With designed needle apertures, one can obtain either smaller or bigger tiny motors. Here, only standard syringe aperture diameter around 0.3 mm is focused for the brief. To evaluate the basic running modalities of the tiny motors, a PMMA material based O-shaped open-top channel with a width of 8 mm was designed and machined (Fig. 8.2b) which is to contain the solution inside and to restrain the locomotion of the liquid metal motors [1]. The alkaline solution was maintained at constant temperature by 70 °C water bath so as to guarantee an appropriate chemical reaction rate. Because of the low thermal conductivity 0.1884 W/m °C of PMMA, there is an evident temperature gradient between the water bath and the channel solution with later around 38 °C. The liquid metal motor was found to work well above certain temperature such as at this specific value. Except for investigating the liquid metal tiny motors in large quantity (Fig. 8.2a), two individual droplet motors (Fig. 8.2b) were also made for detailed analysis purpose. The dynamic motion images were recorded by the digital camera.

According to the experiments [1], there exist certain differences between the locomotion characteristics of a cluster of motors (Fig. 8.2a) and that of two separate droplet motors (Fig. 8.2b). When a cluster of droplets exercise in a closed space, they

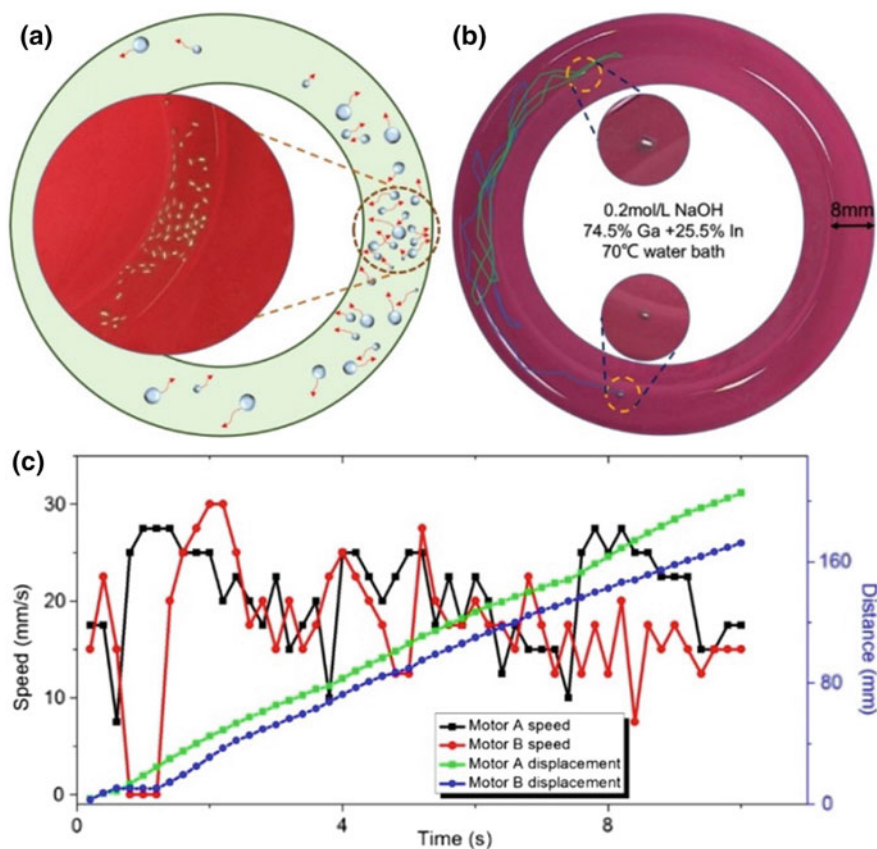


Fig. 8.2 Characterization of the locomotion of typical liquid metal tiny motors [1]. **a** Diagram of many motors running in PMMA open-top channel. **b** Motion trajectory of two individual motors. **c** Instantaneous velocities and displacements of two individual motors. All pictures are reproduced with permission

tend to crowd and affect each other. The locomotion of each droplet then becomes rather hard to discern. While a single sphere or two could distinctly display their running trajectory. In this sense, Fig. 8.2b was used just to characterize the basic behaviors of the tiny motors such as locomotion path, running speed, lasting time, etc. Here, the relative motion velocity was defined as the distance that a motor travels in one second.

The diameters of the two RTLMSpheres in Fig. 8.2b are measured as 1 mm. Through image and data processing, one could track the trajectory of two droplets Motor A and B and calculate their transient velocities. As it was quantified (Fig. 8.2c), the droplet motors swim quickly in aqueous solution in the open-top channel with a pretty high but somewhat random velocity on the order of tens of millimeters per second. Such nonuniform velocity is caused by the dynamic position of aluminum

fuel in the EGaIn droplet. Overall, the magnitude for the average velocity of the motor reached a very high magnitude 10–30 mm/s (Fig. 8.2c), which is somewhat an unusual moving capability. Further, because of the high surface tension of the liquid metal EGaIn, the tiny motors are mostly shrunk into spheres with a diameter from less than half millimeter to millimeters. For a single motor, its lifetime can last for more than a half hour. Depending on different alloy combinations such lifetime is regulatable.

Compared with a cluster of tiny motors (Fig. 8.2a), a single motor has a somewhat unstable motion trajectory which appears as inflexions, cuspidal points, or retrace [1]. The motor may run like shaking and vibrating with a straight velocity component. Sometimes, it may hold standstill for a while, and then reactivate again suddenly. The typical delay time is approximately 0.5 s or less. Analogous phenomenon was also found that when injecting a large amount of droplets into the container, most tiny particles could keep standstill for a very short period of time and then resume to alive full of energy. Overall, motors in a cluster tend to be easily influenced by other motors running nearby.

For quantifying a cluster of droplet motors, image processing is performed to clarify how droplets aggregate and scatter in different positions (Fig. 8.3). With too many tiny motors assembling together, it is rather hard to identify the traveling path and velocity for each of the specific droplet motors. As an alternative, such original snapshots (see upper part image at left-hand side of Fig. 8.3) were converted into grayscale maps, utilizing the gray level difference between luminous spheres and the bleak background. The grayscale maps are ulteriorly transformed to black and white images (see lower part image at left-hand side of Fig. 8.3). The images are divided into four quadrants, which have the same location as a Cartesian coordinate system. By counting the white pixel numbers in each quadrant, we can estimate the droplet motors' transient distribution. It is interesting to find that the transient pixel numbers in each of the quadrant regions I, II, III, and IV are different and appear as an oscillating curve. When two clusters meet, their movements are disturbed and they may change their advancing direction or just run in opposite direction. Such a process takes an approximately 8 s period (Fig. 8.3). This indicates that the liquid metal motors are not uniformly distributed throughout the whole channel. And the metal cluster may choose to stay more in certain quadrant.

Presented in Fig. 8.4 is a sequential motion of the liquid metal motors in large quantity [1]. Here, the time interval for recording the image is one second and the total record lasts about 20 s. These images are analyzed on MATLAB calculation platform. From these subsequent figures, one can observe that, initially ($t = 0$), when the liquid metal pre-fuelled with aluminum was injected into the electrolyte, it would automatically form a large amount of droplet spheres. Then the droplets start to run along the channel (see picture at $t = 1$ s). One can see a stream of droplet motors crowding together while keep running ($t = 2$ s, 3 s, 4 s). They may run clockwise ($t = 3$ s, 4 s) and then anticlockwise ($t = 5$ s, 6 s, 7 s). Such motor clusters may also depart themselves and run oppositely ($t = 7$ s, 8 s, 9 s). Depending on the specific injection, the droplets may not necessarily be in the same size. By measuring the droplet diameters, one can find that the droplet motors at different locations take

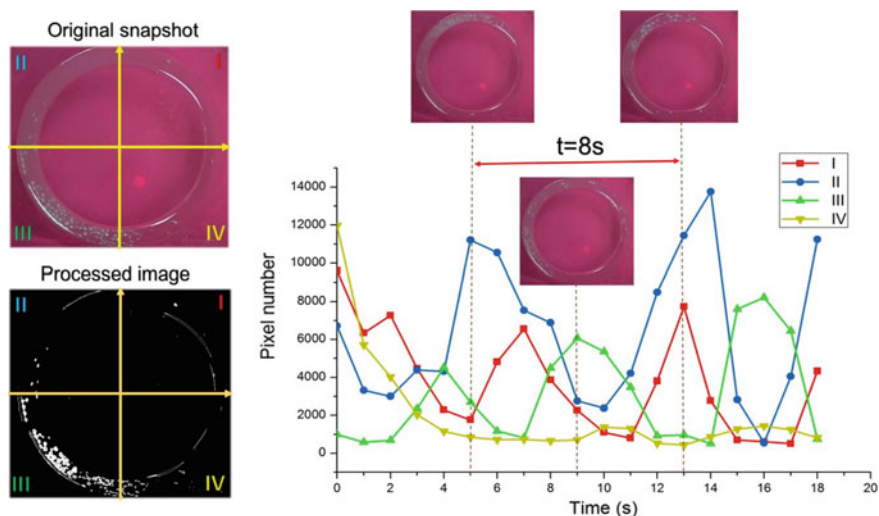


Fig. 8.3 Locomotion of a cluster of liquid metal tiny motors in the open-top channel [1]. Here, each image processed as black and white is placed below its original image. *Note* The channel width is fixed as 8 mm throughout the whole experiments. All pictures are reproduced with permission

different average diameters such as from $D = 0.54, 0.84$ to 1.29 mm (Fig. 8.4), etc. The variation comes from which part of the droplets was sampled.

From repetitive measurements, one can find that motors in the circle are neither stable in channels nor distributed uniformly around different positions [1]. In most times, motors aggregate together and travel in roughly the same direction. When the cluster arrived at a certain space of specific quadrant as shown in the image, there would appear a peak on the corresponding curve of the right-hand side in Fig. 8.4. The peak travels and transforms among different curves indicating the cluster movement from one quadrant to another. The cluster can also split into two smaller clusters or join as one big cluster with some individual motors moving freely away from the big one. Because the size of the motors in a cluster cannot be precisely kept as the same, they have diverse locomotion velocity (also moving direction) thus collision would happen occasionally. Overall, the initial running direction for a stream of liquid metal motors seems to follow its original injection direction. But if two separate streams collide together, the subsequent directions for each of the streams may be disturbed. Clearly, further microscopic interpretations are needed in the near future.

The present principle for spontaneously generating liquid metal tiny motors has generality [1]. To test whether the same phenomenon would also happen in other electrolytes, additional experiments were carried out in the 0.2 mol/L NaCl solution. As is anticipated, the same phenomenon does occur (Fig. 8.5). There are no evident differences between NaCl solution and NaOH case regarding the basic motor behaviors. This is because, no matter what kind of electrolyte is used, galvanic cell reaction would happen. Due to different electrochemical activities between EGaIn

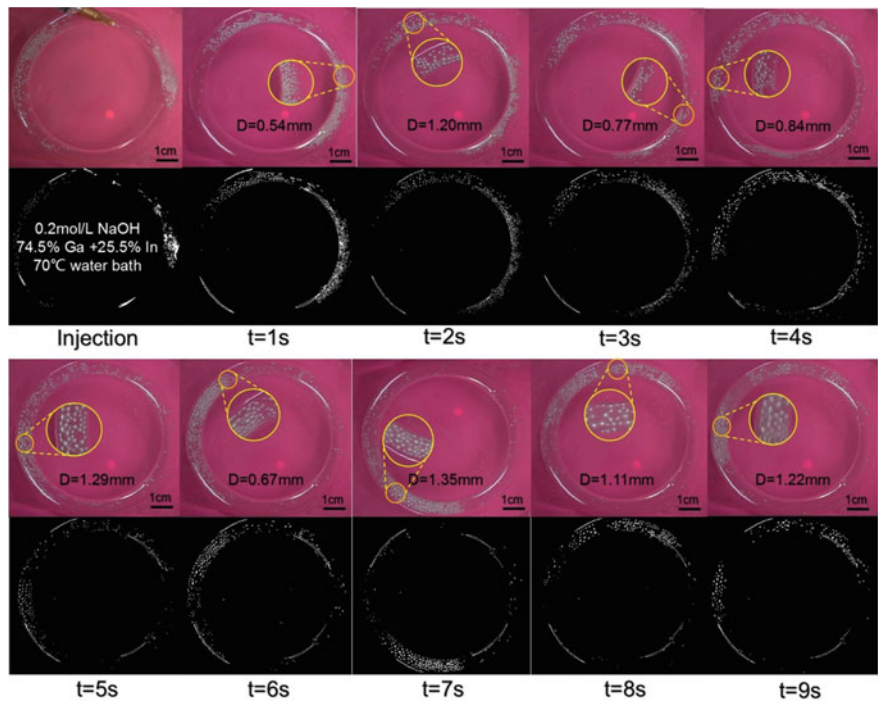


Fig. 8.4 Transient distributions of the running liquid metal motors in four quadrant regions I, II, III, and IV [1]. Here, white pixel number in black and white images was used to estimate the motors distribution. All pictures are reproduced with permission

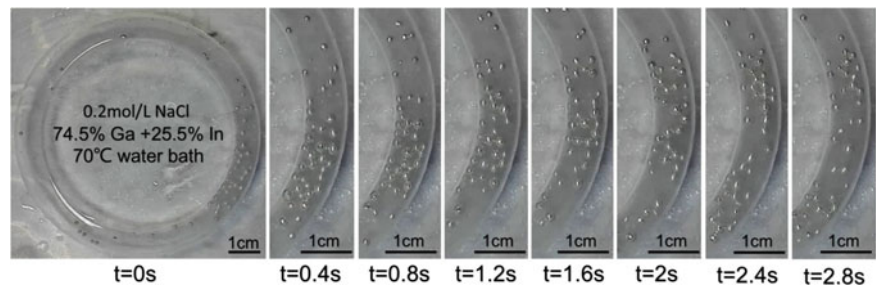


Fig. 8.5 Transient images for the running liquid metal tiny motors in NaCl solution [1]. All pictures are reproduced with permission

and aluminum, galvanic cell reaction would happen between them and the surrounding electrolyte. Droplets are just propelled by the generated interior electricity inside the sphere, the induced flow nearby and the hydrogen bubbles.

It should be pointed out that, the present mechanisms for the self-powered tiny motors are different from the existing ones where small-scale synthetic motors gener-

ally rely on converting the chemical energy into movement and forces [1]. Impressive progress has been made over the past decade and a variety of microscale motors based on different design principles have been exhibited. Most motors are shaped like rods while propelled by microbubbles generation. Gases can come from chemical reaction between the metallic motor coat and acid solution or electrolyte catalysis reaction in which motors perform as a catalyst.

In the above method, tiny motors are not only propelled by the bubbles but also driven by the electricity generated through the galvanic cell reaction. This mechanism is similar to former observation on electricity induced flow of liquid metal. A basic difference between the present work and the former is that all the previous liquid metal machines rely on the driving of the external electrical device while the present one is an entirely self-fuelled machine. Aluminum is adhered to the liquid metal droplet and acts as chemical fuel in Al–water or Al–alkaline galvanic cell reaction. With electricity and bubble driving mechanisms working together, motors can have much higher motion efficiency.

Because of the varied electrochemical activity between EGaIn and Aluminum, the fuel could react with both NaOH and NaCl solution on the surface of liquid metal droplets. It is such a reaction that breaks up the symmetry of the electric double layer. When dispersing the liquid metal droplets inside the electrolyte, the reaction between NaOH and Al proceeds as $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} = 2\text{NaAlO}_2 + 3\text{H}_2 \uparrow$ on the surface of sphere droplets. While in NaCl solution, reaction occurs as $2\text{Al} + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{H}_2$. For NaOH alkaline solution, anodic reaction is $6\text{H}_2\text{O} + 6\text{e}^- = 3\text{H}_2 \uparrow + 6\text{OH}^-$ and cathodic reaction is $2\text{Al} + 8\text{OH}^- - 6\text{e}^- = 2\text{AlO}_2^- + 4\text{H}_2\text{O}$. Clearly, in both cases, it is such interiorly generated electricity and the gases there that drive the liquid metal droplet to run here and there.

According to Lippman's equation, one has $\gamma(V) = \gamma_0 - cV^2/2$ (where γ , c , and V are, respectively, the surface tension, the capacitance, and the potential difference across the electrical double layer of the liquid metal sphere, γ_0 is the maximum surface tension when $V = 0$). Therefore, with the continuously generated electrical voltage from the galvanic cell, the surface tension of the electric double layer of the liquid metal droplets will be varied. When such nonuniform electric field appears, the surface tension becomes asymmetric which would induce imbalance of the pressure difference p and thus the motion of the motors. This is because there exists an approximate relation between p and the surface tension, i.e., $p = 2\gamma/r$, where $1/r$ is the curvature of the droplet surface. In previous researches, it has been found that an external electric field would drive liquid metal droplets to transform between different morphologies and move in the electrolyte. The present motor also follows the same rule. The only difference lies in that it is entirely based on the motor itself rather than the outside electrical field. This allows more freedom for the motors to be flexibly used.

8.4 Macroscopic Brownian Motion of Liquid Metal Motors in Free Space

Unlike the former self-driving liquid metal [10], the motion behavior and driving mechanism for the tiny motors [2] are quite different. It can be observed that such tiny self-powered liquid metal motors, which have a diameter of around 1 mm and were composed of Al–Ga–In alloy, move randomly at a high speed of around 4 cm/s in free space. It perfectly resembles the Brownian motion phenomena. This would add new knowledge to the classical issues in science.

As is well known, since the constant motion of granules on water was discovered by Brown in 1827, tremendous efforts have been made in establishing a theory to characterize the Brownian motion [12]. After almost a half century later, the kinetic theories of heat developed by Maxwell, Boltzmann, and others were merging as a possible explanation. However, it still seemed contradicted with the second law of thermodynamics, which claims that the energy degrades as friction slows down the movement and turns into heat. In 1905, Einstein published a theoretical paper to interpret the Brownian motion [13]. This set up an important bridge between the microscopic dynamics and the macroscopic phenomenon which inspired many subsequent works regarding both thermodynamics and statistical physics [14]. So far, most of the conventional Brownian motions are based on the molecule activities which occur in microscale. There are very limited reports to investigate the phenomena in macro scale.

From an alternative, the liquid metal motors in free space presented a macroscopic Brownian like motion. Particularly, unlike the classical phenomena, the driving force for the current random motion comes from the bubble propulsion from the bottom of the motor, rather than the surrounding molecules. Further, an optical image contrast platform can be established to capture the bubble tails that directly indicated the motion trajectory of each tiny motor. The motion direction and velocity of the tiny motor will be characterized and the driving mechanism lying behind such actuation phenomenon will be preliminarily interpreted.

The Al–Ga–In alloy was prepared in advance using aluminum foil and liquid metal GaIn10 (weight percentage, Ga 90%, In 10%). Here, the mass percentage of Al in Al–Ga–In alloy was prescribed as about 1%. When liquid metal GaIn10 was injected on the Al foil, dissolution happened with liquid metal penetrating into solid aluminum [15]. Since the dissolution of Al in the air might oxidize Al into Al_2O_3 because of its low dissolving speed, we made a particular processing by placing both the liquid metal and aluminum foil into NaOH aqueous solution (0.5 mol/L) to accelerate the dissolving speed. After the aluminum foil was totally dissolved by GaIn10 alloy, a syringe was adopted to produce liquid metal motors just by injecting the alloy into another glass Petri dish filled with NaOH solution (0.5 mol/L). As revealed before [16], with pretty high surface tension, the liquid metal could be injected to form into tremendous separate tiny droplets with relatively uniform diameters. The whole fabrication process took less than half an hour in a quite straightforward way. After a few while, because of the redox reactions occurring among the aluminum, the alloy,

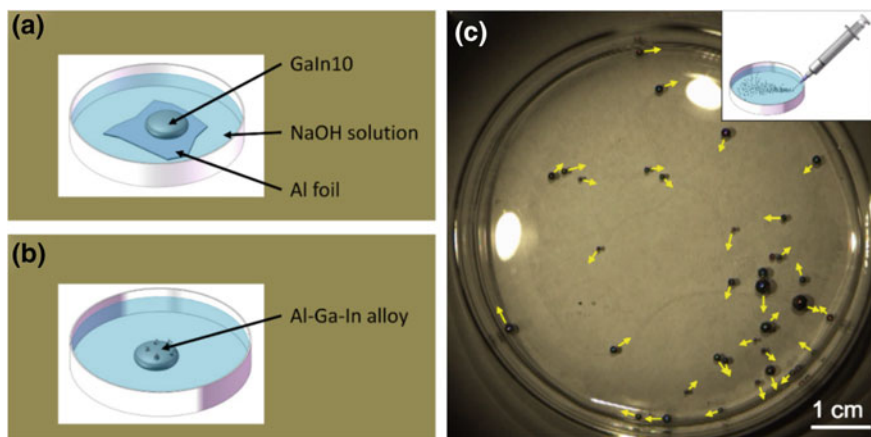


Fig. 8.6 Schematic process for fabricating Al–Ga–In alloy motor droplets [2]. **a** Liquid metal GaIn10 was injected onto Al foil. The mass ratio of GaIn10 and Al foil was 99: 1. Both the GaIn10 and Al foil were immersed in the NaOH aqueous solution (0.5 mol/L). **b** The Al foil was totally dissolved by GaIn10, with hydrogen bubbles arising from the surface. **c** Large amounts of Al–Ga–In alloy droplets were produced by injecting the alloy into another glass Petri dish filled with NaOH aqueous solution (0.5 mol/L). Each droplet began to move swiftly and randomly after a few while. The arrows referred to the motion direction of each tiny motor. The inserted picture indicates that the injection could serve to fabricate tremendous liquid metal motors. All pictures are reproduced with permission

and the surrounding electrolyte, the liquid metal motors with the major diameter of around 1 mm began to move swiftly and randomly with H_2 generated constantly (see Fig. 8.6). Each of the droplets behaved like a tiny motor, which also indicated that the Al was distributed uniformly in the Al–Ga–In alloy. A high-speed camera was used to capture the motion trajectory of the droplets at the frequency of 100 frames per second.

8.5 Dynamic Motion of Al–Ga–In Alloy Droplet Motors

After the alloy was injected into NaOH solution, large amounts of liquid metal motors were immediately generated and dispersed in the Petri dish. After a few while, each small Al–Ga–In droplet began to move swiftly [2], just like a tiny motor in a seemingly random direction with H_2 produced constantly at the bottom of the droplet. By quantifying the subsequent videos, it was found that the motion direction and velocity of the droplets frequently changed with the time. The collision happened inevitably because of the large droplet density. Some of the droplets may become coalesced after collision, some just bounced apart while some new small droplets were pinched off. This dynamic coalescence phenomenon is somewhat similar to the former case as observed on the gently contacting liquid metal droplets [17].

Table 8.1 The diameter of six droplets and the average velocity and total displacement of them during 6 s [2]

	Droplet A	Droplet B	Droplet C	Droplet D	Droplet E	Droplet F
Diameter (mm)	1.2	1.1	1.2	1.0	1.0	0.9
Average velocity (cm/s)	3.79	3.90	3.68	3.55	3.64	3.86
Total displacement (cm)	22.65	23.27	21.94	21.21	21.73	23.04

According to the experiments, the motion trajectory of any droplets in free space was overall unpredictable [2]. Considering that the majority of the tiny motors have reached the diameter of around 1 mm, which implied their macroscopic activities, the present work thus focused on the bulk motion behaviors of motors at this size. Such a phenomenon was termed as macroscopic Brownian like motion [2], although its mechanism is completely different from the classical one. The location of several droplets with different sizes along time can be recorded using a high-speed camera. Through processing the dynamic images, one can obtain the transient locations of six randomly picked droplets every 30 ms for a total 6 s. Assuming that the displacement during each time interval was linear, then the transient velocity at each location can be calculated. The motion trajectories and transient velocity probability distribution of six droplets with similar diameter during 6 s were depicted in Fig. 8.7, respectively. Overall, these results could typically reflect the motion characteristics. For motors with sizes much larger or smaller than the average ones, their speed was somewhat a little bit smaller. However, since such motors amount was very small, they were not taken into account as the samples.

As it can be seen, the motion trajectories of any droplet in the free surface were different [2]. It would turn right or left, speed up or slow down. And the whole process appears rather irregular to a large extent. Besides, one can also see that the transient velocity probability distribution followed the normal distribution. Overall, the droplets moved at a speed of 3–5 cm/s throughout most of the traveling time. For quantitative information, the average velocity and total displacement of each droplet during the 6 s were calculated and listed in Table 8.1. It seems that the average velocity showed no evident relation with the droplet size.

8.6 Driving Mechanisms of Tiny Liquid Metal Motor

Clearly, the trajectory of the current self-powered liquid metal droplets was quite random, which completely resembled the classical Brownian motion [18]. As is well established, the Brownian motion describes a random activity of a microscopic

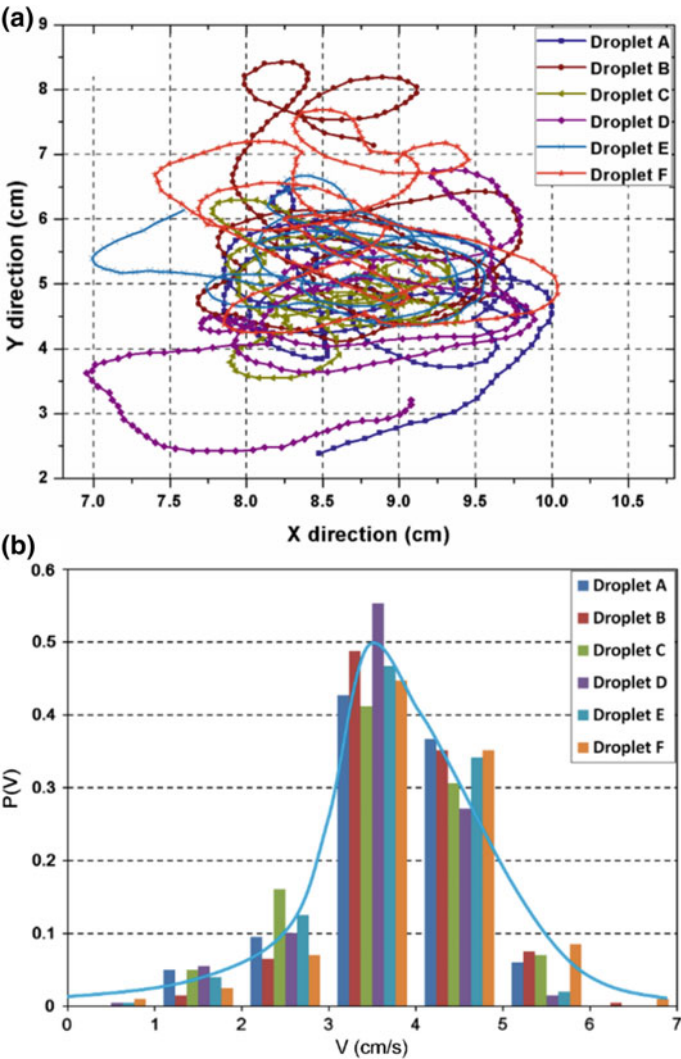


Fig. 8.7 Dynamic motion of six Al–Ga–In alloy droplets during 6 s [2]. The diameters of droplet A, B, C, D, E, F were 1.2 mm, 1.1 mm, 1.2 mm, 1.0 mm, 1.0 mm, and 0.9 mm, respectively. **a** The transient trajectories of six droplets on the two-dimensional free surface of the glass Petri dish. **b** The probability distributions of transient velocities of each droplet. All pictures are reproduced with permission

particle dispersed in liquid or gas. Such motion can be explained by the kinetic theory of heat in that these tiny particles are driven by the surrounding molecules in vigorous motion. It is the collision between the surrounding molecules and the tiny particle that drives it to move randomly. However, unlike such well-known mechanism, the

leading factor for causing the current motion of the liquid metal droplets comes from its interior dynamic force as well as the surrounding effects. As for the classical Brownian motion, particle size was close to the surrounding molecules. Therefore, the collision of the nearby molecules is strong enough to motivate the particle. However, in the present cases, the droplet size was several magnitudes larger than the water molecules. Therefore, the surrounding molecules show little influence on the tiny motor. According to the experiments, the tiny motors were self-propelled by the H_2 bubbles generated from the chemical reaction between Al and surrounding alkaline solution, i.e., $2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2\uparrow$. The detailed driving mechanism of the liquid metal droplets can be explained by the recorded images and process interpretation as presented in Fig. 8.8. In former work, the size of the self-fuelled motor was around 1 cm or even larger and the Al flake was just placed at the back side of the motor. Clearly, the Al flake and the motor formed a primary battery and thus the electrochemical effect offered the main driving force. But in the present work, the Al and GaIn alloy was mixed in advance and then dispersed into an alkaline solution. The Al atoms were uniformly distributed throughout the liquid metal interior. As a result, the electrochemical effect was no longer dominant although it may partially contribute to the behavior. Instead, the H_2 bubbles functioned as the main driving force. This can be reflected by the fact that the running direction of the motor is controlled by the ejection of the bubbles. More experimental observations can be clearly seen in the later section.

As discussed already [19], the liquid metal embrittlement of Al by Ga would accelerate the reaction of Al with an alkaline solution. The penetration of Ga into Al shifts the potential and helps the thinning of passivating Al_2O_3 film. Thus, the reaction lasts rapidly for a long time. For the droplets in repetitive experiments [2], it could be seen that the H_2 bubbles were just generated at the bottom rather than other spots, where the motor contacts the Petri dish floor. For the rest of the parts of the liquid metal motor, no H_2 bubbles were found. This unusual phenomenon might be partially explained by the relatively rough or irregular surface of the glass Petri dish at the microscopic level. It is clearly different compared with the almost perfect contact interface between liquid metal and alkaline solution. Here, such relatively rough spots, in fact, functioned as the reaction sites while the interface between the liquid metal tiny motor and the alkaline solution was quite smooth. This mechanism also partially answers the mystery that some of the liquid metal motors choose to run closely along the wall of the Petri dish. Clearly, the glass wall there also serves as the reaction site. As the reaction happened, Al was consumed and transported from alloy to reaction sites [20]. Besides, some Al particles were brought out by the H_2 bubbles which also reacted and formed bubbles on the glass surface. These bubbles lifted and rotated the droplet at the same time. The bubbles at the bottom also reduced the friction between the tiny motor and the glass floor. The droplet was then pushed forward by the bubbles. Now that the roughness of the glass surface varies, the droplets might be hindered at some spot and thus changed its direction and velocity frequently. Clearly, this finding on the driving mechanism of the liquid metal motor is different from the phenomena occurring on a much larger motor as observed before [8], where the electrochemical-induced surface tension evidently

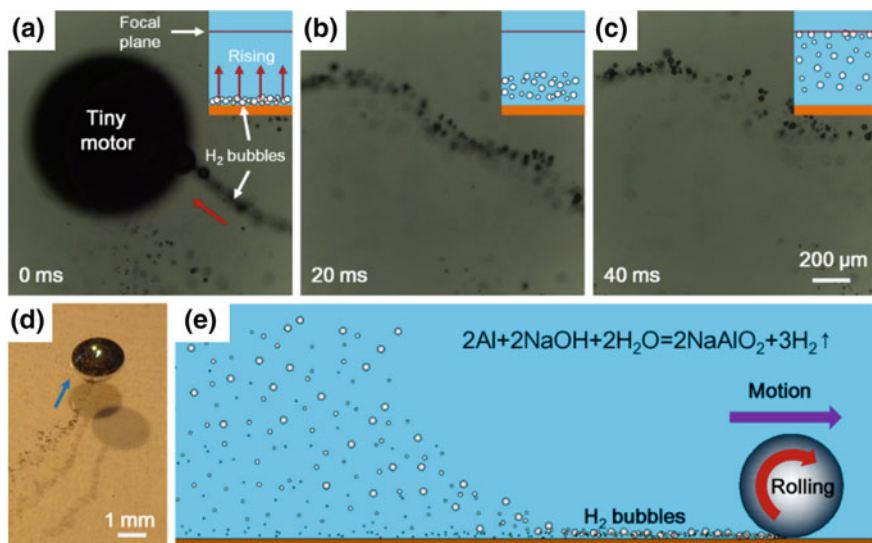


Fig. 8.8 The driving mechanisms of Brownian liquid metal tiny motor [2]. **a**, **b**, and **c** gave the microscopic images regarding the detailed motion of a liquid metal droplet in NaOH solution. The focal point of the microscope was set a little bit higher than the glass floor. H_2 bubbles of different size were generated from the bottom of the droplet and rose up because of buoyancy force. **d** Image taken by camera showing the H_2 bubbles arising from the bottom of the droplet. The two shadows of the droplets were the result of two different background lights. **e** Schematic image of the self-powered liquid metal tiny motor. The H_2 bubbles shifted and pushed the liquid metal tiny motor forward. The motion of the motor was a combination of rolling and translating activities. All pictures are reproduced with permission

drove the moving of the liquid metal. While in the current phenomena, bubble force appears more direct and stronger. Apart from the glass Petri dish, Yuan et al. [2] also tried the same experiments in polystyrene (PS) Petri dish. It was found that the H_2 bubbles were adhered on PS Petri dish, which hindered the movement of the liquid metal motors, while H_2 bubbles would easily detach from the glass Petri dish. Clearly, the roughness of the floor did influence the reaction. Further works are needed to quantify the influences of different floors.

According to Langevin equation [18], the motion of Brownian particle can be described by equation, i.e., $m \frac{du}{dt} = -\lambda u + F(t)$, where m is mass of the particle, u velocity, and λ is the viscous force factor according to Stokes law [21], $F(t)$ is the resultant force of the surrounding fluid particles on the Brownian particle. For the currently investigated liquid metal motor, it also follows a similar equation. However, the resultant force $F(t)$ should clearly be a combination among bubble propulsion force F_p , Coulomb force F_E between surrounding motors due to electrical effects, magnetic force F_B between surrounding motors due to interior field induced, friction force $-F_f$ between the motor and the glass surface. Thus, one can get $F(t) = F_p + F_E + F_B - F_f$. As for the friction force— λu , Stokes law did not fully fit in the

above situation. Assume that the density and viscosity of the NaOH aqueous solution approximate to that of water, then the Reynolds numbers of the fully developed tiny motors as listed in Table 8.1 are all about 40. Since the Stokes law holds true mainly for low Reynolds number flow ($Re \ll 1$), it was unable to describe the viscous force of the tiny motor. Besides, the spherical motors are rolling forward which makes the problem even more complicated. Hence, without losing generality, one can denote the viscous force as $-F_V$. However, for the H_2 bubbles generated from the motor bottom with an average size of about 0.03 mm, the Re number dose gradually increase from zero after detachment of the bubble from the motor. In this case, at the early stage of the droplet motion, the dragging force could be well described by Stokes' law as $D = 6\pi\mu Ua$, where μ is the viscosity of the surrounding fluid, U is the velocity of the droplet and a is the diameter of the sphere. At this stage, it is still difficult to quantify each term in the Langevin equation to characterize the current liquid metal motors. But from this phenomenological equation, one can easily understand that due to the dynamic processes, uncertain substrate environments, and interactions between the motors and the surroundings, the apparent force $F(t)$ as applied on a single motor is, in fact, a random one. Thus, the liquid metal motor just runs in a Brownian-like motion behavior.

Note that it generally took several seconds for the tiny motors to start moving after they were injected into the alkaline solution. This might be explained by the film rupture [22] occurring between the motor and the glass floor. Such fundamental process can be interpreted as shown in Fig. 8.9. When two bulk phases meet, there generally exists a region of finite thickness at the molecular level. An electrical double layer (EDL) [23] would appear at the interface between two different materials. In our cases, the Al–Ga–In liquid metal droplets generally remained spherical in alkaline solution because of its high surface tension relative to the surrounding solution. Besides, both the Al–Ga–In alloy and the alkaline solution were in the liquid phase, thus the interface between the droplets and the alkaline solution was quite smooth. However, the glass Petri dish surface may be rough and it is in the solid state. After the tiny motor reached the glass floor of the Petri dish, there still existed a thin alkaline film between the motor and the glass floor. It took some time for the motor to contact the glass floor before the alkaline solution was squeezed out between them. The rough glass surface then offered the reaction site for the redox reaction between Al and alkaline solution. Clearly, the electron density would become larger at the sharp locations. Thus, when the liquid metal droplet contacted the sharp edge of the glass surface, the electrical double layer excited the redox reaction and H_2 bubbles were hence generated there. Now that the roughness of the glass surface was uncertain, this also partially contributes to the random Brownian motion of the tiny motor.

Further, to better reveal the important phenomena that the H_2 bubbles were in fact generated underneath and behind the droplets, Yuan et al. [2] additionally established an experimental platform with high optical image contrast. The Petri dish was lifted horizontally. Two rays of background light were illuminated from upside and downside, respectively. The camera recorded the images from the bottom of the Petri dish. As can be seen, the motion trajectory can now be perfectly observed with the hydrogen bubble tail along the motion trajectory (see Fig. 8.10).

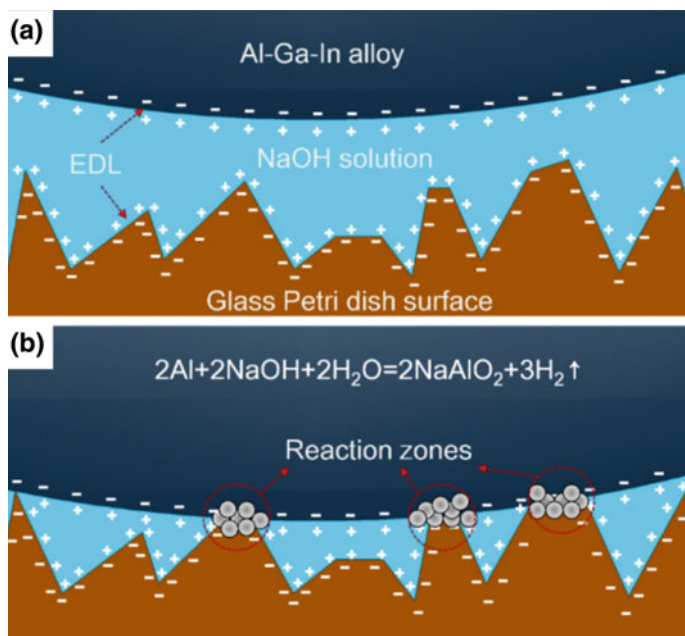


Fig. 8.9 The NaOH solution film ruptures between Al–Ga–In alloy tiny motor and the glass Petri dish floor [2]. **a** Microstructure between Al–Ga–In alloy tiny motor and the glass Petri dish floor. The NaOH solution separated the motor and the glass floor. Electrical double layer (EDL) exists at both interfaces. **b** The NaOH solution was squeezed out of the interval gradually and the motor contacted the glass floor. The contacting sites triggered the redox action between Al and NaOH solution. H_2 were generated from the reaction zones. All pictures are reproduced with permission

In the aforementioned experiments, the images from top down with a white paper below the Petri dish can be captured. In this way, the liquid metal droplets were seen clearly in black while the bubbles appeared not so clear [2]. After lifting the Petri dish and placing background light from both above and below the Petri dish, the bubbles were revealed clearly with almost no shadow (see Fig. 8.10). The trajectory of each tiny motor can now be clearly distinguished with a long bubble tail falling behind. This optical contrast method resembled in principle to the well-known Wilson Cloud Chamber method [24]. Until now, the Wilson Cloud Chamber was used mainly to record the trail of a charged particle in the supersaturated vapor. The ionizing radiation serves as the condensation centers for the vapor and thus the path can be indicated by the tiny liquid droplets. In our experiment, the bubbles in the alkaline solution perfectly depict the traveling path of the Al–Ga–In alloy tiny motor. The bubbles rose because of the buoyancy effect. At the same time, they were imposed by the viscous force of the surrounding solution. Due to the small bubble size (the average bubble diameter was about 0.03 mm), the buoyancy force was quite small (about $5 \mu\text{N}$). So, it would take a certain period of time for the bubbles to reach the liquid level. Thus, the bubble tail of each tiny motor could be 10 cm or longer which corresponds very

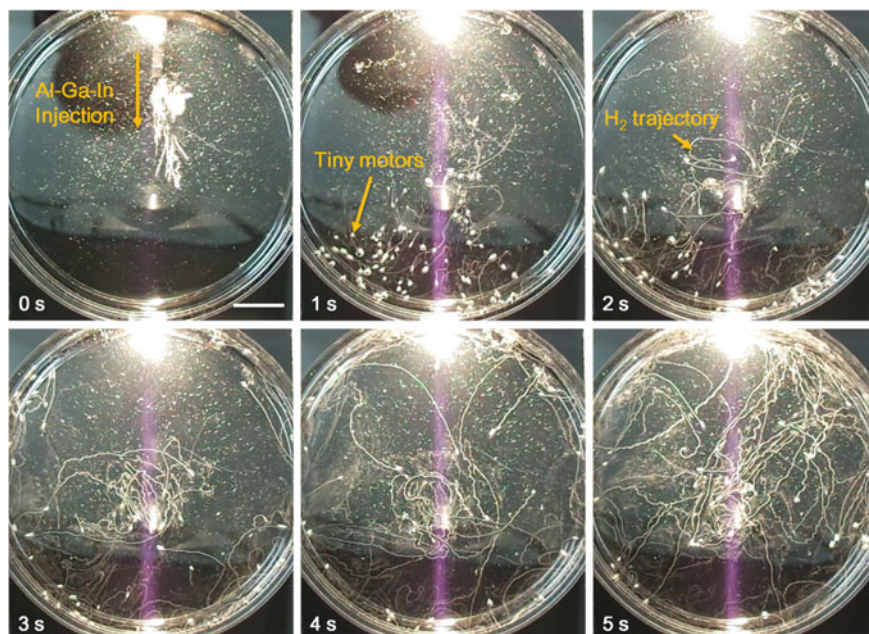


Fig. 8.10 Down top view of the liquid metal tiny motors [2]. At 0 s, the motors were produced by injecting the Al–Ga–In alloy into the Petri dish filled with NaOH aqueous solution (0.5 mol/L). The motors then traveled around on the free glass surface, with H_2 generated constantly from the bottom. The curves in the figure indicated the trajectory of each droplet which is heading the movement. The images at several times from 0 s to 5 s indicate the random Brownian motion behavior of the liquid metal motors. The scale bar was 1 cm. All pictures are reproduced with permission

well to the motion trajectory as image processed in Fig. 8.10. Such experimental method would serve as an important tool for future investigation on the self-powered liquid metal motion behaviors.

8.7 Magnetic Trap Effect of Liquid Metal Motors

The aluminum powered self-running liquid metal motors own many interesting physical properties. For example, the magnetic field can make up a boundary to restrict the motion of such motors. Tan et al.'s work found that [25], for the droplet motors with a diameter below 1 mm, such magnetic trap effect will be strong enough to bounce them off the boundary. Owing to the Lorentz force, the high magnetic field will break up the directional running of the motor. The more aluminum added in the metal droplet, the stronger the trap effect. This phenomenon suggests an important way to control the behavior of the liquid metal motors.

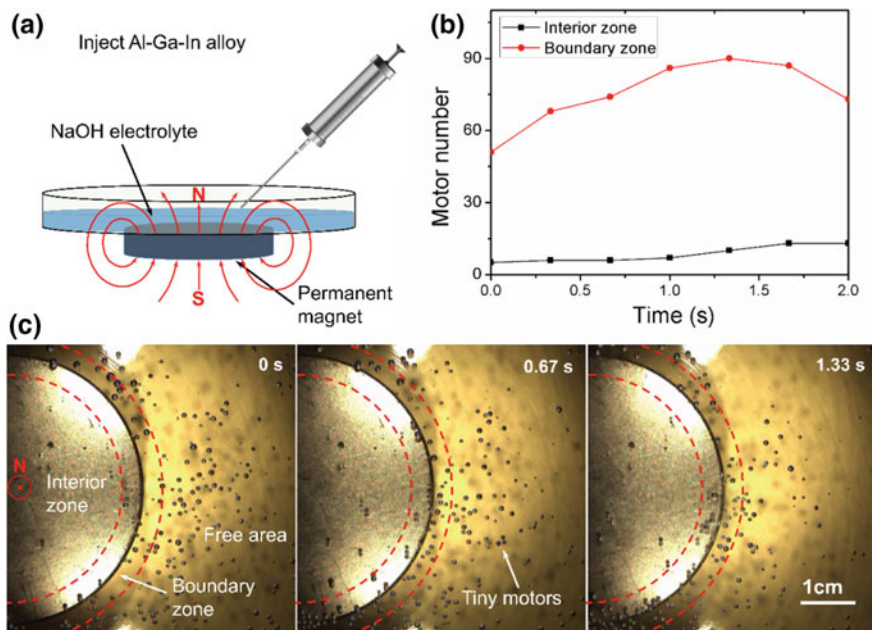


Fig. 8.11 Liquid metal motor under magnetic trap [25]. **a** Schematic for producing many Al–Ga–In motors in a Petri dish. **b** The number of motors along with time in the interior and boundary zone of magnet. **c** Sequential snapshots of tremendous Al–Ga–In motors’ motion under magnetic field

Figure 8.11a illustrates the basic approach to clarify the above issue and the mechanisms lying behind. Through placing a permanent magnet under the Petri dish, the random motion of tiny motors will be regulated obviously. The Al–Ga–In alloy that was adopted as raw materials for making motors was fabricated through adding aluminum into GaIn_{10} (Ga 90%, In 10% in weight) with the proportion of 0.68: 99.32 (Al 0.67% in weight) in a NaOH electrolyte environment. Numerous tiny Al–Ga–In motors, whose sizes are usually less than 1 mm, were produced through injecting the pre-prepared alloy into a glass Petri dish with a syringe. If there are no fields, the motors just keep running automatically and randomly, as disclosed before. But as can be observed, under external magnetic field, the kinematic velocity, and direction of the motors both encounter restriction. Specifically, the velocity of motors will drop suddenly when applying the magnetic field. Then they take a reverse motion or got trapped at the boundary of the magnet.

One can also find that the motor swarm could display a remarkable group phenomenon if the quantity of the tiny motors is sufficient [25]. The numbers of motors in different regions vary with time. Most motors just gather near the boundary of the magnet. To quantify this event, the quantities of motors in different regions were measured as a function of time and compared, respectively. As shown in Fig. 8.11b, the number of motors in the boundary zone will increase with the time going on, which originates from the directional movement of the motors in the free space of the

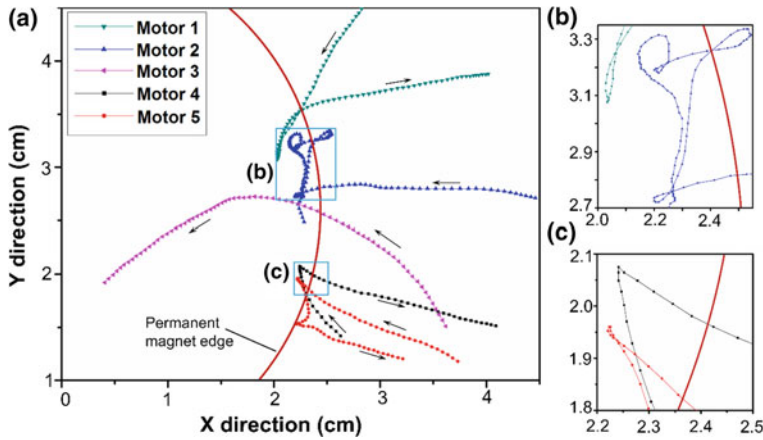


Fig. 8.12 Motion trajectories of five Al-Ga-In motors in free space solution of a Petri dish with a permanent magnet placed underneath [25]. **a** Location paths of five motors. **b–c** Drawings of partial enlargement of **a**

Petri dish. However, the number of motors in the interior zone stays largely constant all the time mainly because of the restriction from the boundary of the magnet to the outside motors, leaving them swirling or just bouncing off.

Figure 8.11 depicted a static view of the droplet motors' behavior which was based on quantitative statistics. However, by trailing the path of each motor, one could find that its speed changes regularly. In Tan et al.'s work [25], five typical samples were chosen to represent most of the motors and their moving trajectories were plotted in Fig. 8.12. With the uniform time interval (0.02 s) between two neighboring points, it can be observed how fast the target object would move. Figure 8.12a depicted a panoramic view of five droplets and Fig. 8.12b, c presented its two partial enlargements for more clarity. For an accurate exhibition, the velocity variation curves of these five motors were plotted in Fig. 8.13.

The motion direction of the motors can be observed in Fig. 8.12, while the velocity can be obtained from Fig. 8.13. It can be seen that [25], motor 1 which ran to the magnet from the free space of the Petri dish and overshot the magnet boundary at time T_1 , moves quite similar to motor 4. The speed of motor 1 and motor 2 dropped suddenly to zero after rushing into the border, then they reversed moving direction and accelerated until dashing out of the magnet at time T_2 . In terms of motor 2, it kept wavering once entering the boundary, with speed also rise and fall while holding the mean at 1.2 cm/s, which was lower than the value of 3.0 cm/s that counted before approaching the edge of the magnet. As for motor 5, its speed decelerated to zero at time T_1 when rushing into the border for the first time, then accelerated oppositely to the outside of the magnet at time T_2 and returned again until contacting the boundary at time T_3 . At this moment, it nearly stopped but still ran to the far distance. The diameters of the five motors selected for the above analysis are slightly different, which were $d_1 = 1.04$ mm, $d_2 = 1.04$ mm, $d_3 = 1.56$ mm, $d_4 = 1.15$ mm and $d_5 =$

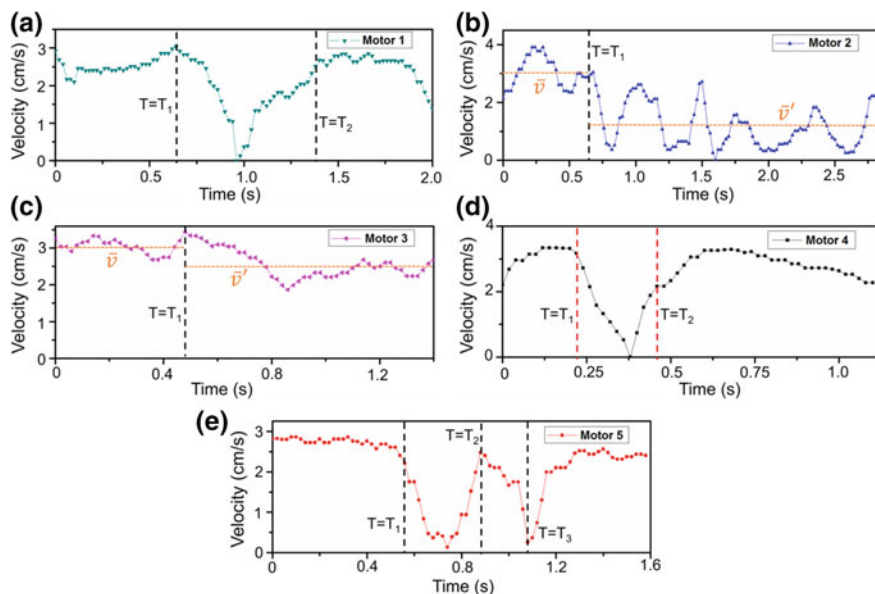


Fig. 8.13 Velocity variation curves of five Al-Ga-In droplet motors [25]. **a** Motor 1. **b** Motor 2. **c** Motor 3. **d** Motor 4. **e** Motor 5

0.83 mm, respectively. Here one can discover that the diameter of motor 3 is evidently larger than others. Though its diameter was amplified only about 50%, accumulating to the volume and the mass, they had enlarged for three times, as well as the inertia. In terms of motor 3, it slightly reduced the speed from 3 to 2.5 cm/s while the other motors shifted down to almost zero when approaching the magnet boundary. Due to larger inertia, motor 3 got rid of the shackles of the magnetic trap and kept forging ahead, though turning its direction for about 60° .

The principle of applying a magnetic field to control tiny Al-Ga-In liquid metal motors is based on its self-driving mechanism [25], which can be interpreted as follows. The tiny motor scattered into NaOH solution will maintain standard spherical shape relying on its strong surface tension as revealed before. If the dimension of the motor becomes relatively large, the spherule will form a plane where it contacts with the bottom of the Petri dish due to gravity. It is clear to see that Al is continuously exuding from the plane to react with the surrounding environment and produces hydrogen, as represented in the chemical formula: $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} = 2\text{NaAlO}_2 + 3\text{H}_2\uparrow$. As shown in Fig. 8.14a, the hydrogen gas stream emitting from a certain direction drives the motor to roll forward, which will reach a balance to maintain the motor rolling until the aluminum inside is consumed. Due to change of the flow field or variety of the bottom surface contacting the motor, the direction in which the hydrogen gas stream ejects will also adjust with them, resulting in the veer of motor motion.

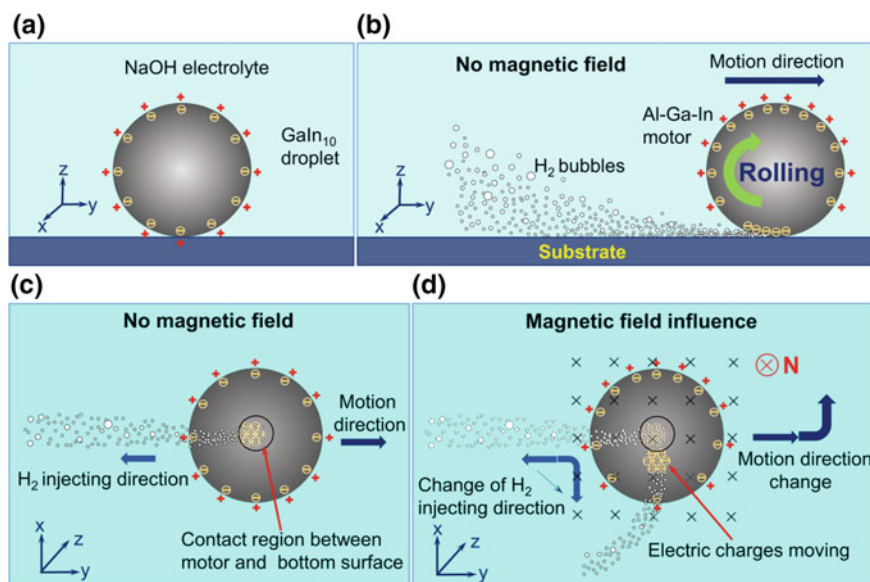


Fig. 8.14 Magnetic effect on the motion of liquid metal motor [25]. **a** Schematic of the electric double layer (EDL) of a GaIn_{10} droplet immersed in the NaOH electrolyte. **b** The mechanism of an Al-Ga-In motor's motion without the magnetic field and schematic of its electrical charges distribution. **c** Bottom view of the self-propelled motor without a magnetic field. **d** Schematic of the motor's electrical charge alteration influenced by the magnetic field in a perspective from the bottom to up

One can attribute the electromagnetic mechanism to affect the motors' motion while simple self-driven motors rely on the mechanical principle rolling with the bubble recoil [25]. First of all, Ga-In liquid metal droplets can react spontaneously in NaOH solution, producing gallates like $[\text{Ga}(\text{OH})_4]^-$ and leaving their surfaces with negative charges. These charges then attract the positive ions in the solution and produce an electric double layer as Fig. 8.14a. The liquid metal added with Al, by extension, will take place of galvanic cell reaction in the substrate of the petri dish where the Al in the liquid metal droplet exudes and reacts with the NaOH solution. In this galvanic cell reaction, the positive electrode is Ga-In alloy of which the chemical equation is expressed as $6\text{H}_2\text{O} + 6\text{e}^- = 3\text{H}_2\uparrow + 6\text{OH}^-$, and the negative electrode is Al sweating continuously from the droplet, whose reaction is $2\text{Al} + 8\text{OH}^- - 6\text{e}^- = 2\text{AlO}_2^- + 4\text{H}_2\text{O}$. Further, one can discover new charges distribution in the place where the liquid metal droplet contacts with the substrate, which is also the reaction zone for the spilling aluminum, as depicted in Fig. 8.14b from side view and Fig. 8.14c from bottom view. Additional explanation is that the hydrogen should be puffed from the surface of the Ga-In positive electrode based on the primary cell mechanism. However, here it emits from the Al electrode where many negative charges gather because the two electrodes were short-circuited. When these motors run in the magnetic field, the charges in their surface will also move according to

Lorentz force formula $F = QvB$, where Q is the magnitude of charge, v the rapidity of the charges' movement, and B the magnetic field flux density. The charges congregation determining the direction of motors' motion will transfer as affected by the magnetic field as shown in Fig. 8.14d, which interrupts the continuous motion of motors because the bubble recoil force cannot just fix one point where Al contacts with the petri dish, reacts with NaOH and gather negative charges.

When the force continuously driving motor forward vanishes, the motor will violently decelerate under actions of friction and viscous resistance [25]. To be highlighted, the slow effect takes subtler forms before the motors enter into the permanent magnet due to weak magnetic field, while the speed variation fluctuates significantly once reaching the boundary. If the motors stop in the magnetic field, Lorentz force will disappear. Then Al will sweat again from the interior of the liquid metal spherule and inject hydrogen to drive the tiny motor itself via a chemical reaction. When reaccelerating to a proper amount along the direction of the boundary, the motors 1, 4, 5 in Fig. 8.12 are lucky enough to get rid of the restrain of the magnet. In general, they move randomly nevertheless because the hydrogen emits in stochastic directions. Towards the interior or along the boundary, there are chances that the motors will take a roller-coaster ride due to continuous unidirectional drive in low speed and the intermittent multidirection resistance in high speed dominated by turn. The fluctuation of velocity and disorder of trajectory will not end as long as the motor is trapped in the permanent magnet, like the motor 2 in Fig. 8.12.

Through the above descriptions, one can see that, two critical factors for motor's motion are the magnetic field flux density and the charge density in the congregation area which is related to the amount of Al in motor [25]. The more Al was added, the more charges will assemble in the reaction area. Therefore magnetic field will restrict the motor more evidently according to the formula $F = QvB$. To verify such a hypothesis, an additional set of controlled trials was made. Figure 8.15a displays that the new tiny motors, which are made by compounding 1.5 ml GaIn₁₀ and 0.145 g Al (1.5% quality ratio), are almost bounded to the outside of the magnet without exception. This contrasted starkly with the previous experiment that the quality ratio is 0.67%, where a part of motors crossed the boundary in Fig. 8.11c. Another evidence lies in that the motor 3 in Fig. 8.12 could easily run across the border with the radius of 1.56 mm and the velocity of 3 cm/s, yet the motors in Fig. 8.15a were still blocked at the border outside with the radius of 2.1 mm and the velocity of 5.8 cm/s. As a contrast, for the cases without the magnet, the motors just keep running randomly. On the Petri dish bottom surface, the magnetic field flux density is the function of the distance from the center (radius). Thus, by measuring the value of a line, the magnetic field flux density distribution of the entire region can be obtained. Figure 8.15b showed the curves along the radius. According to the above electromagnetic mechanism, it can be obtained that the self-propelled liquid metal motor cannot keep continuous movement in the region of the magnetic field with high strength. Thus from the beginning, a cluster of tiny motors will gather in the magnet boundary with their random moving because the magnetic strength is zero in the magnet boundary and two peak value on the two sides. That is to say, the magnetic field around the magnet boundary works like a valley. On the magnet side, the peak value was too high to

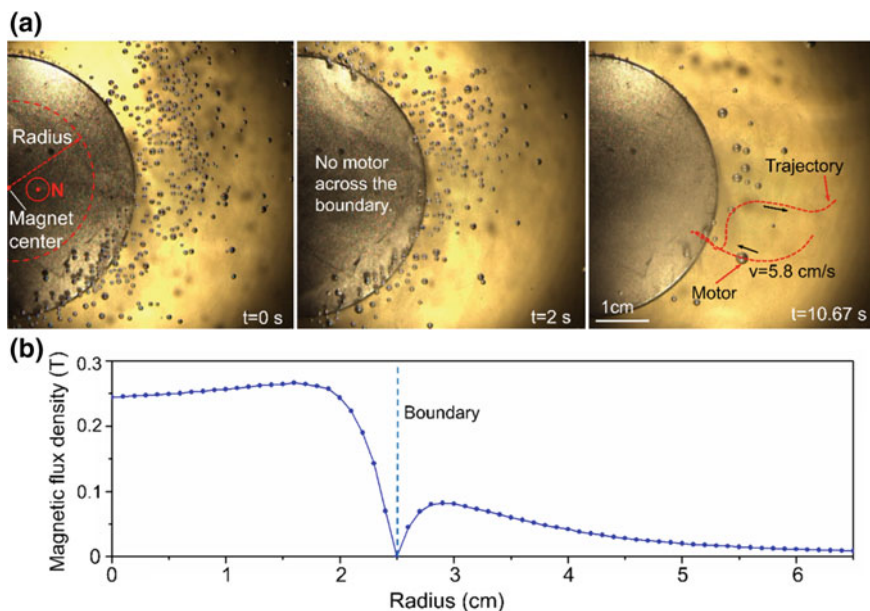


Fig. 8.15 Moving of liquid metal motor under magnetic effect [25]. **a** Many Al–Ga–In motors with Al accounting for 1.51% in weight trapped in the boundary zone of the magnet (0 s and 2 s) and trajectory of a motor with large momentum (10.67 s) (Multimedia view 5a). **b** Magnetic flux density-radius plot on the Petri dish bottom surface

allow the motors to run across. However, the peak value on the outside was relatively low. So soon after, the gathered motors got back from the boundary and scattered in the free zone.

8.8 Conclusion

Overall, self-powered liquid metal tiny motors can be spontaneously fabricated in large quantity via a rather straightforward way. Such motors swiftly running inside the electrolyte are enabled through fueling a tiny piece of aluminum to EGaIn alloy to convert chemical energy into propulsion power. Clearly, the prepared functional solutions can be stored without requesting extra requirement. Once needed, just injecting such mixtures into the desired electrolyte will make tiny motors. The motor amount, size, velocity, etc., can all be well controlled by regulating the related factors.

The self-powered liquid metal Al–Ga–In tiny motors inside the electrolyte free space take the random Brownian-like motion behavior at a high speed of about 4 cm/s. Unlike the classical phenomena observed on molecule level, the current events occur on a macroscale, say in millimeter scale. And the random behaviors come

from the interior driving force of the motors, the uncertain interactions among the neighboring motors, the substrate bottom, and the surrounding electrolyte molecules, etc. Particularly, by introducing a high contrast optical image method, the bubbles behind the liquid metal motor clearly revealed the trajectories of the tiny motors. Mainly due to such H_2 bubbles generated from the redox reaction between Al and alkaline solution, the motors were propelled to move here and there.

Further, the magnetic field could serve as a trap to restrict self-propulsion of the Al–Ga–In motors. Such an effect is rather evident to affect the motors with a diameter below 1 mm, but not for larger ones. The magnetic field would influence the electrical charges generated due to the reaction between Al and NaOH solution. As a result, such modulated electrical charges will break down the motor's continuous motion which was mainly driven otherwise by the H_2 bubble recoil. Such finding suggests that the restriction force was significantly determined by the electrical charge of a chemical reaction. With the increased proportion of aluminum in Al–Ga–In motor, the magnetic trap effect becomes stronger. In the near future, a coil magnet can also be designed to flexibly control the specific motor motion. Such trap effect, combined with its working capacity can be applied to controlling the running range of the motors regarding targeted delivery.

In summary, the basic characteristics and fundamental mechanisms disclosed on liquid metal motors would shed light for future works on complex fluid mechanics, droplet machines including injectable devices as well as the classical Brownian motion phenomenon, etc. The established optical image contrast method also provides an important experimental tool for further investigations along this direction. It also opens the opportunity for designing future soft-robot, tiny machine, or microfluidic systems with high efficiency.

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Chapter 9

Liquid Metal Transient State Machine



Abstract Internally triggered motion of an object owns important potential in diverse application areas ranging from micromachines, actuator, or sensor, to self-assembly of superstructures. This lab (Sheng et al. in *Small* 11:5253–5261, 2015 [1]) proposed and demonstrated a new conceptual liquid metal machine style, the transient state machine that can work as either a large size robot, partial running elements, or just divided spontaneously running swarm of tiny motors. According to the need, the discrete droplet machines as quickly generated through injecting the stream of a large liquid metal machine can combine back again to the original one. Over the process, each tiny machine just keeps its running, colliding, bouncing, or adhesion states until finally assembles into a single machine. Unlike the commonly encountered rigid machines, such transient state system can be reversible in working shapes. Depending on their surface tension, the autonomously traveling droplet motors can experience bouncing and colliding before undergoing total coalescence, arrested coalescence, or total bounce. Further, the liquid metal machine can also be made as color changeable. In this sense, some transformable biomimetic soft machine which was termed as liquid metal “chameleon” has now been possible. As it was demonstrated, the fluorescent liquid metal can be manipulated into various appearances like fluorescent orange, blue, pink, or even send out fluorescence in the dark. It can realize transformation and discoloration by splitting and merging among different colors. If subject to electrical stimulation, such colors would transform from fluorescence into metallic color. These findings are expected to help design future color changeable machines and mold unconventional robot that could automatically transform among different geometries such as a single or swarm, small or large size, assembling and interaction including color, etc. It refreshes people’s basic understandings of machines, smart materials, fluid mechanics, and micromotors. In this chapter, the basic concept of the liquid metal transient state and color changeable machines will be illustrated.

Keywords Transient state machine · Tiny motor
Transformable biomimetic chameleon · Fluorescent liquid metal
Color changeable soft machine

9.1 About Transient State Machine

The room temperature liquid metals such as EGaIn (75% gallium and 25% indium) and galinstan (68.5% gallium, 21.5% indium, and 10% tin) inherits many unusual behaviors that have never been realized before [2–4]. The micro- and nanoscopic motors, thus, made can zip through fluids fuelled purely by chemical reactions. Conventionally, most motors are solid and shaped like rods while propelled by microbubbles generation. Gases can come from a chemical reaction between metallic motor coat and acid solution or electrolyte catalysis reaction in which motors perform as a catalyst. But making similar machines at larger scales is a challenge. Recently, the present lab found that such material can be enabled to quickly move if fed with aluminum as its fuel [5]. In this way, a single drop of the large motor can be generated and would propel itself around the container for approximately one hour. But how to generate tremendous self-powered tiny machines still reserved a challenge. Bearing this point in mind, we further found a rather easy going way to quickly fabricate numerous motors at larger scales which can spontaneously run here and there inside the solution [1]. Each machine works just like an energetic motor. It can be noticed that such self-driven liquid metal machines could compose into a single motor or vice versa which still maintains running state. The liquid metal motors can run separately, either via a single style, or a traveling swarm. And they can assemble together. All these machines come from their common original source, the functional liquid metal solution pre-made and stored in a syringe. This reminds that one can then make a new conceptual machine that can run globally or discretely. It is for this reason we came up to such a fundamental concept regarding machine style: The Transient State Machine [1]. A straightforward direct application from such machine is to mold it as injectable devices, which can run as an integrated large machine or discrete motors that can work independently and can then be collected after finishing each own task. Such machine type would find important applications for some unusual practices in the near future.

The interaction between aluminum and liquid metal, in fact, inherits with rather profound sciences. As revealed by our recent study, a small amount of aluminum can be dissolved in EGaIn to make functional solution which can then be injected into electrolyte to fabricate tremendous tiny motors in a moment. Here, the aluminum acts as chemical fuel for the aluminum–alkaline galvanic cell reaction. Due to the liquid property of the metal flow, the generated droplet can move here and there, just like an energetic motor. All the motors can be collected into a container to make a single self-running machine. If needed, the machine can be reinjected again into electrolyte to make a swarm of tiny motors, which finally would lead to the original large machine through a colliding process. With bubble and electricity driving mechanisms working together, the liquid metal motors can have much higher motion efficiency. A series of experiments were, thus, performed and a group of unexpected phenomena was revealed. The following sections illustrate the most typical colliding and coalescence behaviors of the droplet motors and the conceptual machine type it incubates.

9.2 Preparation of Functional Liquid Metal Alloy

It has been known that pure aluminum could react with water through oxidizing with the oxygen inside the H_2O molecule. Normally, such reaction is prohibited by the very thin passivation layer of aluminum oxide (Al_2O_3) that forms on the metal surface [1]. In order to guarantee a continuous reaction, the passivation layer of the Al_2O_3 must be disrupted. Many different methods have, therefore, been investigated. One approach is to maintain aluminum powder at a high-temperature, high-pressure chamber where it would melt and oxidize with water [6]. Another was to use aluminum–gallium alloys to produce hydrogen [7]. Such technology is expected to be extremely important in future energy area.

At room temperature, aluminum and water could produce aluminum hydroxide and hydrogen via an exothermic reaction. From an alternative different from existing approaches, the liquid metal EGaIn as adopted here would serve to promote this reaction [1]. This is because the gallium prevents a film of aluminum hydroxide from forming on the particle surface during the reaction. As shown in Fig. 9.1a, to make the EGaIn aluminum alloy, a drop of EGaIn (0.1 ml) was immersed into NaOH (0.4 mol/L) solution in a Petri dish. A small piece of aluminum sheet (0.05 g) was adopted to contact with EGaIn until the particles were evenly distributed. Here, the fabricated alloy appears as in liquid phase which is therefore rather easy for injection. During such diffusion process, hydrogen was generated and the alloy takes high-speed self-rotation. To illustrate such self-rotation behavior of the alloy, the ink was used to highlight the process as shown in Fig. 9.1b. Then the alloy was sucked into a 1 ml syringe for late use. If injecting such functional solution into the NaOH (0.4 mol/L) electrolyte, the liquid metal stream would automatically break into a large amount of droplets due to the high surface tension of the liquid metal [2–4], as shown in Fig. 9.1c. According to the observation, each of those alloy droplets runs just like a micro-sized motor. Overall, the droplets kept running randomly. With the time goes on, some of the droplet motors began to collide and coalesce in the channel. The NaOH solution used was maintained at a temperature higher than 38 °C by a hot water bath at 70 °C underneath the dish. This is to accelerate the droplet motors' movements and coalescence. In order to grasp the clear picture of the events, a high-speed video camera (Canon XF-305, Japan) was used to shoot the dynamic process of the colliding and coalescence of the autonomously running liquid metal droplets.

9.3 Force and Velocity of Transient State Motors

Clearly, as is explained before [5], the motion of the liquid metal droplets was induced due to energy conversion inside its chemical reaction with the surrounding electrolyte. Here, a major chemical reaction between aluminum and NaOH solution occurs as $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} = 2\text{NaAlO}_2 + 3\text{H}_2\uparrow$. This is why a lot of bubbles were gener-

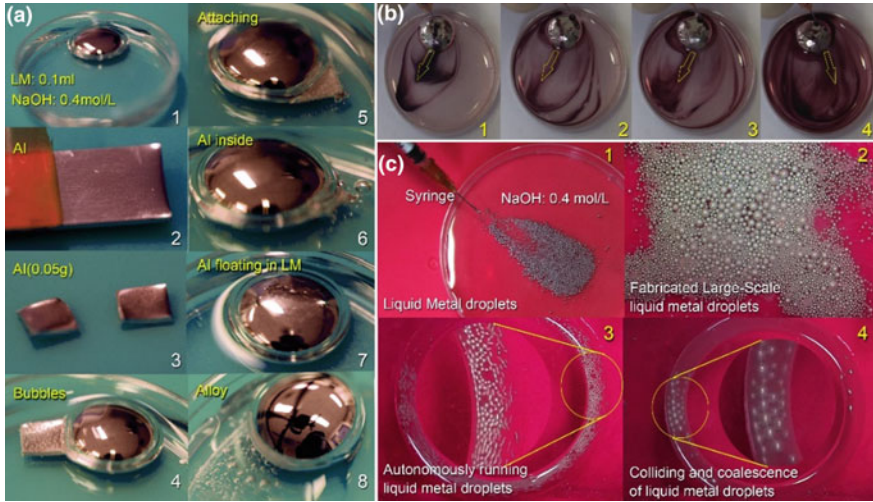


Fig. 9.1 The alloy preparation and fabrication of autonomously running liquid metal machine [1]. **a** Liquid metal pool (0.1 ml) was deposited in a Petri dish and a piece of aluminum (0.05 g) was picked up by tweezers to attach to the liquid metal object (**a1–a4**). A lot of bubbles were generated when aluminum got in touch with the liquid metal in NaOH solution. After approximately 30 min, aluminum was dissolved in liquid metal and the alloy was prepared, with high-speed self-rotation (**a5–a8**). **b** Ink was introduced to highlight the self-rotation of the alloy; ink was dropped from the top of the alloy droplet and then passed through the metal droplet to the front. **c** The syringe was used to inject the alloy into the NaOH solution and to produce a large number of small liquid metal droplets (**c1–c2**). There were a lot of autonomously running droplet motors in the circular channel, and some of which collided and coalesced in the channel (**c3–c4**). All pictures are reproduced with permission

ated. As for the high-speed self-rotation of the droplet motor, it can be interpreted as that the aluminum/EGaIn system, in fact, forms a galvanic cell, where aluminum works as the cathode and EGaIn the anode [1]. Such phenomenon runs the same as the electric field was applied when liquid metal droplet was immersed in water [8]. Figure 9.2 presents the force and velocity schematic of transient motors based on the liquid metal droplet. For a liquid metal droplet moving in the aqueous solution, the driving forces are derived from the reaction force F_b caused by the detachment of the bubbles, and the electric field force F_e from the bipolar electrochemical reaction, which are balanced by the viscous drag force F_d under the steady state. The viscous drag force can be expressed as $F_d = 2\pi RV(3\mu_w + 2\mu_l)/(\mu_w + \mu_l)$ [9], where R is the droplet radius, V is the translational speed, μ_w (about 1.0×10^{-3} Pa s at 20 °C) is the viscosity of water and μ_l (about 2.4×10^{-3} Pa s at 20 °C) for liquid metal, respectively. The velocity field induced by the motion of liquid metal droplet could be analytically solved [9]. Throughout most of the current experiments, the maximum speed of liquid droplets with different sizes was quantified in the range of about 5–30 cm/s, equivalent to 50–300 body length per second. This is an extremely large magnitude regarding various kinds of artificial tiny self-driven motors as made

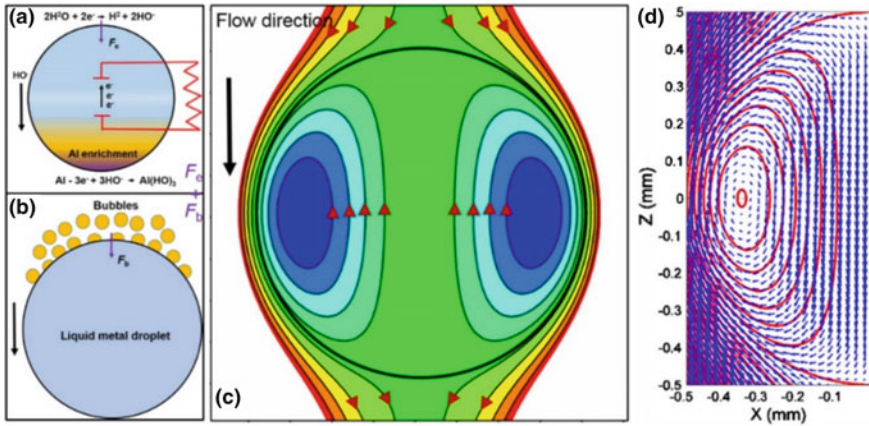


Fig. 9.2 Force and velocity schematic of transient motors based on liquid metal droplet [1]. **a** The endogenous electric field due to bipolar system induced by chemical reaction, which results in a droplet slip velocity relative to the surrounding fluid at the droplet interface; **b** The driving force from hydrogen bubbles detachment; **c** The streamline of the droplet and surrounding fluids induced by the translation speed; **d** The velocity field for liquid droplet with diameter 1 mm and translation speed 5 cm/s. All pictures are reproduced with permission

by human so far. The viscous drag force F_d could be estimated about 450 nN for the liquid metal droplet with diameter 1 mm. Bubbles propulsive force can be estimated by $F_b = \Delta m(v_0 - V)$ [10], where Δm is mass change rate of the bubbles, v_0 is the detached velocity of the bubbles along the translational direction. It is evident that v_0 should be larger than V so as to drive the moving of the liquid metal droplet. The electric field force can read as $F_e = \varepsilon \zeta ER$ [11, 12], where ε is the permittivity of the solution, ζ is the droplet's zeta potential, E is a characteristic magnitude of the endogenous electric field. According to the above definition, one can derive the translational speed as $V = (\Delta m v_0 + \varepsilon \zeta ER) / (\Delta m + 2\pi R(3\mu_w + 2\mu_l) / (\mu_w + \mu_l))$. This relation indicates that the droplet speed is mainly determined by the electric force and the bubble propulsive force. In addition, the amount Δm , v_0 , and E are strongly dependent on the chemical reaction rate, which is determined by the concentration of Al and temperature.

9.4 Schematic for Transient State Liquid Metal Machine

Figure 9.3 presents the basic technical structure of the transient state machine and its typical working style [1]. As explained above, such a machine is able to work in a rather wide category, either small or large, irregular or shapeshifting, quick or slow, assembly or division, etc. For example, if working in a cylindrical pipe as reflected in Fig. 9.3a, the liquid metal machine would conform to that shape. But one can cut the

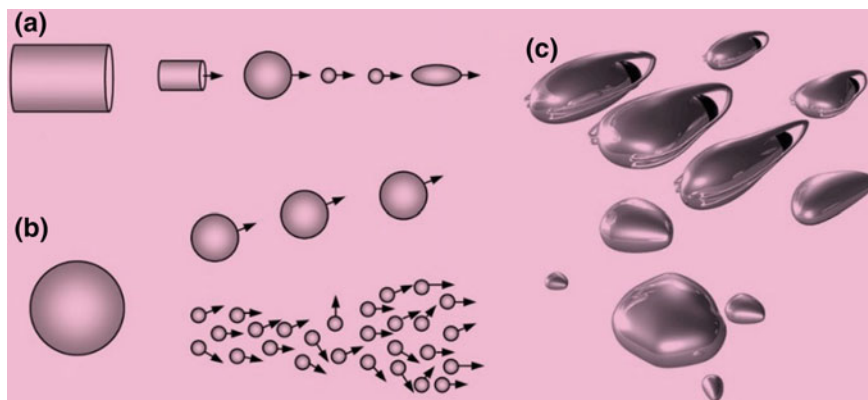


Fig. 9.3 Schematic for the transient state liquid metal machine and its running principle [1]. The device can work by taking multi-size, multi-geometry, and running speeds. That means, all these states are time and spatially variant, although the machine may choose to stay mainly on certain configurations. **a** Cylindrical machine and its components. **b** Sphere machine and its components. **c** Different liquid metal machines via specific combinations among different motors. All pictures are reproduced with permission

original big machine into several separate smaller machines which could then take shapes like cylinder, sphere, ellipsoid, etc., given that space it voyages in allows. For a free space situation, the liquid metal would generally run in a sphere shape due to its very high surface tension of the metal flow. Such a liquid metal can also be divided into several separate smaller sphere motors (upper image in Fig. 9.3b). If injecting the liquid metal solution quickly into the electrolyte, tremendous autonomously running tiny motors will be generated (see the lower image in Fig. 9.3b). Various sized motors can be composed into a specific machine as outlined in Fig. 9.3c.

9.5 Transient State Machine in Different States

Figure 9.4 presents the transient state machine in three different states [1]. As shown in Fig. 9.4a, the functional liquid metal solution pre-made and stored in a syringe, if we injected the functional liquid metal to NaOH solution gradually, a single large moving liquid metal motor was fabricated (Fig. 9.4b). This running liquid metal motor could be collected back by using a syringe (Fig. 9.4c). If quickly injecting out the functional liquid metal to NaOH solution, tremendous discrete droplets motors would be fabricated (Fig. 9.4), with each tiny droplet just keeping its running randomly. With the time goes on, some of the droplet motors began to collide and coalesce in the channel, due to coalescence of all the discrete motors together, a single large motor was finally assembled (Fig. 9.4e) and the transient state machine can be reversible.

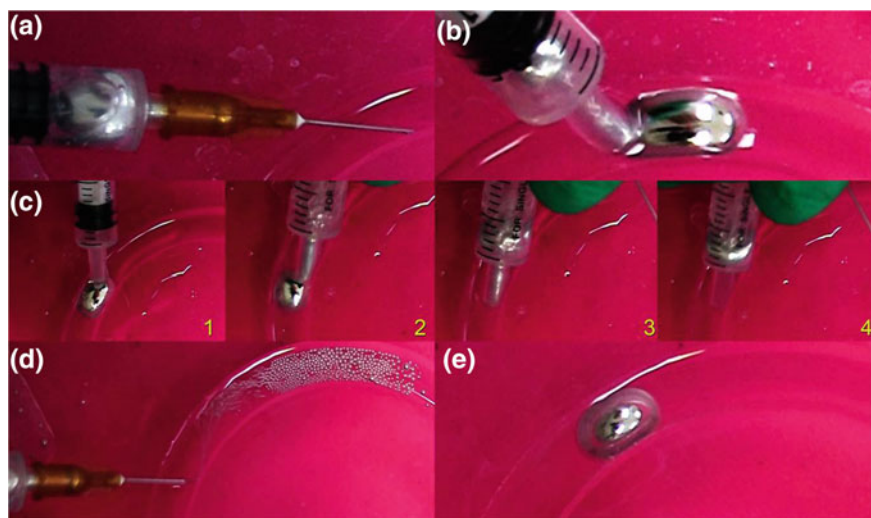


Fig. 9.4 Transient state machine in three different states [1]. **a** In syringe as functional solution; **b** Gradually injecting out the solution to form a single large moving liquid metal motor; **c** Collecting back the running liquid metal motor; **d** Quickly injecting out the solution to form tremendous discrete droplet motors; **e** Final single large machine due to coalescence of all the discrete motors together. All pictures are reproduced with permission

In principle, the surface tension dominates the liquid metal object along with the accumulation and dissolution of the oxide layer [1]. If there is no oxide layer on the outside surface of the liquid metal droplets, the droplets would maintain a spherical shape. As gallium oxide can react with the NaOH solution, the oxide layer will be dissolved in the solution. Therefore, the liquid metal droplets in the NaOH solution generally appear as spheres [2–4]. For the early stage when many tiny liquid metal motors were injected into the electrolyte, they just keep running independently along its original track. However, with the time goes on, these machines' running may become deviating between each other, due to different running direction or speeds either slower or faster. Then evident interactions would occur among the machines. Some of the neighboring droplet machines collide and coalesce because each liquid metal droplet is self-charged without an oxide layer. According to Fig. 9.5a, there was a swarm of liquid metal droplets running in a random style. If the time lasts long enough, these droplets finally coalesced into a single large machine that still keeps running. All these very unusual behaviors refresh people's common understanding of micro-motors. In Fig. 9.5, at the initial moment, there were about 300 liquid metal droplets in the channel. After about 2 min of colliding and coalescence, a large droplet of liquid metal was formed, and the speed of coalescence became lower as time increased, as shown in Fig. 9.5b. To observe their coalescence clearly, the movement speed of these droplets should be reduced. For this purpose, we adopted to use NaOH solution at room temperature for the observation. As shown in Fig. 9.5c,

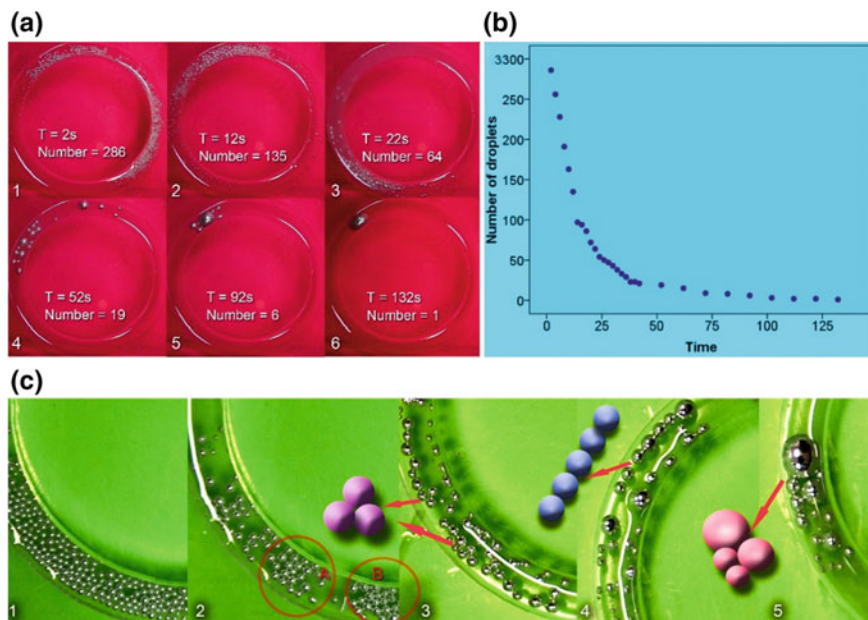


Fig. 9.5 Random running of a swarm of liquid metal droplets spontaneously generated in a moment [1]. **a** Injection of liquid metal into the channel to generate a large amount of dispersed droplet motors (a1). The spheres started to run in a random style (a2). The running direction of the liquid metal spheres was switched (a3). The spheres coalesced into a large liquid metal droplet that still kept running (a4–a6). **b** The number of droplets gradually decreased and decreased more slowly as the time increased. **c** Colliding and coalescence among autonomously running multi-size liquid metal droplets. Randomly running liquid metal droplets formed two groups rapidly (c2). Some of them arranged in a triangle (c3). Some arranged in a line (c4). Some of the big and small ones attracted each other to form an irregular configuration (c5). All pictures are reproduced with permission

after a large number of liquid metal droplets were spontaneously generated, two groups of droplets were formed immediately (Fig. 9.5c-2). During the process of coalescence, some of them arranged in a triangle and some others in a line; while some of them attracted each other to form an irregular arrangement. With self-charged and high-speed self-rotation of each droplet, such arrangements were formed because there occurs a balance between these contacted droplets.

As shown in Fig. 9.6a, there occur lots of interesting phenomena among the motion behaviors of liquid metal droplet swarms in addition to the coalescence [1]. Here, two swarms of liquid metal droplets were generated separately. Then, the two swarms of droplets attracted each other and finally collided and crowded in the middle distance of their positions. After that, they moved in the opposite direction and started another traveling until the next crowding and colliding occurred. Some of the droplets consolidated to bigger ones during a collision. It looks most of the liquid metal machines still keep its original global traveling direction. If there were not enough droplets in the opposite part, the droplets just move towards one direction together.

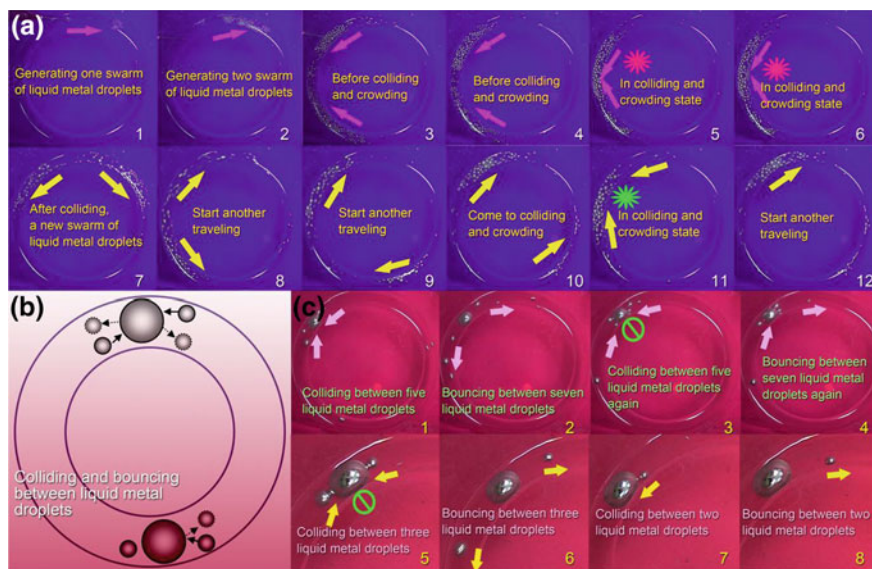


Fig. 9.6 **a** Generation of a swarm of self-running liquid metal spheres and their typical motion behaviors [1]. Generation of two swarms of liquid metal droplets in the channel to observe the phenomenon of their movements (a1, a2). Colliding and crowding between two running liquid metal droplet swarms; after colliding, some liquid metal droplets completed coalescence while others did not; then the new swarm of liquid metal droplets started their another traveling (a3–a12). **b** Schematic diagram for the colliding and bouncing between liquid metal droplets. Some of the small liquid metal droplets were rebounded from one side of the big one, and the others were rebounded from both sides of the big one. **c** Colliding and coalescence among autonomously running multi-size liquid metal droplets; some were bounced back, some grasped, and some smaller ones coalesced themselves together but not with the large one (c1–c4). Bouncing and coalescence between three contacting liquid metal droplets (c5–c8). They were bouncing and colliding several times before they finally coalesced into a larger one. All pictures are reproduced with permission

As shown in Fig. 9.6b, there was also a colliding and bouncing phenomenon between liquid metal droplets. Some of the small liquid metal droplets were rebounded from one side of a big droplet, and the others were rebounded from both sides of the big droplet. If a large droplet encountered a small one, there would be several times of bouncing and colliding before they were coalesced into a larger droplet. All of these droplets kept moving throughout the process of their behavior without interference from outside, as shown in Fig. 9.6c.

For quantifying a cluster of droplet motors, image processing is performed to clarify how droplets aggregate and scatter in different positions [1]. It is rather hard to identify the traveling path and velocity for each of the specific droplet motors with too many tiny motors assembling together. As an alternative, the images of captured videos by different times are divided into four quadrants, as shown in Fig. 9.7a. By counting the pixel numbers of liquid metal in each quadrant, we can estimate the droplet motor's transient distribution. It is interesting to find that, the transient pixel

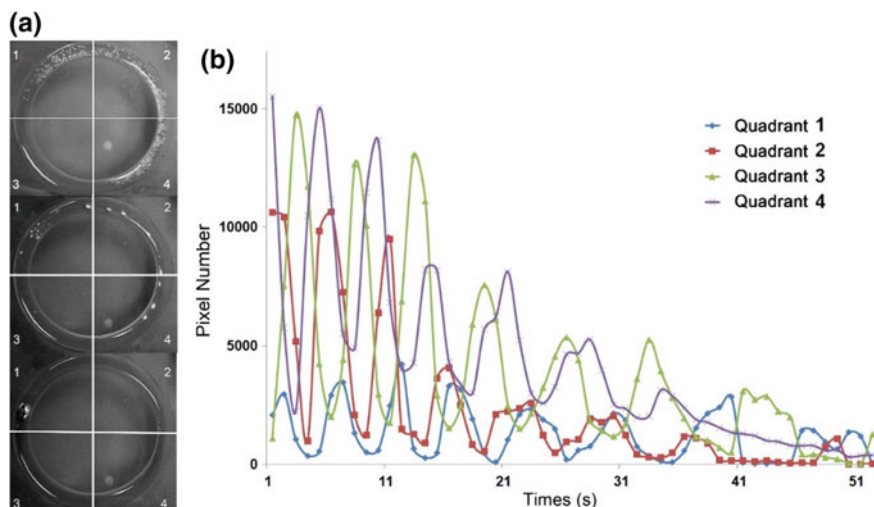


Fig. 9.7 Locomotion of a cluster of liquid metal tiny motors in the channel [1]. **a** The images of a captured experiment by different time are divided into four quadrants. **b** Estimation of the droplet motor's distribution by counting the pixel numbers of liquid metal in each quadrant. The transient pixel numbers in each of the quadrant regions are different and appear as an oscillating curve. Such process approximately takes a 5 s period. All pictures are reproduced with permission

numbers in each of the quadrant regions are different and appear as an oscillating curve. Such a process takes an approximate 5 s period. This indicates that the liquid metal motors are not uniformly distributed throughout the whole channel, and the metal cluster may choose to stay more in a certain quadrant, as shown in Fig. 9.7b.

Clearly, the motors could generate electricity inside itself [1]. This is different from the pure liquid metal droplets alone. Therefore, it was also curious to see what dynamic impacting behaviors between the running liquid metal machine and the liquid metal droplets that were not fuelled with aluminum. Presented in Fig. 9.7 are a group of experimentally found coalescence phenomena of two kinds of liquid metal droplets (with or without aluminum) with liquid metal machine fuelled with aluminum. First, the small droplets were prepared with aluminum. There was bouncing between droplets when the small one came into contact with the coming big machine. After several times moving back and forth between the running machine and the droplets, the small liquid metal droplets moved to coalesce with the liquid metal machine in the opposite direction, and then they were coalesced into a large liquid metal pool without bouncing but still kept moving (Fig. 9.7b). Secondly, a large number of small liquid metal droplets without aluminum were produced in the channel by using a syringe, when the big liquid metal machine fuelled with aluminum got in touch with those small liquid metal droplets, there was no bouncing between droplets when they coalesced, as shown in Fig. 9.8d. During the process of coalescence, the big machine changed its direction several times to coalesce with

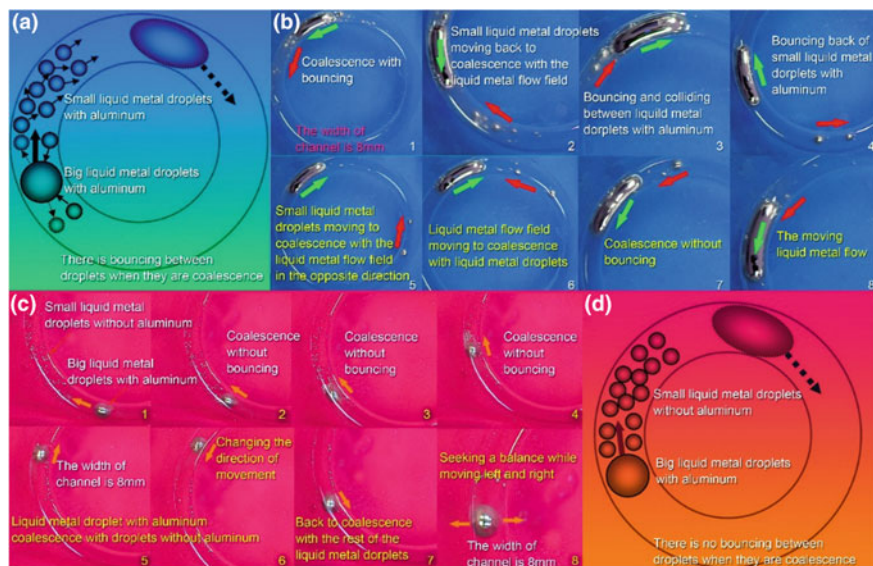


Fig. 9.8 Dynamic behaviors when liquid metal droplets and liquid metal flow field connected each other [1]. There were two kinds of small liquid metal droplets. One was prepared with aluminum and the other was not. The big droplet was fuelled with aluminum. When the big one coalesced with the small ones (with aluminum), there was bouncing between droplets **a**. After several times of moving back and forth between big liquid metal machine and droplets, the small liquid metal droplets moved to coalesce with the running liquid metal machine in the opposite direction, and then they were coalesced to a large metal object without bouncing and still kept moving **b**. When the big one coalesced with the small ones (without aluminum), there was no bouncing between droplets **c**. The big droplet changed its direction several times to coalesce with the rest of the liquid metal droplets, and then the big machine moved left and right to seek a balance **d**. All pictures are reproduced with permission

the rest of liquid metal droplets, and then it moved left and right to seek a balance (Fig. 9.8c).

Overall, coalescence would reduce the system's energy by minimizing the total surface area and corresponding surface energy [1]. As one can see in these experiments, no matter how big the droplets are and how many of them in the channel, they always move back and forth. If there are many of them in the channel, they run together, as shown in Fig. 9.6a. A group of them move back and forth until finally coalesce. Otherwise, if there is only one droplet or a single liquid metal machine, it moves back and forth too, as shown in Fig. 9.8, to find a balance between the movement inside the droplets and the outside of fluid motion.

9.6 Interpretation of Transient State Machine

The above experiments have demonstrated a new conceptual transient state machine style in that the machine can work as either a single big size robot or tremendous discrete spontaneously running tiny motors. According to the need and specific gradually injecting process, a pool of functional liquid metal can be injected to fabricate a single self-running machine. Or the same liquid metal can be quickly injected to form a stream which then would break up into tremendous tiny motors traveling here and there. During their running, colliding, or bouncing, the droplet machines can combine back again to the original one. So it can be seen that the machine, in fact, works in a transient state among different sizes, geometries, components, activities, running dimensions, etc. Such a machine concept is rather different from the existing one. All these unusual capabilities are enabled by the unique properties of the liquid metal and its matching galvanic cell effect. The discovery opens a way for realizing multi-configurational machines. In this sense, the current methodology is rather flexible in making either big or small motors.

In fact, fabrication on varied scale self-powered machine autonomously running inside the solution is very useful in many fields [10–15]. For example, one of the aspiring goals of nanotechnology is the fabrication of miniaturized machines. Methods of manufacturing could be analogous to existing macroscopic versions, or they could be based on entirely new principles [10, 13]. Researchers have designed micro-sized motors that react with chemicals around them in solution to produce jets of bubbles, propelling them forward or actuating moving parts [13]. The advantage of chemical energy-powered objects lies in their similarities to living organisms: These objects take energy from the environment. They are not dependent on the current state of an applied physical field and can move as long as “food” is present [14]. These self-propelled systems are currently in the spotlight of the research community [16]. Such objects are very useful for performing dynamic actions on a macroscopic-scale sensor and actuators for sense-and-act applications. Similar to any other motors, self-propelled constructs are able to convert energy into motion [15].

As gradually realized in recent years [10, 13], there are various sources of energy that can induce motion and they can generally be classified into two categories: physical energy (e.g., light, electromagnetic field, electric field, ultrasonic waves, or thermal gradients) and chemical energy (e.g., chemical fuel, water, hydrogen peroxide, acids/bases, hydrazine, bromine, iodine or a concentration gradient). Thereinto, the chemical energy-powered objects (motors) are independent of external physical field to sustain autonomous motion. The motions of motors were induced by two kinds of energy. According to Rebinder’s effect, liquid metal alloy EGaIn penetrates into aluminum, destroying the oxide skin on the aluminum surface and leading to the activation of aluminum [17]. The present driving force partially follows that of the chemical energy as described in literature [18–22]. With the produced electricity between EGaIn and aluminum, physical energy also plays a role here, as described

previously [8]. Some teams used electric field to control the movements of the conducting objects [23–25]. It looks the gallium and indium-based motor is so far the first motor that could be adopted for making the transient state machine. A certain composition of these metals produces the motor in the liquid phase at room temperature, making the motor deformable when performing tasks under specific conditions. The motor can thus serve as a potential candidate for designing soft robots or self-powered machines in the area. Under a macroscopic scale, its flexibility or rigidity would affect the application of the motors significantly. Theoretically, except for the currently addressed liquid metal, more other classical materials as interpreted in literature [16] can also possibly be tried as a candidate for making the transient state machine which should offer alternative motor behaviors. Clearly, tremendous efforts are urgently needed along this direction in the coming time.

Overall, from the material aspect, different material types or compositions own their specific properties and merits, which would render their performances in realizing the final machine [1]. Regarding the liquid metal material, its unique advantages in making self-powered motor perhaps lie in that: (1) The achievement of a large number of self-powered tiny liquid metal motors is rather straightforward, while no complex fabrication or manipulation procedure is involved. (2) Unlike the liquid mercury or some other organic droplets, such liquid material is nontoxic, which is rather beneficial for making practically useful functional motors. (3) The self-powered motor or motor swarm could quickly move at a pretty high velocity, and it obviates the requirements of external physical energy. (4) At larger scales as discussed before, tiny motors are not only propelled by the bubbles but also driven by the electricity generated through the galvanic cell reaction which is different from existing pure chemically powered motors. (5) The deformability of the current motor can be enhanced by the solution and external electric field. Thus, when the fuel of the motor is depleted or the unidirectional motion is obstructed, the external electric field can be employed to guide the motor for further movement.

At the present stage, the amount/rate of Al in influencing the transient state is a major concern. Actually, through many experiments [1], it has been found that when injecting the liquid metal quickly into the electrolyte, each of these tiny motors may hold stand still for a while, and then reactivate again suddenly. The typical delay time is approximately 0.5 s or less. The higher the proportion of aluminum in the alloy is, the less delay time and faster the moving speed will be. In the above experiments, a small piece of aluminum sheet (0.05 g) was adopted to contact with EGaIn (0.1 ml) until the particles were evenly distributed. Then the alloy was used to generate a larger number of tiny motors. After about 2 min of colliding and coalescence, a large droplet of liquid metal was formed, and the speed of coalescence became lower as the time increased. If more amount of aluminum (0.1 g) was used to make EGaIn–aluminum alloy, the distributed time would take much longer and the colliding and coalescence time would be reduced to about 1.5 min. That is to say, the higher the proportion of aluminum in the alloy is, the faster the whole process of colliding and coalescence will be. And the moving time of the last big motor will be much longer. However, if there is not enough aluminum in the alloy, the tiny motors will stop move due to the viscous drag force after injecting the alloy into the electrolyte. If the composition of

the alloy keeps the same, the droplets could achieve much larger velocities with a smaller size, because a small droplet with a high surface area to volume ratio reacts at much faster rates than a big droplet does.

A fundamental difference between the current driving mechanism and previous works is that the electric field was self-generated here [1], but the electric field relied on an external power source device in previous works. The basic mechanism comes from the galvanic interaction occurring among the liquid metal gallium, the aluminum, and the electrolyte. Aluminum is the cathode and liquid metal works as the anode. The charges on the surface of liquid metal droplets were mainly induced by the chemical reaction between gallium and NaOH, with electricity produced. A varied electrical voltage was generated on the surface of the liquid metal droplet which then induced the change of surface tension. Therefore, under an unsymmetrical surface tension, the liquid metal droplet will be driven to move when the driving force magnitude becomes larger than that of the viscous resistance between the liquid metal and the surrounding liquid. The droplets could achieve much larger velocities in a smaller size, because a small droplet with a high surface area to volume ratio reacts at much faster rates than a big droplet.

Why did the droplets bounce? The familiar bouncing of a ball occurs because of a combination of inertia and elasticity, but various arrangements and velocities based on the observed droplets indicate that here inertia and elasticity do not have a dominant role [1]. A striking consequence of this charge transfer was demonstrated in Fig. 9.4c, in which liquid metal droplets were arranged in a chain. The bouncing demonstrated in Fig. 9.5c appears to be driven entirely by the charge transfer dynamics. Recalling that each droplet is a galvanic cell and the electrical voltage is different due to varied sizes, the reversal of direction following each bouncing indicates that the net charge in the drop switches sign, which means charge must be transmitted during the bouncing.

As the charge consists of dissociated ionic species (for example, H^+ , $[Ga(OH)_4]^-$ and OH^-) in the NaOH solution, the ions must transfer from one droplet to another during each bounce [1]. There are several possible mechanisms for charge transfer, such as conduction through the NaOH solution, dielectric breakdown or electrospray of droplets. Whereas, former studies show that the small liquid metal droplets would be merged into a larger one without bouncing in NaOH solution when they touch each other. If the distance between the droplets approximates to the atom size, the film would rupture and coalescence would commence rapidly with the growth of the liquid bridge between droplets. The oxide layer on the surface of droplets was dissolved in alkaline solution and remained spheroid due to the high surface tension (~ 700 mN/m), indicating that there existed no bridge during bouncing, as shown in Fig. 9.6c. Charge transfer presumably occurs by ionic conduction through the NaOH solution during each bounce.

9.7 About Color-Changeable Soft Machine

Learning from biology, the liquid metal machine can stay at different transient color states. Nature has created a wonderful world full of beautiful colors. As an interesting animal, the chameleon owns the remarkable ability to rapidly change its skin colors during the interactions like courtship, camouflage and male contests [26]. In the engineering area, quite a few of the bionic robots have been fabricated to imitate the color-changing creatures in nature. At the present stage, the liquid metal (LM) EGaIn has a high reflectivity as most of other metals own in the optical aspect. Thus, it often presented a silver-white hue [27]. After utilizing the LM for the fabrication, the functional commodities usually got single appearances as well. From conceptual innovation aspect, it can be envisioned that a big challenge in the field would come to the actualization of LM for full-color appearances which could be applied to a host of unusual practices.

So far, the functional materials thus made by LM only could display a single silver-white appearance. Recently, colorful LM marbles working like transformable biomimetic “chameleons” were demonstrated from LM droplets by encasing them with fluorescent nanoparticles [28]. This unique LM marble can be manipulated into various stable magnificent appearances as one desires, and then split and merge among different colors. Such multifunctional LM “chameleon” is capable of responding to the outside electric-stimulus and realizing shape transformation and discoloration behaviors as well. Furthermore, the electric-stimuli has been successfully introduced to trigger the release of nano/micro-particles from the LM. The fluorescent LM is expected to offer important opportunities for diverse applications, especially in a wide range of functional smart material areas.

9.8 Fluorescent Liquid Metal as Transformable Biomimetic Chameleon

In order to make the color changeable object, the LM marble was fast intentionally oxidized in an oxygen environment and constructed as a thin Ga_2O_3 oxide film with a thickness of 0.5–2.5 nm [29]. The oxide shell has been described with an outstanding adhesion behavior and strongly adhered to whatever surfaces [30]. According to the previous reports, the oxidation films of LM marbles coated with WO_3 , TiO_2 , In_2O_3 , C nanotube and semiconductor nanomaterial [31] have a sea of sensitive electrochemical and photochemical properties. And some of these white LM marbles coated with hydrophobic coverings can even float on the water. Besides, a magnetic LM marble was acquired by covering an LM with nanosized Fe particles, which has a large potential in the magnetic field-driven manipulation, or electrical switching field. Consequently, the coating of the fluorescent grains on the superficies of the LM marbles became the key ingredient due to their unique functions.

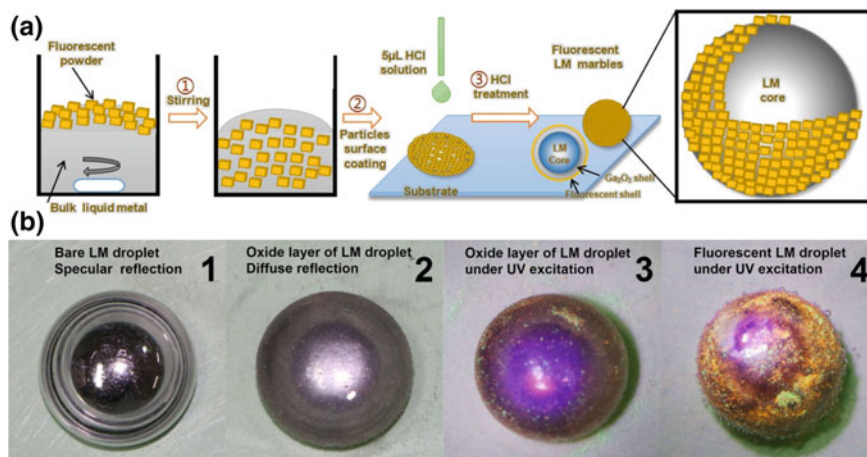


Fig. 9.9 **a** Fluorescent LMs were prepared by stirring a LM marble with nano/micro-fluorescent powders in a beaker; **b** The color-changing of LM: (1) Bare EGaln droplet; (2) Images of a EGaln droplet with naturally formed native oxide layer in ambient air; (3) Images of EGaln droplet with naturally formed native oxide skin under UV excitation; (4) The orange color performance of fluorescent LM was observed under UV excitation [28]. All pictures are reproduced with permission

In the following, we illustrated the primary instance of a spontaneous adhesion of stabilized fluorescent particulates on the superficies of LM droplets to achieve colorizing the LM droplet [28]. The evidence suggested that this fluorescent LM marble was stable, and it can be merged and split between each other. Under the electro stimuli, it can further display the transformation and discoloration behavior of the fluorescent LM marble.

Two attempts have been devoted to fabricating the fluorescent LM droplets [28]: (1) As illustrated in Fig. 9.9a, agitating the LM with rare-earth phosphors in a vessel. The fluorescent powder of 2 g was mixed with the LM of 20 g in a beaker, which was maintained under continuous stirring at 60 °C. The growth of LM oxide film (consists mainly of Ga_2O_3) was accelerated in the atmosphere. The naturally oxidized LM has a viscoelastic oxidative tegument. The fluorescent powders were substantially adhered to the LM droplet's oxidation tegument after being fully stirred for more than 2 h, and the adhesion reason would be discussed in the following result section; (2) Alternative method of overlaying the LM marble was to roll a LM droplet on a fluorescent powder bed, which was overspread with the fluorescent powders. The fluorescence properties prepared by the second method were not as perfect as the first one, which may be due to an insufficient stirring.

After being mixed with the fluorescent powders, the LM became more viscoelastic [28]. It was amorphous and not easy to flow, like a solid. Take a spoonful of the mixture of fluorescent LM, then dealt it with hydrogen chloride (HCl) solution (6% wt%). As an example: A fluorescent LM droplet of 10 mL would be treated with 5 μL HCl. After this treatment, the shape of the fluorescent LM was totally transformed into a

“sphere”, and the physical properties of this marbles have changed from wetting to non-wetting state. The size of the LM droplets depends on the volume of the removal.

Figure 9.9b-1 shows a bare LM Galinstan droplet ($R = 2.04$ cm) with a shiny silver tone. The naturally oxidized LM droplet with a dull gray appearance was presented in Fig. 9.9b-2 as well. Under UV excitation, this oxide skin was presented with a purple hue, as disclosed in Fig. 9.9b-3. And the fluorescent LM droplet with an orange appearance was given in Fig. 9.9b-4. The current discoveries presented a novel opportunity for the implementation of full-color appearances of LM.

9.9 Mechanism of Fluorescent Liquid Metal Chameleon

In the following, the adhesion mechanism between the fluorescent particulates and LM marbles was investigated [28]. Figure 9.10a-1, 2 presented the images of the native oxide tegument which was naturally developed on the surface of a puny micro-fluorescent LM marble ($R = 480$ μm) in ambient air. The oxidized LM droplet has a draped and irregular oxide skin, and the layer was to protect the metal from further oxidation. The LM droplet was fast oxidized even in a mere 0.2% oxygen environment. It has also been revealed that the “tearing morphology” was constructed from the expansion of the LM marble under vacuum in the SEM system. The SEM images of some green and orange fluorescent LM marbles were presented in Fig. 9.10b, c. It can be observed that LM marbles stabilized with fluorescent particulates are multifaceted systems composed of LM cores and solid fluorescent particulates shell. The green and orange fluorescent particles have dimensions from 800 nm to 20 μm , respectively. The native oxide covering played a paramount role in adhesive bonding between the external functional particles and the bare LM marbles, as demonstrated in Fig. 9.10c-2. The results indicated that the fluorescent particles only existed on the surface of an oxide layer, and the particles could not adhere to the smooth and bare LM droplet.

Different synthesized fluorescent LM marbles were manufactured with either relatively small or large sizes, as clearly exhibited in Fig. 9.11a, such as multicolored fluorescences, fluorescent orange, pink, to blue colors, etc. [28]. The oxide film makes it much easier for LM to adhere to the solid surface and also stabilize LMs into different shapes. When constructed, these fluorescent LM marbles were “sphere” in shape, but occasionally adopted an “ellipsoidal” geometry due to their dissimilar surface tensions.

Besides, the addition of fluorescence has not changed the particular physical—chemistry properties of LM droplet. Figure 9.11b presented a photograph of the originally separated LM droplets with pink and green appearances. A straw was used to merge the two different colored LM droplets together, which resulted in a biggish ultimate multicolor LM marble. In Fig. 9.11c, utilizing a blade, it can divide one entire fluorescent LM marble into a couple of slight LM marbles. This cutting manipulation can be performed more than once and one huge fluorescent LM marble can be transformed into multitudinous miniature multicolor LM spheres [28]. Conse-

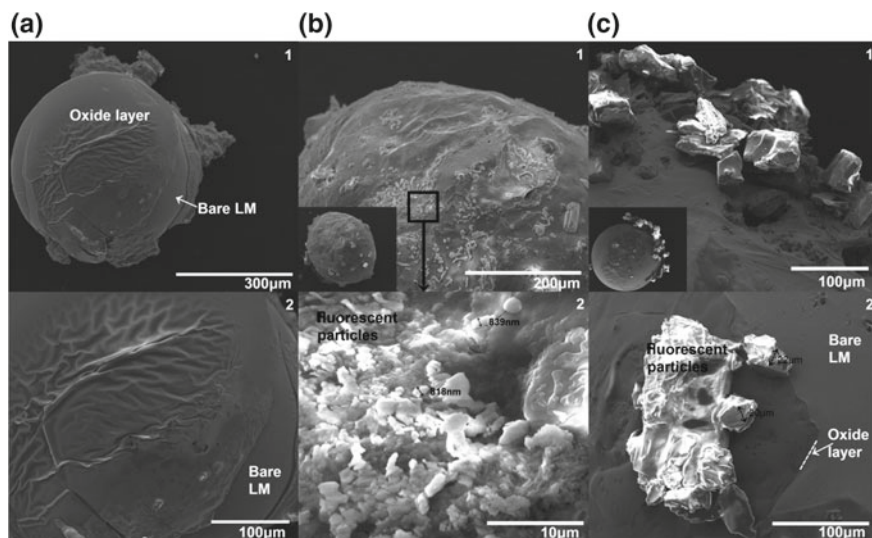


Fig. 9.10 **a** (1, 2) The SEM of oxidized LM with a draped and viscoelastic oxide layer. **b** The SEM images of a green fluorescent LM droplet: (1, 2) LM droplet encapsulated in a coating of 800 nm green fluorescent particles; **c** The SEM images of an orange fluorescent LM droplet: (1, 2) LM droplet encapsulated in a coating of 20 μm orange fluorescent particles [28]. All pictures are reproduced with permission

quently, the fluorescent LM marbles have the power to be split into tens of thousands of multicolor LM marbles or merged together between distinctive droplets.

The color of an object depends on its physics [28]. Objects can display the color of the light leaving their surfaces, which normally depends on the reflectance properties of the surface. Therefore, by testing the V_s -reflectivity of different colorful LM marbles, the optical properties can be known. An excellent V_{is} reflectance (81%) of the bare LM marble with a specular reflection was exhibited in Fig. 9.11d, while the V_{is} reflectance of the oxidized LM marble with an oxide skin diminished to 72%. The oxidized LM has a lower reflectance of light, so its color is darker when compared with the bare LM. When different bands of light were used to excite the fluorescent LM, the fluorescent LM can emit different colors of fluorescence in the dark. As shown in Fig. 9.11e-1, the fluorescent orange, pink, and blue LM marbles displayed excitation peaks around 358, 364, and 535 nm, respectively. The fluorescent emission spectrum of these marbles manifested narrow and symmetric emission peaks at 467, 517, and 600 nm, respectively, as shown in Fig. 9.11e-2. Since the fluorescent particulates are self-luminous materials, the intense bright luminescence of dissimilar fluorescent LM marbles could be perceived by the naked eyes in the dark.

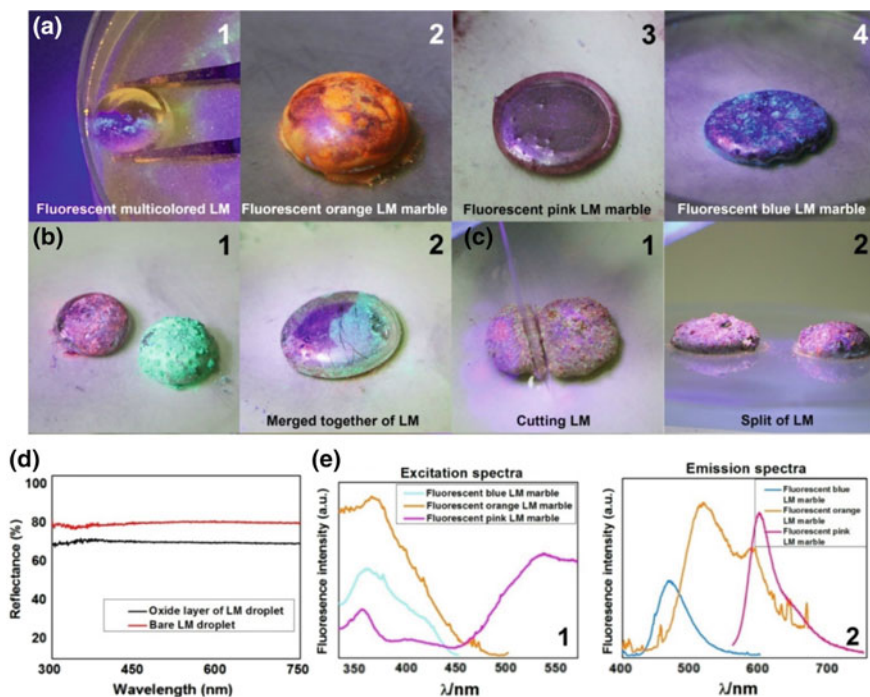


Fig. 9.11 The fluorescent liquid metal marbles [28]. **a** Luminescence of fluorescent LM marbles observed by the naked eye upon excitation with UV light from left to right: (1) Optical image of fluorescent multicolored LM marble ($R = 1.7$ cm), (2) Orange LM marble ($R = 2.3$ cm), (3) Pink LM marble ($R = 3.09$ cm), and (4) Blue LM marble ($R = 3.55$ cm). **b** The merged together color from different fluorescent LM marbles: (1) A fluorescent pink LM marble and a fluorescent green LM marble; (2) The composite fluorescent LM marble constructed from the pink and green LM marbles. **c** The split of fluorescent LM marble: (1) A fluorescent LM marble; (2) Cutting the fluorescent LM marble; **d** The NIR reflectance of bare LM and oxidized LM; **e** The excitation (1) and emission (2) spectra of three different fluorescent LM marbles in the figure (a2–4). All pictures are reproduced with permission

9.10 Transformation and Discoloration of Fluorescent LM Marbles

In the following, a drop of 2 cm diameter fluorescent LM was spread on the surface of the plastic substrate and illuminated with a UV light [28]. The major phenomenon in the basic electrolytic solution (NaOH) and acidic electrolytic solution (HCl) (about 6% wt%) were summarized in Table 9.1 and Fig. 9.12, respectively.

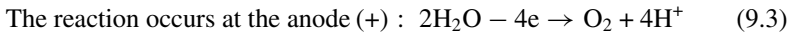
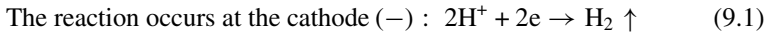
When the fluorescent LM was contacted with the cathode (–) of the copper electrode at the voltage of 15 V, it was found that the fluorescent LM marble slowly released the fluorescent nano/micro-particles [28]. The fluorescence firstly disappeared and the bare LM surface occurred near the cathode at 293 s. The LM changed

Table 9.1 The phenomena of fluorescent LM marbles in different electrolytes

Electrolyte	In NaOH			Phenomena
Case	Anode (+)	Cathode (−)	(+)(−)	
1	Not contacted	Contact LM		Discoloration
2	Contact LM	Not contacted		Transformation
3			Not contacted	Planar locomotion
	In HCl			
	Anode (+)	Cathode (−)	(+)(−)	
4	Not contacted	Contact LM		Discoloration
5	Contact LM	Not contacted		Transformation, turn black
6			Not contacted	Planar locomotion

appearance from its fluorescent orange color into a whole naked one at 380 s. This fluorescent LM was prepared from the fluorescent powder of 2 g and the LM of 20 g. Therefore, almost 9.09% (wt%) phosphor could be completely released from LM in about 420 s. Typical snapshots of this kind of discoloration are presented in Fig. 9.12a and Table 9.1—case 1 and 4, respectively.

When introducing electrical stimulation, the surface layer of Ga_2O_3 was reduced in the cathode, producing bare Ga and indicating significant variations of the adhesion property.



As a consequence, the fluorescent particulates were constantly released from the oxide tegument. The discoloration was also examined and interpreted in NaOH and HCl solutions.

The loading of fluorescence on the LM droplet depends on the area of the epidermis of LM. The volume and surface area of the LM droplet is $4/3\pi r^3$, and $4\pi r^2$ (suppose the radius = r), respectively. And the oxide film and nano/micro-phosphor were only 0.5–2.5 nm and 0.8–20 μm thick, respectively. So the volume of the fluorescence reads as $\approx 4\pi r^2 \times 20 \mu\text{m}$. Thus

$$\text{The loading of the fluorescent material} = (4\pi r^2 \times 20 \mu\text{m}) / (4/3\pi r^3) = 60/r \quad (9.4)$$

Then, suppose there was a LM droplet with a diameter of 2 cm. The loading of fluorescence on the LM droplet is $60 * 2/20,000 = 0.6\%$. That means the loading phosphor on a drop of LM of 2 cm is 0.6%.

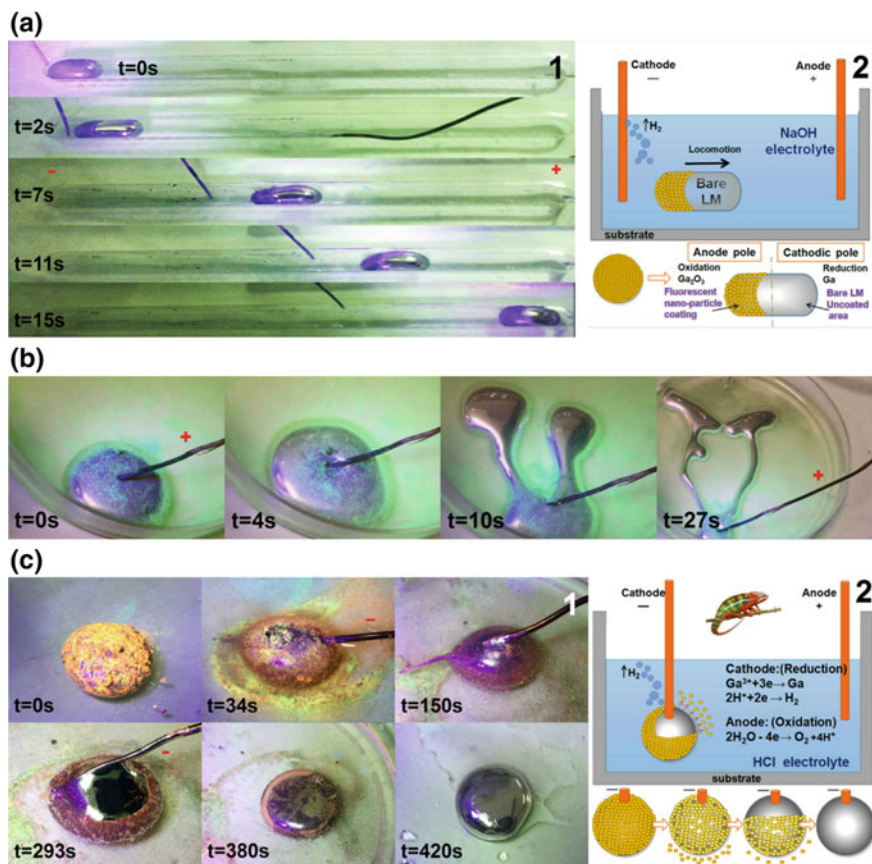
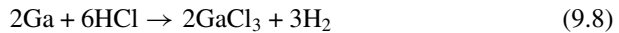
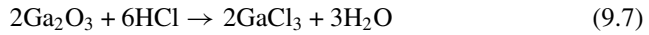
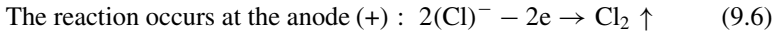
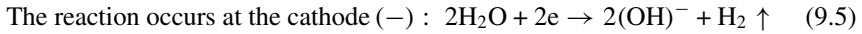


Fig. 9.12 **a** Electrically induced discoloration of the fluorescent LM marbles in a HCl electrolyte: (1) Schematic of the electric field force influencing the discoloration of the fluorescent LM marble in a basic HCl solution; (2) The mechanism of the process to release the fluorescence. **b** Electrically induced transformation of the fluorescent LM marbles in a NaOH electrolyte; **c** Movement of the fluorescent LM marbles in a basic electrolyte when a step voltage of 15 V is applied across the two copper electrodes: (1) Actuation of fluorescent LM marbles; (2) The mechanism of the process of the fluorescent LM marble in electric field [28]. All pictures are reproduced with permission

When the anode (+) was attached to the fluorescent orange LM, the copper-wire cathode (−) was immersed in water, the colorful LM sphere quickly transformed into a flat film with a large area, in Table 9.1–case 2 and 5. Figure 9.12b illustrates the deformation of fluorescent green LM in the basic electrolyte. In the first 4 s, the LM extended gradually; while in the 10 s, the green LM moved close to the cathode, and the oxidation and deformation were observed on the bare surface of LM, which has also been explained in the previous paper [5]. If the fluorescent LM was immersed in HCl, it would quickly become a black flat LM film. The processes were also presented in Table 9.1–case 2 and 4. We speculated that the LM chemically reacted

with HCl and turned into GaCl₃, which was also demonstrated by former research [32]:



When the electrodes were immersed in the electrolyte without contacting the fluorescent LM, the fluorescent LM marble would motivate toward the anode at a speed of 0.5 body length per-second both in NaOH and HCl solutions [28], as displayed in Fig. 9.12c and Table 9.1—case 3 and 6, respectively. What is more, the fluorescent nanoparticles on the surface of the LM marble were changed to nonuniform. The cathodic pole of LM was reduced, and a bare LM with the uncoated area was formed. The Ga₂O₃ integument full of fluorescent powders was created on the anodic pole hemisphere.

By changing the electrode arrangements and the electrolytes, various behaviors of fluorescent LMs were investigated, including deformation, discoloration, and the planar locomotion, respectively. Clearly, using this electric-stimuli can manipulate the LM shapes and colors, which would help stimulate the interesting behaviors of the chameleon in nature. Besides, this is also a first-ever report for an electricity-responsive LM to achieve efficient releasing of fluorescent substances.

9.11 Conclusion

In summary, a transient state liquid metal machine can be realized based on the generation, collision, and coalescence of the self-powered droplet motors. Direct observation and characterization of colliding among a large scale of autonomously running liquid metal droplets disclosed the interactions of a group of droplets, movements of one droplet and a liquid metal machine, and bouncing, colliding and coalescence between two groups of droplet motors and between one large droplet and a group of small droplets or several droplets. The force from the bubble recoil and the imbalance of surface tension induced by the bipolar electrochemical reaction serves as the driving power to overcome the resistance from the surrounding solution, propelling the liquid metal droplet to move autonomously. As the deformability of the liquid metal motors can be enhanced by the solution and electricity, the external electric field can be employed to guide the motor to the destination even when its fuel was depleted. As for the transient state liquid metal machines, no complex fabrications or manipulations are requested and a large number of self-powered tiny liquid metal motors of different sizes can be quickly made in a moment. A very unusual phenomenon still lies in that the smaller motors will maintain their running state until

finally coalescing into several larger machines or just a single motor, while still keeping running. It is based on such unique effect that the new machine style as Transient State Machine can be enabled. Clearly, the behavior of an individual motor or a group of motors swarm is very useful, while their coalescence and the function maintaining can be unique, which suggests an important way to designing future unconventional dynamic machines in the coming time.

Further, a facile and rapid route can be established to fabricate fluorescent liquid metal which could work as a transformable biomimetic chameleon. Such an approach takes advantage of the inherent adhesion properties at the oxide surface of the LM marbles. The original liquid metal with a single silvery-white metal color can be manipulated into full colors. And it still has unique physical/chemical, and optical properties, such as splitting or merging. Such fluorescent LM is able to respond to a particular electric-stimulus and change their original shapes and colors just like a transformable biomimetic chameleon. Moreover, under the electric field stimulation, all these nano or micro materials in the outside layer of the LM can be completely released. Such electro-responsive materials are smarter and more intelligent than ordinary materials. Overall, the fluorescent liquid metal possesses unique virtues in a wide variety of crucial areas, such as functional nanocomposites, controlled/targeted matter delivery, and color changeable bionic soft robot in the coming time.

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Chapter 10

Directional Control of Self-fuelled Liquid Metal Machine



Abstract Self-propelled motors have inspired enormous potential in accomplishing various tasks when navigating themselves in aqueous environment due to the virtue of external energy-free feature and autonomous locomotion. However, without reliable controllability, their potential value will be heavily discounted. In fact, the motion control of small motors in solution is of significance to applications ranging from microfluidics, smart machine, to tiny robot, etc. To realize such object, the present lab had ever proposed an electrical controlling method to flexibly manipulate liquid metal droplet motors powered with aluminum (Tan et al. in Electrical method to control the running direction and speed of self-powered tiny liquid metal motors, 471:20150297–20150306, 2015, [1]). It was discovered that adding aluminum to liquid metal droplets would significantly magnify its electric controlling capability, which provides dozens of times' driving force compared to pure GaIn₁₀ droplets. If switching on the electrical field, the aluminum powered liquid metal droplet would accelerate its running speed to an extremely high magnitude like 40 cm/s under 20 V, as measured in a channel with 1 cm width and filled with aqueous solution. In addition, it was also observed that the motion trajectories of the motors in the free space of a Petri dish nearly reflect the electric field lines in the electrolyte which suggests an important way to visualize such complex physical property. Lastly, the oscillating motion behavior of the motor under small electrical voltage and its continuous running modality can be experimentally discriminated. The findings on the Al–Ga–In motors would have profound impact on developing future controllable microfluidic systems or tiny soft robot that are hard to achieve through conventional methods otherwise. In addition, through coating magnetic material such as nickel cap on the surface of a liquid metal droplet, such self-propelled motor can also be flexibly controlled and steered by external magnet or electric field, which successfully enables the motor to avoid out-of-control trajectory encountered in former approach. This chapter is dedicated to illustrate several feasible methods to realize directional control of self-fuelled liquid metal machine.

Keywords Directional locomotion · Self-propelled · Liquid metal motor
Electrical steering effect · Magnetic control

10.1 Motion Control of Small Motors in Solution

With intensive studies, a variety of applications were increasingly found based on the extraordinary behaviors of Gallium or its alloy, such as elastic antenna [2] and printed electronics [3] which utilized the electrical conductivity and flexibility, and chip cooling [4] with high thermal conductivity and fluidity. Among these properties, the controlled motion of liquid metal objects in aqueous solution has attracted much interest due to its potential biomedical value such as targeted drug delivery [5] and micromachine [6]. Generally, an artificial micromotor “swimming” in aqueous solution was chemically powered that relies on bubble recoil [7, 8]. And some other micrometer scale particles can also be actuated by the electric field force such as the well-known electrophoresis process [9, 10]. Unlike these driving modalities, the actuation of liquid metal objects is based on the asymmetric surface tension induced by an electric field [11, 12]. In certain cases, such a driving form was unable to realize when the applied voltage is low due to a weak driving force.

In the self-propulsion mechanism based motor in centimeter scale through introducing aluminum into liquid metal [13], the Al–Ga–In motors were basically enabled by the asymmetric surface tension owing to an electric potential gradient intrinsically generated from the chemical reaction. Through splitting, the centimeter-scale Al–Ga–In objects can be separated into many tiny motors. However, such small machines just run autonomously via a random behavior. Clearly, controlling their direction and speed turns out to be a tough issue.

Aiming to realize a reliable control of the tiny liquid metal motor, this lab [1] disclosed that the Al–Ga–In motors in a Petri dish filled with NaOH solution can be easily controlled as desired by electric field. And unlike GaIn₁₀ droplets actuation, there generated a very different and much better driving capability on the Al–Ga–In motors. In order to clearly observe the motion of the objects, Tan et al. [1] designed an optical platform and recorded its traveling trails. In addition, experiments were also conducted in a straight channel to measure the motors’ velocity quantitatively which indicates that the velocity of Al–Ga–In motors is much higher than that of pure GaIn₁₀ droplet without aluminum. The main reason comes from the increased negative charge of the droplet surface caused by the chemical reaction between Al and NaOH solution. The higher the negative charge on the droplet’s surface, the stronger asymmetric surface tension it results and thus electric field force.

The basic procedures for fabricating Al–Ga–In motors are as follows. First, Ga–In alloy and filmy aluminum piece in a mass proportion of 99:1 were put into a small beaker. It should be pointed out that many different kinds of Ga alloy with varied ratios of Al can be practical. We chose GaIn₁₀ (Ga 90% and In 10% in weight) in this experiment just for brief. When the aluminum piece touched with Ga–In alloy, it would be corroded slowly. Since Al will be oxidized into Al₂O₃ when exposed to the air, we placed both of them into NaOH solution (0.5 mol/L), which is to guarantee that aluminum piece can be dissolved in Ga–In alloy quickly.

When the aluminum piece finished dispersing in liquid metal, the preparation of the mixed Al–Ga–In alloy was completed. Then, a syringe was used to suck the alloy

and squeeze it into a Petri dish to generate many small droplets. The Petri dish is also filled with NaOH solution (0.5 mol/L). After a 1–4 s pause, these droplets started to run here and there. There are many H_2 bubbles generated constantly at the droplets' bottom where they contact with the Petri dish. These bubbles adhere to the bottom surface of the dish and show a clear trajectory of the droplet motion. To get a clear image on such flow details, an optical method can be designed to capture the motor's motion and bubble trajectories. The Petri dish was fixed to a platform, and a black cloth was set on top of the platform as the background. A digital camera was shot from the bottom-up and two lights from the side. Therefore, the motors and its bubble trajectories can be illuminated by the lights in a dark background.

10.2 The Aimless Motion of Liquid Metal Motor in Petri Dish

In Fig. 10.1, the white lines are not a hand drawing, but actually formed from the H_2 bubble trajectories during motor's traveling [1]. The random images of the motor's trajectories reflect that the motion of the motors is aimless (for example, cases at 0 and 2 s). At the time of 6.7 s, a pair of electrodes was placed inside the solution and the anode is on the left. The electric voltage was set to 20 V DC. Then, an interesting phenomenon was observed that all of the droplets just swim toward the anode very quickly like a cluster of fishes. What is more, these "fishes" shake side to side because of the bubble driving force. When the electric field is switched off, the motion toward the anode stopped and then reverted to a random state (7.6 s). Throughout the progress, the constantly produced hydrogen bubbles appear just like a mist drifted in the solution.

To be more illustrative, one can record the dynamic position paths of five droplets before and after applying electric field [1], as shown in Fig. 10.2a. It should be pointed out that the trajectory images come from another video which is shot by a high-speed camera at the frequency of 100 frames per second. The time interval between two neighboring points is uniform. At the beginning, the droplet motors maintained a random movement in the right-hand side of the Petri dish. After applying an external electric field, all the motors move toward the anode with a very high speed of about 15 cm/s. Significantly, the droplets did not run to the anode along linear paths, but arcs. This is because the electric field vector at a certain point is a combination of electric potential in the anode and cathode. Such electric field distribution determined the driving force and direction. If the velocity direction and driving force are absolutely identical, the trails of the motors should be considered as accurate electric lines in solution. However, the motors' trajectories are determined by its inertia and the driving force. The direction of velocity (tangential direction of the arcs) and driving force is thus somewhat discrepant. So the trajectories were just an approximate reflection of the electric field lines in solution. In brief, the above finding could serve as an intuitionistic index to interpret the potential distribution in electrolyte generated by outside electrical sources which is hard to do otherwise. It should be noted that

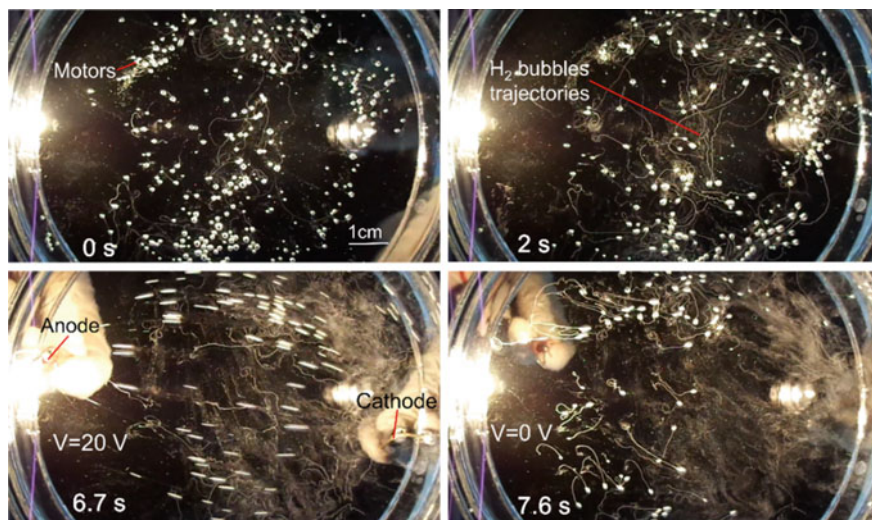


Fig. 10.1 Sequential snapshots of the Al–Ga–In motors that shot from bottom-up with a black background over the Petri dish [1]. The motors were injected to 0.5 mol/L NaOH solution at 0 s and a voltage of 20 V DC was applied between two electrodes at 6.7 s. At 7.6 s, the electrodes were removed. The white lines indicated the trajectories of H_2 bubbles adhering to the dish bottom surface. All pictures are reproduced with permission

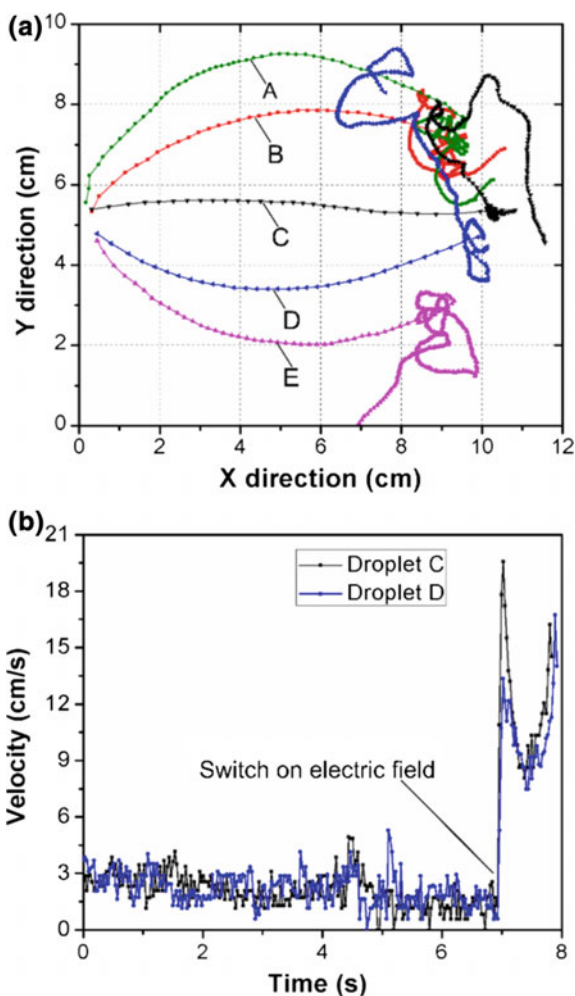
the irregularity of the motor's trails (such as motor A in Fig. 10.2a) was caused by collisions with other motors.

To get a clear quantification, the transient velocities of two objects were captured and shown in Fig. 10.2b. It can be observed that the velocity of the droplets fluctuates around 2 cm/s at the beginning [1]. After applying the electric field, the droplets quickly accelerate to a high speed of nearly 15 cm/s. And then it slows down to about 8 cm/s. When the motor moves close to the anode, its speed accelerates again. The reason lays in that the driving force becomes stronger when the motor moves close to the electrodes.

In fact, the liquid metal droplets without Al could also be actuated by electric field. But this happens only when the electric field is strong enough or the droplet diameter is large enough [1], say between a specific range (about 1 mm to 1 cm for the present case). In this range, the higher the voltage is, the more easily the droplet would be actuated. However, after adding small amount of aluminum to the liquid metal droplet, the actuation performance by electricity achieves huge enhancement. To get accurate result, we measured the displacements of the two kinds of droplets under the same voltage. The experiment was conducted in an open-top polymethyl methacrylate (PMMA) channel with a width of 10 mm, height of 10 mm, and length of 200 mm, which is filled with 0.5 mol/L NaOH solution. The distance between the two electrodes was set to 10 cm.

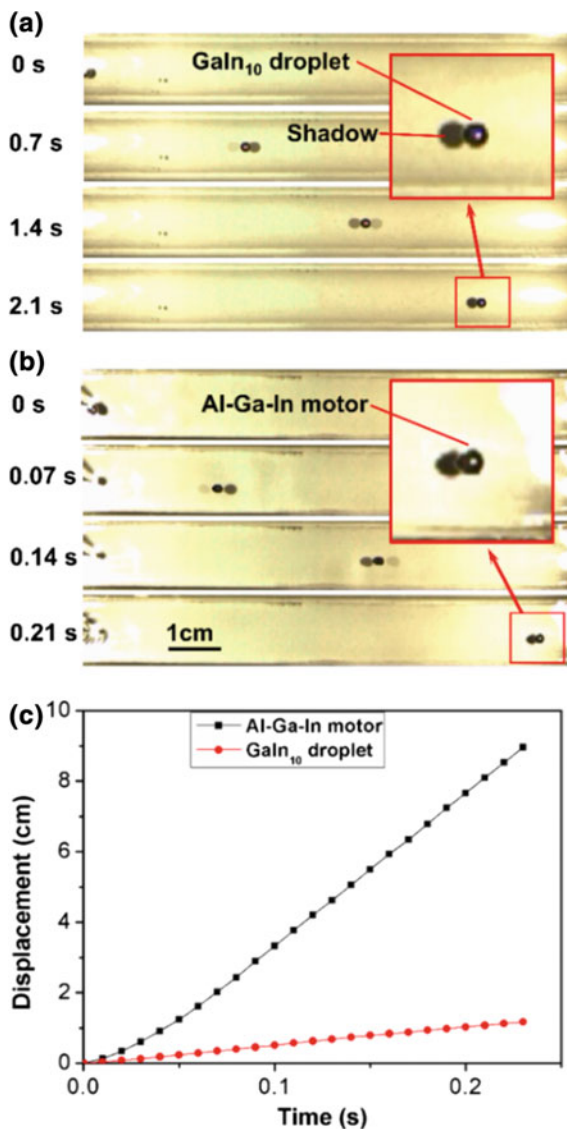
For comparison purpose, one could focus on the Al–Ga–In motors and $GaIn_{10}$ droplets with the same diameter of 1.8 mm [1]. The input voltage is set to 20 V

Fig. 10.2 Motions of five Al–Ga–In motors before and after applying electric field [1]. **a** Location paths of five motors before and after applying electric field (20 V DC). **b** Transient velocities of two droplets chosen from the five motors above. All pictures are reproduced with permission



DC. Figure 10.3a and b shows comparative snapshots of them in several times. Figure 10.3c presents the droplets' displacement along with time. It can be observed that the two kinds of objects accelerate at the beginning. Soon afterward, the displacements increased linearly. Thus, the velocity can be calculated in the state of equilibrium with the Al–Ga–In motor's velocity about 43 cm/s and the other one is about 4.43 cm/s. Such result exhibits a ten times disparity. All these experiments demonstrated the unconventional capacity of the electrical field in controlling the liquid metal micromotors. Previously, existing motors with current size of about 1 mm generally could at most achieve the velocity magnitude of only dozens of millimeters per second.

Fig. 10.3 Motion analysis of Al–Ga–In motors and GaIn₁₀ droplets [1]. **a** Sequential snapshots of a GaIn₁₀ droplet's motion. **b** Sequential snapshots of an Al–Ga–In motor's motion in a straight channel. **c** Displacement along time of an Al–Ga–In motor and a GaIn₁₀ droplet with diameter of 1.8 mm under 20 V DC in a 1 cm width channel that filled with NaOH solution. All pictures are reproduced with permission



10.3 Electrical Actuation Mechanism of Liquid Metal Machine

Without the external electric potential, the driving force of self-propulsion droplets comes from the H₂ bubbles. When the Al–Ga–In droplets were immersed in the NaOH solution, a vigorous reaction will happen between the Al and NaOH because pure Al can be activated by liquid gallium [14]. The reaction can be expressed

as $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} = 2\text{NaAlO}_2 + 3\text{H}_2\uparrow$. It is noteworthy that the H_2 bubbles were just generated at the surface which contacted with the Petri dish. Since the Al is distributed homogeneously in the liquid metal, the reaction would last for a long time. The continuously generated H_2 bubbles pushed the droplets forward and caused the droplets to roll. And the rolling motion left the H_2 bubble trajectory on the bottom surface of Petri dish.

When an external electric voltage was switched on, the driving force of the droplets stems from three parts [1]: asymmetric surface tension, electric field force ($F_{\text{electric field}}$), and bubble propelling force. And the drag force consists of flow resistance (f_{flow}) and frictional force (f_{friction}) between the droplet and the bottom of the channel. The flow resistance can thus be possibly calculated. The Reynolds number of the flow can be expressed as $\text{Re} = \rho v d / \mu$ [15], where ρ is the density of surrounding solution, v is the motor's velocity, d is the diameter of the droplet, and μ is the viscosity of the aqueous solution. Here, assuming that the density and viscosity of the NaOH aqueous solution approximate to that of water, then the Reynolds numbers were 769 for Al–Ga–In motor and 79 for GaIn_{10} droplet (in Fig. 10.3a and b). Owing to insufficient prerequisite condition ($\text{Re} \ll 1$) for Stokes law [15], the equation $f = \frac{1}{2} C \rho v^2 S$ [15] can be chosen to calculate the flow resistance, where C is the dimensionless drag coefficient and S is the front face area of the sphere. And C is equal to $13/\sqrt{\text{Re}}$ when Re ranges from 10 to 10^3 . Thus, the flow resistance is 1.1×10^{-4} N for the Al–Ga–In motor and 3.6×10^{-6} N for GaIn_{10} droplet.

Originally, the gallium will react with the alkali solution, producing gallates like $[\text{Ga}(\text{OH})_4]^-$, which causes negative charge at the liquid metal droplet surface. And the negatively charged surface will attract ions of the solution and forms an electrical double layer (EDL) (Fig. 10.4a). The charged surface affects the surface tension which can be described as Lippmann's equation that is given as $\gamma = \gamma_0 - \frac{1}{2} c V^2$, [16] where γ is the value of surface tension, γ_0 is the maximum value (at $V = 0$), c is the capacitance per unit area of the EDL, and V is the voltage applied on the liquid metal–solution interface. At the beginning, the liquid metal droplet surface was charged with q_0 , and thus the initial voltage is $V_0 = q_0/c$. When an external field is applied, the distribution of electric charge on the surface of droplet is altered, as shown in Fig. 10.4b. This transformation results in an asymmetric surface tension. It should be pointed out that the asymmetric surface will remold the droplet's shape. The surface tension increased in left-hand-side hemisphere, but decreased in right hemisphere, leading to the decreasing radius of left hemisphere (Fig. 10.4b). It can be observed obviously in Al–Ga–In motor movement (Fig. 10.3b), but not in GaIn_{10} droplet due to a weak alteration of the surface tension (Fig. 10.3a). The asymmetric surface tension will induce a pressure difference ΔP between the droplet according to Young–Laplace equation: $P = \gamma (2/r)$, which provides a driving force, ($F_{\text{surface tension driving}}$) to the liquid metal droplet.

As can be seen from Fig. 10.3c, the two kinds of droplets start uniform linear motion since 0.1 s. As a result, to the Al–Ga–In motors, the forces can be related by the equation as $F_{\text{bubble propelling}} + F_{\text{electric field}} + F_{\text{surface tension driving}} - f_{\text{flow}} - f_{\text{friction}} = 0$. For GaIn_{10} droplets, the equation can be expressed as $F'_{\text{electric field}} + F'_{\text{surface tension driving}} - f'_{\text{flow}} - f'_{\text{friction}} = 0$. There is no bubble propelling force of the

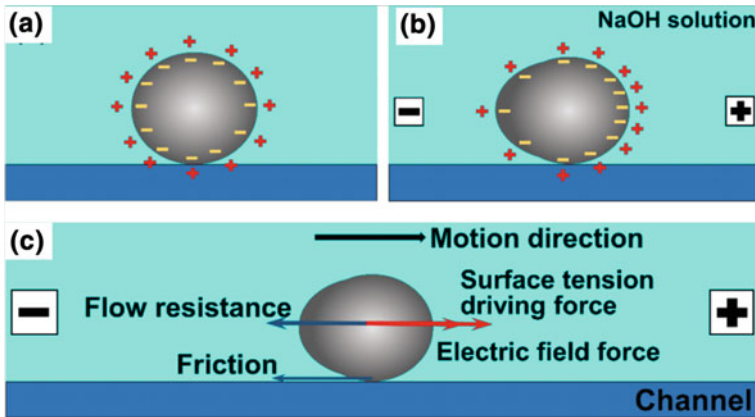


Fig. 10.4 Mechanism of liquid sphere actuation by electric field [1]. **a** Schematic of electric double layer (EDL) model of a liquid metal sphere in alkaline environments. **b** Schematic of varied charge distribution of the EDL and the varied shape. **c** Schematic of forces of liquid metal sphere in movement. All pictures are reproduced with permission

latter. Liquid metal droplets have a very small friction force with the bottom surface owing to its flexibility in a spherical shape. Thus, through ignoring the friction force, the difference of the driving force of the two objects could be obtained as $F_{\text{Al-Ga-In motor actuation}} - F_{\text{GaIn}_{10} \text{ droplet actuation}} = f_{\text{flow}} - f'_{\text{flow}} = 1.06 \times 10^{-4} \text{ N}$, which showed a 29.6 times difference.

The surface tension driving principle adapts to any liquid metal droplets that contain gallium [1]. However, the actuation performance by electricity of Al–Ga–In motors and GaIn₁₀ droplets are very different. Such difference on velocity can even reach 10 times under the same conditions. Through analysis, it can be understood that the primary reason lies in that the chemical reaction between Al and NaOH solution changed the initial electric charge of the droplet surface. It is such an increased initial electric charge that magnified the surface tension driving force ($F_{\text{surface tension driving}}$) [17] and the electric field force ($F_{\text{electric field}}$) [18]. This consists of the key difference between Al–Ga–In motors with GaIn₁₀ droplets. Besides, the generated bubble is also a propelling force ($F_{\text{bubble propelling}}$).

When dispersing the Al–Ga–In motors into NaOH solution, the anodic reaction is proceeded as $6\text{H}_2\text{O} + 6\text{e}^- = 3\text{H}_2\uparrow + 6\text{OH}^-$ and cathodic reaction is $2\text{Al} + 8\text{OH}^- - 6\text{e}^- = 2\text{AlO}_2^- + 4\text{H}_2\text{O}$. The cathode is Al which constantly exuded from the alloy, and liquid metal serves as the anode. When the external field was applied, the anodic reaction slowed down which caused the H₂ production to reduce. The higher the voltage is, the lesser the H₂ it produces, as shown in Fig. 10.5. Since the production of H₂ was reduced, more negative charge would distribute on the surface of the droplets.

In Fig. 10.5, one can find an interesting phenomenon that the bubble trajectory is in fact discontinuous. This is due to that the electric-induced force pointed to the

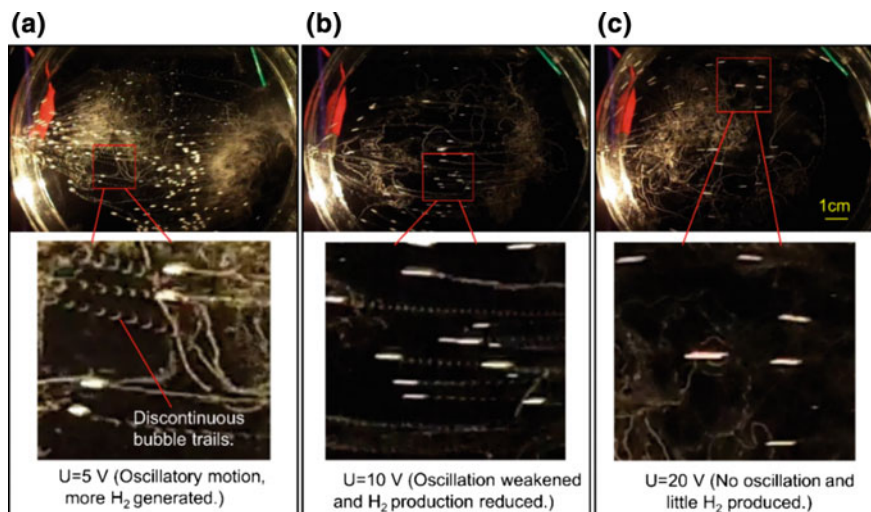


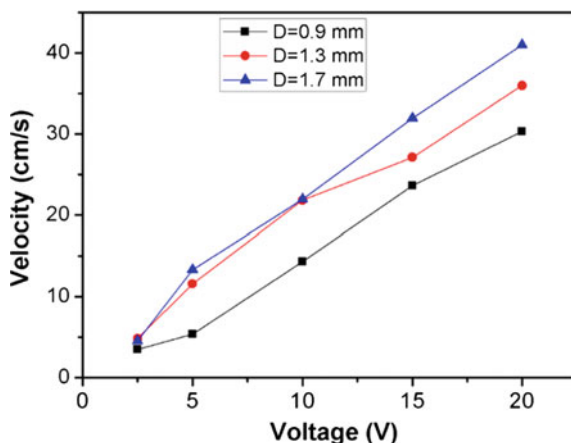
Fig. 10.5 Comparison of H_2 trajectories of the Al–Ga–In motors under different applied voltages in a free Petri dish that is filled with 0.5 mol/L NaOH solution [1]. **a** $U = 5$ V; **b** $U = 10$ V; **c** $U = 20$ V. All pictures are reproduced with permission

barycenter which makes the droplet to translate forward [1]. However, the bubble driving force pushes the droplet rolling, and the direction of the force was varied, to the left, right, or forward. When the two kinds of motions were combined, the translational forward movement would be accompanied by a rolling or oscillating behavior. At a low voltage (such as 5 V), the driving force induced by electric field ($F_{\text{electric field}}$ and $F_{\text{surface tension driving}}$) was relatively weak. So the oscillating movement was obvious and the left H_2 bubbles were large in amount, as shown in Fig. 10.5a. With the increase of the electric field (10 V), the actuated force strengthens which causes a weakened oscillating motion and decreasing H_2 production, as shown in Fig. 10.5b. When the applied voltage was up to 20 V, there are no H_2 bubble trails left and the oscillating movement disappeared due to a high electric driving force (Fig. 10.5c).

The velocity of the Al–Ga–In motors is dominated by the driving voltage and its diameter. Figure 10.6 presents the velocities with several diameters of 0.9, 1.3, and 1.7 mm under different voltages. The velocity shows an apparent difference when the voltage is strong enough (more than 10 V), but only little difference was found under a low voltage. This is merely due to the fact that the friction force accounted for a large proportion of the drag force when the velocity of the droplets is low, while it takes up only a very small percentage under a high speed.

Overall, it was demonstrated that when a small amount of aluminum is added to the liquid metal alloy, the electric driving performance of such Al–Ga–In droplets will be significantly increased compared to the cases that not added [1]. The droplets could easily accelerate to a rather high speed, say 40 cm/s under 20 V voltage.

Fig. 10.6 Velocity–voltage plot in equilibrium state of Al–Ga–In motors with different diameters which was measured in a 1 cm width channel filled with 0.5 mol/L NaOH solution and the distance of electrodes is 10 cm [1]. Picture is reproduced with permission



Further, the force analysis of these two kinds of droplets showed approximately 30 times difference between the Al–Ga–In motor and the GaIn_{10} droplet without Al. In addition, the recorded trajectories of the Al–Ga–In motors in a free Petri dish were found to closely approximate to the electric lines in solution. This suggests a straightforward way to visualize the electrical field distribution of electrolyte, which is hard to do otherwise. Owing to the strong driving force under a low voltage, it is expected that the Al–Ga–In motor would have a prosperous application in diverse areas like microfluidic systems as the driving elements, tiny soft robot as cargo delivery engine, and the like.

10.4 Self-propelled Liquid Metal Motors with Magnetic Property

For a larger size machine, Zhang et al. [19] exhibited an improved self-propelled motor in millimeter scale controlled and steered by external magnet or electric field. A nickel cap is elaborately electroplated on the surface of a liquid metal droplet. The onboard fuel aluminum foil not merely triggers the autonomous movement but also makes the nickel cap adhere more tightly to the droplet. Such motor, composed of nickel cap, aluminum, and liquid metal, runs with a velocity of 3 cm/s for more than 3 hours in aqueous solution without any employment of external energy. In addition, the integration of nickel cap renders magnetic field exploitable to easily change the direction or position and control the start–stop of the motor remotely. Furthermore, external electrical field is a feasible choice to expedite the movement and guide the motor directionally in a reliable manner. More importantly, as a conceptual experiment, when partially loaded with soft alginate-based biomaterial containing aluminum nanoparticles as drugs, such motor is still capable of self-propulsion,

exhibiting steerable motion for drug delivery. The remarkable features of such soft material enabled motor, such as flexibility, controllable self-propelled movement, and drug delivery application, represent a critical step toward functional intelligent soft robots or machines.

As is explained, the self-fuelled movement is imperfect since the droplet holds an uncontrollable behavior with independent trajectory. Therefore, it is crucial to seriously take the controllability into consideration when designing artificial self-propelled motors/machines for meeting the demands of practical applications [19]. The movement of these motors should be able to be turned on or off and slowed down or speeded up at will. Actually, with regard to controllability, numerous excellent investigations on the micro/nanomotors have been conducted to maintain the motors navigating in a steady direction toward their destination [20]. On the whole, there are several feasible approaches for precise control of these micro/nanomotors, including magnetic guidance [21–25], potential modulation [26], light illumination [27, 28], thermal gradient [29], and chemical stimuli [30, 31]. Thereinto, magnetic field and electric field are usually adopted for their unique advantages. Magnetically directed movement of self-driven motors, which is usually implemented through the cooperation of an intermediate ferromagnetic layer (Fe, Co, or Ni) inside motors, is typically preferable due to the selectively applied force and remote management. However, in terms of most soft materials to manufacture macroscopic self-propelled motors, such as organic droplets [32–35] or liquid metals, it is problematic that these soft materials are immiscible with ferromagnetic materials which are usually in the form of powder or solid lump. Consequently, magnetic guidance is theoretically inoperative over these soft objects since the adhesion between soft materials and ferromagnetic materials is not tight enough, especially under the circumstance of synchronous locomotion. Despite that the electric field is a versatile tool as it is easy to be adjusted and arranged in complex patterned arrays, not all the soft materials, such as hydrogel and organic oil, which are nonconductive, respond to electric field.

To further promote the potential application of liquid metal motors, it is important to develop methods for controllable self-propulsion. Magnetic field and electric field are promising to control the liquid-metal-based motors since both ferromagnetic materials and liquid metals have metallic property and actuation has already been realized on liquid metal droplets under the exposure of electric field [19]. Here, the manipulation of the small-scaled self-propelled motors based on liquid metal EGaIn (75% gallium and 25% indium) is explored by applying external magnetic field or electrical field. A thin nickel (Ni) layer is partially electroplated on the surface of the soft droplets in response to the switch of external magnetic field. A piece of aluminum (Al) foil provides onboard fuel source for the self-propulsion and prevents the detachment of Ni cap from liquid metal. Additionally, the enhancement and directional guidance of the autonomous movement are demonstrated and evaluated under the exposure of external electrical field. As alginate-based biomaterials are soft and usually utilized in drug delivery systems for tissue engineering [36], here alginate hydrogel containing aluminum nanoparticles (Al-NPs) are partially loaded on the self-propelled motors to testify their delivery performance. The feasibility of controllable self-propulsion over such macroscopic soft motors for drug delivery

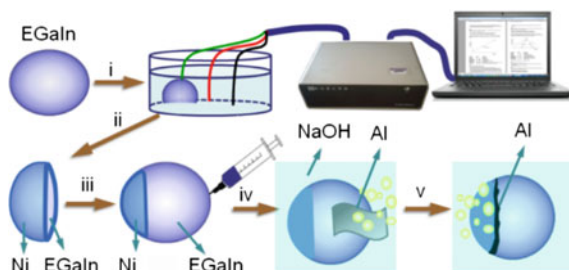


Fig. 10.7 Sketch for the fabrication of the magnetic soft motor [19]. (i) Put EGaIn droplet into nickel plating solution; (ii) Electroplate Ni cap on liquid metal droplet; (iii) Adjust the dosage of liquid metal; (iv) Contact Al foil with Ni/EGaIn droplet; (v) After amalgamation between Al and liquid metal. All pictures are reproduced with permission

presents significant expectations on developing future soft robots or machines either under the guidance of on-demand applications or from the view of fundamental scientific exploration.

10.5 Preparation of Ni/EGaIn Droplet and Ni/al/EGaIn Motor

The preparation process of the magnetic soft motor is shown in Fig. 10.7. When exposed to an ambient air environment, the surface of EGaIn droplet gets oxidized instantaneously, which influences the behavior of the droplet evidently due to the drastically reduced surface tension [19]. The oxidized droplet is easily distorted in nickel plating solution, maintaining a pronounced nonspherical shape. The nickel plating solution contains 20 g/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 350 g/L $\text{Ni}(\text{SO}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$, and 35 g/L H_3BO_3 . A Pt (99.99%) wire and an Ag/AgCl (3 M KCl) are served as counter electrode and reference electrode, respectively. A copper wire is inserted into the liquid metal droplet to work as the working electrode. The electroplating is carried out by an electrochemical workstation (CHI660E, Chenhua, China) at -1.0 V for 600 s, yielding a Ni cap coated on the upper surface of the liquid metal droplet. Such Ni/EGaIn droplet is rinsed in deionized water. The size of the Ni cap can be easily trimmed according to the volume of EGaIn droplet. In addition, since the flexibility of the liquid metal is not severely compromised by the thin Ni cap, the EGaIn dosage can be adjusted by injecting or extracting the liquid metal through the bottom gap to modulate the coverage of the cap. When transferring the Ni/EGaIn droplet into sodium hydroxide (NaOH) solution, it resumes a spherical shape due to the recovery of surface tension via the dissolution of the oxidized skin on liquid metal. A piece of Al foil is added by contacting the liquid metal surface, which supplies the fuel for self-propulsion. After several seconds, the formed Ni/Al/EGaIn motor starts to move autonomously.

10.6 Preparation of Hyd/al/EGaIn-Al Motor and Hyd/Ni/al/EGaIn-Al Motor

Sodium alginate solution (1.0 wt%) is prepared and mixed with Al-NPs (diameter of 80 nm) at a concentration of 30 g/L. Calcium chloride (CaCl_2) solution to ionically crosslink alginate is prepared with a concentration of 0.05 mol/L. A 50 μL Ni/EGaIn droplet is placed on a plastic plate with the Ni cap upside. A drop of sodium alginate solution containing Al-NPs is added on the Ni/EGaIn droplet by a microsyringe, and then CaCl_2 solution is added on the top of sodium alginate solution. Immediately, sodium alginate solidifies into a hydrogel cap on the upper surface of the Ni/EGaIn droplet, forming into a Hyd/Ni/EGaIn-Al droplet. The hydrogel cap can be trimmed by microscissors. The hydrogel cap is coated on the upper surface of EGaIn droplet to form a Hyd/EGaIn-Al droplet by the same way. After transferring the Hyd/EGaIn-Al droplet and Hyd/Ni/EGaIn-Al droplet into NaOH solution, Al foil is utilized to contact the EGaIn surface to form Hyd/Ni/Al/EGaIn-Al motor and Hyd/Al/EGaIn-Al motor, which can be self-propelled to move in NaOH solution.

A commercially available neodymium-iron-boron (NdFeB) permanent magnet (magnetic flux density of ~ 0.35 T and size of $\Phi 20$ mm * 10 mm) is utilized to change the direction or control the pause-start of the Ni/Al/EGaIn motor. The magnet can be placed out of the NaOH solution. The voltage between two graphite electrodes is generated by a direct power supply (PS-305D, Long Wei, Hong Kong, China).

The straight channel for the experiments to be carried out with the application of magnetic or electric field has a length of 15 cm, a width of 6 mm, and a depth of 6 mm. A Y-shaped channel used to test the path selection of the magnetic self-propelled motor is 8 mm in width and 6 mm in depth with angles of 150° , 150° , and 60° at the intersection. Channels are fabricated by computer numerical controlled (CNC) machine.

Videos are captured by a high-speed camera (Canon XF-305, Japan). The transient images and velocity data are extracted from these videos. To observe the appearance of the liquid metal motor more clearly, a digital microscope connected with a computer through USB interface is employed with a magnification of tenfold.

10.7 Ni/EGaIn Droplet Under Magnetic or Electric Field

Figure 10.8a and b shows that a magnet is utilized to validate the adhesion force between Ni cap and EGaIn droplet [19]. In a straight channel containing NaOH solution, the Ni/EGaIn droplet can be attracted by the magnet and move as a whole, indicating that the solid Ni layer and the liquid metal droplet cohere tightly. In addition, within certain velocity range, it is feasible for the magnet to passively drag the Ni/EGaIn droplet here and there randomly. Figure 10.8b implies that the introduction of Ni layer successfully endows the Ni/EGaIn droplet with magnetic property. The Ni cap enables Ni/EGaIn droplet to move passively in aqueous solution,

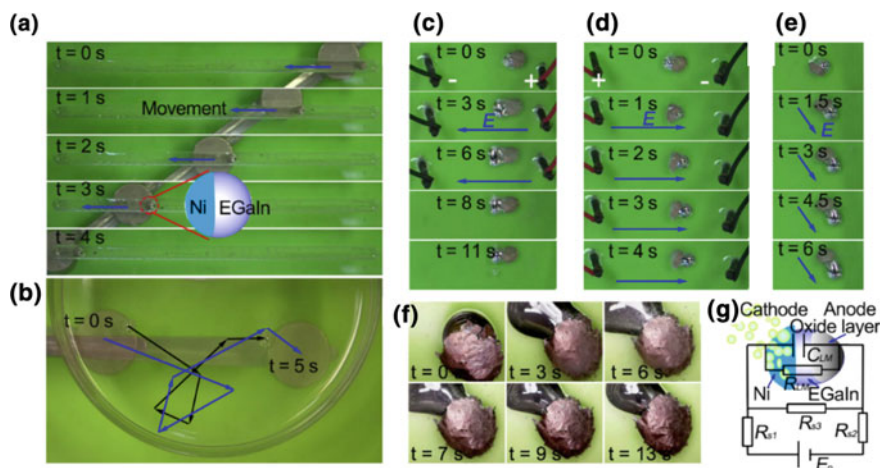


Fig. 10.8 50 μL Ni/EGaIn droplet under the application of magnetic or electric field in 0.1 mol/L NaOH solution [19]. **a** The Ni/EGaIn droplet moves under the guidance of a magnet in a straight channel. **b** Trajectories of the Ni/EGaIn droplet and magnet under the random guidance over 5 s with the interval of 1 s in a Petri dish (with a diameter of 7 cm). The snapshot captured at 5 s and the tracking lines are overlapped on the snapshot captured at 0 s. **c–e** The deformation of Ni/EGaIn droplet under the exposure of electric field in different directions. **c** The voltage is 15 V, and the distance between two electrodes is 4 cm. **d** The voltage is 15 V, and the distance between two electrodes is 4.5 cm. **e** The voltage is 20 V, and the distance between two electrodes is 4.5 cm. **f** The magnified figure of the deformed Ni/EGaIn droplet captured by a portable digital microscopy. The electric field is removed at $t = 6$ s. **g** Equivalent circuit when direct power is applied on Ni/EGaIn droplet: R_s is the electrolyte resistance between two electrodes and Ni/EGaIn droplet, R_{LM} and C_{LM} are the charge-transfer resistance and the capacitance of the electric double layer between Ni/EGaIn droplet and the solution, respectively, E_p denotes the direct power supply. All pictures are reproduced with permission

while it hinders the liquid metal to be actuated in NaOH solution under external electric field. As is shown in Fig. 10.2c–e, external electric field generated by a DC power supply is applied between two inert graphite rods (a diameter of 2 mm) in a glass Petri dish. A 50 μL Ni/EGaIn droplet is placed between the two electrodes. Under the exposure of 15 V, the liquid metal flattens toward the cathode, while the Ni cap remains pinned at its original location, forming a prominent tail. When exchanging the electrodes, the liquid metal turns around and deforms toward the cathode as before (Fig. 10.8 c, d). The deformation of the liquid metal is more obvious when the voltage is about 20 V (Fig. 10.8e). Under a stimulus of 25 V, the force induced by external electric field renders Ni cap to separate from liquid metal, and then the bare EGaIn droplet is actuated to move toward the anode rapidly alone. Unlike *p*-type CuO nanoparticles coated on the surface of the liquid metal marble, which are evenly distributed at first, and then migrate toward the anode in response to external electric field, the Ni cap keeps quiescent and is facing the anodic electrode.

Many bubbles are observed on the Ni tail with the DC power on (Fig. 10.8f), and the number of bubbles declines sharply when the power is off. In the galvanic cell

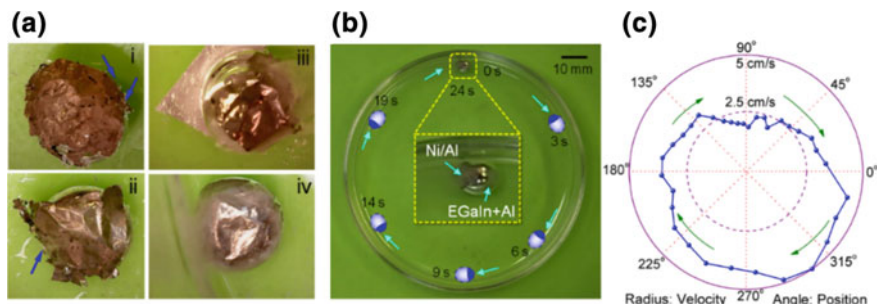


Fig. 10.9 The self-propulsion of Ni/Al/EGaIn motor [19]. **a** (i) and (ii) are a 50 μL Ni/EGaIn droplet in 0.1 mol/L and 0.25 mol/L NaOH solution, respectively. (iii) and (iv) are the amalgamation process between Al foil and Ni/EGaIn droplet in 0.1 mol/L NaOH solution. (iii) is the Al foil penetrating into the liquid metal, and (iv) is the appearance of Ni/Al/EGaIn motor. **b** Spatiotemporal evolution of Ni/Al/EGaIn motor in a Petri dish containing 0.1 mol/L NaOH solution. **c** Position–velocity plot during one lap for a Ni/Al/EGaIn motor in 0.15 mol/L NaOH solution. The time interval between every two points is 0.2 s. All pictures are reproduced with permission

Ni/EGaIn system, Ni cap works as the cathode and EGaIn droplet is the anode. With the application of electric field, the liquid metal always chooses to face the cathodic electrode since it ensures the liquid metal to be the anodic pole (Fig. 10.8g), which is consistent with the galvanic cell Ni/EGaIn system and reduces the interfacial energy between the two materials. As is characterized in Fig. 10.8g, the deformation is mainly induced by the progressive formation of the solid oxide skin, which reduces the surface tension of liquid metal. With the external electric field superimposed on the Ni/EGaIn galvanic cell, the electrochemical reaction is accelerated evidently.

10.8 Self-propulsion of Ni/al/EGaIn Motor

Generally, a slow chemical reaction occurs between NaOH solution and EGaIn droplet (mainly gallium since it is the dominant ingredient) at room temperature without any visible bubbles [19]. With the addition of Ni cap, a few macroscopic bubbles evolve gradually on the surface of Ni cap in 0.1 mol/L NaOH solution, while a multitude of bubbles emerge simultaneously in 0.25 mol/L NaOH solution (Fig. 10.9a (i) and (ii)). The main reason for the accelerated reaction is that as Ni has a more positive potential than gallium, the galvanic reaction between Ni and liquid metal facilitates the oxidation of liquid metal, and it can be further promoted by increasing NaOH solution concentration. Along with the dissolution of gallium to produce gallates $[\text{Ga}(\text{OH})_4]^-$, hydrogen bubbles are generated on the surface of Ni cap (Fig. 10.9a (i) and (ii)). It is noticeable that the accelerated reaction is troublesome since the reaction renders the Ni cap prone to detach from liquid metal.

In our previous research on the self-propulsion of Al/EGaIn motor, a small piece of Al foil is able to initiate the autonomous locomotion in NaOH solution. However,

unlike Al/EGaIn motor, no movement is observed on Ni/EGaIn droplet. To impose the self-propulsion capability on Ni/EGaIn droplet, a piece of Al foil is utilized to provide the onboard fuel. Figure 10.9a (iii) and (iv) shows the amalgamation between Al foil and Ni/EGaIn droplet in 0.1 mol/L NaOH solution. The Al foil penetrates into the liquid metal droplet immediately after it contacts with liquid metal part. In contrast to Al/EGaIn motor, bubbles emerge on the Ni cap of the Ni/Al/EGaIn motor instead of Al foil. After the liquid metal swallows Al foil, part of the Al foil forms into small fragments, aggregating around the Ni cap, while the rest Al foil forms into Al-EGaIn amalgam, similar to copper–mercury amalgam [37]. Coincidentally, the addition of Al foil induces Ni cap to adhere to the liquid metal droplet much more tightly, and the Ni cap is no longer prone to fall apart from the droplet along with the consumption of Al. Thus, Al is beneficial to the cooperation between Ni and liquid metal.

As is aforementioned, the onboard fuel source Al is capable of releasing energy through the interaction with both liquid metal and the solution to support the self-propulsion of the Al/EGaIn motor [19]. In the present experiments, the addition of Al foil enables the Ni/Al/EGaIn motor to move autonomously through a solid Ni cap that is partially coated on the surface of the liquid metal droplet. The self-propulsion of the liquid metal motor with the load of Ni cap indicates that such motor has a potential of carrying cargo. Figure 10.9b depicts a 50 μ L Ni/Al/EGaIn motor navigating along the wall of a Petri dish (diameter of 7 cm). It takes about 24 s for the motor to swim a lap in 0.1 mol/L NaOH. A typical Ni/Al/EGaIn motor is able to travel for more than 10 m in 5 min with a peak velocity up to 5 cm/s, exhibiting a superb performance (Fig. 10.9c).

The velocity during one lap varies with the location of Ni/Al/EGaIn motor (Fig. 10.9c), while the average velocity per lap is relatively stable (Fig. 10.10a). During 40 laps in 0.1 mol/L NaOH solution, the average velocity per lap for Ni/Al/EGaIn motor stays around 1 cm/s, and for Al/EGaIn motor, it triples, demonstrating that the load of Ni cap impedes the self-propelled movement. Fortunately, the impetus is sufficient to overcome the increased resistance. Figure 10.10b exhibits the distance of the motors with/without Ni cap during 1000 s in 0.1 mol/L NaOH solution. The journey for Al/EGaIn motor and Ni/Al/EGaIn motor is, respectively, about 25 and 9 m. It is observed that in the first 400 s, the velocity of the Al/EGaIn motor is larger. Fresh NaOH solution is re-added when Ni/Al/EGaIn motor slows down in 0.15 mol/L NaOH solution, and consequently, the velocity recovers.

As the self-propulsion depends on the conversion of chemical energy into kinetic energy, the release rate of chemical energy affects the performance of the motor significantly [19]. A series of experiments are conducted on Ni/Al/EGaIn motor in NaOH solution with different concentrations since solution concentration is one of the main factors to affect the chemical reaction rate (Fig. 10.10c). Al/EGaIn motor is also investigated in order to manifest the difference between the two motors. As a result, in 0.1 mol/L NaOH solution, the velocity difference between Ni/Al/EGaIn motor and Al/EGaIn motor is evident, and the difference diminishes along with the increase of concentration. Increasing the solution concentration to 0.15 mol/L induces Ni/Al/EGaIn motor much more prompt, which can be comparable to a typ-

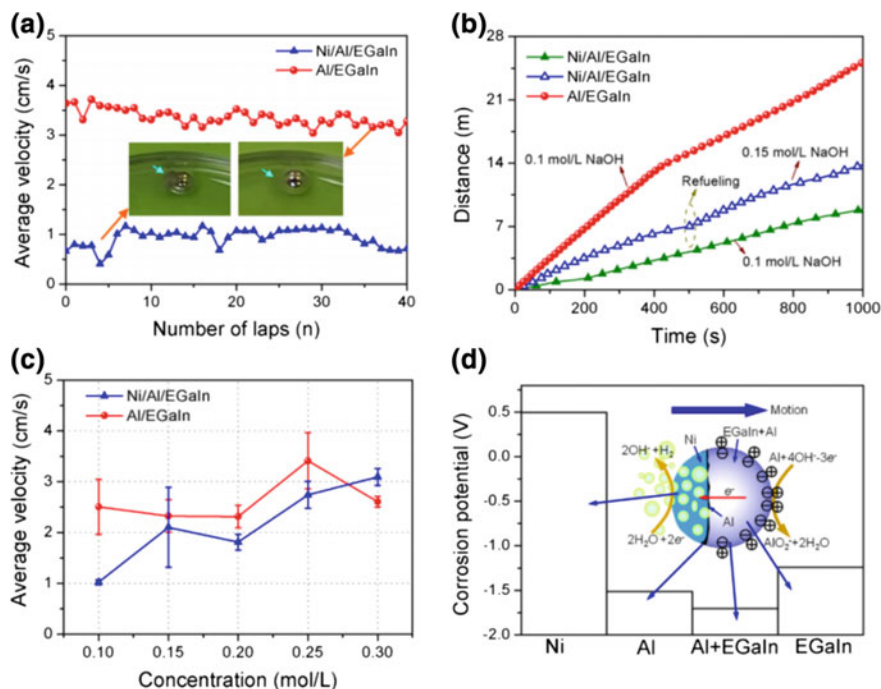


Fig. 10.10 The autonomous movement of liquid metal motors (50 μL) with/without Ni cap [19]. **a** Average velocities per lap of Ni/Al/EGaIn motors and Al/EGaIn motors during 40 laps in 0.1 mol/L NaOH solution. **b** Displacement–time plots of liquid metal motors with/without Ni cap during 1000 s. **c** Average velocity of Ni/Al/EGaIn motor and Al/EGaIn motor in NaOH solution with different concentrations. Each point is tested four times. **d** The corrosion potential (vs. 3 M Ag/AgCl) for the four parts of Ni/Al/EGaIn motor. All pictures are reproduced with permission

ical Al/EGaIn motor in 0.1 mol/L NaOH solution (Figs. 10.9c and 10.10c). Both Ni/Al/EGaIn motor and Al/EGaIn motor are energetic in 0.25 mol/L NaOH solution. In 0.3 mol/L NaOH solution, the velocity of Al/EGaIn motor starts to decline as in the NaOH solution with higher concentration, Al foil penetrates into liquid metal much more quickly, which decreases the contact area of Al with solution. In contrast, Ni/Al/EGaIn motor moves a little faster in 0.3 mol/L NaOH solution since the existence of Ni cap slows down the amalgamation. Therefore, though Ni cap obstructs the autonomous movement in some degree, the performance can be improved by increasing the concentration of NaOH solution. Apart from the concentration of NaOH solution, it is noticeable that the surface coverage of the Ni cap and the volume of the liquid metal affect the self-propulsion of Ni/Al/EGaIn motor as well. Generally, the surface coverage of Ni cap is adjusted between 1/4 and 1/3 as it will not severely influence the fluidity of the soft motor. If the coverage is too large, it is difficult for Ni/Al/EGaIn motor to move autonomously. But if the coverage is too small, it is hard to utilize magnetic field to handle the motor. Different from the self-

propelled magnetic nano/micromotors, the volume of the Ni/Al/EGaIn motor here mainly focuses on millimeter scale, as it is meaningless in terms of the soft property when Ni/Al/EGaIn motor is too small. In macroscopic scale, larger Ni/Al/EGaIn motor moves slower since it needs more energy to overcome larger resistance.

It has been elucidated that the main mechanism for the self-propulsion of Al/EGaIn motor is originated from the galvanic reaction between Al and gallium [19]. In the present Ni–Al–EGaIn system, as part of Al foil forms into fragments and the rest is amalgamated with EGaIn, the Ni/Al/EGaIn motor can be divided into four parts: Ni, Al, Al + EGaIn, and EGaIn. Theoretically, the standard electrode potential (vs.SHE, 25 °C) of Al, Ga, In, and Ni is, respectively, -1.66 , -0.56 , -0.345 , and -0.246 V. Therefore, Al has the most negative potential, and Ni has the most positive potential, which means that among the four metals, Al is the most active one to lose electrons, while Ni is much more stable. In 0.1 mol/L NaOH solution, the corrosion potentials of the four parts are measured by electrochemical workstation, as is shown in Fig. 10.10d. It is observed that Al has a lower corrosion potential than EGaIn, and the corrosion potential of Al is more negative when it is activated by liquid metal. In addition, Ni has a positive corrosion potential as Ni is corrosion resistant in NaOH solution. Therefore, it can be speculated that the galvanic reaction over a Ni/Al/EGaIn motor includes the Al dissolution and hydrogen evolution (Fig. 10.10d). The addition of Ni cap facilitates the reaction since Ni has a more positive potential than EGaIn, which is the main reason that bubbles evolve on Al foil for Al/EGaIn motor while they occur on Ni cap for Ni/Al/EGaIn motor (Fig. 10.9a).

10.9 Manipulation of Self-propelled Ni/Al/EGaIn Motor by Magnetic Field

It is intriguing for Al/EGaIn motor to move autonomously in aqueous solution. However, once the locomotion is initiated by the addition of Al, it will not stop unless it is blocked or the fuel runs out [19]. Due to lack of controllability, it is a huge challenge to apply such motor to fulfill complex tasks. As is aforementioned, the Ni/EGaIn droplet can be dragged passively by a magnet (Fig. 10.8a, b), which indicates that the travel of the self-propelled Ni/Al/EGaIn motor on a predetermined path can also be achieved via magnetic field. Figure 10.10 presents a Ni/Al/EGaIn motor manipulated by a commercially available NdFeB magnet during self-propulsion. As is shown in Fig. 10.11a, the autonomous locomotion can be initiated or stopped repetitively through the switch of magnetic field. When the magnet approaches the rear of the motor (on the Ni cap side), the running motor slows down and reverses to the edge of the magnet to seek balance. If the magnet is placed in front of the motor, it expedites the navigation until the motor arrives at the proximity of the magnet (Fig. 10.11b). Moreover, the velocity can be accelerated to be up to 7 cm/s, which implies that within certain distance range, even though the exact location of the Ni/Al/EGaIn

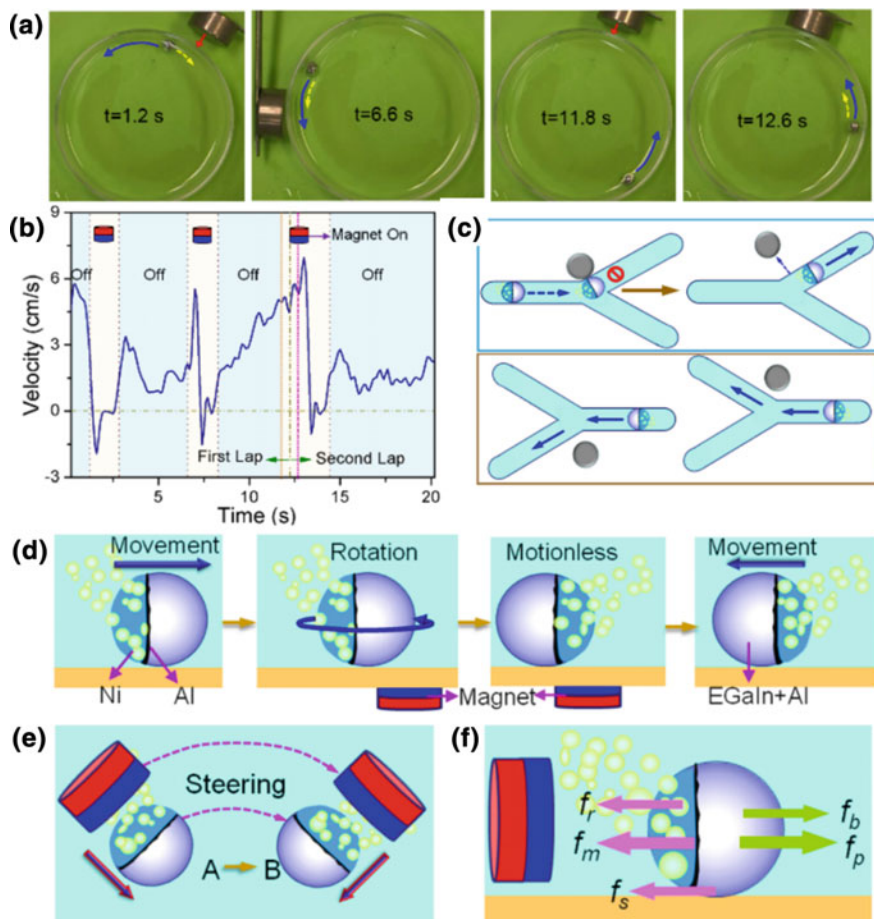


Fig. 10.11 The manipulation of a 50 μL Ni/Al/EGaIn motor by a magnet in 0.15 mol/L NaOH solution [19]. **a** A series of the time-lapse snapshots for the “stop and go” behavior of Ni/Al/EGaIn motor under the alteration of the magnetic field during the autonomous locomotion in a Petri dish (diameter of 7 cm). **b** The velocity of the motor in (a). **c** The manipulation of the motor by a magnet in a Y-shaped channel. The upper image denotes that the closer magnet (stronger magnetic field) stops/starts the motor at the intersection like a switch, and the bottom image shows that weak magnetic field can be utilized to choose the direction at the intersection. **d** The rotation of the motor along with the existence of the magnet in a horizontal plane. **e** The alteration of both position and direction over the motor steered by a magnet. The thick arrows point to the movement direction after the magnet is removed. **f** Schematic of forces affecting the movement of the motor. All pictures are reproduced with permission

motor is not confirmed, the magnet can still be utilized to stop the movement of the motor quickly and precisely once the magnet position is determined.

As the Ni cap is capable of being attracted by a magnet, the adjustment of magnetic field affects the orientation of Ni cap directly, which masters the direction of the

autonomous movement [19]. In Fig. 10.11c, a magnet can serve as a switch to guide Ni/Al/EGaIn motor through a junction. In the Y-shaped channel, if the magnet is very close to the channel junction, the motor will be pulled over near the magnet. With the removal of the magnet, the motor continues to move autonomously along the channel at the magnet side. If the magnet is about 5 mm away from the channel at the junction, the weak magnetic field can be utilized to guide the motor without contributing to the motor velocity. That is to say, the magnetic flux density at the Ni cap can be adjusted to control the behavior of Ni/Al/EGaIn motor. Higher magnetic flux density induces the start–stop of the motor, while lower magnetic flux density can be employed to steer the direction of the motor effectively, similar to nano/micromotors. Figure 10.11d illustrates the scenario that the rotation of Ni/Al/EGaIn motor is achieved via a magnet, and after withdrawal of the magnet, the motor moves reversely. In addition, the disturbance by the magnet enables the motor to alter the direction flexibly, rendering the Ni cap to resemble a steering wheel. Moreover, the magnet can be employed to attract the moving motor from the original track to another location, and meanwhile directionally manipulate the autonomous movement (Fig. 10.11e). Therefore, through the adjustment of the magnetic induction, different motion behaviors of the Ni/Al/EGaIn motor can be precisely achieved.

Theoretically, the movement of Ni/Al/EGaIn motor is promoted by the bubble thrust force f_b and electrochemical propulsion f_p , while it is hindered by the resistance f_r from the solution, the friction from the substrate f_s , and the drag force f_m from the magnet (Fig. 10.9f). Thereinto, the bubble thrust force can be expressed as

$$f_b = N \frac{\Delta m}{\Delta t} (v_0 - v) \quad (10.1)$$

where N denotes the number of bubbles detached from the motor, Δm is the mass change by a single bubble, Δt is the time for bubble detachment, v_0 is the initial horizontal speed of a bubble, and v is the speed of the motor [38]. The electrochemical propulsion force can be expressed as

$$f_p = \varepsilon \zeta E R \quad (10.2)$$

where ε is the permittivity of the solution, ζ is the droplet's zeta potential, E is a characteristic magnitude of the endogenous electric field, and R is the radius of the motor [39]. The flow resistance is described as

$$f_r = (1/2) C \rho \pi R^2 v^2 \quad (10.3)$$

where C ($C = \frac{24}{\text{Re}} + \frac{6}{1+\sqrt{\text{Re}}} + 0.4$, Re is the Reynolds number of the motor) is the resistance factor, and ρ is the density of the solution. The rolling friction from the substrate f_s is negligible due to the fluidity of the liquid metal [40]. The drag force from the magnet can be estimated as

$$f_m = k \frac{\mu_0 m^2}{2\pi d^4} \quad (10.4)$$

where k is the coefficient for the alignment of the Ni cap relative to the magnet, d denotes the distance between the motor and the magnet, $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$ is the permeability of free space, and m is the magnetic moment. It can be seen that larger distance reduces the drag force sharply. The horizontal resultant force is characterized as

$$F = f_b + f_p - f_r - f_s + n \cdot f_m \quad (10.5)$$

where n is the positive (or negative) when motor runs toward (or away) from the magnet. The flow resistance for a 50 μL Ni/Al/EGaIn motor running at 2 cm/s is about $4.0 \times 10^{-6} \text{ N}$. It is hypothesized that when Ni/Al/EGaIn motor reaches a balance at the horizontal direction without the magnetic attraction, the propulsion force (f_b and f_p) is a little larger than the flow resistance. When the motor needs to be stopped by the magnet (the flow resistance is zero), the attraction force in the horizontal direction should be larger than the propulsion force. As the attraction force f_m is very sensitive to the relative position between the motor and the magnet, the autonomous movement is highly controllable. Besides, as long as the fuel Al is depleted or the impetus is insufficient to overcome these resistances (which means f_b and f_p decrease gradually to zero with the consumption of Al), magnetic field can contribute to the velocity and guide the motor to the destination, and thus the emergency is handled in time.

10.10 Control of Self-propelled Ni/al/EGaIn Motor by Electric Field

It is observed that the Ni cap is unfavorable for the actuation of Ni/EGaIn droplet by electric field. Here, a series of experiments have been conducted to explore how external electric field affects the motion of Ni/Al/EGaIn motor [19]. As a result, different from the Ni/EGaIn droplet, which only deforms toward the cathodic electrode, the Ni/Al/EGaIn motor moves as a whole. In a Petri dish, the self-propelled motor is accelerated obviously and moves only toward the anodic electrode. For better quantitative measurement of the acceleration, experiments are carried out in a straight narrow channel containing NaOH solution under certain voltage, as is shown in Fig. 10.12a. The enhancement of the movement is manifested in Fig. 10.12b. In 0.1 mol/L NaOH solution, Ni/Al/EGaIn motor swims at a velocity less than 1 cm/s, while with the application of electric field, the average velocity reaches up to 6 cm/s (Fig. 10.12b). In 0.25 mol/L NaOH solution, such motor moves at a velocity less than 2 cm/s, and under the same voltage, the motor performs better than that in 0.1 mol/L NaOH solution. In addition, the average velocity of Ni/Al/EGaIn motor in 0.25 mol/L NaOH solution reaches up to 8 cm/s, which exhibits appreciable accel-

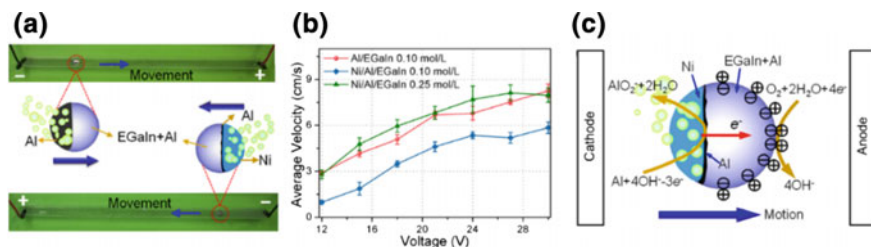


Fig. 10.12 Influence of electric field on a 50 μL liquid metal motor with the addition of Ni [19]. **a** The sketch for Ni/Al/EGaIn motor and Al/EGaIn motor to move under the exposure of external electric field. **b** Average velocity of a 50 μL Al/EGaIn motor with/without Ni cap in a straight channel containing NaOH solution under the exposure of different voltages. Each point is measured at least four times. **c** sketch of Ni/Al/EGaIn motor under a direct power supply. All pictures are reproduced with permission

ation. In contrast, with the exposure of electric field, the performance of Ni/Al/EGaIn motor in 0.25 mol/L NaOH solution is slightly better than that of Al/EGaIn motor in 0.1 mol/L NaOH solution, as is shown in Fig. 10.12b. These experiments elucidate that external electric field can be employed to enhance the performance of the Ni/Al/EGaIn motor, especially in higher concentration of NaOH solution.

Under the exposure of external electric field, the fluidity of the EGaIn droplet enables liquid metal to choose the orientation to reduce the interfacial energy. As a result, the liquid metal selects to face the anode side [19]. Both Ni/Al/EGaIn motor and Al/EGaIn motor move toward the anode (Fig. 10.12a), implying that the liquid metal part works as cathodic pole. Hence, it is inferred that the reduction reaction occurs on the liquid metal surface, as is presented in Fig. 10.12c. Correspondingly, the Al fragments which aggregate around the Ni cap are the anodic pole since Al has a much more negative potential than both Ni and EGaIn. On the cathodic pole, the reduction reaction includes the reduction of oxidized gallium and oxygen. According to the principal of the chemical kinetics, oxygen reduction, which generates hydroxyl ion, is prior to the oxidized gallium reduction [19]. As the content of the oxidized gallium is limited, the oxygen reduction dominates on the cathodic pole. On the anodic pole, Al dissolves to lose electrons. These electrons flowing internally from Al to the liquid metal involve into the reduction reaction preferentially near the Al, which leads to the generation of a potential gradient along the liquid metal surface (Fig. 10.12c). Such potential gradient induces an imbalance of the surface tension on the liquid metal, which actuates the motor to move forward to the anode. The potential drop posed by external electric field is critical for Faradaic reactions at the cathodic pole and the anodic pole [41]. Larger applied voltage increases the potential drop, which accelerates the electrochemical reaction. Thus, the electrochemical propulsion force is increased, which is favorable for the autonomous movement. The concentration of NaOH solution affects both the endogenous electric field and the potential drop. As for the endogenous electric field, higher concentration accelerates the galvanic reaction, which generates larger intensity of endogenous electric field.

For the potential drop, increasing the concentration of the solution induces more charges in electrolyte and reduces electrolyte resistance, which enhances the voltage drop across the motor and increases the velocity. Overall, the external electric field accelerates the motor, and under the same voltage, higher concentration further expedites the motor.

From the above, external electric field can be utilized to control the movement direction since both Ni/Al/EGaIn motor and Al/EGaIn motor move directionally toward the anode. In addition, the velocity can be enhanced through the adjustment of electric field and the concentration of NaOH solution [19]. In exceptional circumstances, such as the fuel Al of the self-propelled motor is depleted or there are some obstacles on the way, the electric field can supply extra impetus for the motor to arrive at the destination. In a word, the electric field can be a versatile tool to control the direction and velocity of the self-propelled Ni/Al/EGaIn motor, and it is also very useful for the failure remedy.

10.11 Self-propelled Motor for Drug Delivery

As a conceptual experiment, Al-NPs embedded in the hydrogel work as drug, and meanwhile they induce the hydrogel to anchor to liquid metal more tightly [19]. In the absence of Al foil, the Hyd/EGaIn-Al droplet (Fig. 10.13a) remains immobile. With the exposure of external electric field, the Hyd/EGaIn-Al droplet is actuated to move toward the anodic electrode (Fig. 10.13b). Similarly, the Hyd/Ni/EGaIn-Al droplet can be dragged by a magnet passively. To initiate the self-propulsion, a small piece of Al foil is utilized to provide the fuel in NaOH solution. With the load of hydrogel, both the Hyd/Al/EGaIn-Al motor and Hyd/Ni/Al/EGaIn-Al motor are capable of moving autonomously at a velocity of about 2 cm/s (Fig. 10.13b), which demonstrates that the two motors have potential in delivering drugs without any assistance. The size of the hydrogel cap affects the self-propulsion much more evidently than that of the Ni cap. As is shown in Fig. 10.13d and e, during the self-propulsion, the behavior of the Hyd/Ni/Al/EGaIn-Al motor can also be controlled by magnetic or electric field. It is noteworthy that with the application of external electric field, the movement of the motor can be accelerated toward the anode obviously. However, the hydrogel may depart from the motor for speeding (mainly more than 5 cm/s).

Overall, a controllable self-propelled motor based on liquid metal can be fabricated through partially electroplating a Ni layer on the liquid metal surface and adding a small piece of Al foil to trigger the autonomous movement [19]. Such Ni/Al/EGaIn motor with a volume of 50 μL own the ability to move at an average velocity up to 3 cm/s in a Petri dish, and the self-propulsion can last for hours without any extra external energy. Additionally, the Ni/Al/EGaIn motor owns the capability of being flexibly manipulated via external magnetic field or electric field. The magnetic field can be utilized to steer the motor by efficiently changing the direction or position as well as controlling the start-stop. Besides, under the exposure of electric field, the motor moves directionally from cathode to anode, and it can be accelerated with

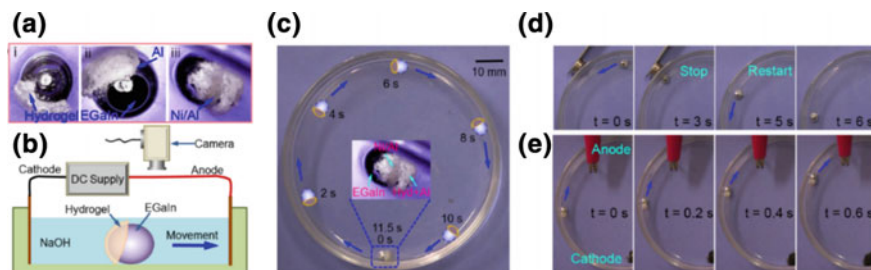


Fig. 10.13 The self-propelled motor for drug delivery [19]. **a** The appearances for the Hyd/EGaIn-Al droplet, Hyd/Al/EGaIn-Al motor, and Hyd/Ni/Al/EGaIn-Al motor, respectively. **b** The sketch for Hyd/EGaIn-Al droplet to move under the exposure of external electric field. **c** Spatiotemporal evolution of a 50 μL Hyd/Ni/Al/EGaIn-Al motor in a Petri dish containing 0.2 mol/L NaOH solution. **d** A series of the time-lapse snapshots for the “stop and go” behavior of Hyd/Ni/Al/EGaIn-Al motor under the alteration of the magnetic field during the autonomous locomotion in a Petri dish (diameter of 7 cm). **e** The acceleration of Hyd/Ni/Al/EGaIn-Al motor with the application of external electric field. All pictures are reproduced with permission

an average velocity up to 8 cm/s. Magnetic field can produce a drag force on the Ni cap to impede the autonomous movement in a noncontact way, while electric field improves the impetus by regulating the electrochemical reaction in the aqueous solution. Hence, the pause of the motor can be realized by way of magnetic field control, and the acceleration can be achieved reliably via electric field. Thus, a desirable directional movement can be implemented by magnetic field and electric field. More importantly, combined with the soft biomedical materials hydrogel, the liquid metal motor can be utilized to deliver drugs, and the transportation is controllable in response to magnetic field and electric field. The highly controllable self-propulsion enables the liquid metal motor to advance the field of soft robot design as well as the intelligent machines to perform challenging tasks in the near future.

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Chapter 11

Environment Enabled Liquid Metal Machine



Abstract Simulating nature to manufacture self-powered device or motor has been an important goal in science and engineering. Conventional spontaneous motions of an object were generally achieved through the Marangoni flow of organic liquid or water solution. Regarding the metallic materials, mercury had ever been developed as beating heart as a kind of self-propulsion example. However, the serious safety concern of such medium restricts its extensive application. From an alternative, Yi et al. (Breathing to harvest energy as a mechanism toward making a liquid metal beating heart, 6:94692–94698, 2016 [1]) discovered an important mechanism to realize gallium-based liquid metal beating heart through introducing a breathing mechanism in analogy to living organisms. With the unique configuration of a semi-submerged liquid metal droplet partially immersed in alkaline solution, such a system would produce a surface tension gradient perpendicular to the three-phase contact line which subsequently leads to the oscillation of the droplet and the surrounding solution. This finding suggests a feasible way to fabricate self-oscillating liquid metal motors without external electricity or fuels input. Except for such air driving mechanism, more environmental factors such as heat can also be applied to power the liquid metal system given appropriate designing. The present chapter illustrates the basic behaviors of such environment enabled liquid metal machines and their self-actuating driving mechanisms.

Keywords Environmental effect • Liquid metal machine • Beating heart
Breathing enabled propulsion • Thermo-pneumatic effect • Heat driving system

11.1 About Breathing Enabled Liquid Metal Machine

Spontaneous motion of droplet has attracted a great deal of attention over the past few decades. Since the famous phenomenon of “tears of wine” was revealed, a typical model of Marangoni flow has been well known that surface tension gradients can cause liquids to flow against the force of gravity [2]. Based on such mechanism, interesting stories have been developed rapidly. It was reported that the aniline

oil can show either circular or beeline motion in a circular Petri dish filled with solution due to the chemical nonequilibrium [3]. The directional motion can be generated in many ways, such as differences in metal ions concentration [4], pH gradient [5], and wettability gradient [6]. Cira et al. demonstrated that two-component liquid droplets such as propylene glycol and water deposited on clean glass can cause motion of the neighboring droplets over a distance [7]. For such two-component droplets, evaporation induces the gradient of surface tension and then a Marangoni flow sets in. Further, Wang et al. [8] demonstrated the automatically running PVC system which was driven by the surrounding water. Such self-propelling behavior is regulatable through an embedded ZnO micro-/nanostructured hollow sphere structure [9]. These self-propelled explorations are beneficial for the fabrication of bionic robot, application in microfluidic systems, and physical analog of biological organism. Generally, the elements of the self-propelled system include water and organic solvent. In contrast, related works on Marangoni effects of metallic material are exceedingly rare.

It is worth noting that a classical bionic model, the mercury beating heart is perhaps the most popular self-propelled oscillator which is consisted of a mercury droplet covered with aqueous acid or basic solution and an iron nail. The iron triggers the chemical reactions occurring on the surface of Hg drop, inducing the variations of the surface tension and further leading to the oscillations. Such phenomenon was first reported by Lippmann [10]. A hundred years later, many researchers conducted comprehensive experiments on the phenomenon of mercury beating heart at different conditions and elaborated the related mechanism [11, 12]. Thereafter, variations of the autonomous beating heart system were developed widely. Distinctive phenomena, such as deformation of circle, triangle, square, diverse multi-pointed stars [13, 14], and rotational motion [15], can be achieved by adjusting the experimental conditions. Although these studies provide outstanding insights into bionic system, the poisonous and polluttional characteristics of mercury restrict in a large extent its extensive applications. Clearly, finding a new strategy through a green metal material to obtain a spontaneous oscillator is of particular significance.

Over the years, this lab has made efforts to probe into the biomimetic behaviors via safe liquid metal. It was found that gallium-based liquid metal can transform into different morphologies, including large-scale reversible deformation, rapid merging of separate metal droplets, controlled self-rotation, and planar locomotion [16, 17]. In these cases, electrical field is required as major power resource. Such deformability of liquid metal is similar to that of amoeba which can alter its own shape according to the demand. Apart from this, it is found that the magnetic field has a certain influence on the motion of nonmagnetic liquid metal. When the liquid metal sphere is set between a pair of concentric ring electrodes in the NaOH solution on the permanent magnet, the sphere is capable of rotating centrifugally around the central electrode [18]. To get rid of the limit of external energy supply and further simplify the driving method, our group disclosed a synthetic self-fueled motor based on liquid metal [19]. The liquid metal “eats” Al flake as fuel to power its swimming. The mechanism has been figured out that the energy produced by the chemical reaction between gallium, Al, and solution is converted into mechanical activity for driving

the motion of droplet. Such activities are comparable to those of organism, i.e., ingestion, digestion, conversion, and locomotion. Further, such self-fuelled liquid metal machine still displays additional behaviors like autonomous convergence or divergence [20, 21], macroscopic Brownian motion [22], and the motion restriction resulting from magnetic trap effect under the magnetic field [23].

Via a rather easy going way, Yi et al. [1] found a new mechanism to compose the Ga-based liquid metal beating heart. Such self-propelled system includes a liquid metal droplet and alkaline solution. To trigger the oscillation of this system, a special configuration is designed where a part of the droplet is exposed to ambient air and the other is immersed in the alkaline solution. The liquid film around the metallic droplet presents the regular and periodic motion. It can be noted that such unique semi-submerged design results in Marangoni gradients consisting of the gallium oxide diffusing along the droplet interface and gallium hydroxide spreading at the solution/air interface, which provides the impetus source for the oscillation. Thereinto, breathing air to harvest energy is similar to animals' physiological activity in nature.

11.2 Experiments on the Breathing Driven Liquid Metal Beating Heart

Liquid metal GaIn alloy (Ga 90%, In 10% by weight) was utilized to realize the spontaneous movement. The solution environment, i.e., NaOH solutions (0.5 mol/L), was prepared with deionized water and A.R. grade NaOH (99% purity). A liquid metal droplet was produced into a glass dish containing NaOH solution by a disposable injector without needle. The volume of the droplet was 0.4 mL with the diameter of 1.1 cm. To eliminate the interference of wall contact, the liquid metal was located in the center position of container. The solution level should be slightly lower than the top of the liquid metal droplet so that liquid metal can be partly exposed to the air and the remainder can be submerged into NaOH solution.

The dynamic behavior of the liquid metal beating heart system was recorded by a digital camera (Canon 60D, Japan). The films were captured at 25 frames per second (fps), with 1920×1080 pixel resolution. Due to the high light reflection on metal base, it is difficult to distinguish the boundary between liquid metal and the solution with naked eyes. To improve the contrast, NaOH solution was dyed with red ink. In addition, the side view of the liquid metal droplet with the alkaline solution surrounded was also captured by the Canon camera. To observe the flow characteristics of the solution intuitively, nylon fabric fragments in millimeter scale as tracers were randomly positioned into the liquid metal beating heart system. The fragments are enough light in weight that can float on NaOH solution and drift with the flow of fluid. Moreover, fluorescent polystyrene particles with the mean size of $1.84 \mu\text{m}$ (purchased from SpheroTech) were utilized to display the flows of solution.

QIClick camera (QImaging) on an Olympus BX51 upright microscope was employed to capture the motion of fluorescent beads at a rate of 10 fps.

11.3 Cyclic Oscillation of Liquid Metal Droplet

Experiments disclosed that the crown area exposed in the air of liquid metal droplet was able to enlarge and shrink spontaneously and periodically in NaOH solution without any external power supply [1]. It seems like that the liquid metal droplet takes deep breath periodically. The continuous oscillation lasted for 1 min 40 s, and then the solution calmed down gradually. Before and after the regular movement, the interfacial solution rotated along the surface of liquid metal droplet in one direction. To investigate the relationship between the time and diameter of the exposed crown area quantitatively, several stable cycles from oscillation can be selected for analysis (Fig. 11.1a, b). If the moment of the exposed part with minimum diameter was set as 0 s, the diameter would expand to the maximum within 5.2 s, and shrunk rapidly to the minimum within only 1.4 s. Since then, the following five cycles were extracted from the movie to clarify the motion pattern (Fig. 11.1c). It shows that the dimension of the exposed part can recover to the original size during these six cycles. And the maximum diameter of the exposed part is almost the one-and-a-half times as large as the minimum diameter. The corresponding oscillation period of these six cycles is 6.095 ± 0.335 s ($T_{\text{expand}} = 4.930 \pm 0.262$ s, $T_{\text{shrink}} = 1.165 \pm 0.106$ s), which proves that such variation is quite regular as the heart beating with certain stable frequency.

From the top view, it is hard to distinguish whether the movement is resulted from metallic droplet or the surrounding solution. Thus, side photos of this beating heart system were taken. From the related videos of the oscillation from two different angles, it was found that the solution nearby the interface obviously demonstrated the back-and-forth movement around the metal droplet [1]. In turn, the oscillation of the solution leads to the slight vibration of liquid metal droplet as well. Consequently, the oscillation of the beating system is mainly caused by the periodic fluctuation of the interfacial solution. This significantly differs from the mechanisms of traditional mercury beating heart system where oscillation is caused by the motion of mercury droplet itself. It is noteworthy that such test is simply utilized to clarify the source of the obvious oscillation.

11.4 Tracing the Dynamic Behaviors

In the tracing experiment, the movement of nylon fabric fragment was recorded to describe the situation of the flow field [1]. Figure 11.2a shows the overlaid time-lapse images of fragments at different time. The arrows represent the motion directions of fragments. These fragments can be divided into two groups according to their

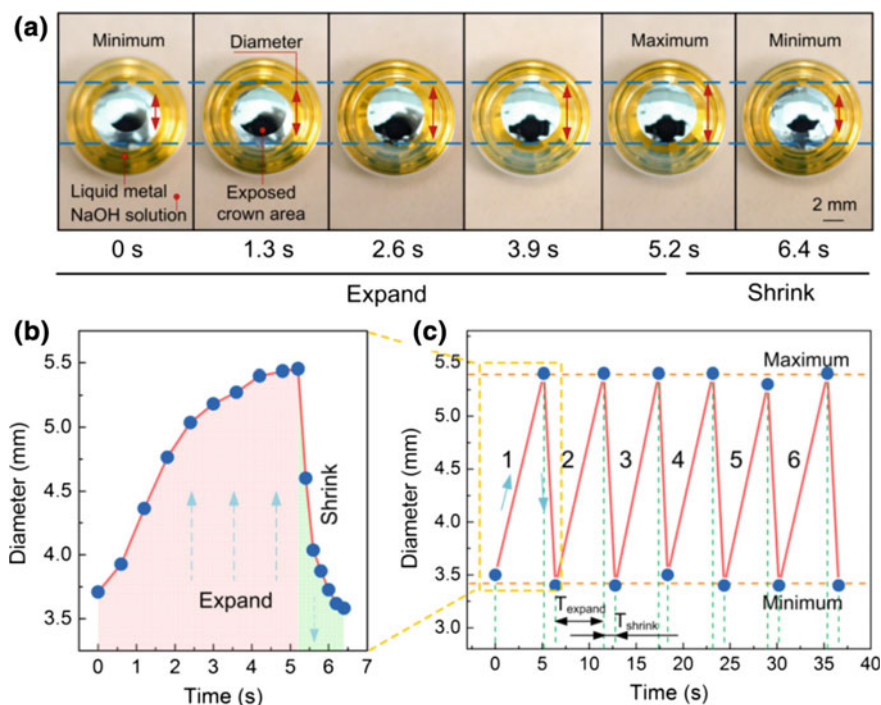


Fig. 11.1 Beating heart behaviors of liquid GaIn metal droplet [1]. **a** The semi-submerged liquid metal droplet resulting in the periodic oscillation of surrounding solution. The red arrows indicate the diameter of exposed crown area. The blue-dotted lines are marked according to the maximum diameter of exposed crown area for the comparison on dimensional changes at different time. **b** The dimension variations on the part of liquid metal droplet exposed to the air versus time in one cycle. **c** The periodic oscillation curves in several cycles. All pictures are reproduced with permission

moving behaviors. One group of fragments near the droplet rapidly moved to the gas–solution–metal contact line, which was affected by the oscillation of the solution. Accordingly, an effective area can be determined within the blue circle as shown in Fig. 11.2a, region 1. The other group of fragments was far from the droplet which slightly fluctuated depending on the natural state of the solution. Such area outside the red circle is classified as region 2 in Fig. 11.2a. The region between red and blue circles does not involve any nylon sample, so this area is not considered and discussed in current test. In region 1, a typical fragment termed as sample 1 was selected and its position was labeled with interval time. At first, this sample moved with the initial fluctuation of the solution as the other fragments did in region 2. After 25 s, the solution surface became stable. Since then, the fragments in region 2 were nearly static in situ. Meanwhile, sample 1 began to alter its motion direction and went straightly toward the center of the droplet along with each oscillation of the solution surface around the droplet. Figure 11.2b shows the relative displacement of sample 1 between two adjacent time intervals in Fig. 11.2a. From 50 to 100 s, there was

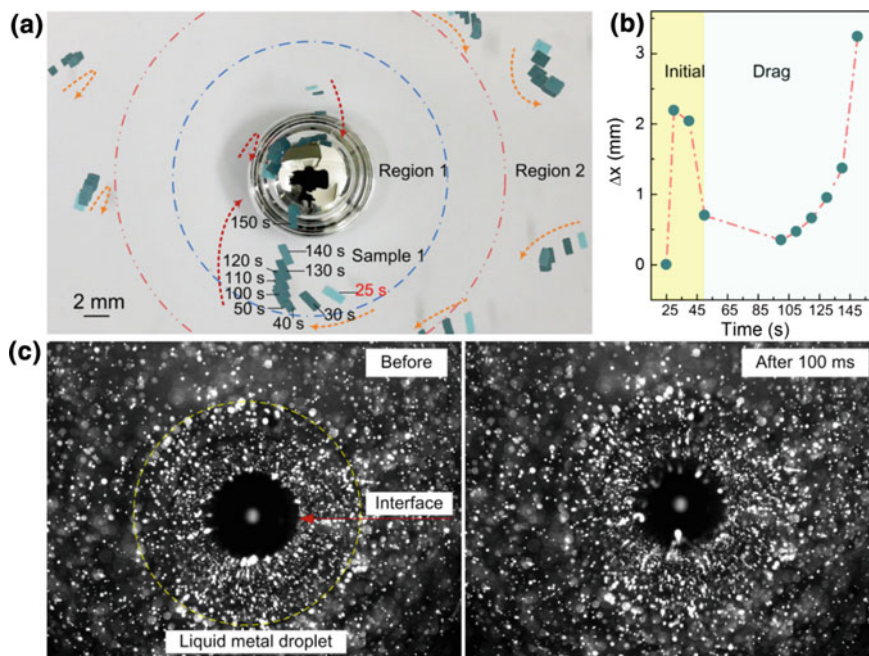


Fig. 11.2 The flow characteristics of solution around the droplet [1]. **a** Overlaid time-lapse images of nylon fragments moving with the flow of the solution for 125 s. **b** The relative displacement between labeled fragments in adjacent intervals. **c** Images of fluorescent beads ($1.84 \mu\text{m}$) tracing the flow direction of solution. All pictures are reproduced with permission

no large displacement of sample 1. Because some fragments near the droplet have contacted the interface and disturbed the periodic motion of the interfacial solution. After adjusting and adapting for about 50 s, the oscillation of the three-phase contact line recovered and the velocity of sample 1 significantly increased as it moved closer to the droplet. Evidently, the liquid metal beating heart system is capable of producing certain level of dynamic power, which can be developed as mini motor to deliver or collect objects in solution.

It has been found that the nylon fabric experiment can intuitively embody the flow characteristics of liquid metal beating heart system, and thus the effective scope can be determined. However, the nylon samples with large size here cannot accurately reflect the actual flow field of the oscillation. Moreover, these light fragments floating on the liquid surface simply describe the surface status of the solution. Therefore, fluorescent polystyrene particles were utilized to further visualize the flow field around the droplet (Fig. 11.2c). Due to the limited vision field of the microscope under high magnification, a liquid metal droplet of several hundred micrometers in size was adopted to demonstrate its surroundings. Such small droplet formed into sphere and suspended in the solution. It was found that such tiny droplet can realize the oscillation as that in large size. However, it takes 100 ms for the exposed crown to

change from its maximum area to the minimum, which is much shorter than that of droplet with bigger size in Fig. 11.1. It proves that the oscillation frequency is related with the dimension of the droplet [1]. In addition, the tracer particles at the interface fluctuated with the solution and gathered from the edge to the center of the droplet. Such microscopic observation also shows that the particles near the top interface appear more mobile than those near the bottom. It indicates that there are regional differences in moving speed of surrounding solution induced from oscillation of the beating heart system.

11.5 Mechanisms of the Breathing Enabled Self-propulsion

To clarify the principle of this self-propelled system, deionized water and NaCl solution (0.5 mol/L) were employed in comparison with NaOH solution [1]. Figure 11.3a demonstrates the status of droplets in three different solutions. There were no obvious changes in morphology of droplets in water and NaCl solution. The surface of these droplets was rough, lacking brightness compared to that of droplet in NaOH solution. In such two situations, oscillation did not occur even if the droplets were semi-submerged.

It is well known that Ga-based alloy surface is susceptible to be oxidized when exposed to air, causing a thin, solid film covering the surface of the alloy [24]. For GaIn alloy here, the content of gallium is dominant. Thus, the main constituent of its oxide film is Ga_2O_3 . This oxide film can be dissolved effectively in NaOH solution but not in water or NaCl solution. Moreover, the performance of liquid metal in air and NaOH solution was studied due to the semi-submerged of liquid metal droplet. Figure 11.3b shows the morphology of liquid metal droplets in air and NaOH, respectively. Contour features of droplets were both extracted from the bottom and side views. It shows that the contact angle of the droplet in NaOH solution (θ_1) is larger than that in air (θ_2), indicating the higher surface tension in NaOH solution. This result is consistent with the conclusion as previously reported that the oxidation lowers the surface tension of the liquid metal significantly [25].

For oscillation, one can define the wetting parameter M according to the force balance as follows: $M = \gamma_{DS} - \gamma_{DA} + \gamma_{SA} \cos \theta_a$, where γ_{DS} , γ_{DA} , and γ_{SA} represent the surface energy of the droplet/solution, the droplet/air, and the solution/air, respectively; θ_a represents the angle between γ_{SA} and γ_{DS} . The direction of M is in X -axis, shown in Fig. 11.3c. X -axis represents the direction of the interfacial tangent. Initially, M is larger than 0 due to $\gamma_{DS} > \gamma_{DA}$, when the contact line reaches position 1. In Fig. 11.3c, position 1 indicates the peak of the dynamic solution surface around the droplet; positions 2 and 3 are the different moments of the surface proceeding down toward; the lowest height of the interfacial surface is shown in the position 4. The resulting stresses are large enough to shift the interfacial solution several millimeters downward along the droplet surface, and hence the exposed diameter subsequently increases. Moreover, there is a phenomenon that effectively supports this statement as well. During the course of droplet being exposed from solution

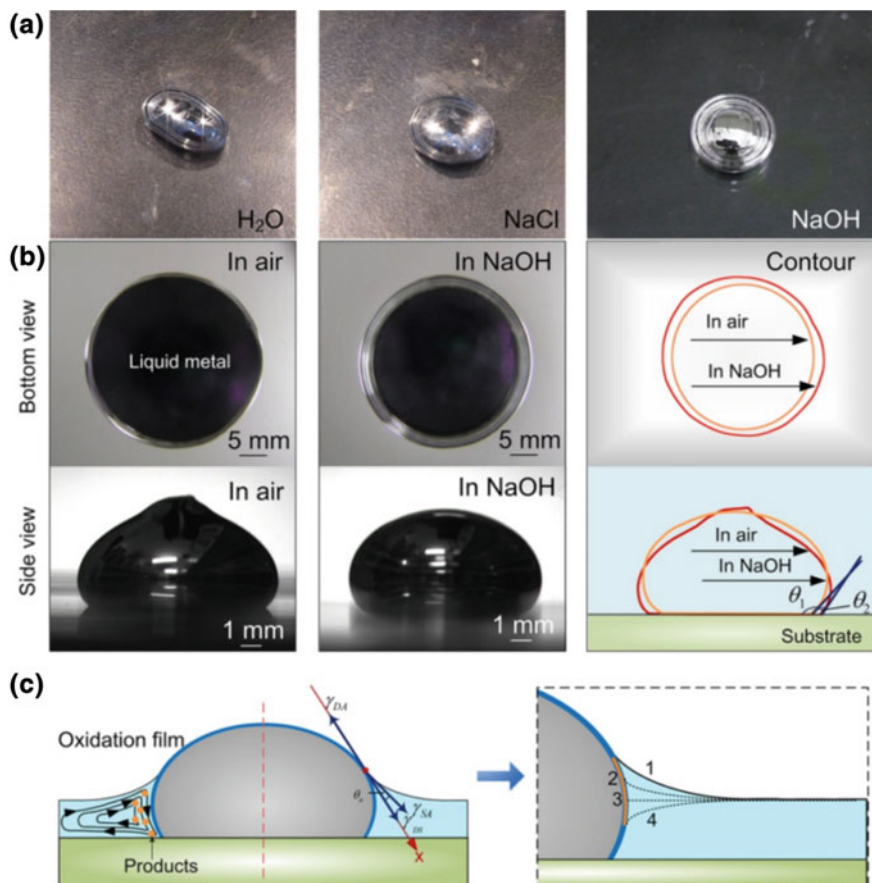


Fig. 11.3 The characteristics of interfacial interaction of air, NaOH solution, and liquid metal droplet [1]. **a** The comparison of performances among liquid metal in water, NaCl solution, and NaOH solution. **b** The bottom and side views of liquid metal droplet in air and NaOH solution, respectively. **c** Mechanical analysis of triple-line (left) and schematic illustration of the flow field around the droplet (right). All pictures are reproduced with permission

at the beginning, the liquid surface first went down until the exposed diameter of droplet reached maximum. Such maximum diameter is larger than that under the condition of stable and balanced liquid surface. It proves that the interfacial solution is subjected to the downward drag force since the very beginning.

In the fluctuation area, the lower the height of solution is, the longer the reaction time between the solution and the oxide of gallium will be [1]. Therefore, the difference in the interfacial tension of the two patches beside the boundary becomes smaller since the interface solution goes down from position 1–4 (Fig. 11.3c). Meanwhile, the value of θ_a gets larger which decreases $\cos\theta_a$ markedly. Therefore, the downward motion of the solution is decelerated due to M becoming smaller. These

statements are in accordance with the result shown in Fig. 11.1b. Once the liquid surface descends to the lowest degree, i.e., position 4, the direction of γ_{SA} will turn to the opposite position. Such sudden comprehensive alteration leads to $M < 0$, inducing the inverse motion direction of M . As long as $M < 0$, the interfacial solution goes upward along the outer face of the droplet. Moreover, the distant hydrostatic pressure tends to push the solution with lower surface adjacent to the droplet back to the horizontal. The whole procedure is similar to the vibration of a spring.

It is well known that changes in the interfacial tension under nonequilibrium conditions play an important role in directional sensing [3]. For semi-submerged droplet, a different interfacial tension is triggered between the interfaces of droplet/solution and the droplet/air, respectively. Remarkably, the metal ions localized around the droplet can result in the inhomogeneous interfacial tension [26]. Therefore, there are two sources of Marangoni gradients in this system: the diffusion of gallium oxide along the droplet interface and gradients at the solution/air interface due to the spreading of gallium hydroxide. Notably, the Marangoni flow moves toward the region with higher interfacial tension [27], and thus an asymmetric flow field is created around the droplets (Fig. 11.3c). The flow generates local vortex of surrounding solution, which is also the reason why nylon fabric in certain region can move toward the droplet.

Additionally, further repeated experiments were conducted under oxygen-free, i.e., argon gas, atmosphere [1]. The GaIn alloy before being used was adequately washed in NaOH solution to guarantee that its oxide was completely removed. It was found that the oscillation can still be observed in this situation. There were six apparent oscillation periods, lasting for 25 s. However, such oscillation time of liquid metal in oxygen-free situation is shorter compared to the one in the air environment. It can be concluded that the oxygen is beneficial to increase the difference in surface tension between two sides of the interface.

In a rather long period of time, the oscillation amplitude remained almost constant under the air condition. However, at the beginning and terminal of the oscillation, the interface experienced the inducing and adjusting period, respectively. During these stages, the interfacial solution rotated around the droplet (Fig. 11.4a–c). The rotation occurs due to the inhomogeneous oxidation of the surface on liquid metal droplet. Such inhomogeneity results in different motion amplitudes of surrounding solution at different interfacial positions [1]. The solution which goes higher toward the center of the droplet will flow to the lower nearby position. Thus, the rotation is triggered and the rotational direction is random. With the reaction proceeding, the difference in Marangoni gradients was reduced, and thus the oscillation amplitude got smaller. Additionally, the concentration of NaOH solution in microenvironment around the droplet gradually decreased due to consumption, especially that of the liquid film near the upper solution surface. It can be confirmed by the fact that if one shakes the liquid metal droplet with dish, the oscillation will restore the activity. This is attributed to the complement of fresh NaOH solution and the redistribution of oxide film on the surface of droplet. Another reason for the solution ceasing the oscillation is the accumulation of gallium hydroxide on the interfacial surface of droplet (see Fig. 11.4d). The solid gallium hydroxide produced from the reaction

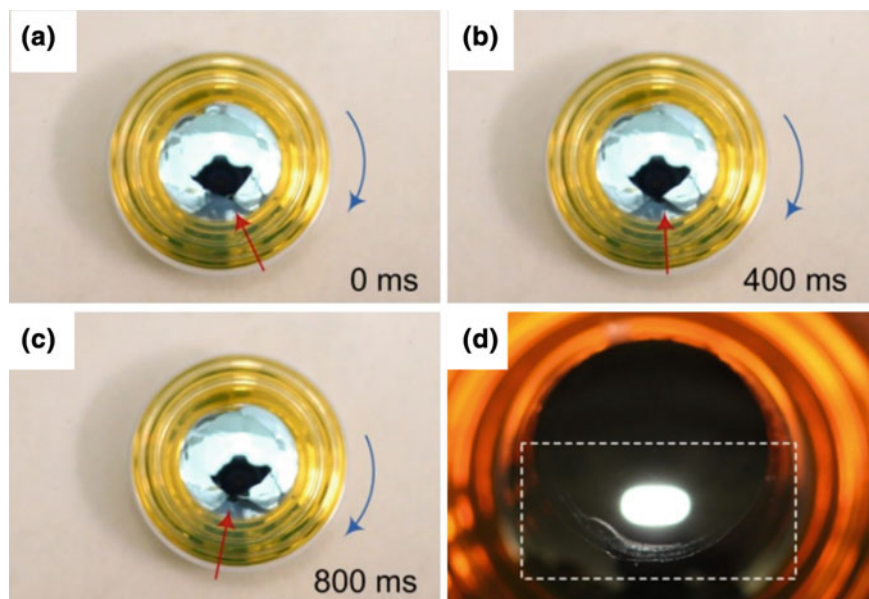


Fig. 11.4 The disturbed activities of the liquid surface around the droplet at the start and end of oscillation [1]. **a**, **b**, and **c** are the photos of liquid surface rotating in clockwise direction; **d** Local image of liquid droplet at the end of oscillation. All pictures are reproduced with permission

between gallium, and the alkali solution results in the barrier boundary restricting the motion of solution. Consequently, the balance of the system will be established.

In summary, the self-propelled liquid metal beating heart can harvest energy via breathing mechanism without external power supply [1]. Such system has unique design that the droplet is semi-submerged in NaOH solution and partially exposed to the air. The different characteristics of the liquid metal droplet performing in these two environments lead to the surface tension gradient across the interface of three phases on the droplet which induces the Marangoni flow. The studies on Marangoni effect are common, but the one applied in sphere realizing periodic oscillation is rare to see. Interestingly, such system imitates not only the motion of living creature but also the energy acquisition strategy. Without using external electricity or fuel, the ambient air provides one energy source for the spontaneous motion of liquid metal in alkaline solution, which is in close analogy to the breathing behavior of living organism in animal. Conventional beating heart is generally composed of mercury and sulphuric acid, which are harmful and dangerous. Conversely, nontoxic Ga-based liquid metals offer an alternative approach to realize beating heart behaviors. Particularly, such beating heart owns the advantages of low-cost, being easily accessible, and quick to make. This finding would shed light on a variety of future applications, such as self-propelled motor in microfluidics and biomimics system for partially duplicating the biological activity in nature.

11.6 Heat-Powered Thermo-Pneumatic Liquid Metal Machine

Except for the above breathing mechanism enabled liquid metal machine, the environmental heat can also be adopted as a power to drive the liquid metal machine. Tang et al. [28] disclosed a self-driving thermo-pneumatic liquid metal system which can be developed certain controllable power system even robot. The driving force that pushes the liquid metal against flow resistance and gravity is provided by a resistively heated volatile fluid based on thermo-pneumatic principle. The tested harvester prototype demonstrated its capability to extract thermal energy between small temperature gradient, at a scale of 10 °C. During a 5-h operation, it further demonstrated robust liquid metal recirculating performance at a time-average volume flow rate of 14 mL/min with a heat charge of 12.25 W. The prototype also managed to self-adjust to variable working conditions which indicated the reliability of the system. Advantages of this method include simple-structural design, rigid-motion free, and low-temperature actuation. These advantages make it uniquely suited for solar energy and low-grade heat harvesting, high heat flux electronics cooling as well as autonomous machines actuating.

A conceptual prototype for the thermo-pneumatic liquid metal machine system was constructed in Fig. 11.5. The harvester mainly consists of two sealed chambers with the heat sink chamber mounted above the heat source chamber and two connecting tubes between them [28]. An electrical heating module (Fig. 11.5c) is welded at the bottom of the heat source chamber as a simulative heat source. Heat transfer toward the heat source chamber is enhanced by a miniature grooved copper plate, while heat transfer toward other directions is reduced by a polytetrafluoroethylene (PTFE) base. The heat that transported to the heat sink chamber is dissipated to the ambient by a copper heat exchanger. Three temperature probes are mounted accordingly to measure the temperature of the heating module ($T_{\text{Heat module}}$), the heat source chamber ($T_{\text{Heat source chamber}}$), and the heat sink chamber ($T_{\text{Heat sink chamber}}$). For visualization purpose, transparent polymethyl methacrylate (PMMA) and PTFE are used to fabricate the chamber walls and their connecting tubes, respectively.

In order to achieve self-actuation, several principles should be considered when constructing the prototype [28]. First of all, the liquid metal injected into the heat source chamber should submerge both ports of the two connecting tubes. Isopentane is then introduced to fill the heat source chamber which will cover the liquid metal surface due to density difference. EGaIn oxides removal before liquid metal injection and air expelling after isopentane filling are required. EGaIn oxides were dissolved using alkaline solution and air was expelled by heating in this study. Once the EGaIn is covered with inert isopentane atmosphere, further oxidation could be prevented. It is also important to set up an asymmetric design of the two connecting tubes so that liquid metal can rise through one of them and return from the other. Accordingly, the inner diameters of the rising tube and the returning tube are designed differently and both ports of the returning tube are placed lower than that of the rising tube with one port just below the heat sink chamber.

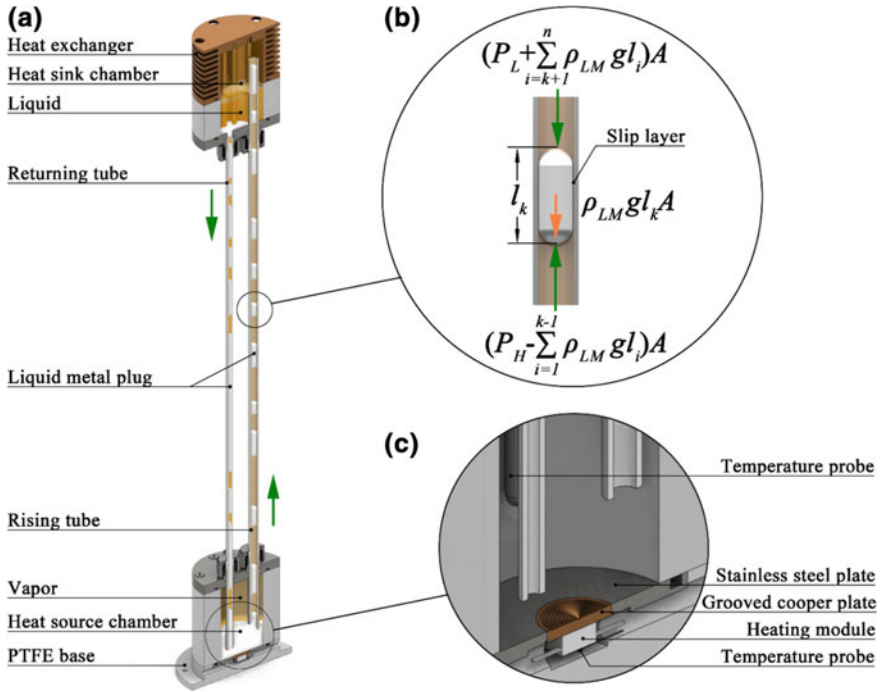


Fig. 11.5 Heat-driven thermo-pneumatic liquid metal machine or energy harvester [28]. **a** Schematic of the prototype showing system parts. The inner diameter of the heat source chamber and the heat sink chamber are both 28 mm and height of the two chambers are 40 and 45 mm, respectively. The copper heat exchanger has fins on both sides to enhance heat transfer. Inner diameter of the rising tube d_{Ri} and the returning tube d_{Re} are 4 and 2 mm, respectively. Tube length between the two chambers is 240 mm. **b** Force analysis of an arbitrary liquid metal plug. P_H and P_L refer to the vapor pressure of the heat source chamber and the heat sink chamber, respectively; ρ_{LM} the density of liquid metal; g the gravitational acceleration; l the length of the liquid metal plug; A the effective thrust face of the liquid metal plug which equals to the cross-sectional area of each tube; Subscripts are used to indicate individual liquid metal plug. The two terms $\sum_{i=1}^{k-1} \rho_{LM} g l_i$ and $\sum_{i=k+1}^n \rho_{LM} g l_i$ represent the pressure gradient caused by the liquid metal plugs below and above the target plug, respectively. **c** Detailed view inside the heat source chamber. The grooved copper plate is 1.4 mm thick and 11.28 mm in diameter and it is welded at the center of a stainless steel plate. The heating module has a cross section of $0.60 \times 0.64 \text{ cm}^2$ and a thickness of 0.20 cm. All pictures are reproduced with permission

When heat was charged, vaporization of isopentane inside the heat source chamber was first observed during experimental investigation [28]. The harvester demonstrated two different operating phases during observation. When both ports of the two connecting tubes were immersed in liquid metal, the induced vapor could not pass through the rising tube and was held up inside the heat source chamber. The pressurized then vapor pushed the liquid metal below toward the low-pressure heat sink chamber against gravitational force and viscous drag. During this phase, which was referred to as the hold-up phase, up-rising liquid metal columns were observed

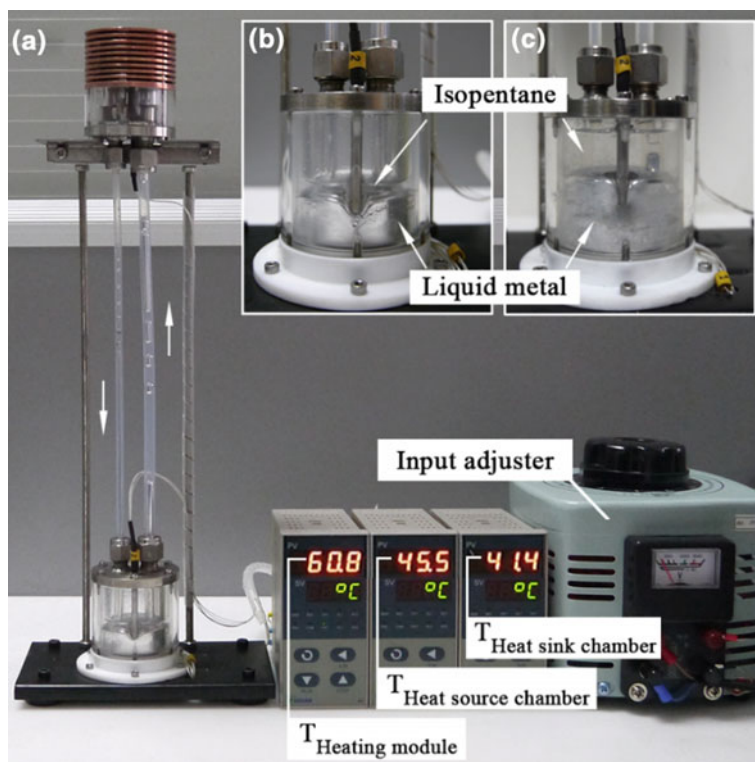


Fig. 11.6 **a** Experimental setups of the tested prototype to show its working process. **b** Liquid metal and isopentane distribution in the heat source chamber during operation. **c** Liquid metal and isopentane stored in the heat source chamber one hour after heat charge terminated [28]. All pictures are reproduced with permission

in both connecting tubes. Once the vapor reached the entry port of the rising tube, it squeezed in the tube, torn up the liquid metal columns, and then pushed the liquid metal upward plug by plug to the heat sink chamber. Heat carried by the working fluids was dissipated at the heat sink chamber, and isopentane vapor is condensed to its liquid state. In the returning tube, contrary to the flow direction of the rising tube, a downward liquid metal flow accompanied with condensed isopentane would be induced because of the asymmetric design. In this recirculating phase, liquid metal recirculating was realized. These two phases repeated successively during long-term operation. This cyclical operating process of the prototype is shown in Fig. 11.6a. A detailed view of working fluids distribution inside the heat source chamber during operation can be found in Fig. 11.6b.

Force analysis of liquid metal plugs in different connecting tubes can be used to demonstrate the self-recirculating mechanism [28]. Assumption can be made that effects of the viscous drag are negligible given the fact that radial contact force between the liquid metal plugs and the tube wall is weak and an isopentane slip

layer will form between their surface which significantly reduces the viscous drag. The contribution of isopentane mass to the gravitational force can be also eliminated because its density (612 kg/m^3 for liquid and 3 kg/m^3 for vapor at 300 K , 10^5 Pa) is frictional to that of the liquid metal (6280 kg/m^3). In this sense, as shown in Fig. 11.5b, the motion of liquid metal is only controlled by predominate pressure gradient and gravity. Here, one can introduce the liquid metal filling ratio $\alpha = \sum_{i=1}^n h_i/L$ and the diameter ratio $\gamma = d_{\text{Ri}}/d_{\text{Re}}$, where L indicates the length of the connecting tube. Then, $\alpha_{\text{Re}}L_{\text{Re}} = \gamma^2\alpha_{\text{Ri}}L_{\text{Ri}}$ according to mass conservation. The resultant force F can be obtained by fore summation: $F = (P_H - P_L - \rho_{\text{LM}}g\alpha L)A$. Liquid metal plugs in the rising tube and the returning tube should satisfy $F_{\text{Ri}} > 0$ and $F_{\text{Re}} < 0$, respectively, to achieve a recirculating. Thus, we get $1 < (P_H - P_L)/\rho_{\text{LM}}g\alpha_{\text{Ri}}L_{\text{Ri}} < \gamma^2$. When further consider the pressure gradient between the two chambers $P_H - P_L$ as a function of temperature gradient ΔT . So the thermal-pneumatic self-recirculating mechanism can be interpreted as $1 < f(\Delta T)/\rho_{\text{LM}}g\alpha_{\text{Ri}}L_{\text{Ri}} < \gamma^2$. This inequality governs the temperature gradient needed to actuate a specified system based on the properties of the working pair and the design parameters. And for energy harvesting of different energy sources where available temperature gradient is set, it further provides a quantitative basis for the system design.

11.7 Working Performance of the Heat-Powered Liquid Metal Machine

Figure 11.7a presents the temperature variations of different system parts when constant heat (12.25 W) is charged and then terminated [28]. Temperature gradients among the heating module, the heat source chamber, the heat sink chamber, and the environment establish gradually which indicates the thermal-pneumatic actuation nature of the system. When heating power is terminated, the temperature gradients fade away and the vapor pressure between the two chambers become the same. Then, the gravitational force drives the liquid metal and the condensed isopentane back to the heat source chamber so that the system returns to its initial state, as shown in Fig. 11.6c. The cyclical operation process of the prototype is demonstrated in Fig. 11.7b, c. The intermittent liquid metal flow will lead to a fluctuation in heat dissipating from the high power density heating module. So the temperature variation at the heating module is more significant than the other two locations. The cycle length of the system appears to be different at different operating time when comparing Fig. 11.7b, c. This may be attributed to the fact that the system is a dynamic one that works on self-balance of its internal forces. So any factor that influences the acting forces would cause a disturbance and lead to a new balance. This self-adjusting capability of the thermo-pneumatic liquid metal machine system makes it flexible to a different heat charge which is favorable to adopting the system to variable working conditions. The prototype has demonstrated robust performance of 5-hour non-stop working which indicates the reliability of the self-driving thermal-pneumatic method.

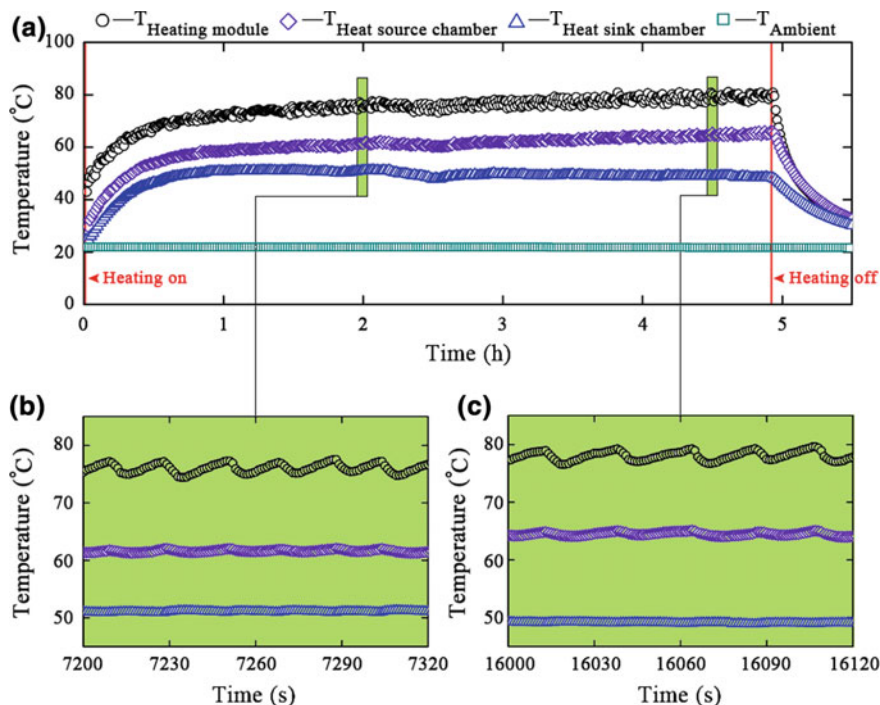


Fig. 11.7 a Temperature variations at different system parts as a function of time with a constant 12.25 W heating power. b, c Zoom-in view at different time points to show the periodical working feature of the prototype [28]. All pictures are reproduced with permission

In order to give a comprehensive evaluation of the harvester prototype, more performance parameters are presented in Fig. 11.8. Comparisons are made by charging different heating loads to the heating module [28]. The prototype starts periodic pumping at 1 W heating load with the heat chamber temperature just 8 °C higher than the ambient temperature. A system can work at such a temperature range is particularly suited for harvesting solar energy and low-grade heat. As the heating power increases, the liquid metal recirculating speed becomes faster which manifests as a decline in cycle length and an increase in volume flow rate. When the heating load increases to 25.2 W, the temperature of the heating module and the heat source chamber reach 122.6 and 94.3 °C, respectively. The harvester produces a liquid metal volume flow rate of 25.57 mL/min with a 6 s time cycle. Further power increase was not conducted in this study considering the PMMA constructing material might loss thermal stability working at higher temperature. Though, the system is expected to function in higher temperature range judging from its working mechanism and working fluids property. The system can be also treated as a cooling loop for high heat flux devices. In this sense, the heating module is regarded as a simulated electronic component and its temperature and surface heat flux become the variables of interest.

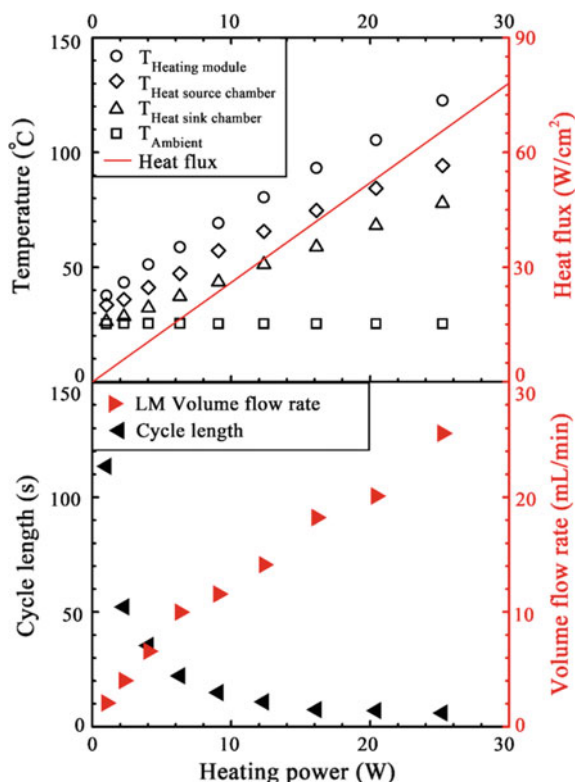


Fig. 11.8 Performance of the thermo-pneumatic liquid metal machine prototype under different heating powers [28]. Temperatures were recorded when the prototype established its quasi-equilibrium state under each working condition. Heat flux was obtained by dividing the heating power by the contacting surface of the heating module (0.384 cm^2). The cycle length of the liquid metal flow was assumed the same as the temperature cycle length. 10 quasi-equilibrium cycles were recorded using high-speed camera to investigate the cyclical operation process of the prototype. The pictures were replayed frame by frame to accumulate the liquid metal plug length l when it passed through the rising tube within the 10 cycles. Based on the total time, the accumulation of the liquid metal plug length and the known tube diameter (4 mm), the time-average liquid metal volume flow rate were calculated. All pictures are reproduced with permission

The current prototype may fail to meet the requirement for extreme conditions. But it should be pointed out that the temperature gradient within the system (temperature gradient between the heat source chamber and the heat sink chamber) is small and the main temperature gradient exists between the system and the heat source (heating module) and the heat sink (ambient air). The small heat resistance within the system contributes to its low flow resistance and the high thermal conductivity of the liquid metal. More efficient heat dissipation can be achieved by enhancing heat transfer at both the heat source end and the heat sink end.

The use of a volatile–conductive working pair may have alternatives for operations under different temperature ranges. The compatibility of the volatile fluid and the liquid metal, compatibility of the liquid metal, and constructing material should also be considered [28]. Low melting point, nontoxic gallium-based liquid metal alloys could be a desirable conductive fluid candidate from room temperature to 2000 °C temperature range when non-oxidizing atmosphere can be created. In general, volatile fluid selection should be based on the temperature–pressure saturation relationship of the fluid as well as its environmental effects. Water-based nanofluids [29] have enhanced electrical and thermal conductivities while still maintain the volatile nature of water. Water-based nanofluid energy harvesting system brings no environmental hazard which makes it an appealing plan for further study.

Overall, the thermo-pneumatic liquid metal machine is rather reliable in realizing self-actuation, self-adjusting, and low-temperature operation. All these features make it a promising strategy to develop various heat-driven liquid metal machines even robot systems which can fully utilize environmental thermal energy. Further, theoretical and practical study can be continued along this direction.

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Chapter 12

Nanoparticles Enabled Liquid Metal Motions



Abstract Jumping is a special, however, hard to achieve capability by a liquid metal machine. But under certain assistance, such behavior can also be partially realized. In a recently found electron discharge effect due to point contact between liquid metal and solid metal particles in electrolyte (Tang et al in Appl Phys Lett 108: 223901–223905, 2016 [1]), it was disclosed that adding nickel particles induces drastic hydrogen generation and intermittent jumping of sub-millimeter EGaIn droplet in NaOH solution. Observations from different orientations indicated that such jumping is triggered by pressurized bubble under assistance of interfacial interactions. Hydrogen evolution around particle provides clear evidence that such electric instability is originated from the varied electric potential and morphology between the two metallic materials. The point-contact-induced charge significantly enhances the near-surface electric field intensity at the particle tips and thus causes electric breakdown of the electrolyte. Further, with a particle raft, electrohydrodynamic liquid metal surface convection can even be triggered. Such phenomenon would be very useful to trace the flow of the liquid metal which is hard to do otherwise. This chapter is dedicated to present a basic understanding on the fundamental route to realize particles stimulated liquid metal motions which can help develop potential machine thus involved.

Keywords Nanoparticle effect · Interfacial interaction
Jumping liquid metal droplet · Particles triggered motion · Flow tracing
Particle raft image contrast

12.1 Interfacial Interactions on Liquid Metal Droplets

It has long been realized that the transition from the rigid crystal lattice of a solid metal to its movable liquid state leads to fundamental differences between the bulk properties of the two [2]. Attempts to reveal these differences have renovated our knowledge of metallic materials. Distinct surface morphology between the two metallic phases belongs to this category. Solid metal surface has complex small-scale structure that

deviates its true surface area from geometric value [3]. On the contrary, the surface of a liquid metal is highly ordered. X-ray reflectivity measurements provide direct evidences of atomic surface layering at liquid metal surfaces in both vacuum [4, 5] and electrolyte [6]. Interfacial interactions will take place as the metal responses to excitations of the electrolyte [7, 8]. Interfacial interactions are essentially affected by distribution, adsorption, and transportation of charge species at atomic level [9]. And these processes are responsible for capillary and electrostatic interactions at surfaces, films, and bio-membranes [10, 11]. Understanding the underlying mechanisms is of fundamental importance and it is also desirable to manipulate these subtle processes for actuation [12, 13], passivation [14], and catalysis [15] purposes.

Tang et al. experimental findings and theoretical interpretations [1] disclosed the electron discharge effect and its related mechanical and interfacial behaviors induced by the contact of liquid metal droplet (LMD) and solid metal particles (SMPs) in electrolyte environment. The liquid metal, solid metal particle, and electrolyte that used are EGaIn (Eutectic Gallium and Indium, 75.5% gallium, and 24.5% indium by weight percent), nickel particle, and aqueous NaOH (1M), respectively. In the experiment, liquid metal is first injected into a Petri dish which has been pre-filled with deionized water to produce sub-millimeter LMDs [16]. A pipette is then used to transfer one single LMD to an electrolyte-filled sample container. SMPs, mixed in water previously, are instilled into the sample container thereafter. Optical microscope is mounted at different orientations for in situ recording of experimental phenomena.

12.2 Jumping Liquid Metal Droplet in Electrolyte

The point-contact-induced jumping behavior of a sub-millimeter LMD in 1M NaOH solution is illustrated in Fig. 12.1a–c. Initially, the spherical LMD remains stable in the electrolyte. Soon after SMPs are introduced, the LMD becomes activated. Accompanied with drastic bubble generation, it jumps intermittently on the substrate which is spread with microparticles. It is intriguing to find that when the LMD jumps from one location to another, a “footprint” is left behind [1]. Side view observations reveal that when some bubbles detach from the LMD surface and rise upward, the remainder will accumulate at the bottom region (Fig. 12.1f). With fast and consistent bubble generation, small bubbles coalesce into much larger bubble base (Fig. 12.1g). Eventually, acting as a pressurized gas spring, the inflated bubble base ejects the LMD away while the bubble base itself is left behind so as to pave a path of “footprints” (Fig. 12.1h). A more quantified process can refer to Fig. 12.2 while a transition detail for the jumping liquid metal droplet can be found in Fig. 12.3.

Based on side view observation [1], the force analysis of the LMD is presented in the inset of Fig. 12.4 in which f_1 and f_2 indicate the forces provided by individual bubbles (only two bubbles are shown) and F represents their resultant force (the contribution of the rising bubbles is neglected), m and a are the mass and acceleration of the LMD, respectively, and G_{LMD} is the resultant force of gravity and buoyancy. It is also indicated that the nature of the substrate will influence the jumping behavior

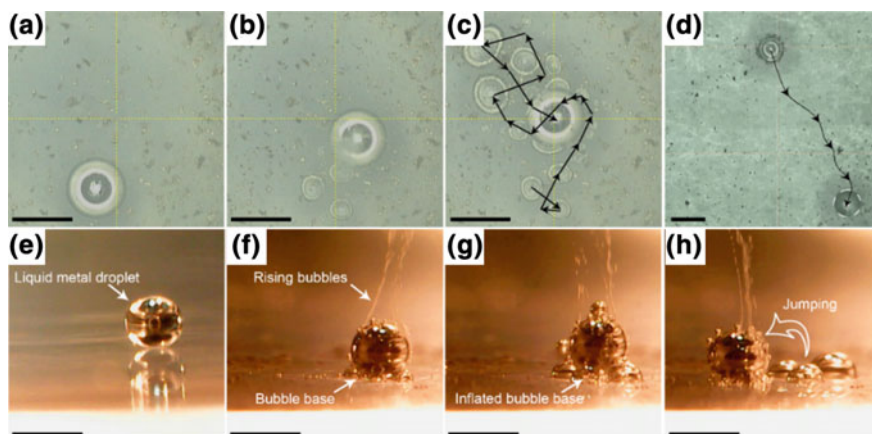


Fig. 12.1 **a–c** (top view): Time-lapse images of intermittent jumping behavior of an LMD on hydrophobic polypropylene substrate with the jumping path indicated with arrows. **d** (top view): Rolling LMD on hydrophilic quartz substrate. **e–h** (side view): Time-lapse images of one jumping process and the related interfacial phenomena (Scale bar: 500 μm) [1]. All pictures are reproduced with permission

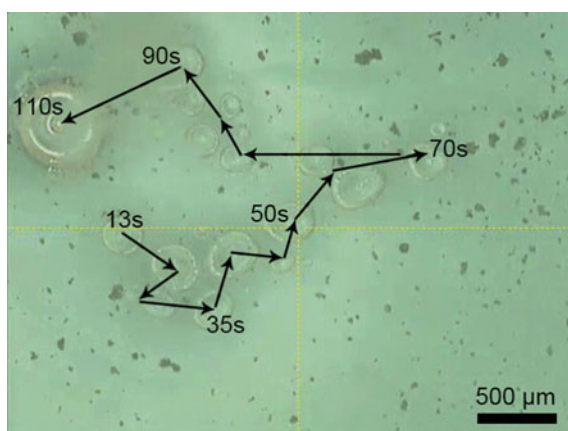


Fig. 12.2 Tests on the combination of EGaIn–Fe–NaOH (group 1) (Top view) [1]. This combination shares very similar results with the combination of EGaIn–Ni–NaOH which is described in the main text. The jumping path and locations of the LMD at different time points are indicated. Picture is reproduced with permission

by affecting the contact angle [17] θ_1 and θ_2 . In general, bubbles tend to adhere to hydrophobic surfaces ($\theta > 90^\circ$) and escape from hydrophilic ones ($\theta < 90^\circ$). So a hydrophobic substrate is favorable for bubble base adhesion while a hydrophilic LMD surface is favorable for LMD to detach from the bubble base. When changing the hydrophobic polypropylene sample container to a hydrophilic quartz container,

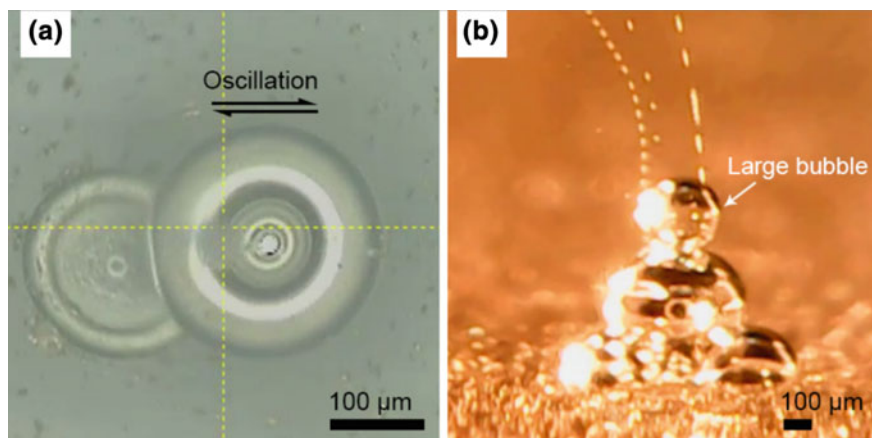


Fig. 12.3 **a** Oscillation of the LMD of the combination of EGaIn + Ni + HCl (Top view); **b** A large bubble stays on the top of an LMD (Side view). These results indicate an enhancement of the adhesion force between the bubble and the LMD surface [1]. All pictures are reproduced with permission

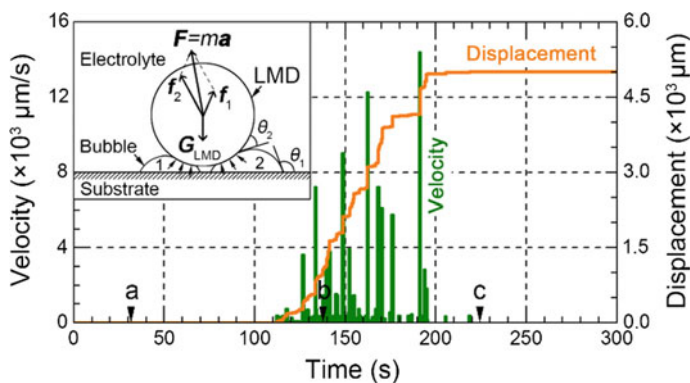


Fig. 12.4 Jumping velocity and displacement characterization [1]. Inset: Force analysis of the LMD. Picture is reproduced with permission

bubble adhesion is not observed (no “footprint”) and the LMD moves by rolling instead of jumping (Fig. 12.1d). So the type of substrate is crucial for the jumping behavior.

The velocities plotted in Fig. 12.4 are average values that are calculated with a time interval of 1/30 s, and the evaluation of each displacement is within an error of $\pm 10 \mu\text{m}$. The letters *a*, *b*, and *c* indicate the time points at which Fig. 12.1a–c are photographed, respectively [1]. The whole process can be divided into three stages. After SMPs are introduced (time point *a*), the LMD shows no instant activation evidence. Instead, it goes through an initializing period. This is attributed to the existence of an adhesion barrier [18] for the SMPs to build effective contact with the

LMD. The initializing process can be accelerated by making a perturbation (either slightly shaking the sample container or dropping an electrolyte drop). When the droplet is activated, it jumps intermittently on the substrate. Its velocity can reach as high as 14,400 $\mu\text{m/s}$, corresponding to a relative velocity of nearly 30 body length per second. The magnitude of its displacement adds up to about 10 body length in about 100 s ($R_{\text{LMD}} = 240 \pm 1 \mu\text{m}$ measured by a measuring microscope). During the intervals of fast jumping, there are also more moderate wagging behaviors (velocities well below 1000 $\mu\text{m/s}$). After the active stage, the droplet becomes motionless as the bubble-generating speed becomes too slow to assemble a bubble base with sufficient thrust.

12.3 Conspicuous Mechanics of Jumping Liquid Metal Droplet in Electrolyte

The jumping behavior has conspicuous mechanics [1]. However, the underlying mechanisms of the point-contact-induced bubble generation and the site-specific bubble accumulation still remain ambiguous. Gas chromatography analysis shows that the bubbles contain hydrogen only. And it is confirmed that either the LMD or the nickel particles alone is stable in the electrolyte. Clearly, the observed hydrogen evolution implies that the local electric field intensity should be strongly enhanced so as to cause an electric breakdown (electrolysis) of the electrolyte [19, 20]. According to the Jellium model [21, 22] and the Gouy–Chapman theory [23], the Coulombic attractions between the screening electrons of the metal and the countercharges of the electrolyte (such as H^+O [24] and Na^+ in present situation) lead to the establishment of an electric double layer (EDL). And the metal–nonmetal transition from metal ions to gallate species [25] results in the formation of a protective passivation film (PF) (Fig. 12.5a). Here, the PF was treated as a dielectric layer set between the EDL (Fig. 12.5b). Equivalently, part of the original charge density σ_0 is neutralized by a polarization charge density of σ_p . As a result, the dielectric layer reduces the electric field intensity from its original value $E_0 = \sigma_0 / \epsilon_E$ to an equilibrium value $E_{\text{eq}} = \sigma_0 / (\epsilon_E + \chi_e)$, where ϵ is the permittivity, χ_e is the electric susceptibility of the PF, and $\sigma_p = \chi_e E_{\text{eq}}$. The mathematical physics that describes the electric field that surrounds a conductor is the solution of the Laplace equation subjected to specific boundary conditions. Though the exact solution to an arbitrary surface is inaccessible, the near-surface electric field structure can be described as [26–28]

$$E = f(\Delta\Phi)f(\kappa_M) = \Delta\Phi \frac{2\kappa_M}{\exp(-2\kappa_M \Delta n) - 1} \Big|_{\Delta n \rightarrow 0} \quad (12.1)$$

where $\Delta\Phi$ is the potential gradient across a small distance Δn , κ_M the mean curvature, the terms $f(\Delta\Phi)$ and $f(\kappa_M)$ denote the contributions of electric potential and surface curvature, respectively.

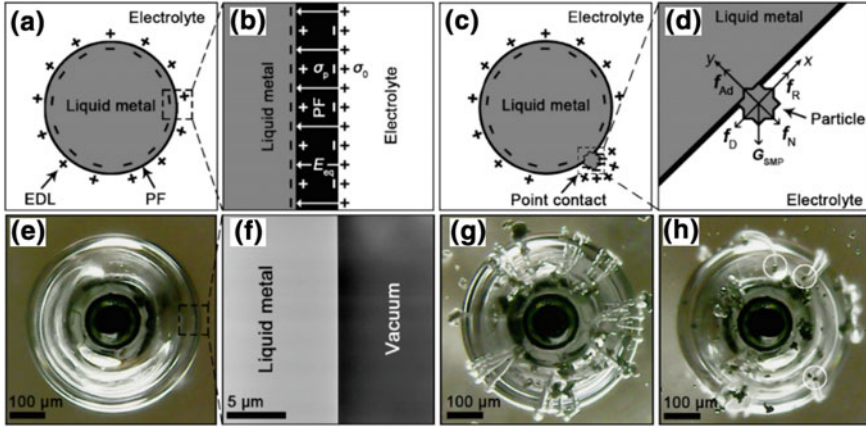


Fig. 12.5 Schematics of **a** the interfacial EDL and PF structures; **b** The dielectric PF model; **c** Point-contact-induced surface charge accumulation; **d** Force analysis of SMP adhesion. **e** (Top view): Optical microscopic image of an LMD immersed in NaOH solution. **f** SEM image of the liquid metal/vacuum interface. **g** (Bottom view): SMP accumulation and bubble generation. **h** (Bottom view) SMPs (inside the circles) surfing on the LMD surface. Note that a hydrophilic concave quartz sample container is used during bottom view recording [1]. All pictures are reproduced with permission

According to Eq. (12.1), the electric instability stems from two intrinsic differences between the two metallic phases [1]. One is the electric potential difference (galvanic effect), and the other is the inherent morphology. When isolated, there exists an arbitrary surface potential gradient across each metal/electrolyte interface, $\Delta\Phi_0$, SMP-E and $\Delta\Phi_0$, LMD-E , respectively. When the two are brought into contact, the two metals become equipotential and the potential of the particle/electrolyte interface will shift to a more negative value ($\Delta\Phi_0$, LMD-E , potential gradient of the metallic contact is neglected). Since $\Delta\Phi_0$ cannot be directly measured, electrode potential (Zeta potential) ζ is generally used as a reference [29, 30]. By introducing Nernst equation, the contribution of the potential shift at the SMP site can be derived $f(\Delta\Phi)_2/f(\Delta\Phi)_1 = \zeta_{\text{Ga-E}}/\zeta_{\text{Ni-E}} = 1.83$, where the subscripts 1 and 2 indicate the circumstances before and after contacting, respectively, $\zeta_{\text{Ga-E}} = -1.32 \text{ V}$ [31] and $\zeta_{\text{Ni-E}} = -0.72 \text{ V}$ [32] are the calculated electrode potentials of gallium (the primary element of EGaln [33]) and nickel in 1M NaOH solution, respectively.

The Bond number of a sub-millimeter EGaln droplet in 1M NaOH solution is $\text{Bo} = 4(\rho_{\text{LMD}} - \rho_{\text{E}})gR_{\text{LMD}}^2/\gamma = 0.018$, where ρ_{LMD} and ρ_{E} are the densities of the liquid metal and electrolyte, respectively, g is the gravitational acceleration, and $\gamma(0.62 \text{ Nm}^{-1})$ [34] is the surface tension of the liquid metal. The domination of surface tension ($\text{Bo} \ll 1$) implies that the LMD is highly spherical (Fig. 12.3e). The liquid metal surface is also featureless, and the liquid metal/vacuum interface has a sharp boundary (Fig. 12.3f). In fact, measurements have unambiguously demonstrated that the liquid metal surface has no measurable roughness [4, 5]. So a uniform

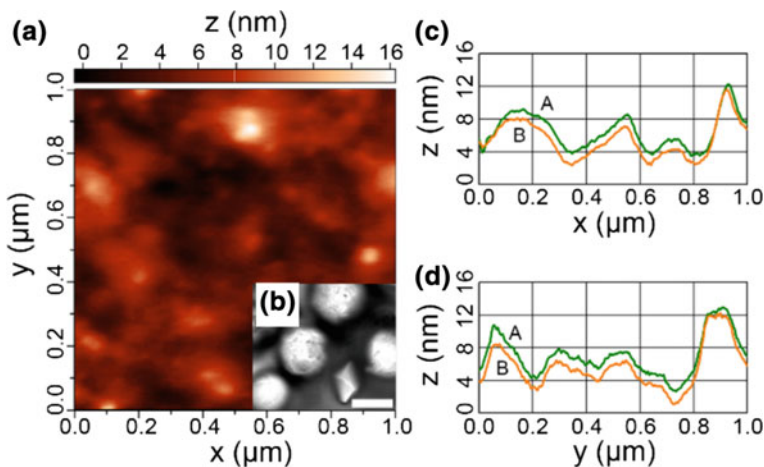


Fig. 12.6 **a** AFM image shows the morphology of an $1\ \mu\text{m} \times 1\ \mu\text{m}$ area on an SMP. **b** SEM image shows the size and shape of the SMPs (scale bar: $5\ \mu\text{m}$). **c**, **d** Sectional surface profile along x direction ($y = 0.5\ \mu\text{m}$) and y direction ($x = 0.5\ \mu\text{m}$), respectively. The curves A and B represent the profiles measured during forward and backward scanning, respectively, and their consistent profile indicates the reliability of the measurement [1]. All pictures are reproduced with permission

charge distribution on the LMD surface can be expected. But the surface of an SMP is thought to have complex morphology. Atomic force microscopy (AMF) has been used to characterize the minuscule area on a single SMP. As shown in Fig. 12.6, it is safe to take the radii of the principle curvatures at the SMP tips to be $r_1 = r_2 = 1\ \text{nm}$ which corresponds to a mean curvature of $\kappa_{M, \text{SMP}} = 10^9\ \text{m}^{-1}$. As a comparison, that of the LMD is $\kappa_{M, \text{LMD}} = 4.2 \times 10^3\ \text{m}^{-1}$. Since interfacial processes mostly take place at the EDL region, we take $\Delta n = \lambda_D = (\varepsilon_0 \varepsilon_r N_A k_B T / 2F^2 I)^{1/2} \sim 0.26\ \text{nm}$ in $f(\kappa_M)$ calculation, where λ_D is the Debye length (characteristic length of the EDL), ε_0 is the permittivity of free space, $\varepsilon_r = 58$ [35] is the dielectric constant of 1M NaOH, N_A is the Avogadro constant, k_B is the Boltzmann constant, T is the temperature, F is the Faraday constant, and I is the ionic strength of the electrolyte. Then, the contribution of curvature-induced charge concentration at the particle tips can be determined: $f(\kappa_M)_2 / f(\kappa_M)_1 = 1.28$. Though the accuracy of $f(\kappa_M)$ closely depends on which value Δn is assigned and the estimation of λ_D exist inevitable derivation, the result shows that when the surface curvature is comparable to the inverse Debye length λ_D^{-1} , the electric field intensity at the EDL region can be considerably enhanced. This can be compared to the so-called “tip effect” which in the present case is of nanoscale and occurs when the high-curvature SMP surface contacts with the uniformly charged LMD surface.

When both the galvanic effect and the tip effect are considered, the electric field enhancement factor becomes $E_{\text{SMP},2} / E_{\text{SMP},1} = f(\Delta\Phi)_2 f(\kappa_M)_2 / f(\Delta\Phi)_1 f(\kappa_M)_1 = 2.34$. Apparently, the polarized particle tips deviate from the local electric field intensity largely from its equilibrium value

[1]. Discharging from the SMP surface, electrons bond with hydrated protons attracted at the EDL to generate hydrogen molecules. Meanwhile, metal ions are neutralized by hydroxyls oriented at the liquid metal surface so that a unidirectional current can be formed. Since the transfer of two electrons forms one hydrogen molecule, the electrical process and the mechanical motion can be bridged by employing the ideal gas law [36].

$$\frac{d\mathbf{F}}{dt} = m \frac{d\mathbf{a}}{dt} \propto \frac{(1-c)ART}{2FV} i \quad (12.2)$$

where c is the ratio of hydrogen which rises away directly, A is the contact area between the LMD and the bubble base, V is the total volume of the bubble base, R is the gas constant, and i is the electron discharge intensity. A and V can be treated as constants upon jumping. According to Ref. 0, the current density on the particle size is about 1 A cm^{-2} with respect to its geometric area and a polarized potential of $\zeta_{\text{Ni-E},2} = -1.68 \text{ V}$. A rough estimation [37] gives $d\mathbf{F}/dt \sim 3.2 \times 10^{-5} \text{ N s}^{-1}$. The value of the gravitational force and buoyancy are $3.6 \times 10^{-6} \text{ N}$ and $8.4 \times 10^{-7} \text{ N}$, respectively. Upon jumping, the vertical component of $\mathbf{F}$ should be equal to the resultant force of gravity and buoyancy ($2.8 \times 10^{-6} \text{ N}$). By comparing different kinds of forces, one can conclude that the current intensity is strong enough to induce an abrupt acceleration (jumping) of the LMD.

The answer to the final question regarding bubble accumulation at the LMD bottom is the dominating of gravitational force of the SMPs [1]. Apparently, as it may be, it provides crucial implications for interfacial interactions. As shown in Fig. 12.5g and h, the fact that micro-sized particles slip easily along the spherical surface to the bottom is another proof of high smoothness of the LMD surface. It also indicates that appropriate particle size is critical for the jumping behavior. Since the gravitational force of nanoparticles will be overwhelmed by the thermal motions of the electrolyte molecules, a homogeneous nanoliquid will lead to homogeneous particle coating [38] rather than site-specific accumulating. Larger SMPs are also not favorable because they may fail to wedge into the droplet–substrate slit to embed a bubble nuclei. In our experiment, SMPs of several to tens of microns are effective to trigger LMD jumping. Force analysis of the surfing SMPs on the LMD surface (Fig. 12.5h) is shown in Fig. 12.5d, where f_{Ad} and f_{N} are the radial adhesion force and contact force, respectively, f_{R} is the tangential rising force provided by the rising bubbles, f_{D} is the viscous drag, and G_{SMP} is the resultant force of gravity and buoyancy. The adhesion force has the form of $f_{\text{Ad}} = f_{\text{NE}} + \eta q^2 / 16\pi \epsilon_0 R_{\text{SMP}}^2$, where f_{NE} is the nonelectrostatic forces (Van der Waals force and capillary force), η is a constant, q is the particle charge, and R_{SMP} is the equivalent SMP radius. The second term on the right side of equation refers to the contribution of the electrostatic force. Since q is proportional to both the surface area and the charge density of the SMP, charge concentration will increase the electrostatic force which is also an important contribution to SMP adhesion and LMD jumping.

12.4 Further Mechanism Discussion

In order to generalize the above findings, Tang et al. [1] further validated the results using different combinations, i.e., replacing EGaIn with gallium, or the particle material with iron (Fe), as well as the electrolyte with aqueous HCl (1M). Bubble generation which indicates the electron discharge effect is observed in every tested combination. Since the interfacial electric field intensity, the wettability of electrolyte on substrate, and LMD surface are material-dependent, in our further experiments on different combinations, the observed hydrogen evolution speed as well as the motions of the LMD, SMPs, and bubbles reveals different features.

Overall, the jumping behavior is a mechanical motion assisted by interfacial interactions which include electron discharge, hydrogen evolution, bubble accumulation as well as particle adhesion. The theoretical model suggests that both the galvanic effect and nanoscale tip effect are the underlying mechanisms. For the EGaIn–nickel particle NaOH combination, the galvanic effect has a greater contribution. The results show that the liquid metal surface exhibits different natures in comparison with solid surfaces and it can be manipulated for actuation purpose. The phenomena also provide a glimpse on interfacial charge distribution and transportation problems.

12.5 Particles Triggered Liquid Metal Surface Convection

To those who have been trying to understand the origin of geodynamo or to create a prototype at laboratory scale, and also to those who want to advance metallurgical processing, the regimes of complex liquid metal (LM) flow are of particular interest. Besides such geophysical and industrial implications, self-sustained motion of LMs also holds a promising future in smart fluid systems. Clearly, understanding the flow behaviors of LMs would bring straightforward benefit to liquid metal-based science and technologies. So far, direct measurement or visualization of the flow field of LMs remains challenging due to their nontransparent yet highly reflective metallic nature. Tang et al. [39] demonstrate that tiny metal particles can serve as both driving sources and flow tracers to actuate and at the same time, to quantify large-scale surface convection of gallium-based LMs. Details regarding the flow regimes as well as the quantitative information of the surface-tension-driven flow are accessed via particle image velocimetry (PIV) flow visualization. Moreover, the questions regarding how the tiny particles drive the flow and why the flow can be self-sustained are also interpreted.

A binary immiscible fluid pair, GaIn alloy (75.5 wt% Gallium, and 24.5 wt% Indium), and sodium hydroxide solution (NaOH, 0.5 mol L⁻¹), is adopted for conceptual demonstrations [39]. The volume of the LM and the solution is controlled so that the LM, which owns superior surface tension, can be partially immersed in the solution. In the present study, ~12 mL LM and the same amount of solution are used for a circular glass Petri dish (94 mm in diameter). Cu particles (particle size:

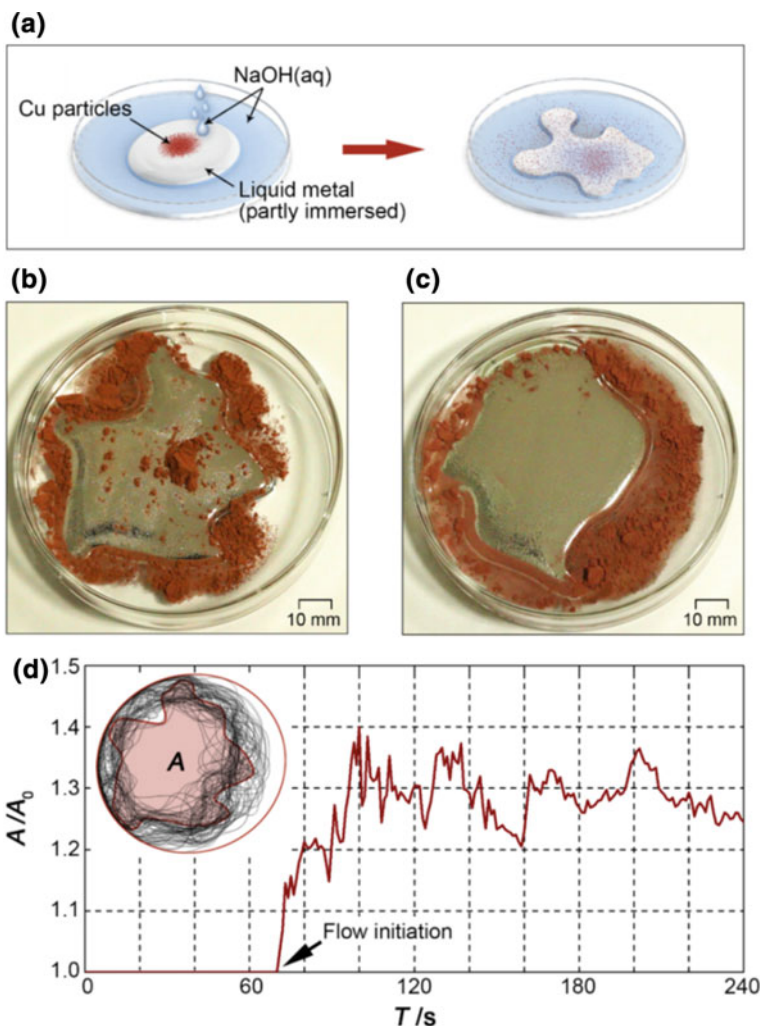


Fig. 12.7 **a** Schematic illustration of the experiment. **b, c** Images of the rolling LM puddle during random convection **b** and steady convection **c**, respectively. **d** Variations of the upper surface area A of the LM puddle in the first 240 s. The inset figure overlaps the outlines of the LM puddle in every 4 s. The value of A presents the filled area of the outlines and A_0 indicates the surface area before flow initiation [39]. All pictures are reproduced with permission

$\sim 50 \mu\text{m}$) are gently placed on the upper surface of the LM puddle. Till then, the system is able to maintain a stable state (Fig. 12.7a). However, a strong hydrodynamic instability, which is sufficient to induce continuous surface convection and large-scale shape transformation of the LM puddle, is observed right after wetting the Cu particles with a few solution drops.

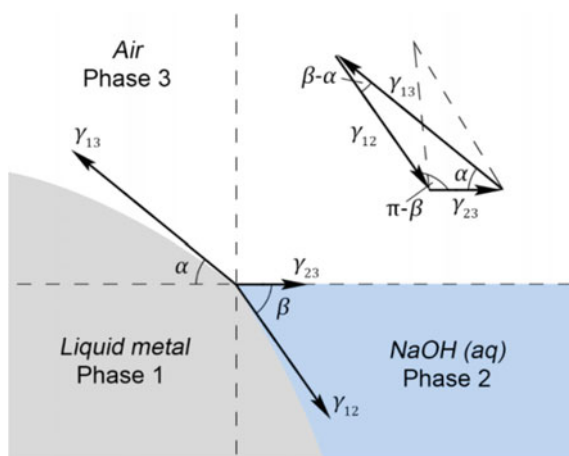
Rolling with the particles in the shallow solution, the LM puddle transforms into various shapes with tortuous outlines and its flow behavior can be mainly divided into two stages [39]. At the early stage, when Cu particles pile up on the LM surface, the LM puddle rolls rapidly at all directions, causing the particle piles to avalanche (random convection, Fig. 12.7b). Overspread particles are transferred from the LM surface to the solution side during this stage. When most of the particles are transferred to the solution side and the LM surface is spread with dispersive particles, the flow becomes steady and more uniform (steady convection, Fig. 12.7c). A survey of the upper surface area A of the LM puddle indicates that the puddle is flattened when the flow is initiated (Fig. 12.7d). Furthermore, the zigzag fluctuating of A suggests that, during continuous rolling and transforming, the LM puddle is also stretching and retracting itself at the same time, resulting in continuous variations of its thickness.

In general, the configuration of the two immiscible fluids is determined by the surface tensions of the three contacting phases, i.e., the LM (phase 1), the NaOH solution (phase 2), and the ambient air (phase 3). Here, we do not differentiate between the two terms, surface tension and interfacial tension. For each equilibrium condition, the system will automatically adapt itself to a configuration which satisfies surface–tension balance. And geometrically, the three surface tension vectors form the Neumann’s triangle [39]

$$\frac{\gamma_{12}}{\sin \alpha} = \frac{\gamma_{13}}{\sin \beta} = \frac{\gamma_{23}}{\sin(\beta - \alpha)} \quad (12.3)$$

where γ_{12} , γ_{13} , and γ_{23} are, respectively, the surface tension between phase 1/phase 2, phase 1/phase 3, and phase 2/phase 3, while α and β represent their orientation constraints (Fig. 12.8). Equation 12.3 implies the fact that surface tension variations lead to new configurations of the system. And fluid motion will be induced when the system adapts itself to such new configurations.

Fig. 12.8 Surface tension balance at the three-phase contact line and the Neumann’s triangle [39]. Note that the dashed triangle implies that the change of surface tension also changes the configuration of the system. Picture is reproduced with permission



In the present work, there are two possible ways through which the procedure of adding solution drops breaks the surface tension balance of the system. Treating the dry LM surface with NaOH solution on one hand alters its surface tension by dissolving the oxide layer on the part of the surface which is exposed to the ambient air [39]. However, for a considerably large LM volume, the influence of this chemical process should be marginal (This can be validated by simply repeating the procedures without the particles). On the other hand, when a second metallic phase is further considered, the electrochemical effect rises due to the differences in the electrical nature (zeta potential) and morphology between the LM and the particles [39]. The LM and the wet Cu particles form numerous tiny galvanic couples at the contact points due to such differences. Just like joining capacitors with different capacitances, the galvanic contacts will cause a potential shift to the system. Fortunately, as shown in Fig. 12.9a, the overall potential shift of the present system can be directly monitored during the fluid motion (against a saturated calomel electrode, SCE). It can be found that the potential ε (electrode potential) of the LM puddle remains a constant (-1.52 V) before flow initiation (i.e., the wetting of the particles). Right after the particles being wetted by the solution drops, a sharp jump of ε is detected. After that, ε never returns to its initial value, nor does it stay unchanged. Instead, it keeps long-term fluctuating at a higher voltage range Δ . The result suggests that the hydrodynamic instability of the system is accompanied by an electrochemical instability.

To testify whether the abovementioned electrochemical instability can induce such large-scale hydrodynamic flows to the system or not, the dependence of the LM surface tension γ with respect to ε is measured using a standard pendent-drop method (Fig. 12.9b). The voltage U applied between the working electrode E_W (pendent LM drops) and the counter electrode E_C , which changes ε between E_W and the reference electrode E_R , is used as the control parameter (Fig. 12.9c). Theoretically, the surface tension of a liquid is subject to its surface potential according to the electrocapillary theory

$$\gamma = \gamma_0 - \frac{1}{2} C_0 (\varepsilon_{pzc} - \varepsilon)^2 \quad (12.4)$$

where γ_0 is the surface tension of the potential of zero charge ε_{pzc} (corresponding to a polarization voltage of U_{pzc}) and C_0 is the EDL capacitance. As shown in Fig. 12.9d, direct observations find that a small change of ε (within ~ 1 V) greatly alters the shape of the LM drops, indicating significant influences of ε on γ . Based on the profiles of the photographed pendent drops and the density of the fluids, the relation between ε and γ can be obtained (Fig. 12.9e). Since the dependence of surface tension γ with respect to its electric potential ε is experimentally determined, the Marangoni surface stress τ which drives the flow can be explicitly expressed as [39]

$$\tau = \frac{d\gamma}{dx} \mathbf{n} = \frac{d\gamma}{d\varepsilon} \frac{d\varepsilon}{dx} \mathbf{n} = f(\varepsilon) \mathbf{E} \quad (12.5)$$

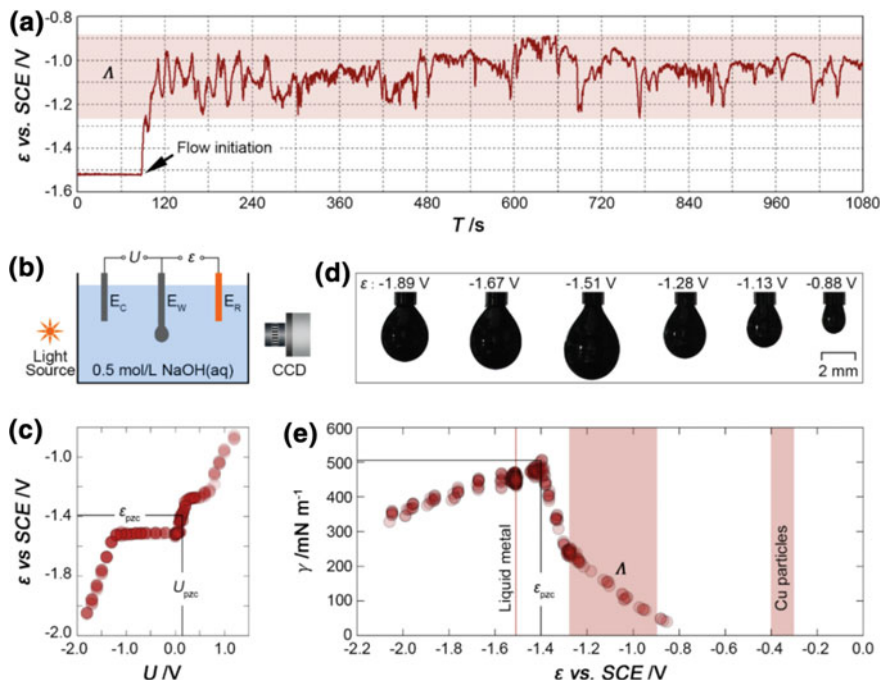


Fig. 12.9 **a** Electric potential ε of the LM puddle before and after flow initiation. The filled region represents the fluctuating range Δ of ε . **b** Schematic setups of the pendant-drop electrocapillary test. E_C —Counter electrode, E_W —Working electrode, E_R —Reference electrode (SCE). **c** The development of ε as a function of U . **d** The profiles of the LM pendant drops at different values of ε . **e** The development of γ as a function of ε . The potential range Δ as well as that of the Cu particles in 0.5 mol L^{-1} solution is also indicated. Note that the data markers are overlapped in figure c and e so that the color becomes deeper where more data markers are plotted [39]. All pictures are reproduced with permission

where $f(\varepsilon) = d\gamma/d\varepsilon$ is already known from Fig. 12.9e, $\mathbf{n}$ denotes the unit vector of $\boldsymbol{\tau}$, and $\mathbf{E}$ is the electric field along the surface. The surface-tension-driven nature and the electrocapillary origin of the surface flow are both revealed by Eq. 12.5. Combining Fig. 12.9a and e, one will further notice that ε of the LM before flow initiation ($-1.52V$) corresponds to a high surface tension state ($\gamma \sim 450 \text{ mN m}^{-1}$). While when ε shifts to the higher voltage range, $\Delta \in (-1.27, -0.90 \text{ V})$, the LM ends up with a low surface tension state, $\gamma \in (240, 40 \text{ mN m}^{-1})$. Consequently, such large surface tension gradient should be reasonable to generate strong instability and large-scale fluid motion. Moreover, further measurement finds out that the much higher ε of the wet Cu particles with respect to that of the LM should be the cause of the shift of ε to the intermediate range Δ (Fig. 12.9e).

Being aware of the electrocapillary origin of the flow, we further present details of the flow patterns to explain why the flow can be self-sustained [39]. As shown in Fig. 12.10a, instead of wetting the Cu particle with solution drops, the particle pile is

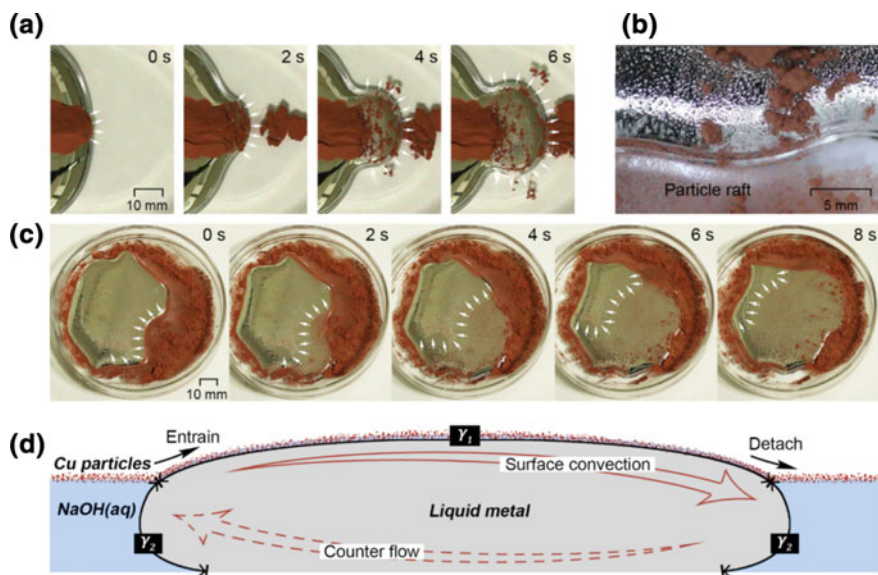


Fig. 12.10 **a** Time-lapse images showing the local deformation of the LM puddle. **b** A zoom-in look at the near-boundary region showing the particle raft formed by the hydrophobic Cu particles detaching from the LM surface. **c** Time-lapse images showing the LM entrains Cu particles from the solution side and carries them across its surface. The advancing particle front is indicated by an array of arrows. **d** A schematic drawing showing the LM surface convection regime and the accompanying particle circulation [39]. All pictures are reproduced with permission

made to approach the LM–solution contact line to initiate fluid motion. In this case, the convection (deformation) only takes place at the particle-covered region while the rest of the LM puddle remains motionless. The observed local deformation suggests that the Cu particles take effect individually and their influences are restricted closely at the particle sites. Such site-specific electrical polarization induced by the numerous tiny battery-like particles differs largely from conventional overall polarizations realized with external sources [39]. It is also because of this unique feature, localized flow and diverse transformation of the LM puddle could be possible.

While the flow is initiated by the giant electrocapillary effect owing to the electrical property of the particle material, the long-term surface convection is guaranteed by the circulation of the Cu particles [39]. To achieve particle circulation, the hydrophobicity of the Cu particle surface is found to be crucial. Hydrophobicity enables the particles to detach the LM surface when they are carried to the contact line, resulting in the formation of a particle raft floating on the solution (Fig. 12.10b). The hydrophobicity of the Cu particles also sheds light on the thickness of the NaOH film on the liquid metal surface. Since the hydrophobic particles can only immerse partially in the solution, they will float on the solution film even when its thickness is not comparable to the particle size. The absence of such situation in the

experiment indicates the NaOH film thickness is relatively small with respect to that of the particle size.

In fact, after the random convection stage, most of the particles are washed off from the LM surface through this self-cleaning process. In order to keep sufficient particles on the LM surface to maintain continuous motion, the system performs another particle-transporting process [39]. During this process, the LM entrains particles from the solutions side and then transports them across its surface during the steady convection stage (Fig. 12.10c). This particle-entraining process, together with the particle-detaching process, completes the whole particle circulation. It should also be noted that the hydrophobic particles will be washed off by the solution and the LM under the solution surface is particle-free. Given the site-specific polarization of the particles, a surface tension gradient between the particle-covered region above the solution (γ_1) and the particle-free region below the solution (γ_2) is expected. Driven by such surface tension gradient, a global surface convection of the LM puddle will be induced. And because continuity must conserve, a global counter flow beneath the surface is also expected (Fig. 12.10d).

By now, as sketched in Fig. 12.10d, a general picture of the flow can be interpreted as follows [39]: The wet Cu particles induce large surface tension gradient through the electrocapillary mechanism. And the resulted surface tension imbalance breaks the equilibrium of the system and initiates hydrodynamic flow. The rolling LM puddle keeps circulating the hydrophobic Cu particles so that sufficient galvanic contacts can be formed on its surface to maintain persistent flow.

12.6 Tracing Liquid Metal Surface Convection with a Particle Raft

After considerable experimental observations of the particle-driving flow, it occurs that the unique feature of the system also offers the benefit to use the particles as tracers to capture flow details [39]. Starting from this point, the flow field was further visualized with the assistance of PIV system. It can be seen from the visualized flow fields that the characteristic multidirectional flow behavior during the random convection stage and the unidirectional flow behavior during the steady convection stage can both be well captured using this method (Fig. 12.11a and b). And the visualized flow fields show that high-velocity regions mainly lie at the LM side, which confirms that the flow is driven by the surface tension gradient of the LM.

The PIV analysis also permits quantitative access to the flow field [39]. The results show that the typical velocity of the surface convection is on the scale of several millimeters per second. The variations of the velocity $V(u, v)$ at a fixed point (Eulerian approach) in the flow field during the random convection stage and the steady convection stage have also been plotted. The frequent fluctuations of velocity magnitude and the shifting of flow directions (sign-shifting of u and v) in Fig. 12.11a give a clear indication of the random convection behavior. While the

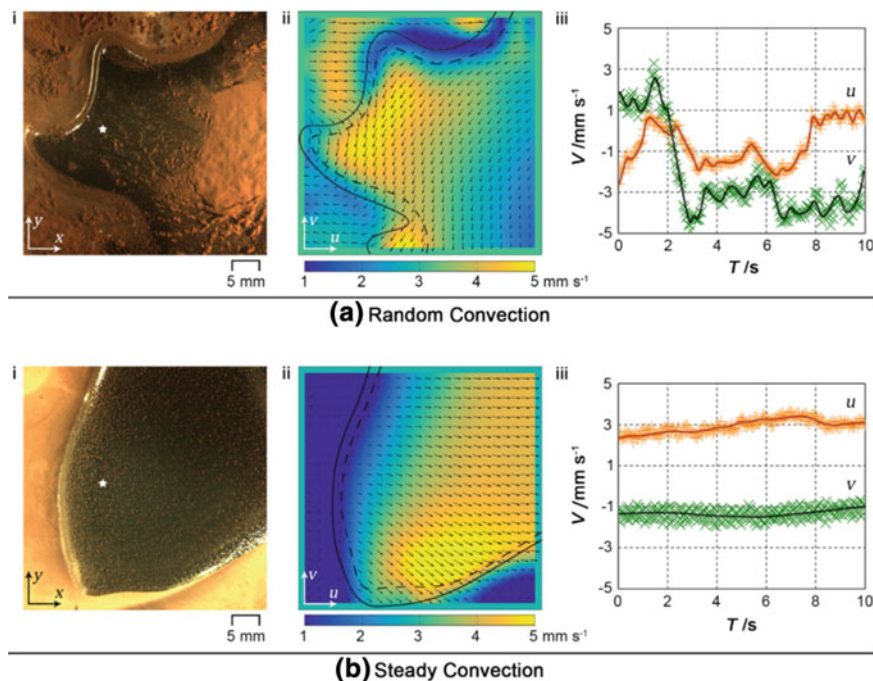


Fig. 12.11 **a, b** PIV flow visualization of the random convection stage **a** and the steady convection stage **b**. Subfigures: i-optical image, ii-visualized flow field and velocity distribution (the solid line and the dashed line indicate the LM outline and the LM–solution contact line, respectively), and iii-velocity variation of the fixed location marked in subfigure i [39]. All pictures are reproduced with permission

flow during the steady convection stage in Fig. 12.11b experiences minor change in velocity magnitude and flow direction, which qualitatively distinguishes itself from the random convection stage. Such continuous unidirectional flow behavior during the steady convection stage also puts forward a conveyor-belt-like use of the system as a self-driving all-liquid surface pump.

In addition, small-scale flow regimes of the LM surface convection can also be captured using PIV analysis [39]. As shown in Fig. 12.12a, when traveling along with the surface convection, particle piles are found to scatter on the LM surface. The expanding rim of the particle pile indicates there exists a secondary flow accompanying the main surface convection. By subtracting the absolute velocity V_A with the mean velocity of the particle pile V_0 , the relative velocity V_R of the particles (velocity with respect to the moving LM surface) can be obtained. It shows clearly that V_R at the particle pile region exhibits a radial distribution, which reveals the outward expanding behavior of the particles. Also, a vortex at the particle pile region can be found from the vorticity color map. Acting as a secondary flow source, such velocity and vorticity distribution further confirm that the flow is activated by the

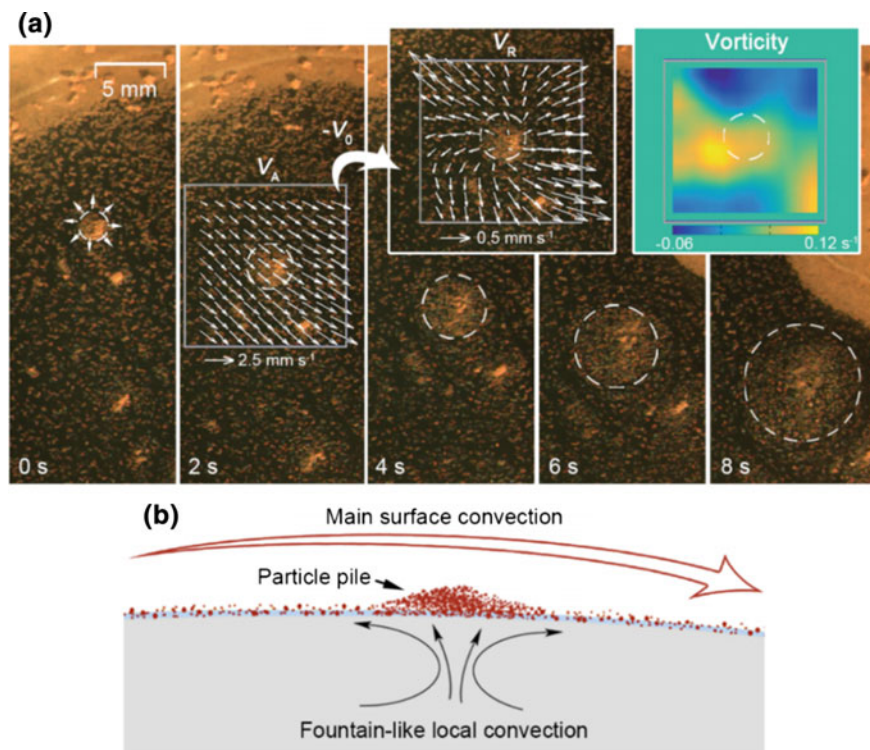


Fig. 12.12 **a** A small particle pile scatters on the LM surface accompanying the main surface convection. The dashed circles outline the rims of the particle pile at different time points. The vector fields of the absolute velocity V_A and the relative velocity V_R at the particle pile region are indicated. $V_R = V_A - V_0$, where $V_0 = (1.0 \text{ mm s}^{-1}, 1.3 \text{ mm s}^{-1})$ is the mean velocity. Also, the vorticity distribution is further presented in the color map. **b** A schematic drawing showing a fountain-like local convection takes place at the particle pile region [39]. All pictures are reproduced with permission

particles. This secondary surface flow also indicates a fountain-like local convection beneath the surface due to mass conservation (Fig. 12.12b). Conclusion thus can also be made that the flow behavior of the system can be further complicated due to ununiform particle distribution.

For further discussion, it should be noted that the hydrophobicity of the particle material is a prerequisite [39]. It has been validated that the same particle material with nanoscale size ($\sim 50 \text{ nm}$ Cu particles) is infeasible due to their particle-size-induced hydrophilicity. Also, alkaline solutions cannot be replaced by acid ones, though both of them can remove the LM oxide layer. This is because an acid solution, e.g., HCl solution, will disperse the Cu particles inside the LM [39]. Typically, the flow can last more than 1 h in the experiments until the upper surface of LM is dried via evaporating. However, the flow can be reinitiated when the particle raft on the LM

surface is wetted again. This suggests that the flow can be maintained as long as the particular configuration of wet particles on partially immersed LM is satisfied.

In summary, large-scale long-term electrohydrodynamic instability of the LM—solution system can be readily induced and also be maintained using metal particles [39]. Tiny particles can cause large surface tension gradient to the LM when wetted, which is responsible for the fluid motion. It was also disclosed that the LM keeps circulating the particles during the surface convection so that the flow can be self-sustained. Such flow behaviors are guaranteed by the electric potential as well as the hydrophobicity of the particle materials. The PIV technology could be a very useful way to capture the flow patterns and analyze the characteristic flow regimes of the self-running liquid metal system. The phenomena reveal complex flow behaviors which may shed light on other LM flows. Also, the flow actuation strategy and the flow visualization method can also be applied to other immiscible fluid pairs.

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Chapter 13

Substrate Enabled Liquid Metal Machine



Abstract Although liquid metals such as eutectic gallium–indium and gallium–indium–tin have been found extremely important in making various kinds of soft machines, there however always exists a big challenge to flexibly and stably control the shape of liquid metal due to its extremely high surface tension. Along this direction, the present lab (Hu et al. in *Adv Mater* 28:9210–9217, 2016 [1]) made a fundamental discovery that the bouncing bright liquid metal droplet in alkaline electrolyte can be transformed to a flat and dull puddle when placed on graphite surface. Through the intrinsic interactions between liquid metal and graphite, the liquid metal puddle on graphite can be manipulated as desired into various stable shapes with sharp angles in semi-open space via a simple and highly feasible way. Moreover, it was also disclosed that the electric field can be flexibly applied to control the transformation, locomotion even anti-gravity behavior of liquid metal puddle on graphite. Such phenomena are fundamentally different from those observed before when placing liquid metal on glass substrate. Further, if the liquid metal was fed with aluminum in advance, the graphite-like substrate would induce a group of very unusual amoeba-like behaviors for such self-driven liquid metal machines. With basic science value and practical significance, these finding suggests a pivotal strategy for liquid metal patterning as well as developing future soft mobile machine owning three-dimensional locomotion capability. It also adds new knowledge for understanding the liquid metal science. This chapter presents the typical strategies and mechanisms in manipulating the liquid metal and the allied machine systems inside the electrolyte environment.

Keywords Liquid metal · Substrate effect · Shape control · Amoeba-like behavior

13.1 Transformation of Liquid Metal Droplet on Graphite in Electrolyte

With intriguing and valuable behaviors, the multifunctional materials of nontoxic liquid metal (LM), such as eutectic gallium–indium (GaIn) or gallium–indium–tin

(GaInSn), are found more and more important applications in wide areas such as flexible and stretchable electronics [2, 3], microfluidics [4, 5] to soft devices [6, 7], and chip cooling [8–10]. Although LM has already been investigated in some primary fields, further development is still not so successful as anticipated due to many unknown intrinsic properties of the liquid metal. Among those, the high surface tension of liquid metal, which is ten times that of water [11], has been a big challenge for flexibly manipulating the liquid metal structure. With large surface tension, the liquid metal usually forms a droplet when interfaced with air or liquid, which makes it hard to be shaped into desired structures for specific applications. To overcome this difficulty, tremendous efforts have been made recently such that LM was encapsulated into various molds via injection [12], gold-assisted deposition [13], localized stiff cell filling [14, 15], or dual-trans printing [16]. However, the shaping mainly depends on enclosed molds and the surface tension of LM remains high in those studies. Surface tension of LM is also reported to be altered electrochemically [6, 17–20]. However, the surface tension across the whole LM as reported in those studies was not so uniform and stable since the electrochemical reactions over the LM surface are hard to control, which makes it difficult to form stable LM shapes. So far, the strategy to control the surface tension of LM remains to be explored since it has vital effects on shaping LM for various practical controls as desired.

Apart from LM shaping, the high surface tension also evidently influences the locomotion of LM droplets in water. For example, the LM would move in the flow channel as a round spherical droplet due to the high surface tension. If the surface tension becomes much lower, the LM is more likely to be deformed under external force, which in turn would influence the locomotion. However, the locomotion of LM with much lower surface tension was rarely reported up to now. As an unusual liquid-state metal material, LMs have already presented many promising properties for soft robot design and manufacture including electrically [20] or electrochemically [6, 7, 19] drivable behaviors. Moreover, researches on soft robots have kept gaining much attention in mobile machine design [21–23]. The key challenge for soft machine manufacture lies in the development of controllable soft bodies using materials that can integrate sensors, actuators, and computation elements together to enable the body to deliver the desired behavior. The material with better stretchability and adaptability remains to be explored.

In Hu et al. work [1], an intriguing and distinct phenomenon is discovered that when the spherical LM droplet was placed on graphite substrate immersed in electrolyte, it would easily become a dull, flat puddle. The mechanism underlying this straightforward transformation is due to the formation of oxide layer on droplet induced by the potential elevation upon contact with graphite. With significantly reduced surface tension, the shaping of LM in the semi-open space in electrolyte can be achieved via a much easier operational way. Moreover, with unusual properties induced by the interaction with graphite, the dedicated locomotion of LM on graphite plane and slope when subject to electric field were also clarified. The series of fundamental findings are expected to be important for developing powerful ways for manipulating liquid metal in liquid environment and thus soft machines in the near future.

It is known that LM EGaIn or GaInSn would form bouncing spheres in electrolyte due to its high surface tension in room temperature. It has also been reported that liquid metal droplets can transform from a sphere into a film under application of an external electric field [20, 24]. This transformation is due to the surface tension changes induced by the electric field, which is quick and reversible by removing the electric field. In Hu et al. work [1], LM droplet can quickly transform into flat, dull puddle when placed on graphite substrate immersed in alkaline electrolyte (0.5 mm NaOH solution in this work). The static images of LM droplets on glass or graphite substrate immersed in 0.5 mm NaOH are shown in Fig. 13.1a. Besides, oxidized membrane was observed on the LM puddle, which was composed of β -Ga₂O₃ confirmed by Raman measurements (as the appearance of a 600 cm⁻¹ peak shift, Fig. 13.1b) [25]. The surface tension was reduced by the interaction with graphite substrate without external electrical energy supply. When separated from the graphite, the dull, flat puddle quickly becomes a bouncing spherical droplet again in NaOH solution within 0.5 s.

The mechanism underlying this flatten deformation is mainly related to the surface tension change induced by the formation of oxide layer on LM puddle. The quick formation of this oxide layer should be caused by the electrochemical reaction induced by graphite. Thus, it was predicted that the potential drop across the LM–NaOH interface was increased upon the LM–graphite contact. To testify this prediction, zeta potential of graphite nanoparticle in NaOH was measured to evaluate the surface potential of graphite. At pH 11.6, the zeta potential of graphite was –31.6 mV, which indicated that it was a positive potential drop across the graphite–NaOH interface. Upon the contact with graphite, the negative potential drop across the LM–NaOH interface could be significantly pulled up in order to reach to equal potential with graphite (Fig. 13.1c). Thus, the above prediction was proven that the LM was electrochemically oxidized with abundant electrons quickly outflowed from LM to graphite, which reduced the surface tension as a result. The zeta potentials of other conductive substrate material including Cu and steel were also measured. Similar flattening behavior of LM droplet was also observed on copper substrate which however should be mainly caused by the diffusion of gallium with copper. The zeta potential results also confirmed that this flattening is not related to interface potential changes as the potential drop across the copper–NaOH was negative, similar to that of LM and NaOH. While on steel substrate, such obvious flattening of LM was not observed, which was also consistent with the zeta potential result. These results further confirmed that the potential drop across the contact substrate and electrolyte interface plays the key role in such flattening behavior of LM [1].

As the surface tension of LM droplets was reduced by LM–graphite interaction, the bouncing LM droplets quickly became flattened dull puddle. To quantify the transformation, the diameters of the same LM droplets on common glass and on graphite surfaces were measured [1]. As shown in Fig. 13.1d, the diameter of LM droplets measured on graphite surface increased with the original droplet size in linear manner and the slope k is around 1.30. Moreover, several basic geometrical LM shapes including line, triangle, rectangle, and ring were formed with simple slide molds as shown in Fig. 13.1e. Compared with LM on glass surface, the LM

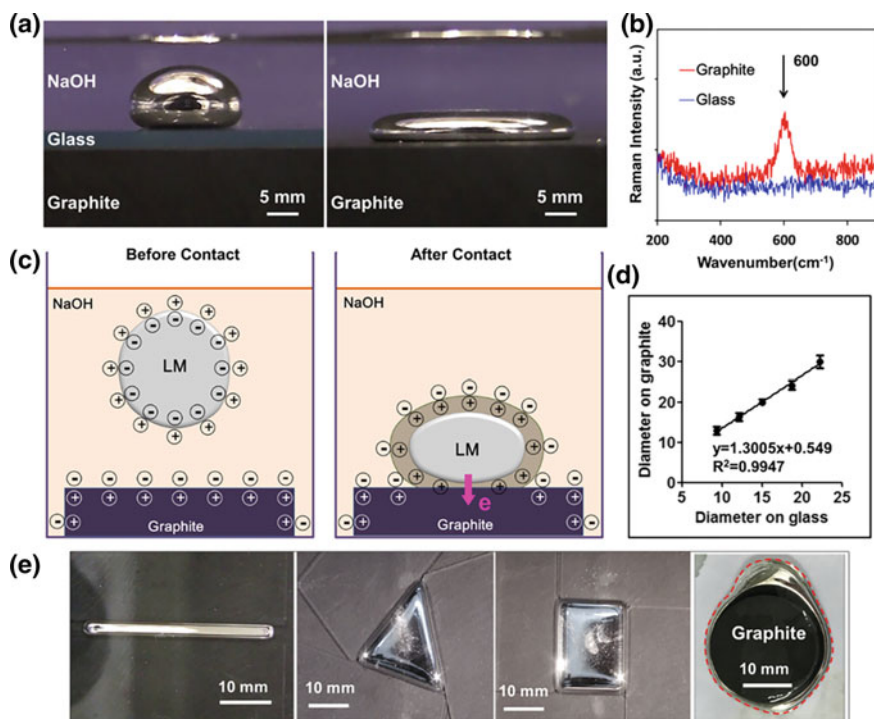


Fig. 13.1 The transformation of LM droplet on graphite in electrolyte [1]. **a** The static images of LM droplet on glass (left) and on graphite substrate (right) in NaOH, respectively. LM presented quasi-sphere on glass substrate and became flat on graphite. **b** Raman spectra of LM droplet on graphite (red) and on glass (blue) in the 200–900 cm⁻¹ region. **c** The schematic figure of LM interacting with graphite substrate. The LM was electrochemically oxidized as the potential drop across LM–NaOH was pulled up due to contact with graphite. **d** The quantification of diameter changes of LM on glass and on graphite. **e** Four typical basic shapes of LM manipulated by glass slides including ling, triangle, rectangular, and ring (red-dotted line indicate the LM). All pictures are reproduced with permission

droplets were easy to be shaped with sharp angles by slides, while the LM droplet on glass retained a quasi-circle shape, which implied the effect of the higher surface tension. When the slides were removed, the LM on graphite still maintained the general shapes. This result also proved the significant reduction of surface tension of LM on graphite substrate. It would provide valuable and promising methods for LM planar structure fabrication.

The interaction of LM droplets with graphite substrate enabled the bouncing smooth LM sphere to be transformed into a dull, flat puddle [1]. When slightly poked with a glass rod, the LM puddle acted like a dull clump of clay. From the observation and discussion above, the interaction between LM droplets and graphite substrate has rendered the LM droplet with distinct physical and chemical properties, which is quite different from those on common glass substrate. In order to further

illustrate the unique properties thus offered, the LM puddle locomotion and transformation on graphite surface induced by electrical field were also investigated. The LM and graphite surface were completely immersed in alkaline electrolyte, which was 0.5 mM NaOH in all experiments in the present study. External electrical field was administrated by two steel-wire electrodes connected to a 10 V DC power supply. Through changing the electrode and substrate arrangement, a series of investigations were carried out. The experimental setup and major phenomenon as revealed are summarized in Table 13.1.

13.2 Transformation Induced by Direct Connection with Electrode

In the first two cases (Case 1 and 2), the transformation of LM puddle directly connecting with electric electrode was examined and interpreted (Fig. 13.2a) [1]. The previous study has reported some transformation of LM droplets on common glass substrate with application of external electric field. Clearly, through introduction of the graphite, much abundant phenomena were observed where flexible manipulations of liquid metal can be achieved. An LM puddle with an area of 241.7 mm^2 was placed on the graphite immersed in NaOH. The area here and below indicated the two-dimensional image of LM puddle from the bird view in Fig. 13.2b. Electric field was provided by 10 DC power supply with two steel-wire electrodes. When the anode contacted LM puddle itself (Case 1, Table 13.1), the LM puddle stretched into large, thin film with an area of 662.4 mm^2 in 1 s. The LM droplet on glass substrate had similar phenomenon when contacted with anode. The LM film contracted again into dull puddle by disconnecting the anode with the LM film. In these transformations, the contact with anode could raise the potential of the LM puddle, which further reduces the surface tension of the LM puddle based on the Lippman's equation. When the LM puddle was contacted with cathode (Case 2, Table 13.1), the flat LM puddle quickly transformed into a sphere with a smaller area of 48.5 mm^2 . However, the LM droplet on glass substrate was repulsive to cathode, which made it even hard to connect LM with cathode. The typical snapshots of same LM puddle transformations in Case 1 and 2 are displayed in Fig. 13.2b.

13.3 Electric Field Induced Planar Locomotion of Liquid Metal on Graphite

In addition to the transformation, the planar locomotion of LM puddle on graphite under electric field was also investigated [1]. The LM droplet was placed on graphite immersed in NaOH and quickly became dull flat LM puddle. External electrical field was applied by two steel-wire electrodes connected to a 10 V DC power supply. The

Table 13.1 The experimental settings and main phenomenon [1] in the investigation of LM interaction with graphite substrate based on Ga₆₅In₂₂Sn₁₃

Cases	Voltage	Anode	Cathode	Test subject	Main phenomena
1	DC, 10 V	Contact LM; fixed	Not contacted; fixed	Transformation	The flat LM puddle quickly stretched into thinner LM film
2	DC, 10 V	Not contacted; fixed	Contact LM; fixed	Transformation	The flat LM puddle quickly transformed into a sphere
3	DC, 10 V	Not contacted; fixed	Not contacted; fixed	Planar locomotion	The flat LM puddle continuously elongated and moves toward cathode
4	DC, 10 V	Not contacted; fixed	Not contacted; not fixed	Planar locomotion	The flat puddle of LM elongated, moved toward cathode and could make a turn in any direction with cathode
5	DC, IOV	Not contacted; not fixed	Not contacted; fixed	Planar locomotion	The LM puddle moved toward cathode with a notch at the rear end
6	DC, IOV	Not contacted; not fixed	Not contacted; not fixed	Upslope locomotion	The slope locomotion of LM puddle was realized

electrodes were immersed in NaOH without contacting graphite or LM. Therefore, this provided a planar electric field for LM puddle locomotion. It has been discussed above that the LM puddle was positively charged. So it was not surprising that the puddle slowly moved toward the cathode when the electrical field was applied in NaOH (Cases 3, 4, and 5, Table 13.1). When both anode and cathode were fixed and amounted relatively far away from LM, the LM elongated and moved to the cathode with the rear end dragged like a tail (Fig. 13.3a). When it moved close to

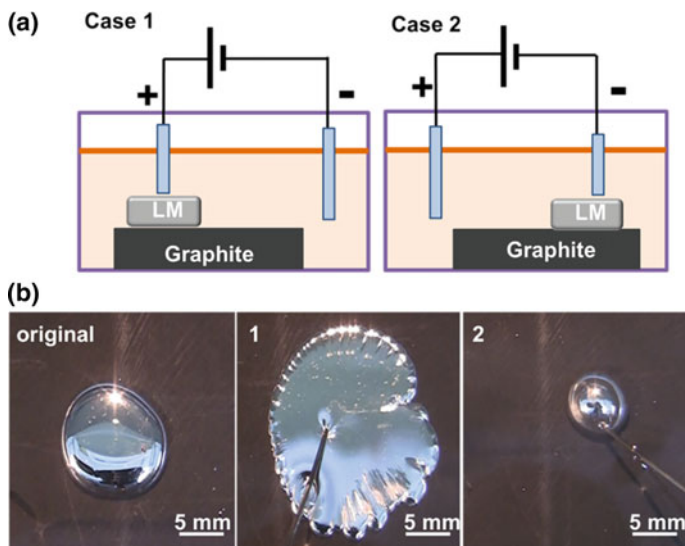


Fig. 13.2 The transformation of LM on graphite induced by direct connection with electrode [1]. **a** Scheme of the experimental Case 1 and Case 2. Case 1: The transformation of LM on graphite directly connecting external power anode. Case 2: The transformation of LM on graphite directly connecting external power cathode. **b** The images of an LM puddle on graphite and its transformations in experimental Case 1 and Case 2. All pictures are reproduced with permission

the cathode, the LM puddle branched at the head end, which may be caused by electrochemical reactions. When the cathode was not fixed and made turns close to LM puddle (Case 4, Table 13.1), the head end of the LM puddle made turns along with the cathode movement and the tail was dragged along more slowly (Fig. 13.3b). To further investigate the kinetics of the locomotion mode in Case 3, the directional locomotion of LM in certain electric field was examined. The anode and cathode of external 10 V power were separated by 10 cm to provide the desired electric field. When the electricity was switched on, the LM puddle continuously elongated and moved toward cathode with the rear end dragged like a tail (Fig. 13.3c), which was quite different from the quick and smooth movement of LM droplets on glass surface. More specifically, it was observed that the thick oxidized surface moved relatively slow and gradually shrunk to the rear end like a tail while at the head end, the bright metal with less thick oxidized surface quickly runs to the cathode. The transient displacement of both rear and head ends of the two sized LM puddles is recorded and shown in the inset of Fig. 13.3c. It can be observed that larger sized LM moved faster than the smaller one as a whole. More specifically, when both heads reached the end point (here about 7 cm from the start point), the LM puddle with larger size also displayed larger deformation, namely, the distance between head and rear. The LM puddle also moved generally faster under electric field with higher intensity.

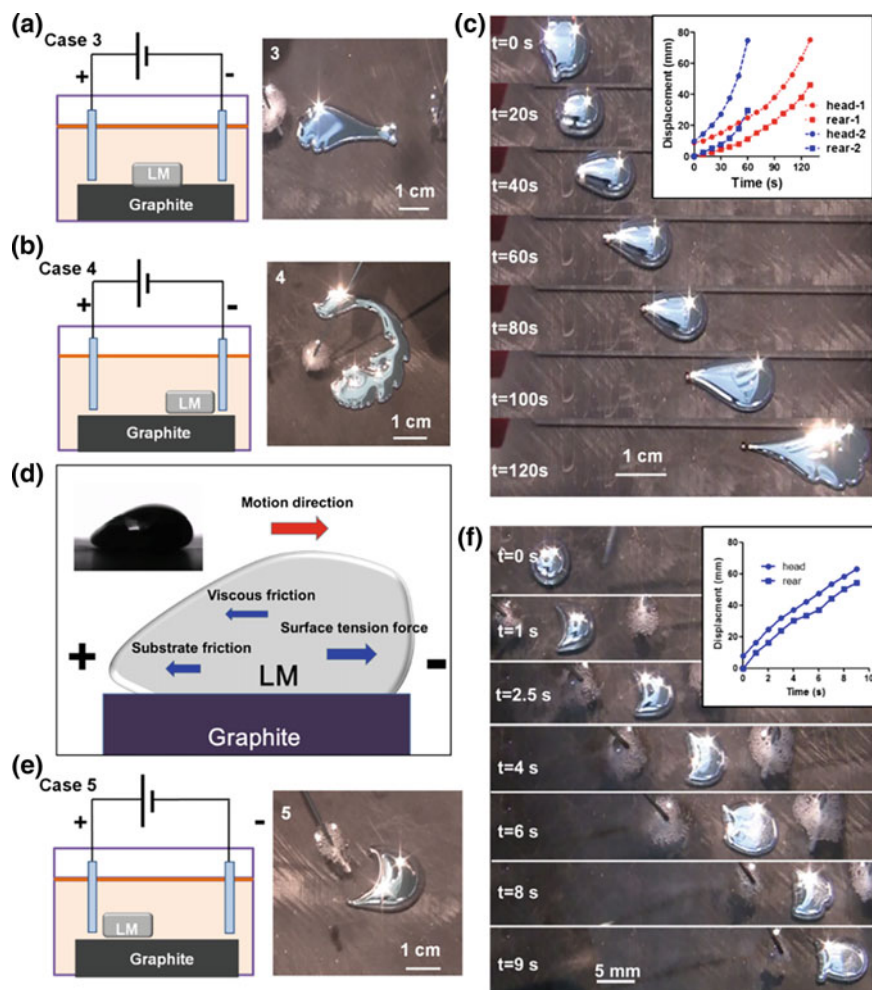


Fig. 13.3 The planar locomotion of LM on graphite induced by electric field [1]. **a** The scheme of experimental Case 3 and its experimental images. Case 3: The power electrodes were fixed at the opposite sides of LM on graphite. Both electrodes were relatively far away from LM (over 2 cm). **b** The scheme of experimental Case 4 and its experimental images. Case 4: The power cathode was close to LM on graphite and make turns manually. The anode was fixed relatively far away from LM. **c** Sequential snapshot for an LM directional locomotion in NaOH in Case 3. Inset. The transient displacements of head and rear end of two sized LMs. LM 1: diameter 8.5 mm. LM 2: 9.6 mm. **d** The force analysis of LM on graphite induced by electric field. Inset. The deformation of LM puddle on graphite when electric field was applied. **e** The scheme of experimental Case 5 and the experimental image. **f** Sequential snapshot for an LM directional locomotion in NaOH in Case 5. Inset. The transient displacements of head and rear ends of an LM (8.5 mm in diameter). All pictures are reproduced with permission

The mechanism of morphological transformation and planar locomotion of LM droplet in common glass Petri dish in NaOH under electric field has already been discussed in previous reports [13]. The driving mechanism was similar here. To summarize, the deformation and directional locomotion of LM droplets in electrolyte were mainly due to the surface tension changes induced by the potential gradient generated by the electric field. The electric field induced the imbalance of electron distribution in LM puddle, which generated a potential gradient from the head to the rear end. At the head end, the voltage drop across the EDL will become lower on the rear end, which results in a higher surface tension and thus a higher pressure on this end according to Lippman's equation. As a result, the LM puddle was deformed and propelled toward cathode of external power supply. The deformed snapshot of LM puddle is shown in Fig. 13.3d inset, and the force analysis is depicted in Fig. 13.3d.

However, there are fundamental differences in LM locomotion between current findings and previous efforts in which the substrate are insulated [1]. First, the LM puddle moved toward cathode rather than the anode because the LM puddle was positively charged due to the oxide layer. Second, the deformation of LM puddle on graphite was much larger under electric field. This was because the surface tension of LM was significantly reduced, which make the LM more deformable under certain pressure. Moreover, the oxide layer presented the mechanic properties as a solid, which also influences the locomotion. The thick solid oxide surface could enhance the friction with graphite surface, and thus was left behind to the rear end. While the LM puddle facing the anode got rid of the thick oxide and moved freely more like a fluid although thin oxide layer should still exist over the head part. Therefore, it appeared that the bright head end of LM puddle moved much faster than the rear end with dark oxide surface (Fig. 13.3c).

In those two directional locomotions in Cases 3 and 4, the anode was placed relatively far away from the LM, say about 2 cm away. When the anode was not fixed and placed close to the rear end of LM at a distance around 0.5 cm, the LM puddle was observed to move more quickly with a meniscus at the rear end (Fig. 13.3e). When the anode and cathode moved together at a distance of approximately 3 cm and the anode was close to the rear end of the LM puddle at a distance around 0.5 cm, the LM puddle was observed to move more quickly than that in Case 3 (Fig. 13.3a). The quantified transient locomotion displacement of an LM puddle also proved this (Fig. 13.3f inset). In such case, apart from providing the electric field to induce the charge imbalance along the LM, the anode also played another important role in the locomotion of LM. Here at the rear end, the LM was electrochemically reduced and the surface tension increased, which pulled the LM backward to form the reverse meniscus. Thus, the anode worked like a propeller and the LM moved faster than that in Case 3.

Based on the above observations and discussions, the LM puddle presented some unique properties in the planar locomotion due to the large surface friction between LM puddle and graphite substrate [1]. Besides, when the LM puddle moved under electric field with the "anode propeller" (Case 5), it wriggled like a worm. Though

they have no feet, such worms display amazing ability, say moving even on sharp slope via a wriggling style. Inspired by this, the slope locomotion of LM puddle was also examined (Case 6, Table 13.1).

13.4 Electric Field Driven Upslope Locomotion of Liquid Metal on Graphite

According to the experiments and also common sense, the sharper the slope is, the more difficult it would be for the LM to climb under the same electric field [1]. In the present experiments for slope locomotion, a 10° graphite slope with a length of 7 cm was prepared. It was neither too flat nor too sharp, which was better for us to present the generalized locomotion properties of LM puddle on graphite slope. In this case, the LM droplet was gently placed on graphite slope. The cathode was placed on the upward side close to the head end of LM puddle and anode was placed on the downward side at the rear end as indicated in Fig. 13.4a. The distance between the two power electrodes was around 2.5 cm. The voltage was set at 10 V. A gap at about 2–3 mm had to be kept between the bottom of the electrodes and the graphite surface to avoid notable charging of graphite as well as the LM puddle on it. When no electric field was applied, the LM puddle slid down due to its own gravity. When the electricity was switched on, the LM puddle slowly wriggled up the slope. The head end was continuously branching and the rear end was propelled by the “anode propeller.” The front view snapshots of slope climbing of the LM puddle are shown in Fig. 13.4b, and the plan view of branching LM on slope is displayed in the inset of Fig. 13.4b. As the head end was branching, the LM puddle may be divided into separated parts along the upslope locomotion. Thus, the anode and cathode had to coordinate with the locomotion of LM to avoid dividing. In the example shown in Fig. 13.4b, the cathode was at a distance of around 1–1.5 cm ahead of the head end of LM puddle and the anode was around 0.5 cm behind the rear end. If the cathode was too far away from the head end, the LM puddle would not move upward due to the insufficient driving force. If it is too close, the head end kept branching and cannot move on. In addition, if the anode was too close to the rear end of LM puddle, the repulsive force from anode could lift up the rear end, making it detached. The detached LM puddle would then become a sphere at once and quickly roll downslope. Unlike the planar locomotion, the upslope locomotion of LM was significantly affected by the component of gravity (Fig. 13.4c). Subjected to those forces, the LM with lower surface tension crept upslope like a worm, which was intriguing and unique.

Subsequently, the general kinetic properties of LM puddle upslope locomotion on graphite were examined [1]. The transient displacements of two sized LM puddles (6.7 and 8 mm, respectively) on graphite slope were recorded in Fig. 13.4d. The distance between two electrodes was around 2.5 cm, and the LM puddles were not divided separately along the upslope locomotion. Obviously, the larger LM puddle moved more quickly than the smaller one. When the LM puddle was too small

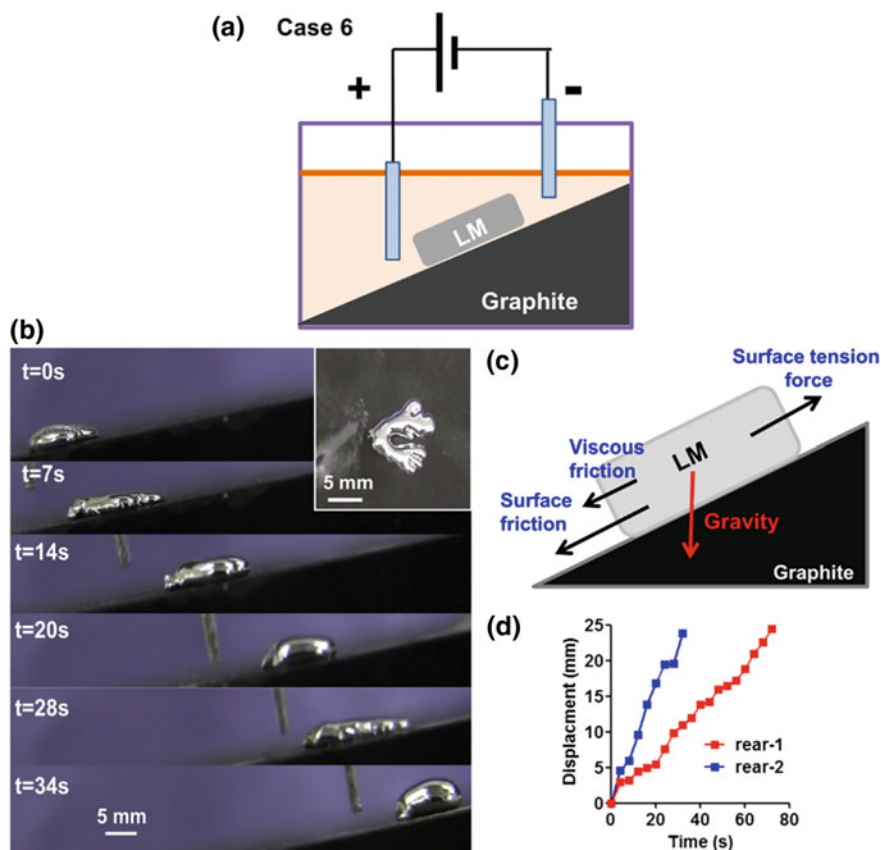


Fig. 13.4 The upslope locomotion of LM on graphite under electric field [1]. **a** The scheme of experimental set in slope locomotion. **b** Sequential snapshot for LM slope locomotion on graphite in NaOH from the front view. Inset: The plan view image of a branching LM puddle (8 mm in diameter) during slope locomotion. **c** The force analysis of LM on graphite slope during locomotion. **d** The transient locomotion of two sized LM puddles on graphite slope. The displacement of rear ends was recorded. The rear 1 (red rectangle) indicates the smaller LM puddle with a diameter of 6.7 mm. The rear 2 (blue rectangle) indicates the larger one with a diameter of 8 mm on graphite. All pictures are reproduced with permission

(diameter less than about 3 mm), it may be quickly electrochemically oxidized. Thus, it was somewhat difficult to induce obvious locomotion.

Similar to the controllable planar locomotion of LM droplets, the upslope locomotion of LM puddle on graphite substrate could be also regulated by changing the electrical field intensity [1]. Thus, regulated upslope locomotion can be programmable. In principle, the speed and slope angle of this upslope locomotion can be controlled by regulating the electric field intensity and electrode position. However, the arrangement of electric field and electrode position was more complex. In the upslope locomotion, the distance between electrodes and the LM puddle had

to be carefully controlled to avoid the LM dividing or detaching from the graphite. When the electric field intensity increased, the electrochemically induced branching at the head end became more remarkable, which requires the careful manipulation of anode to coalesce and propel the branched LM puddle in order to realize the upslope locomotion. Moreover, the increase of electric field intensity may induce electrochemical reactions on LM, which could affect the surface charge distribution as well as the surface tension. As a result, the stressed condition of LM puddle would also change.

Overall, manipulation of LM shape is highly feasible via graphite substrate effect. The induced transformation uniformly reduced the surface tension of LM in electrolyte without external energy supply, which is valuable in applications such as LM-based structure patterning [1]. Based on this discovery, electric-field-induced planar transformation of LM on graphite surface was also clarified. Moreover, the unique planar and upslope locomotion of LM on graphite was disclosed with the application of low-voltage DC electric field, which may provide new insight for potential soft device manufacture. Furthermore, the electrochemical properties of LM also suggest further explorations worth of pursuing in the near future.

13.5 Liquid Metal Amoeba Enabled by Substrate Effects

Through introducing the graphite as the controlling material, more complicated machine styles such as amoeba-like machines can still be realized. As is known to all, the unique motion of amoeba with deformable body has long been an intriguing issue across physics, bionics, and mechanics for soft robot design. So far, most of the artificial machines are still hard to achieve the complicated amoeba behaviors including the stretching pseudopodia. Through introducing a multi-materials system, Hu et al. [26, 27] further discovered a group of amoeba-like behaviors of self-driven motions of liquid gallium alloy on graphite immersed in alkaline solution. The underlying mechanisms were disclosed to be the surface tension variations of the liquid metal machine caused by its electrochemical interactions with aluminum and graphite in NaOH electrolyte. This multi-material system would shed light on packing and structure design of future soft robot with diverse deformation capability. Moreover, it also sets up a bridge to connect the physical to the vital, which is provoking and profound in inspiring human's pursuit of advanced artificial machine.

The cognition and imitation of unique behavioral movements in biological world have always been the core pursuit of scientists in diverse fields such as physics [28–31], biology [32–34], and engineering [22, 35, 36]. However, the evolution of nature has endowed life species with rather elaborate functions that artificial machine could hardly achieve. Even for the tiny animals with simplest structures, their behaviors are still too complicated to be fully interpreted or imitated. For example, the amoeba, a single-cellular organism in nature, could extend its temporary structures called pseudopodia in order to move and feed [32]. The overall shape of such amoeba cells may change as rapidly as their pseudopodia are extended. These free deformable

movements of amoeba with pseudopodia require the fine coordination of cytoskeleton (microfilament) under complicated mechanism within the biological system [37], which still reserved to be a big challenge for an artificial machine to precisely imitate.

Despite its complexity, the amoeba-like behavior recently especially attracted great attention in developing flexible and soft devices [21, 38, 39]. Generally, two strategies are adopted in the design of amoeba-like machines or actuators with the extensive deformability and adaptability. The first one is to connect several modular units together to compose the deformable structure [40–43]. However, the deformability of such systems is usually restricted by their physical structures and amoeba-like pseudopodia are rarely achieved. The other approaches just directly adopt flexible or stretchable sensing materials as actuators [44–47]. Although these actuators in some extent own the deformable body and even amoeba-like pseudopodia, the deformation relies much on external driving forces, which significantly reduces the flexibilities of the machine in free space.

In the following [26], diverse morphological transformations of liquid metal machine made of gallium alloy GaInSn (67:12:13 in mass ratio in this study) (LM for short) with striking external resemblance to amoeba were illustrated when the LM droplet amalgamated with certain amount of Al (LM–Al droplet for short) was placed on graphite substrate immersed in alkaline electrolyte (0.5 m NaOH in this study). Within this multi-material system, soft and deformable LM droplet behaves just like the amoeba body. In fact, such LM amoeba behaviors, which are the integrated results from physical and electrochemical interaction with Al and graphite, even appear more complex than that of real biological amoeba in nature.

13.6 Transformations of Liquid Metal–Al Droplets on Graphite

All the liquid metal (LM) droplets used in the experiments were GaInSn alloy prepared from gallium, indium, and tin with purity of 99.99%. These raw materials with mass ratios of 67:12:13, respectively, were added into a beaker and then heated to 100 °C. A magnetic stirrer was used to stir the mixture uniformly after the metals were all melted. All NaOH electrolyte used in the experiment of this study was freshly made at 0.5 mm. The graphite plate with purity of 99.9% takes size as 10 cm × 10 cm × 1 cm in length, width, and height, respectively. As the aluminum foil is too light to weight, in our experiments a big piece of aluminum foil was weighted and was cut into small pieces with the same sizes (1.6 mg = 1 piece) for preparation. A drop of LM was initially injected into NaOH solution in glass Petri dish. Small piece of Al foil was placed in touch with the LM droplets via forceps. Thus, Al was attached to the LM droplet and gradually broken into smaller granules since the gallium would destroy the intergranular bonds of Al foil and penetrate into Al grain boundaries [7, 48]. Some of the Al granules were dispersed inside the LM, while others accumulated together into big granules on droplet surface. When the Al

foil was dispersed into small granules without apparent big debris, the LM droplets containing Al (LM–Al droplet in short) were gently transferred by sucker onto the graphite substrate immersed in NaOH solution. Then, the transformations of LM–Al droplet were observed and recorded by digital video equipment, Sony HDR-PJ670. In the experiments, the graphite surface was ensured to be the horizontal to avoid interference factor from gravity unless otherwise indicated. To evaluate the relation of Al content with the transformational categories, various amount of Al foil ($1.6 \text{ mg} = 1 \text{ piece}$) was dispersed in LM droplets with certain volume ($500 \mu\text{L}$). These LM–Al droplets were then placed on the graphite surface for observation. For each Al concentration, 20 trials were carried out and their transformations were statistically categorized as shown in Fig. 13.5b.

Figure 13.5a exemplified the most typical autonomous amoeba-like morphological transformations of LM–Al droplet [26]. LM amoeba with different numbers of main extensions was also observed, which display large resemblance to the pseudopodia. For brief, these extensions were called LM pseudopodia in the following sections. Actually, three types of heteromorphous transformations of LM–Al droplet on graphite were observed and categorized as Case 1–3 based on the distinct prop-

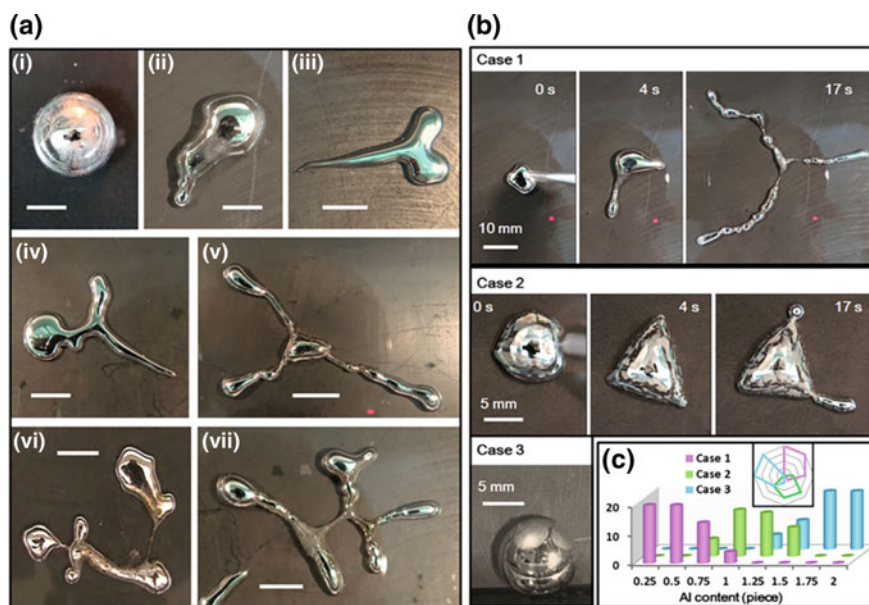


Fig. 13.5 Appearance of liquid metal amoeba [26]. **a** i. The LM–Al droplet prepared in NaOH on glass Petri dish. ii–vii. Amoeba-like transformations of LM–Al droplets on graphite. The LM amoeba presents one main “pseudopodia” in ii, three in iii and iv four in vi and five in vii. Scale bars: i and ii, 3 mm; iii and iv, 5 mm; v, 1 cm; vi and vii, 6 mm. **b** Consecutive snapshots of three typical heteromorphous transformations of LM–Al droplet in Case 1–3. **c** LM droplets with various Al contents (20 trials for each content. For Al content, 1 piece = 1.6 mg) presented different behaviors as categorized in Case 1–3. Inset. All pictures are reproduced with permission

erties of their appearances (Fig. 13.5b). In Case 1, the round LM–Al droplet in short quickly spreads out with formation of pseudopodia as it contacted the graphite in NaOH, during which few bubbles were observed on LM–Al surface. In Case 2, upon contacting the graphite, the bright and shining droplet quickly became gray and gloomy pebble at first. Subsequently, the round LM pebble deformed and the gloomy surface continuously cracked. LM pseudopodia were also observed. Along with these transformations, abundant bubbles were observed on LM surface. In Case 3, the LM–Al droplet moved smoothly similarly as it does on the glass substrate. Vortices were observed on LM surface. The behaviors of LM–Al droplet in Case 1 and 2 presented remarkable resemblance to those of amoeba.

Initially, the relation between Al content in LM and these transformations was examined (Fig. 13.5c) [26]. The LM droplets containing varied Al content presented different behaviors, which all fell into the categorized three cases. Generally, when the Al content was relatively low, the LM–Al droplet would behave as Case 1 described. As the Al content increased, the droplet behaviors were more likely to be categorized into the Case 2. When the LM droplet absorbed enough Al, it would present the behavior in Case 3. There was some overlap in this categorization, which should be caused due to small variations of different graphite substrates. The radar plot (Fig. 13.5c, inset) presented obvious mutual distinctions among these behaviors in three cases based on Al content, indicating that the Al content in LM plays an important role in the classification of these three categories.

The current diverse transformation refers to a complex multi-material system involving LM, Al, graphite, and the alkaline electrolyte surrounding them. The general interactions among these components should be crucial to understand these complicated behaviors. It has been disclosed that the bouncing spherical LM gallium alloy droplet quickly becomes flat and dull when placed on graphite substrate in NaOH electrolyte [1]. A thin layer of oxide is formed on the LM surface electrochemically upon contact with the graphite substrate, which reduces the droplet surface tension significantly. The interaction between LM droplet and Al in NaOH has also been revealed in previous reports [7, 48]. Briefly, Al can disperse into LM and form galvanic cells with LM, which influences the charge distribution over the droplet and produces hydrogen bubbles. When those components were incorporated together, it was predicted that the Al on LM droplet would form galvanic cell with graphite substrate through LM, since the LM droplet was conductively contacted with graphite (Fig. 13.6a). At the cathode, the Al was oxidized and electrons outflowed to graphite through LM. At the anode (graphite), water received the electron and hydrogen was produced. Bubbles were observed with bubbling behaviors from graphite gaps after some time of LM–Al droplet interaction with graphite substrate since graphite could store hydrogen [50], which validated this assumption (Fig. 13.6b). Moreover, when the LM–Al droplet was separated from graphite, many more bubbles were observed on droplet than the same one contacted with graphite (Fig. 13.6c), which further verified that galvanic interaction happens between Al and graphite substrate in NaOH solution. From the above discussion, it suggests that the status of LM–Al droplet on graphite in this study was determined by two main electrochemical factors: the electrochemical reduction by Al reactions and the

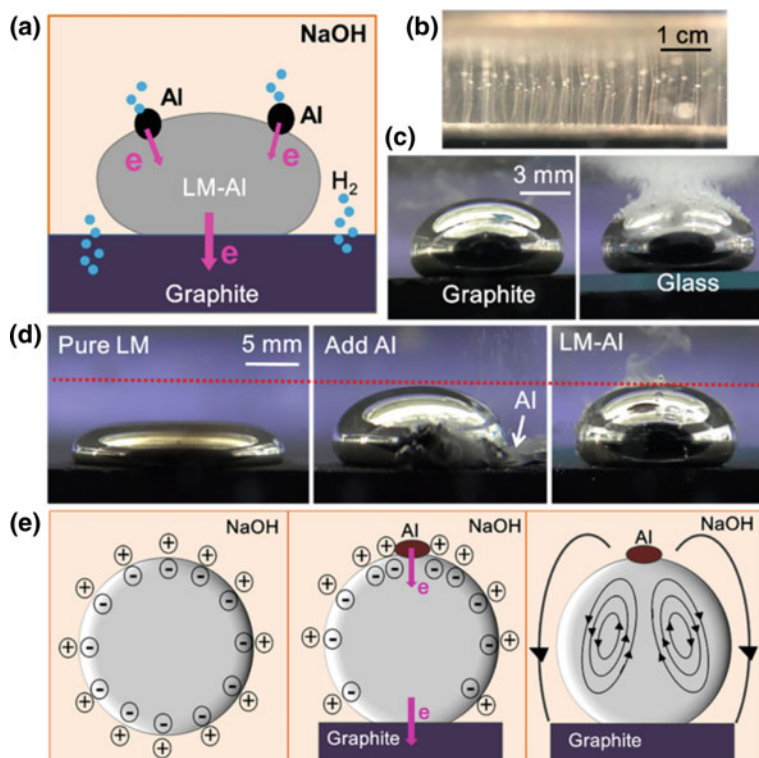


Fig. 13.6 **a** Schematic diagram of the electrochemical interactions among Al, LM, and graphite. **b** Hydrogen was bubbling from the gap of graphite surface. **c** Same LM droplet containing high Al in Case 3 on graphite (left) and glass (right) substrate. **d** Electrochemical Al reaction increased surface tension of LM droplet on graphite. **e** The surface tension gradient on LM–Al droplet induced by electrochemical reaction of Al and the interaction with graphite [26]. All pictures are reproduced with permission

electrochemical oxidation induced by the interaction with graphite. More detailed, the electrochemical oxidation by graphite comprised of two parts: the quick oxidation upon contact through the potential difference across the graphite–NaOH interface and the continuous oxidation through galvanic reaction with Al.

To further investigate and explain these transformations in a more comprehensive and logical way, the phenomenon in Case 3 was examined [26]. Unlike the LM droplet without Al which becomes flat on graphite substrate due to the oxidized layer, the LM–Al droplet in Case 3 generally maintains the surface tension similarly as it was on the insulated substrate (Fig. 13.6c). The bouncing spherical appearance of LM–Al with metallic luster strongly implied that the electrochemical reduction by Al reaction was remarkably more intensive than the oxidation by graphite, which affects the surface tension through inhibiting the formation of oxide layer on droplet. To demonstrate that the Al oxidation would affect the surface tension of LM–Al droplet,

comparative experiments were carried out. A pure LM droplet without Al was placed on graphite initially. Thin oxide layer was formed on its surface, which reduced the surface tension significantly. Then, a piece of Al flake was added into the flattened droplet via forceps. As Al was absorbed gradually, the flattened droplet became obviously contracted (Fig. 13.6d). The previous study on insulated substrate as well as the comparative experiments on graphite substrate confirmed that electrochemical Al reaction could remove the oxide layer on LM droplet and increase its surface tension. When the Al continued to be consumed, the droplet may stop moving around with dark oxide membrane appeared on its surface, which also validated the redox status of LM–Al droplet as described.

Noteworthy, obvious surface vortices were observed with Al granules aggregating on the droplet surface especially when the droplet became a little leaned against the insulated plastic wall (Fig. 13.6b), whose angular velocity could be 24.4 rad/s or even higher [26]. The generation of vortices should be related to the imbalanced pressure difference between electrolyte and LM generated through electrochemically or electrically induced potential gradients across the electric double layer (EDL) of LM droplet [20, 49]. In the present case, Al granules were observed aggregated on the top of the droplet. When the electrochemical reaction of Al went on, the electrons flowing internally from Al to the LM droplet preferentially deoxidized the oxidized LM near Al at the top. At the bottom, the electron flowed from LM to graphite, which enhanced the oxidation of LM near the graphite. Thus the charge across the EDL was altered, which induces an imbalance of potential gradient as well as the surface tension gradient along the droplet (Fig. 13.6e). Here, apart from the electrochemical reaction of Al, the electrochemical reaction with graphite should also contribute to the surface potential imbalance across the EDL of droplet. As a result, intense surface flows as vortices were observed.

Compared with that in Case 3, the LM droplet with less Al content in Case 2 presented a totally different behavior, giving striking external resemblance to amoeba movement [26]. Three stages were divided based on the observational properties in order to better explain the amoeba-like behavior including the body deformation and pseudopodia extension. In the first stage (Stage 1), the round shining LM–Al droplet quickly turned gray pebble upon contact with the graphite in less than 1 s (Fig. 13.7a), suggesting that the quick electrochemical oxidation by graphite dominates the LM droplet. Unlike the thin oxide layer of LM droplet without Al, which was dull but still with metallic color, the oxidized layer on the LM–Al droplet was dark gray with no metallic luster, suggesting that Al oxide may be included in this oxidized metal layer. Besides, bubbles were mostly observed on the gloomy cracks but not on the silver-white LM body, implying that there was certain Al in the oxidized membrane and few Al in the newly exposed LM.

Right after the oxide membrane covered the droplet, local deformations took place and the round shape of LM droplet changed to an irregular one like the amoeba body (Fig. 13.7a, Stage 2). It is speculated that the electrochemical reaction of Al reduced the oxide layer at the LM–NaOH interface (Fig. 13.7b). The oxide membrane was observed to break out with bright LM gushing out, which provides some evidences for this speculation [26]. At the same time, the electrochemical oxidation by graphite

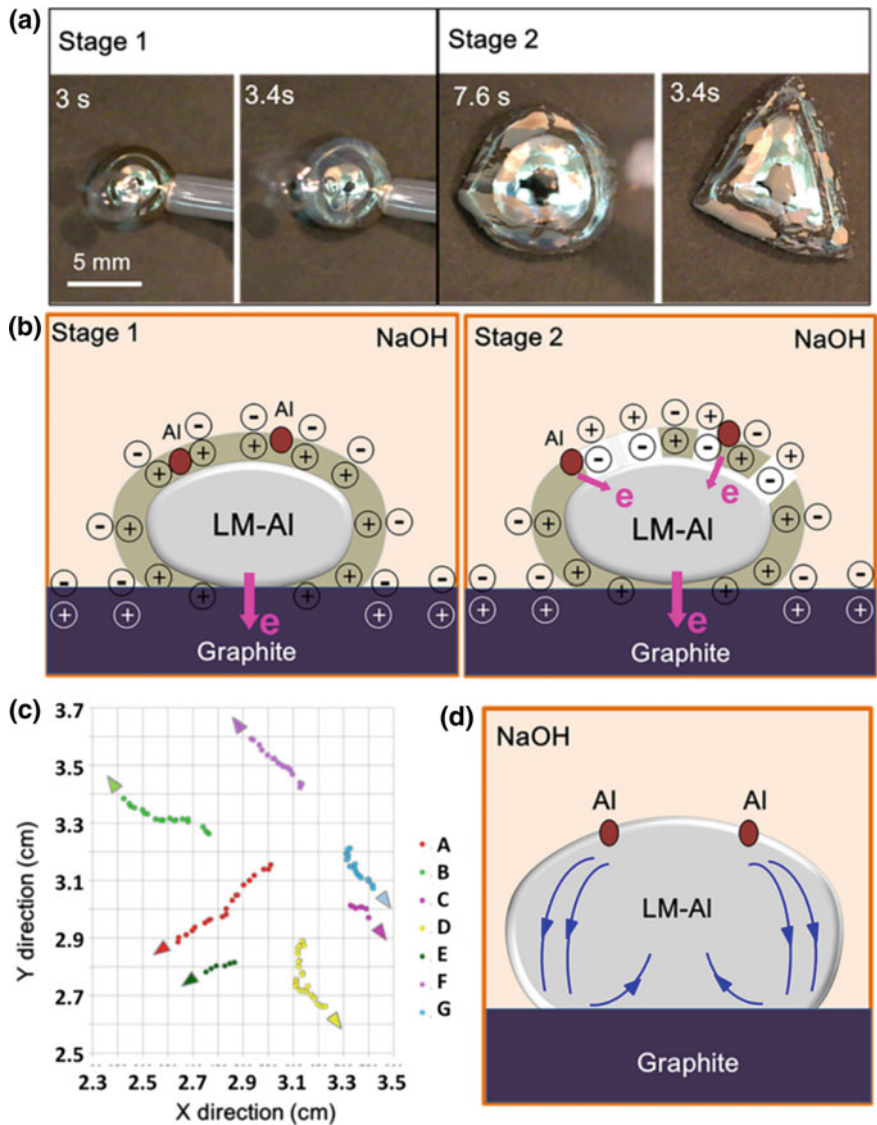


Fig. 13.7 **a** The transformation of LM–Al droplet in stage 1 and 2 in Case 2. **b** The schematic diagrams of the electrochemical status of LM–Al droplet in stage 1 and 2. **c** The trajectory of oxide cracks in Stage 2. The arrows indicate the moving directions of cracks. Each point was taken every 0.2 s. **d** The surface tension gradient generated along the LM–Al droplet which induced the LM flow indicated as the arrows [26]. All pictures are reproduced with permission

also continuously oxidized the newly exposed LM, significantly reducing the surface tension. Thus, it was observed that the oxide surface on the top continuously cracked and dispersed to the periphery as the redox went on. The trajectory of the oxide cracks also confirmed this out-dispersing (Fig. 13.7c). While at the LM–graphite interface, the LM rolled to the bottom, tucking to the central at the bottom, which strongly implies that contact angle between droplet and graphite remained little changed, indicating that the surface tension was almost not changed. Two reasons may be responsible for the little change of surface tension. First, the electrochemical oxidation by graphite through galvanic interaction is likely to maintain the oxide layer of droplet at the bottom. Second, the electrochemical reaction of Al at the LM–graphite interface was rather weak due to lack of electrolyte, which inhibited the reduction of oxide layer. As a result, the surface tension gradient was generated along the top surface to bottom at the LM–NaOH interface (Fig. 13.7d).

In the third stage (Stage 3), slender LM pseudopodia gradually stretched out from the LM amoeba body (Fig. 13.8a). According to the discussion for Case 2, the surface tension gradient induced the LM surface out disperse from top to bottom and tuck to center [26]. Consider the ideal situation in which the Al was evenly distributed on LM droplet and the droplet maintained the round shape in the top view when placed on graphite substrate. The surface tension gradient induced the LM flow from top to bottom, which would push the bottom to the central. If at all directions, the gradient force was equal that to push bottom part to the central, the LM droplet should contract to the central and may form convection under certain status, which may be an analogy to the Rayleigh–Benard convection. However, in real situation, the surface tension around the whole droplet was not uniform due to the imbalanced distribution of Al as well the contact variation with graphite substrate. Based on the Young–Laplace equation $\Delta p = 2\gamma/r$ (r is the radius of the droplet), if there is a position where the surface tension (γ) was lower, the pressure difference between the LM and electrolyte (Δp) was also lower. Thus, the LM at higher pressure difference propels the LM out from the points where the pressure difference was relatively lower, which leads to the initiation of pseudopodia. Notably, these points discussed above were almost close to the three-phase boundary where the pressures were considered horizontal. Thus, gravity was not needed to consider. At the top part of LM–Al droplet, gravity has to be overcome in order to propel the LM, which is apparently more difficult. Thus, the LM should reach out at the points where the surface tension was lower than that nearby at the periphery of droplet.

For the extension of these pseudopodia, the force analysis at the reach out points was made [26]. As the LM reached out at the points where surface tension was lower, it was observed to be continuously stretched out at those points to form long extensions like pseudopodia. It was speculated that the surface tension of those points where LM already reached out and formed corner was also lower than that at the smooth margin. According to Young–Laplace equation, the interfacial tension of curved surface at one side is

$$\Gamma = \Delta p / \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (13.1)$$

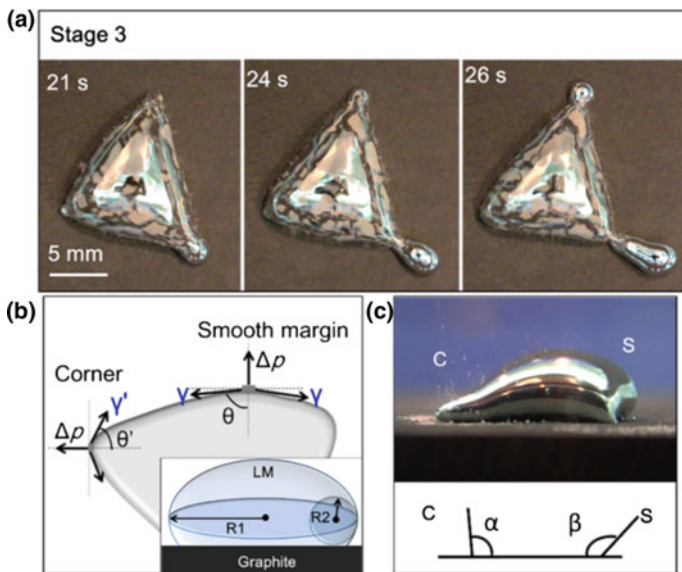


Fig. 13.8 **a** The consecutive snapshots of LM pseudopodia stretching out. **b** The force analysis indicates that the surface tension at corner was lower than that at the smooth margin in the top view. The inset indicates the R_1 and R_2 in an LM droplet on graphite substrate in the horizontal view. **c** The side view image of an LM–Al droplet with pseudopodia. C: Corner; S: Smooth margin. The contact angle at the corner (α) was observed smaller than that (β) at the smooth margin [26]. All pictures are reproduced with permission

where Δp is the pressure difference between the LM droplet and the electrolyte ($\Delta p > 0$), and $1/R_1$ and $1/R_2$ are the principal curvatures for the curved surface at the margin of droplet in the top and horizontal view, respectively (Fig. 13.8b, inset). R_1 is perpendicular to R_2 . For a sessile droplet, R_2 generally maintains approximately the same at the points around the periphery. However, R_1 depends much on the shape of the droplet from the top view. In the deformed droplet in Fig. 13.8b, $\frac{1}{R_1} = \cos \theta$. Thus the interfacial tension can be deduced as

$$\gamma = \Delta p / \left(\frac{1}{R_2} + \cos \theta \right), \quad (13.2)$$

In quasi-steady state, Δp ($\Delta p > 0$) and R_1 are considered equal at every hemisphere on the same horizontal level [26]. At the smooth margin, θ is obviously larger than that at the corner (θ'). Thus, it is deduced that the interfacial tension at the smooth margin γ' is larger than γ such that at the corner ($\gamma' > \gamma$). Thus, the LM was further stretched out at those deformed corners, which formed the slender and long pseudopodia. The side view of an LM–Al droplet with pseudopodia showed that the contact angle between droplet and substrate at the pseudopodia stretched-out corner is obviously smaller than that at the smooth margin (Fig. 13.8c), validating the low

surface tension of droplet at the corner. Thus, it is proved that the LM was more likely to further extend to form slender pseudopodia from the points at the corner.

Based on the above discussion, the phenomenon in Case 1 now became clear. In Case 1, the Al content was much lower in droplet [26]. Thus, gray oxide layer containing much Al oxide was not observed as in Stage 1 in Case 2. Moreover, the surface tension of droplet should be lower than that in Case 2, rendering more deformability of droplet. Thus, it was observed that the LM–Al droplet directly spreads out upon contacting with the graphite substrate (Fig. 13.5a, Case 1) without processing the slowly twisting and cracking Stage 2 in Case 2. The stretched LM pseudopodia should also be caused by the redox-induced surface tension imbalance as described in Case 2. During the transformation in Case 1, LM pseudopodia gradually stretched out, which kept a relatively small contact angle with the graphite substrate similar to that of pseudopodia formed in Case 2 shown in Fig. 13.8c. As a whole, the contact angles of droplet in Case 1 (around 137° data measured from Fig. 13.6c) are larger than that in Case 2 and 3 (pseudopodia side: 96° ; smooth margin side: 136° , data measured from Fig. 13.8c), which is consistent with our conclusion that the surface tension of droplet in Case 3 is generally larger than that in Case 2 and Case 1.

In these heteromorphous transformations of LM–Al droplets over present experiments, the electrochemical reduction by Al reaction and the electrochemical oxidation by graphite were two crucial factors in determining the amoeba behaviors as described above [26]. The LM droplet here had apparently much larger deformation than those caused by other factors such as ionic [49] or surface charge imbalance [20]. Apart from these two integral factors, there are other factors which also influence the transformation significantly. For example, if there was big Al aggregating on the droplet, the bipolar electrochemical reaction of Al would strongly influence the transformation of droplets. Moreover, as the graphite was a loose and porous material, the roughness and surface topography may vary at different places, which should influence the contact angles of LM droplet on graphite and in turn the surface tension of LM droplet at local positions. This finding also suggests the self-adaptive property of such LM amoeba, which has practical values in developing robots for complex environment [50].

In a word, intriguing self-driven amoeba-like transformations of LM–Al droplets can be realized through introducing multi-material system [26]. The fundamental mechanism underlying these LM–Al droplet machine motions has been revealed to be the surface tension variations induced by the synergistic effects of electrochemical reactions of Al and the electrochemical interaction with graphite. This finding, which closely resembles the amoeba biology in nature, would promote peoples' basic understanding of the soft characteristics of liquid gallium alloy machine fueled by Al. Moreover, the revealed multifunctional behaviors of hybrid liquid metal material systems particularly offer new insights for design of future soft devices and bionic robots which should own surprisingly large and diverse shape transformation capability.

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Chapter 14

Chemicals Enabled Liquid Metal Machine



Abstract If well designed, chemicals can help in realizing very complicated liquid metal machine styles. In a large sense, such strategy resembles that of bionics and suggests an important way for the manufacture of soft robots which are not possible otherwise. Among the many different robots, the realization of serpentine locomotion has been a core goal pursued for decades among worldwide researchers. However, there still remains tough challenges in the area due to the complexity of the systems involved. Recently, a straightforward approach was discovered to generate the discretized self-growing and serpentine motion behaviors of liquid metal mollusk based on a new phenomenon observed on liquid metal (LM: $\text{Ga}_{67}\text{In}_{21}\text{Sn}_{12}$) immersed in specific solutions [1]. The dynamic process that liquid metal can automatically produce and move like tremendous slim snakes in acidic copper salt solution was revealed and the underlying mechanisms were clarified and interpreted. It was revealed that the self-growing serpentine locomotion of liquid metal is driven by the localized surface pressure difference related to the surface tension imbalance originating from the numerous tiny Cu–Ga galvanic couples through the electrocapillary mechanism. Particularly, the significant effect of the acids on inducing the continuous serpentine locomotion of liquid metal was disclosed and comparatively evaluated. The discretely self-growing serpentine locomotion of liquid metal induced by copper ions is very different in its dynamics and configurations from the formerly discovered integral large-scale shape transformation of the liquid metal. This chapter illustrates some basic insights and forms in developing future autonomous soft systems and bionic multifunctional robots with complicated capabilities.

Keywords Chemical effect · Self-growing · Serpentine locomotion
Cu–Ga galvanic couple

14.1 About Snake-like Motions of Soft Robots

Conventionally, rigid-bodied robots may encounter the bottleneck of compliance due to their limited adaptability. Soft robots, which can deform their bodies in a continuous way, own the potential to exhibit unprecedented adaptation, sensitivity, and agility with a relatively large number of degrees of freedom [2–5]. In nature, creatures tend to evolve better compatibility with the environment and form a lot of unique and exquisite features. Among them, softness is especially a prominent one. In this sense, biology has been serving as an important source of inspiration for the manufacture of soft robots [6–10]. However, traditional machines and materials are often facing with significant difficulties in achieving even a simple biological motion activity. For example, the snakes, common species, can move quickly through muscle contraction without the assistance of legs. Such free and deformable serpentine locomotion requires fine coordination of the muscles under a complicated mechanism [11, 12], which is still a challenging task for many traditional machines. Although it is of great complexity, the serpentine locomotion has recently attracted numerous attentions in the investigation and development of soft devices [13–15]. Besides, another challenge for developing soft robotics is to realize the functions of self-growing, evolution, and self-recovery through simple methods.

Liquid metal (LM: $\text{Ga}_{67}\text{In}_{21}\text{Sn}_{12}$) owns many distinctive properties which are different from conventional materials [16–18]. A group of fascinating interfacial phenomena of LM systems was kept discovered, such as self-running machines, LM surface convection, self-actuation Cu wire in the LM droplets, etc. [19–22]. Mechanisms lying behind those phenomena are involved in many aspects, including thermodynamic, electrochemistry, or chemical reaction [23, 24]. These rich features enable it to be widely used in a wide range of applications including the soft bionic robot [25], flexible electronics [26–28], 3D metal printing [29, 30], etc. Therefore, the LM, with outstanding versatile capabilities and deformable behavior, is expected to be applied to the future manufacture of soft robots. Until now, the combination of LM and soft robots is in progress [31, 32]. However, many complex motions or mechanisms of a soft robot still remain to be revealed on LM.

Chen et al.'s work [1] observed the phenomenon of self-growing and serpentine locomotion of LM in the acidic copper sulfate (CuSO_4) solution was first discovered. It revealed that the LM immersed in the acidic CuSO_4 solution will spontaneously generate tremendous discrete slim protrusions. Such slim protrusions continuously grow and move like a snake until all the LM is dispersed into thin strips. More intriguingly, the speed of the self-growing and serpentine locomotion can be controlled by the acid strength and the dynamic process can be induced many times. The serpentine locomotion is driven by the surface pressure difference which is related to the surface tension imbalance, curvature, and acidity. The phenomenon of self-growing serpentine locomotion of LM provides a straightforward method to realize snake-like movement, which is expected to generate a positive impact on the coming soft robot field.

14.2 Approaches to Realize and Characterize Serpentine Liquid Metal Machine

Over the current experiments, the LM used were $\text{Ga}_{67}\text{In}_{21}\text{Sn}_{12}$, which were prepared by stirring and heating gallium (Ga, 67wt%, 99.99% purity), indium (In, 21wt%, 99.99% purity), and tin (Sn, 12wt%, 99.99% purity) together to 150 °C for 2 h until metal alloy is formed. Here, a magnetic stirrer was applied to stir the mixture uniformly [1]. HCl solutions with different pH concentrations were prepared with concentrated hydrochloric acid and diluted water. Similarly, CuSO_4 solutions were prepared with anhydrous copper sulfate crystals and distilled water. They were all purchased from Beijing Lan Yi Chemical Products Limited Liability Company (Beijing, China). The mass concentrations of HCl solution and CuSO_4 solution used in this experiment were 10 and 18%, respectively. All the experiments were conducted at room temperature (about 20 °C).

The imaging data of the self-growing and serpentine locomotion during the experiments was recorded by the Sony Digital Video (FDR-AX40). The concentration of ions in the solution was tested by means of the inductive-coupled plasma emission spectrometer (ICP; Varian725-ES). The electric potential V of the LM was measured by a millivolt voltmeter with one electrode (copper wire) inserted in the LM marble and the reference electrode (SCE: Saturated calomel electrode) in the solution. The micromorphology of the LM was observed by means of scanning electron microscopy (SEM; S-4800, Hitachi, Ltd.). After the end of the reaction, the element distributions of LM were evaluated by using energy dispersive spectrometry (EDS; 6853-H, HORIBA, Ltd.).

14.3 Basics of Serpentine Locomotion

According to the principle of surface energy minimum, LM marbles tend to form an ellipsoid due to the largest surface tension of any known room-temperature fluid [1]. However, LM marbles immersed in acidic CuSO_4 solution will generate tremendous discrete snake-like extensions (pseudopodia) spontaneously (Fig. 14.1). These pseudopodia continued to grow just like slim snakes until the entire LM marble was consumed and became a lot of dendritic strips (Fig. 14.1c). Given these characteristics, such phenomenon was named as the self-growing serpentine locomotion of LM induced by copper ions. More intriguingly, through measuring the total length of the extended pseudopodia (Fig. 14.1d), it was found that the movement speed of the serpentine locomotion under more-acid condition is about ten times faster than that of the less-acid case (Fig. 14.1c), which means that the velocities of serpentine locomotion can be regulated by adding different amounts of acid. A detailed dynamic process of liquid metal serpentine locomotion can be found at Fig. 14.2.

This self-growing serpentine locomotion phenomenon refers to a complex multi-material system including LM, HCl and CuSO_4 solution. Interface reactions that

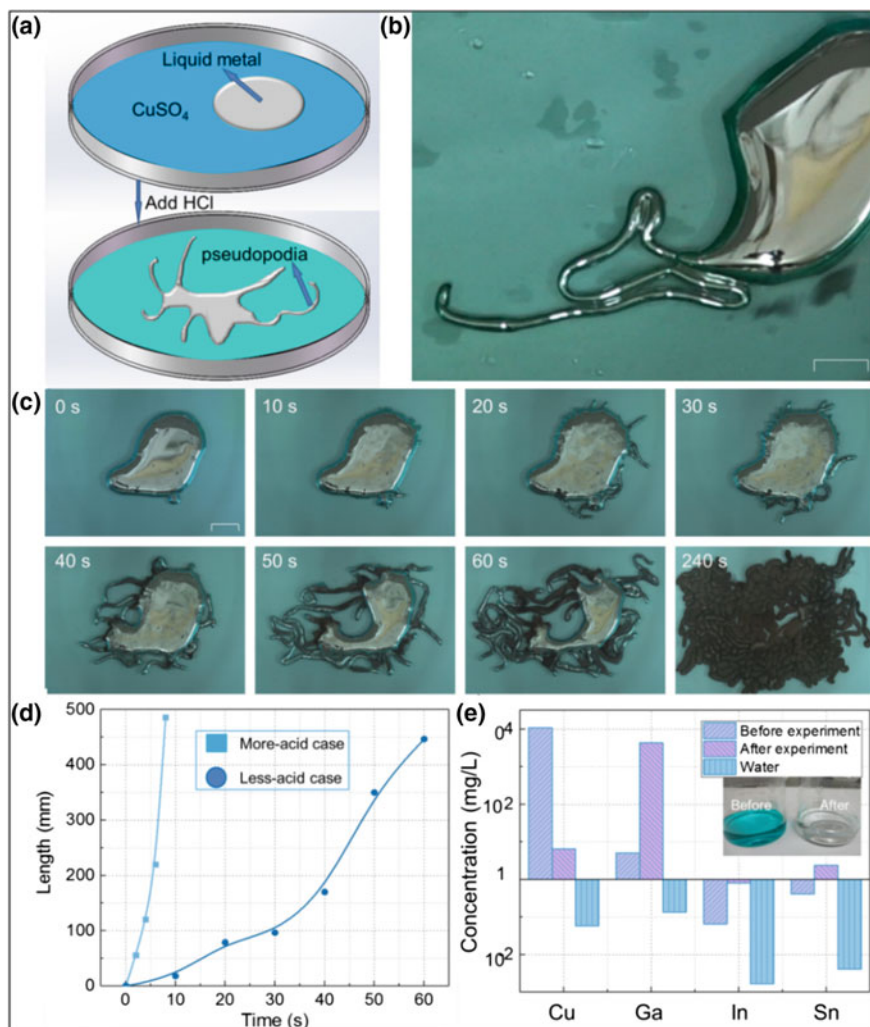


Fig. 14.1 **a** Schematic illustration of the experiment. **b** A bird view of the snake-like protruding pseudopodia. **c** Time-lapse images of the phenomenon of the discrete serpentine locomotion. **d** A graph of the length of all pseudopodia over time. Here, more-acid case refers to a 1:2 volumetric ratio of HCl (20 ml) to CuSO_4 (40 ml), less-acid case refers to a 1:4 volumetric ratio of HCl (15 ml) to CuSO_4 (60 ml). The amount of LM is 5 ml. **e** Analysis of the concentration of various elements (Cu, Ga, In, and Sn) in the solution before and after the experiment. Scale bars, 10 mm [1]. All pictures are reproduced with permission

occur on the LM surface are vital for understanding the complex serpentine locomotion [1]. It was observed clearly that particles appeared in the interface between the LM marble and the solution during the experiments (Fig. 14.1c), which was inferred as copper particles. From the previous literature, one can see that the electronegativity

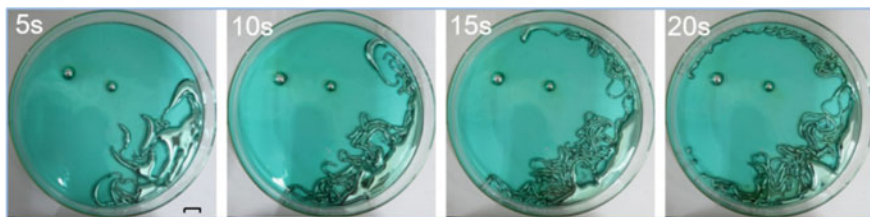
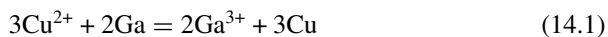


Fig. 14.2 Time-lapse images showing the serpentine locomotion of the LM marble in the strong acid ambient. Scale bars, 10 mm [1]. All pictures are reproduced with permission

of gallium is weaker than that of the copper [33], which means gallium has stronger reducibility than copper and the displacement reaction will occur in the interface between copper and gallium, leading to the precipitation of copper particles on the LM surface. This replacement reaction is described as follows:



In order to confirm the occurrence of replacement reaction between gallium and copper, inductive-coupled plasma emission spectrometer (ICP) test that focuses on the analysis of elemental concentrations was utilized [1]. As is shown in Fig. 14.1e, the solution contained a large number of copper elements (10,953 mg/L) before the start of the serpentine locomotion. After the end of serpentine locomotion, the solution contained a large amount of gallium (4323.6 mg/L) and a small amount of copper (6.5 mg/L), as well as a very small amount of indium (0.79 mg/L) and tin (2.38 mg/L). The test results show that copper element are consumed and a large amount of gallium element is produced during the dynamic process, which indicates that the replacement reaction occurs between the gallium and the copper.

14.4 Surface Tension Imbalance Originating from the Cu–Ga Galvanic Couples

Generally, interfacial tensions arise between two different phases. The LM marble placed in CuSO_4 solution will be affected by surface tension of the three contacting phases, i.e., the LM (phase 1), the CuSO_4 solution (phase 2), and the glass (phase 3), as illustrated in Fig. 14.3a. Geometrically, according to Young's equation [34], the relationship between surface tension is as follows:

$$\gamma^{23} = \gamma^{13} + \gamma^{12} \cos \theta \quad (14.2)$$

where γ^{12} , γ^{13} , and γ^{23} are, respectively, the surface tension between phase 1/phase 2, phase 1/phase 3, and phase 2/phase 3. The change of surface tension will stimulate the movement of LM marble to satisfy surface tension balance.

Therefore, the variation of surface tension plays an important role in the current study of the LM interface. LM marbles immersed in the CuSO_4 solution were dominated by surface tension related to the solution properties. With the addition of HCl solution, changes in surface tension will break up this balance, resulting in movement and deformation of the liquid metal (Fig. 14.3a). At the same time, a new ion with green color ($[\text{CuCl}_4]^{2-}$) formed, which is responsible for the change of the solution color from blue to green (Fig. 14.3b). In such a solution environment, copper particles were precipitated from the solution and appeared on the surface of the LM marble [1].

Clearly, Cu particles accumulated on the LM surface and formed galvanic cells with the Ga, which influenced the charge distribution over the droplet [1]. According to the different potential, it is deduced that Ga loses electrons ($\text{Ga} - 3\text{e}^- = \text{Ga}^{3+}$) in the system. Then electrons outflow to the solution through the Cu particles, as illustrated in Fig. 14.3b. At the Cu anode, hydrogen ion (H^+) receives those electrons

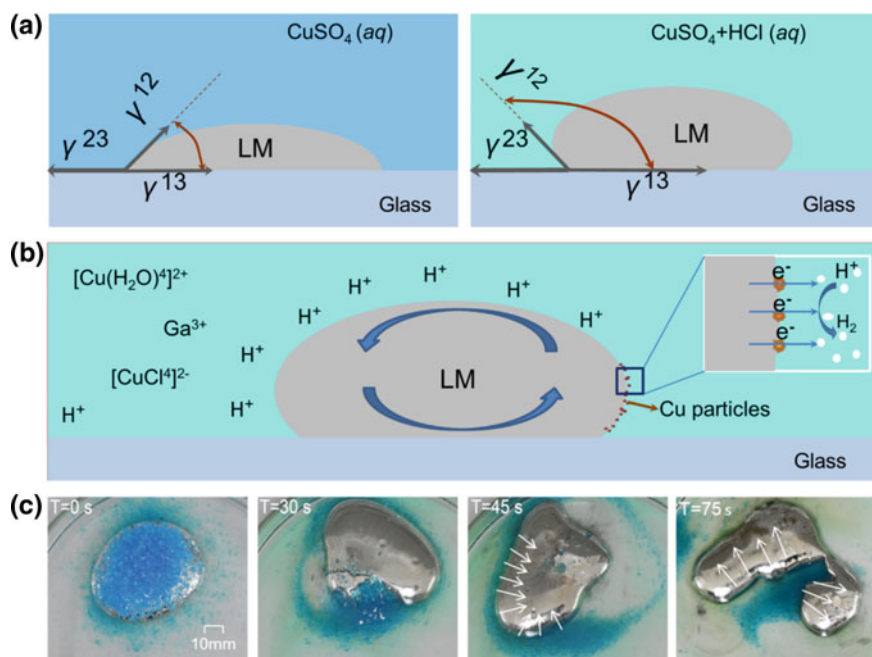


Fig. 14.3 **a** Schematic of the surface tension of the LM marble in CuSO_4 solution and acidic CuSO_4 solution. **b** Diagram of Cu–Ga galvanic cell and the direction of surface convection of the LM marble. **c** Time-lapse images of the surface convection of the LM marble induced by CuSO_4 granules. The direction of LM surface flow is indicated by an array of white arrows [1]. All pictures are reproduced with permission

and hydrogen is produced ($2\text{H}^+ + 2\text{e}^- = \text{H}_2\uparrow$). Bubbles were observed to come out from the LM marble, which supported the explanation of galvanic interaction taking place on the interface between the LM marble and the CuSO_4 solution. The surface potential altered due to the formation of the primary cell, resulting in the appearance of the surface tension gradient. It induced surface flow due to the Marangoni effects (Fig. 14.3b), which were also observed in other studies [35, 36]. More specifically, the flow induced by the surface tension imbalance was initiated from the interfacial region with lower surface tension towards the region with higher surface tension.

Another experiment was carried out to better explain the role played by divalent copper ions (Cu^{2+}) and the direction of convection caused by Cu–Ga galvanic couples (Fig. 14.3c) [1]. LM marble placed in acid ambient kept stable until CuSO_4 particles were added into the surface of the LM marble. After several seconds, the convection of LM marble took place, which illustrated that Cu^{2+} can induce the convection of LM marble. Beyond that, a black substance appeared in the solution which belongs to the oxide of the LM oxidized by divalent copper ion (Cu^{2+}). It can be observed clearly that the surface flow of LM marble began in the low surface tension region where the LM marble contacted CuSO_4 particles and ended in the high surface tension region, eventually forming a convective circulation (Fig. 14.3c), which is consistent with analysis. During the dynamic process of serpentine locomotion, the direction of LM surface flow has also been pointed out (Fig. 14.4).

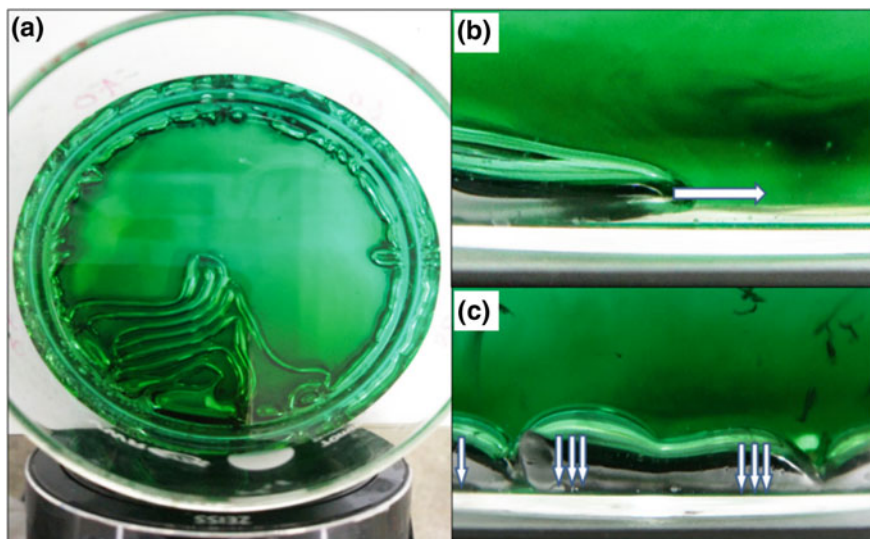


Fig. 14.4 **a** Experimental setups for filming the side. **b** A side view of the direction of serpentine locomotion. **c** A side view of the direction of surface convection of liquid metal. Here, white arrows indicate the direction of movement [1]. All pictures are reproduced with permission

14.5 Factors to Affect Serpentine Locomotion of Liquid Metal Machine

Surface potential The electric double layer (EDL) will form when the LM is placed in the solution due to the inherent properties of matter, which can be modeled as a charged capacitor. Based on the Lippmann's equation [37], the surface tension is related to the voltage of the EDL. Lippmann's equation is as follows:

$$\gamma = \gamma_0 - \frac{1}{2}CU^2 \quad (14.3)$$

where γ_0 is the original surface tension of the LM marble, C and U are the capacitance and voltage across the EDL. The change of U will greatly alter the surface tension of the LM marble, leading to significant influence on the shape of LM marble. Therefore, modifying the LM behavior by adjusting the EDL is completely practicable. Through the previous analysis, we can get such a conclusion that the surface tension imbalance is related to the change of surface potential originating from the form of Cu–Ga galvanic cell, which is a vital reason for the self-growing serpentine locomotion. To better describe the surface potential quantitatively, the surface electrode potential of LM marble was measured by a millivolt voltmeter (against a saturated calomel electrode, SCE) during the self-growing serpentine locomotion (Fig. 14.5a). The schematic setup of the LM marble surface electric potential test is illustrated in Fig. 14.5b. Here, the volume ratio of HCl to CuSO₄ is prescribed as 1:4.

It can be obtained clearly that the surface electrode potential of LM marble showed a shift from about 0 to -0.15 V when serpentine locomotion was induced [1]. The surface potential of the LM marble placed in CuSO₄ solution was nearly 0 V due to the oxidized surface and it became -0.15 V instantly with the adding of HCl solution. Meanwhile, LM pseudopodia stretched from the marble spontaneously and moved like a slim snake. As the serpentine locomotion of LM ceased, the surface potential returned to near 0 V, which shows that there is a good correspondence between the surface potential and the motion behavior of the LM marble. The measurement of the surface potential clearly points out the change of surface potential (V), which also corresponds to the dramatic altering of the surface tension (γ) according to the Lippmann's equation.

Influence of curvature on serpentine locomotion. From the above discussion, it can be understood that the LM convection and serpentine locomotion is induced by surface pressure difference related to the unbalanced surface tension originating from the Cu–Ga primary cell through the electrocapillary effect [1]. According to the Yang–Laplace equation, [38] the pressure difference between electrolyte and LM can be described as follows:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (14.4)$$

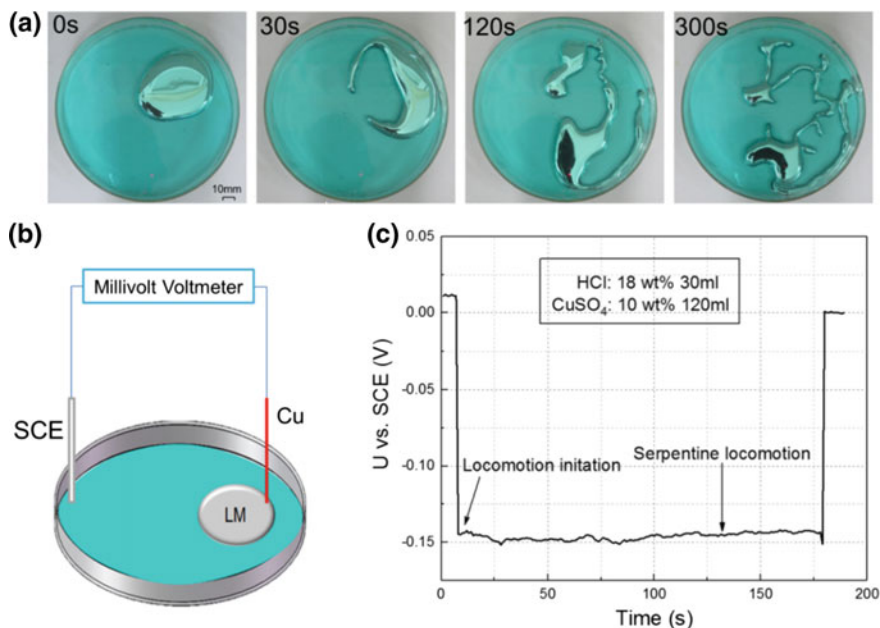


Fig. 14.5 **a** Time-lapse images showing the serpentine locomotion of the LM marble. **b** Schematic setups of the LM marble electric potential test. **c** Electric potential V of the LM marble during the dynamic process [1]. All pictures are reproduced with permission

where R_1 and R_2 are the principal radii of curvature at the interface, respectively. The surface pressure difference is related to the LM surface tension and surface curvature. Therefore, the curvature is another important factor affecting the surface pressure difference, which is also verified by our measurement. Experimental results show that the serpentine locomotion took place easily when the LM marble leaned against the wall of the dish (Fig. 14.6a), which illustrates that the protruding of pseudopodia is related to the surface curvature of the LM marble. In order to better expound on the effect of curvature, the force analysis is adopted (Fig. 14.6c).

The LM was in the quasi-steady state when the serpentine locomotion was going to take place. At the smooth region, θ' was obviously larger than that at the corner (θ), resulting in $\cos \theta' < \cos \theta$. Thus, it was deduced that the surface pressure difference at the smooth margin (Δp_c) was smaller than that at the corner (Δp_s) based on Yang-Laplace equation (Eq. 14.3). In other words, the corners which own large surface curvature are driven by a greater pressure difference. Thus, the serpentine locomotion took place easily at those deformed corners, which further formed the slender and long pseudopodia. Artificially induced curvature can also stimulate the spontaneous serpentine movement, which further proved the reasonableness of the curvature analysis (see Fig. 14.6d). In a conclusion, the difference in curvature also has a great influence on the serpentine motion, which was consistent with the results of our analysis based on the Yang-Laplace equation.

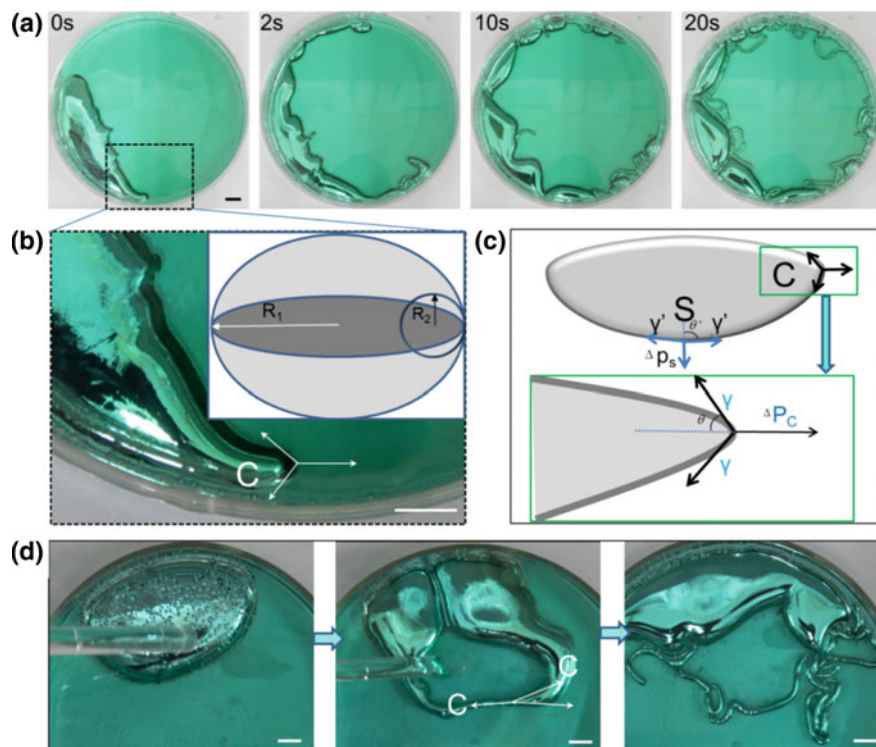


Fig. 14.6 **a** Time-lapse images showing the serpentine locomotion of the LM marble owning the large curvature. **b** Selected enlarged images showing the corner. **c** The force analysis of the LM marble placed in the acid copper solution. Here, the γ represents the surface tension of LM, Δp indicates surface pressure difference. C means corner, S refers to smooth region. R_1 and R_2 are the principal radii of curvature at the interface, respectively. **d** Artificially formed curvature excites serpentine locomotion [1]. All pictures are reproduced with permission

By now, a general deformation picture of the self-growing serpentine locomotion can be interpreted as follows [1]: the precipitated Cu particles induce large surface tension gradient through the electrocapillary mechanism. The surface tension imbalance breaks the equilibrium of the system and initiates hydrodynamic flow. The intense change of the surface tension and different surface curvature cause the pressure difference between the LM and the solution, resulting in asymmetric deformation. Asymmetrical deformation continues to develop and eventually becomes tremendous discrete slim pseudopodia.

Particle internalization Besides, in order to achieve continuous serpentine locomotion, particle internalization between LM and Cu particles precipitated from the acidic solution (LM-phagocytosis effect) also plays crucial roles in LM serpentine locomotion [1]. Particles internalization means precipitated Cu particles will be swallowed by the LM marble in the acidic solution [39], which can be observed clearly

on the surface of the LM marble immersed in the acidic copper sulfate solution. The continuously precipitated Cu particles were constantly swallowed by the LM marble. The two processes maintained the dynamic balance between the precipitation of Cu and LM-phagocytosis resulting in continuous serpentine movement.

After the end of serpentine locomotion, surface morphology and the composition of LM marble were analyzed through the scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). It was found [1] that there were many small particles inside the LM after swallowing copper particles (Fig. 14.7a). The elemental analysis of regions I and II showed that the small particles in the interior are Cu (Fig. 14.5b, d), which indicates that precipitated Cu particles are successfully swallowed by the LM marble. Finally, the copper–gallium alloy (CuGa_2) will be formed after the end of self-growing serpentine locomotion. Such CuGa_2 own excellent wetting properties and application prospects, which has been investigated by former researchers [40, 41].

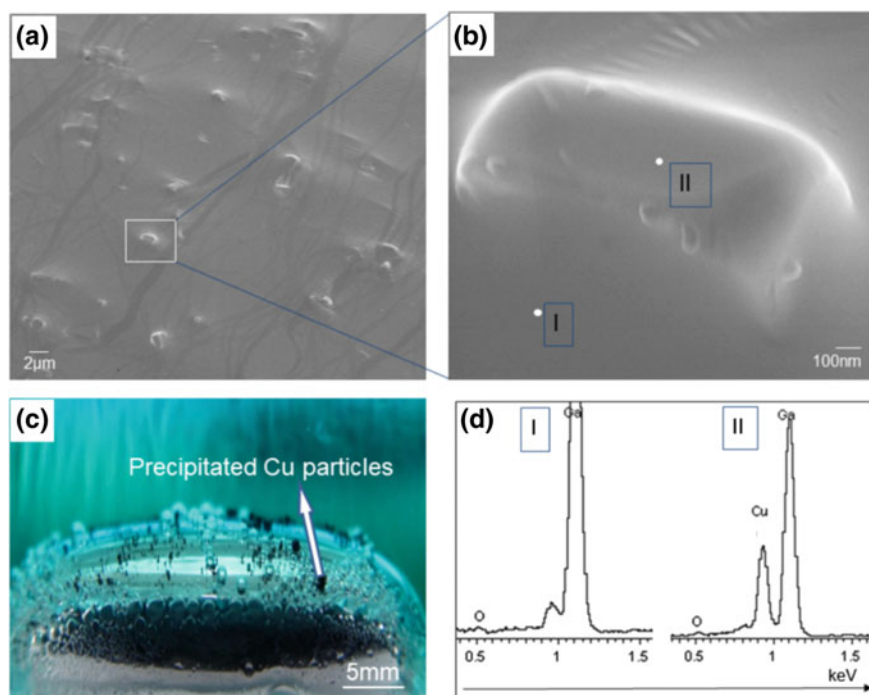


Fig. 14.7 **a** Scanning electron microscope (SEM) image of the LM marble after swallowing copper particles. **b** Higher magnification of the SEM image. **c** Precipitated copper particles were swallowed on the surface of LM marble. **d** Composition analysis of LM marble after the end of serpentine locomotion through energy dispersive spectrometer (EDS). Scale bars, 10 mm [1]. All pictures are reproduced with permission

Effect of acid on serpentine locomotion The discrete serpentine locomotion took place with the addition of HCl, which leads us to think about the role of acids. It was established that an oxide layer will appear on the LM surface when it is exposed in air [42]. Similarly, an oxide layer can be found on the LM surface when the LM was added into the CuSO_4 solution (Fig. 14.8). The oxide layer will significantly reduce the surface tension of LM and restrict its ability to deform [43]. Therefore, it is necessary for the serpentine locomotion to break down the oxide layers. Here, the oxide layer can be dissolved by HCl, which is responsible for the observed shape transition and allow LM to maintain a large surface tension.

In order to better illustrate the role of acid, comparative experiments were implemented in the acid-free condition [1]. It can be observed that the LM presented a flattened shape due to the oxidized surface and copper tree appeared on the LM surface due to the accumulation of precipitated copper particles (Fig. 14.9). The

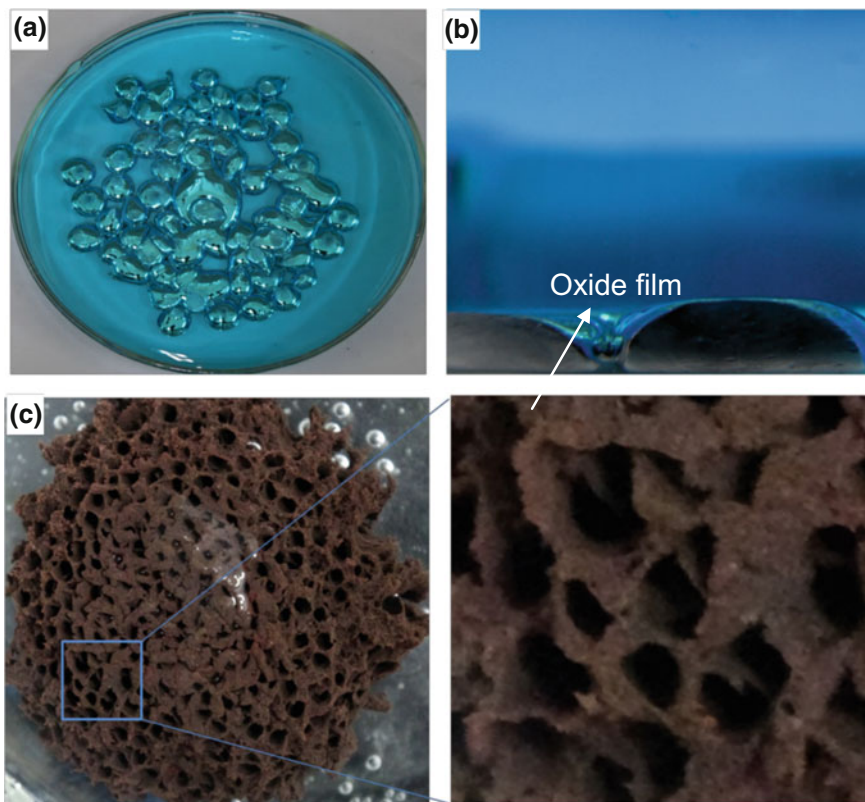


Fig. 14.8 **a** A bird view image of the pie-shaped liquid metal in CuSO_4 solution. **b** A side view image of liquid metal with an oxide film in CuSO_4 solution. **c** Reticulate copper tree appeared on the liquid metal surface in the absence of acid [1]. All pictures are reproduced with permission

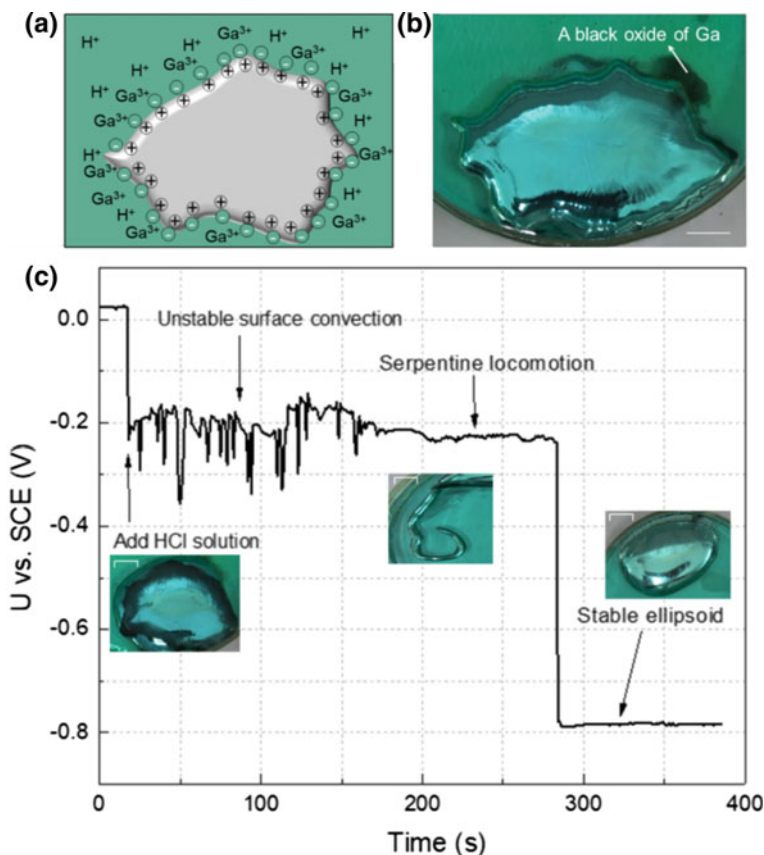


Fig. 14.9 **a** Schematic diagram of the EDL of LM marble in the case of more acid. **b** A bird view of LM marble in unstable surface convection. **c** Electric potential U of the LM marble during the dynamics process. Scale bars, 10 mm [1]. All pictures are reproduced with permission

serpentine locomotion no longer took place in the acid-free condition, which means that acidity is a prerequisite for this phenomenon.

Another experiment was conducted to explore the effect of acid amount on the LM deformation [1]. Compared to the previous experiment, more acids were used in this experiment. Concretely, the volume ratio of HCl to CuSO₄ is 1:1.8. Different from the previous phenomenon that serpentine locomotion occurred immediately with the addition of acid, LM marble convection appeared first when the acid was added in the case of more acid. In the stage of unstable surface convection, the LM marble tended to extend LM pseudopodia (Fig. 14.9b). Then, the serpentine locomotion appeared and stretched quickly. It can be seen that there exist a transition from convection to serpentine locomotion (see the Fig. 14.10). Eventually, the LM marble regained ellipsoid shape due to the strong acidity, which was different from the case of less acid. In the case of less acid, the LM marble was eventually covered by precipitated

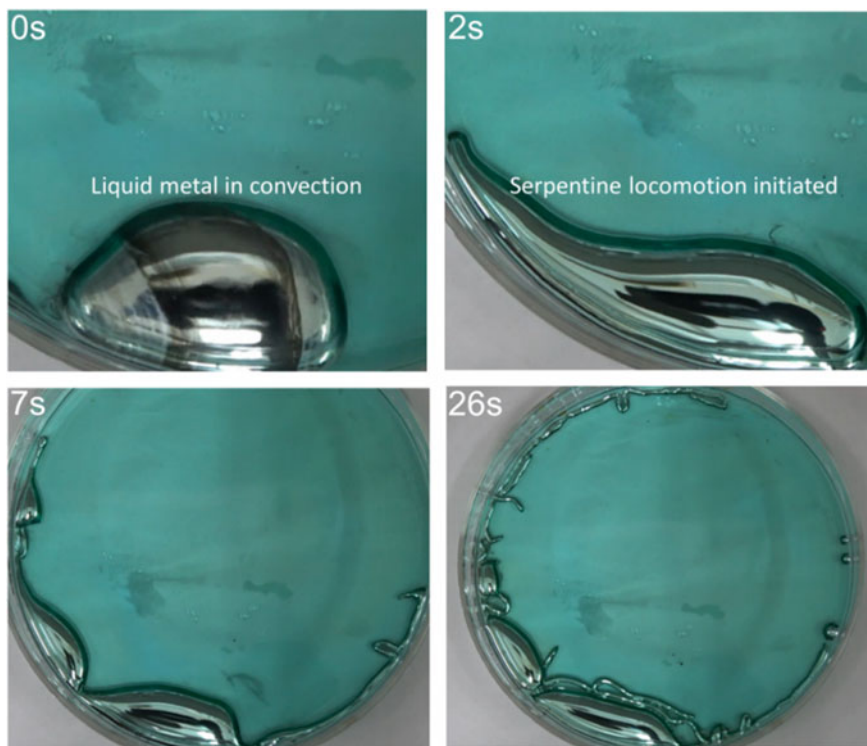


Fig. 14.10 The transition from convection to serpentine locomotion [1]. All pictures are reproduced with permission

Cu instead of returning to ellipsoid. To more accurately reveal the effect of acid on serpentine locomotion, the LM surface potential under the case of more acid has also been tested.

The measurement of the surface electrode potential, in this case, was also carried out [1] using the same method as before, the results are illustrated in Fig. 14.9c. Coinciding with the observed experimental phenomena, it can be divided into three stages. During the process of unsteady convection, the waveform of the surface electric potential presented a serrated shape and fluctuated around -0.2 V. Then, the surface electric potential was stable (about -0.23 V) while serpentine locomotion took place, which was different from the previous test data (about -0.15 V) under the condition of less acid. Eventually, the LM marble regained ellipsoid shape with a stable surface electric potential (-0.8 V). As a result, different acidity greatly affects the surface potential of the LM, resulting in a different surface tension gradient.

With the increasing acidity (the volumetric ratio of HCl and CuSO_4 is greater than 1–1.8), it is more difficult to convert surface convection into serpentine locomotion due to the damping effect of LM under the surface of the layer of Ga salts [1]. As is shown in the Fig. 14.9a, the electrical double layer (EDL) is largely influenced

by the ions in the solution. In strong acid solution, tremendous gallium ions (Ga^{3+}) originating from the displacement reaction gather in the surface of the LM marble, resulting in the form of layer of Ga salts, altering the surface potential and hindering the further deformation. Conversely, the layer of Ga salts easily breaks down to allow the large deformation of the LM in the case of less acid.

To sum up, acidic solutions not only allow LM to maintain a large surface tension by dissolving the surface oxide layer, but also provide the appropriate environment for LM to swallow the precipitated copper particles [1]. Besides, the speed of the self-growing and serpentine locomotion can be controlled by acid strength. However, the serpentine locomotion has not been successfully stimulated due to the limitation of the surface layer under the case of too strong acid or too weak acid. Hence, the appropriate acidic solution is indispensable in the self-growing serpentine locomotion.

From the above interpretations, one can know that copper granules are precipitated on the surface of LM due to the potential difference between copper and gallium [1]. Such granules can form countless tiny Cu–Ga galvanic cell and alter the surface tension of LM, leading to the unbalanced surface pressure difference, which is the main reason of serpentine locomotion. Besides, curvature, LM-phagocytosis effect, and acidity all own a large effect on serpentine locomotion.

The last thing to explain is that the self-growing serpentine locomotion can be triggered many times after the end of the movement. The triggering methods include not only the artificial curvature but also the addition of copper ions (see the Fig. 14.11).

The serpentine locomotion set forth herein stems from the imbalance of surface tension [1]. It is superb if the surface tension of the LM in motion can be known in real time. However, the measurement of surface tension is based on the principle of force balance, which makes it difficult to test in time the surface tension of moving LM. Even so, one can still obtain the relative magnitude of surface tension through the observation of contact angles. The salt solution used here is CuSO_4 solution and it should be noted that other copper salt solution (such as CuCl_2) can also achieve the same effect, which is verified by related experiments.

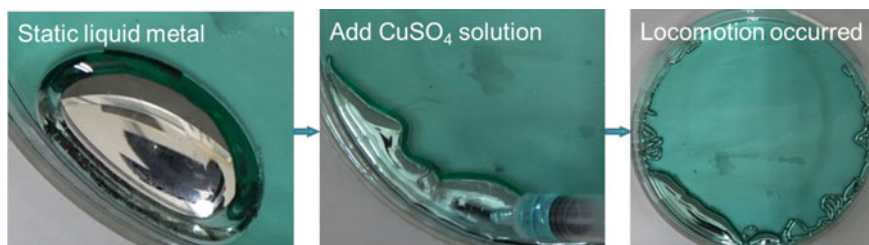


Fig. 14.11 The addition of copper ions once again excites serpentine movement [1]. All pictures are reproduced with permission

14.6 Conclusion

In summary, driven by the surface pressure difference originating from surface tension imbalance, discrete self-growing and serpentine locomotion of LM can be induced. This refreshes the basic physical and chemical effects of LM and advances the understanding of electricocapillary effect. LM which reacts with copper ions can be considered as a smart soft matter. It provides new insight into further exploration and has an important application value in many fields such as ionic smart response sensors, self-growing LM circuit, autonomous soft systems, etc. Moreover, the finding on self-growing serpentine locomotion induced by copper ions provides a completely novel strategy to achieve the bionic serpentine locomotion, which has vital values in developing future potential soft bionic LM robots, especially those multifunctional and deformable robots which own the ability to self-grow, evolve, and self-recovery.

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Chapter 15

Hybrid Liquid Metal Machine



Abstract Clearly, liquid metal alone cannot solve everything. However, if combining with other materials or structures, liquid metal would aid to make complicated system, which is not possible otherwise. This chapter illustrates a typical way to fabricate a kind of oscillating system made of hybrid liquid metal and rigid needle. As is known to all, oscillation is a widely seen dynamic phenomenon (Jenkins in *Phys Rep* 525:167–222, 2013 [1]; Cross and Hohenberg in *Rev Mod Phys* 65:851–1112, 1993 [2]; Pikovsky and Kurths in *Phys Rev Lett* 78:775–778, 1997 [3]) in mechanical (Hendricks in *Science* 3:775–776, 1884 [4]), electrical (Tesla in *Proc IEEE* 87(7):1282, 1999 [5]), biological (Aschoff in *Science* 148:1427–1432, 1965 [6]), chemical (Petrov et al. in *Nature* 388:655–657, 1997 [7]) systems, etc. Oscillatory chemical reactions such as Belousov–Zhabotinsky (BZ) reaction (Petrov et al. in *Nature* 361:240–243, 1993 [8]), mercury beating heart (Lin et al. in *Proc Natl Acad Sci U S A* 71:4477–4481, 1974 [9]) are classical examples of nonequilibrium thermodynamics switching between different patterns. This lab (Yuan et al. *Adv Sci* 3:1600212, 2016 [10]) found the first ever oscillation phenomenon of a copper wire embraced inside the liquid metal machine via chemical and mechanical coupling. Previously, it was revealed that gallium-based liquid metal owns rather important value to serve as shape transformable material (Zhang et al. in *Adv Mater* 27:2648–2655, 2015 [11]; Sheng et al. *Adv Mater* 26:5889–5889, 2014 [12]) due to its unique property of high electrical conductivity, excellent fluidity, and low melting point. In addition, feeding the liquid metal with aluminum would lead to self-powered motors which could keep long-term actuation performance in alkaline solution (Zhang et al. in *Adv Mater* 27:2648–2655, 2015 [11]) due to surface tension gradient and H_2 propulsion mechanism. The study discovered even more unusual effects that apart from self-actuation, such liquid metal machine would trigger a copper wire to reciprocally move back and forth across the liquid metal body. When contacting a copper wire to the liquid metal motor, it will be wetted and swallowed and then oscillates horizontally like a violin bow at the frequency of about 1.2 Hz. Moreover, the oscillation could be easily regulated and speeded up by touching a steel needle on the liquid metal motor surface. This fundamental phenomenon can be explained by the wetting behavior difference due to chemical reaction. Given appropriate designing, such autonomous oscillator composed of hybrid solid and

liquid metal structures can be developed as a core switch element in periodically regulating devices to realize various particular fluidic, electrical, mechanical, and optical functions. The present finding refreshes the basic understanding of the soft machines commonly conceived in textbook as well as add new knowledge to the wetting science (Gennes et al. in *Phys Today* 57:66–67, 2004 [13]). It also opens a basic way to fabricate self-powered wire oscillator using liquid metal as the main machine body. Further, through combining with other external material, substrate, and environmental factors, more hybrid liquid metal machines can still be made. Some of such typical strategies will be discussed thereafter.

Keywords Hybrid liquid metal machine · Wire oscillation · Resonance · Wetting

15.1 Oscillation Behavior of Copper Wire in Liquid Metal Machine

To make hybrid machine, the liquid metal containing aluminum granules was placed in a rubber O-ring (diameter 10.6 mm) to avoid self-motion [10]. A copper wire (length 20 mm, diameter 0.19 mm) inserted inside the liquid metal oscillated horizontally from side to side (Fig. 15.1). The oscillation motion could last for about half an hour. The whole system was immersed in aqueous NaOH solution (0.5 M). Hydrogen was mainly generated from the bottom of the liquid metal [14] and the copper wire surface contacting the solution (Fig. 15.1a, b). The H_2 generation on copper wire surface was mainly from Al granules deposited on wire surface when it went through liquid metal. It can be proved by the fact that when the copper wire was pulled out of the liquid metal, the surface still kept producing H_2 for about two minutes (Fig. 15.2). Particularly, the middle part of the wire produced H_2 for a longer time since it was embedded inside the liquid metal all the time with almost no Al consumption. This process resembled the monolayer deposition as found before [15]. Apart from the copper wire, a group of comparative experiments was also carried out to test whether more metal wires can work as the oscillator candidates. Particularly, Ni, Ti, Ag, and steel wires were investigated. However, as indicated by the experiments, the liquid metal could not wet Ni, Ti, and steel wires, while Al granules would not attach on the Ag wire surface. Therefore, all these tested three wires were not suitable for making oscillating machine although more other materials can be tried in the near future. For brief, only copper wire machine will be focused here. According to the experiments, after the copper wire moved to one edge of the liquid metal machine, it would stay there for a while before moving back to the other edge. The period of the oscillation was about 0.8 s. The phase portrait of the oscillation is shown in Fig. 15.3, which resembled the harmonic oscillation.

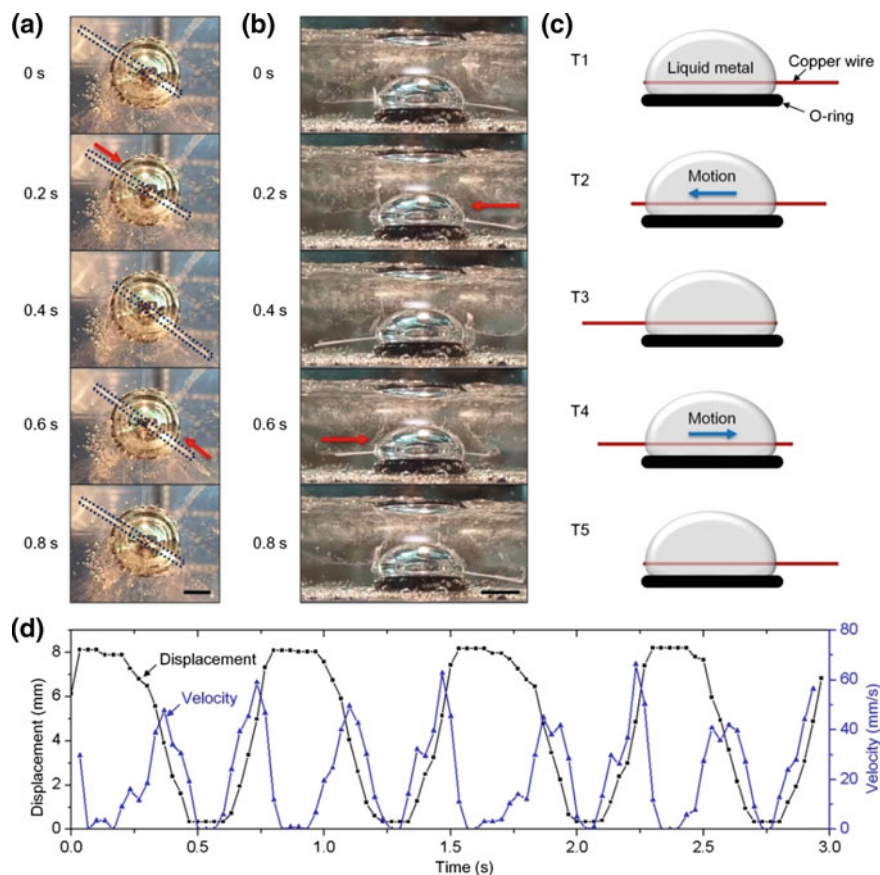


Fig. 15.1 Oscillation behavior of copper wire in liquid metal machine [10]. **a** Top-down view (scale bar, 5 mm). **b** Side view (scale bar, 5 mm). **c** Position of the copper wire during one period. **d** Time evolution of the copper wire during 3 s. All pictures are reproduced with permission

15.2 Quantifying the Oscillation Behavior of Hybrid Liquid Metal Machine

Fabrication of the liquid metal motor was similar with previous work [14]. Liquid metal GaIn_{10} (10 wt% In) was injected onto a piece of Al foil in a 10 ml beaker filled with 0.5 M aqueous NaOH solution. The mass ratio of GaIn_{10} and Al foil was about 200:1. Liquid metal GaIn_{10} would gradually penetrate into Al grain boundaries. After 10 min, Al foil was totally decomposed into small granules by liquid metal. Some of the granules would float on liquid metal surface and accumulated together while others were dispersed inside liquid metal [13]. The prepared liquid metal (approximately 0.4 ml) was then moved onto a rubber O-ring (diameter 1 cm) in case of self-motion induced by surface tension gradient [10]. The whole system was

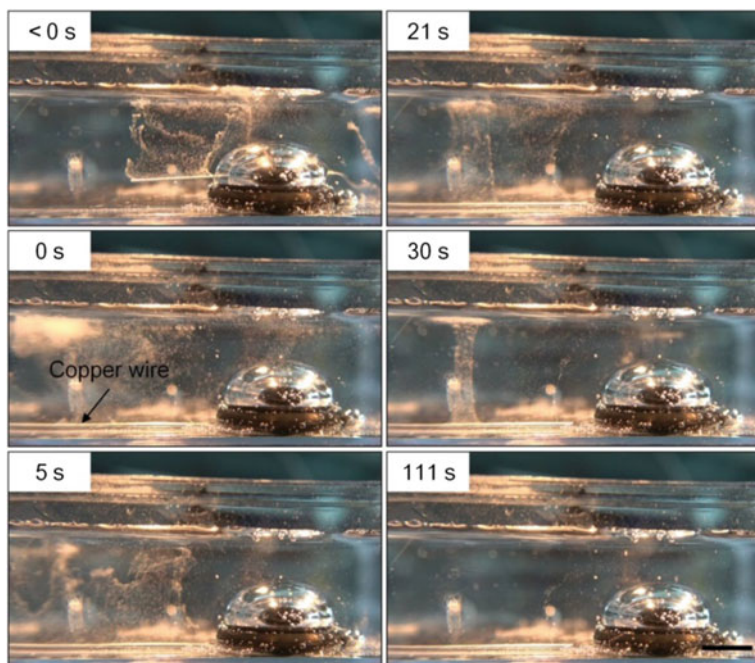


Fig. 15.2 H_2 generation on the copper wire after being pulled out of liquid metal (scale bar, 5 mm) [10]. All pictures are reproduced with permission

immersed inside 0.5 M aqueous NaOH solution in a square plastic Petri dish. Since the copper wire would be totally wetted by liquid metal after oscillation, coating the copper wire (length 2 cm, diameter 0.19 mm) via GaIn_{10} can be done in advance before inserting it inside the prepared liquid metal to shorten the fabrication time. Initially, the copper wire just stayed at one side and did not move. The wire can be pulled out from the liquid metal and repeated the inserting process several times until the surface was covered with enough tiny Al granules from the liquid metal. Oscillation then happened spontaneously with H_2 bubbles rising from the copper wire surface constantly (Fig. 15.1a, b).

15.3 Interpretation of the Oscillation Phenomenon

To investigate the oscillation rhythm in detail, the data for the time interval of the copper wire oscillation during 50 periods can be collected (Fig. 15.4). We defined four states of the copper wire during one period according to the time and position in order to facilitate the following discussion (Fig. 15.4a). Statistics showed that the pausing time (process A–B and C–D) varied with time [10]. Occasionally, such

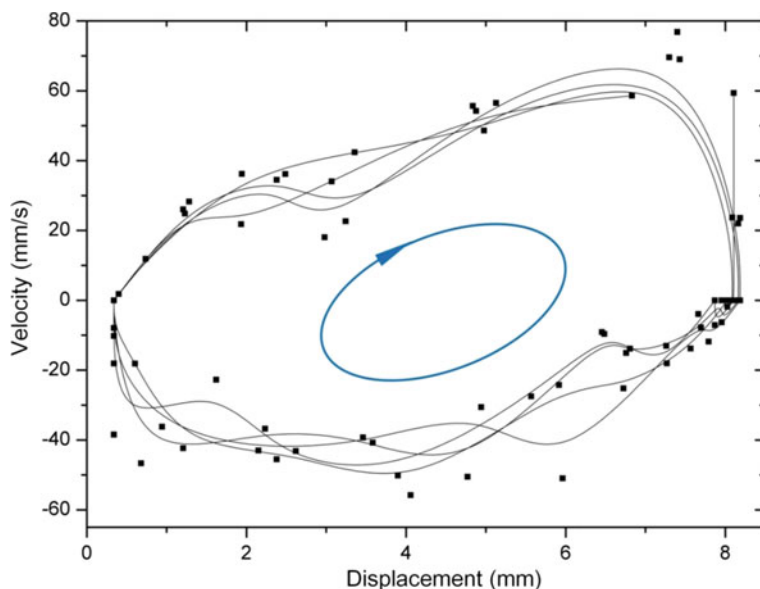
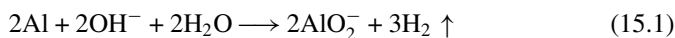


Fig. 15.3 Phase portrait of the oscillation process [10]. The data were fitted by Spline curve. All pictures are reproduced with permission

pausing time could be up to minutes (Fig. 15.5). The moving time (process B–C and D–A) was almost the same (Fig. 15.4b), which took about 0.22 s.

This oscillation behavior can be explained by the dynamic imbalance of the wetting force on two edges of the copper wire contacting liquid metal [10]. The dragging force induced in three-phase region competes on two edges and results in the oscillatory behavior (Fig. 15.6). The wetted copper wire surface was quite rough (Fig. 15.6b) compared with bare copper wire (Fig. 15.6a) since tiny solid Al granules would attach on it when moving through the liquid metal body. Assume that the copper wire was moving from left to right (Fig. 15.6c), and the left part would carry solution in the rough surface inside the liquid metal. On the other hand, the solution carried by the right part of the wire had reacted with Al granules, producing H_2 in large quantities



These H_2 reduced the contact area between liquid and solid wire, reducing the dragging force along the wire. Thus, the dragging force on the left-hand side becomes higher than that on the right-hand side.

The contact angle between copper wire and liquid metal machine can be described by the Cassie–Baxter equation [16, 17], i.e.,

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (15.2)$$

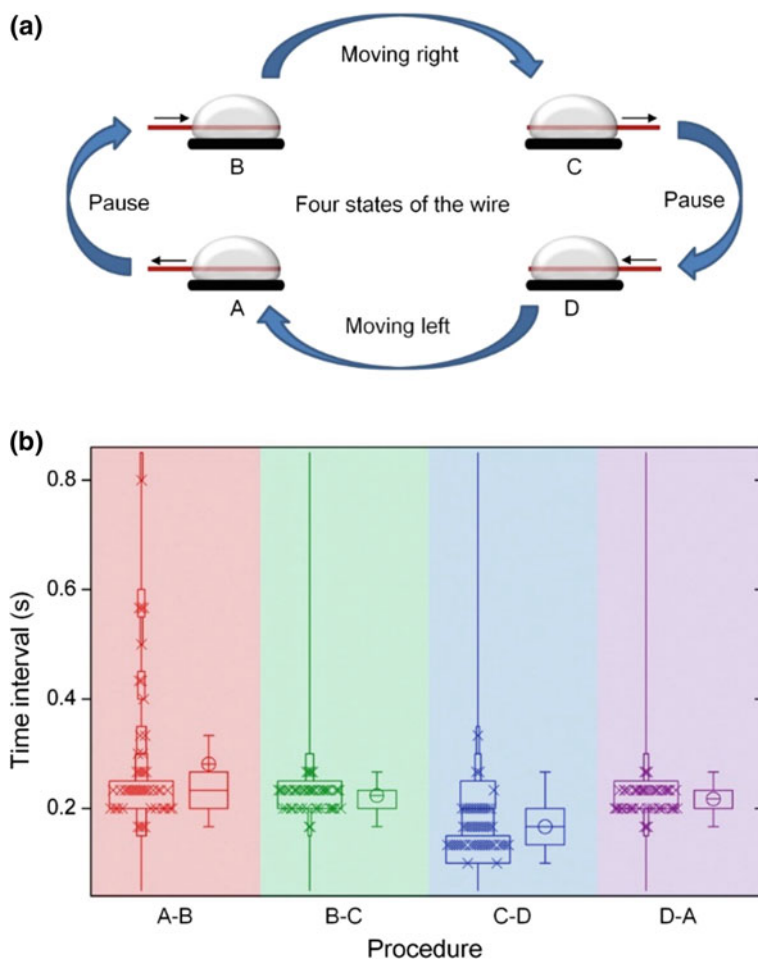


Fig. 15.4 Statistic analysis of the oscillation phenomenon [10]. **a** Different states during a typical oscillation period. The copper wire moved to the left-hand side (A), pausing for a while (B) before moving to the right-hand side (C), pausing again (D) before moving left to state A. **b** Time interval between the four states during 50 period times. The box chart indicates the 25, 50, and 75% of the data (the crosses on the left represent the data). The whisker shows the outlier range with coefficient number to be 1.5. The circle indicates the mean of the data. The following box charts follow the same setting. All pictures are reproduced with permission

where θ_c represents the apparent contact angle, and f_1 is the total area of solid under the drop per unit projected area, with θ_1 as the contact angle on a smooth surface of material 1. Likewise, f_2 is defined in a similar way.

Since the contact angle was determined just by the contact line region [17, 18], as depicted in Fig. 15.6c, one could ignore other regions far from it. In the present case, the contact angle at left part of contact line and right part are expressed as

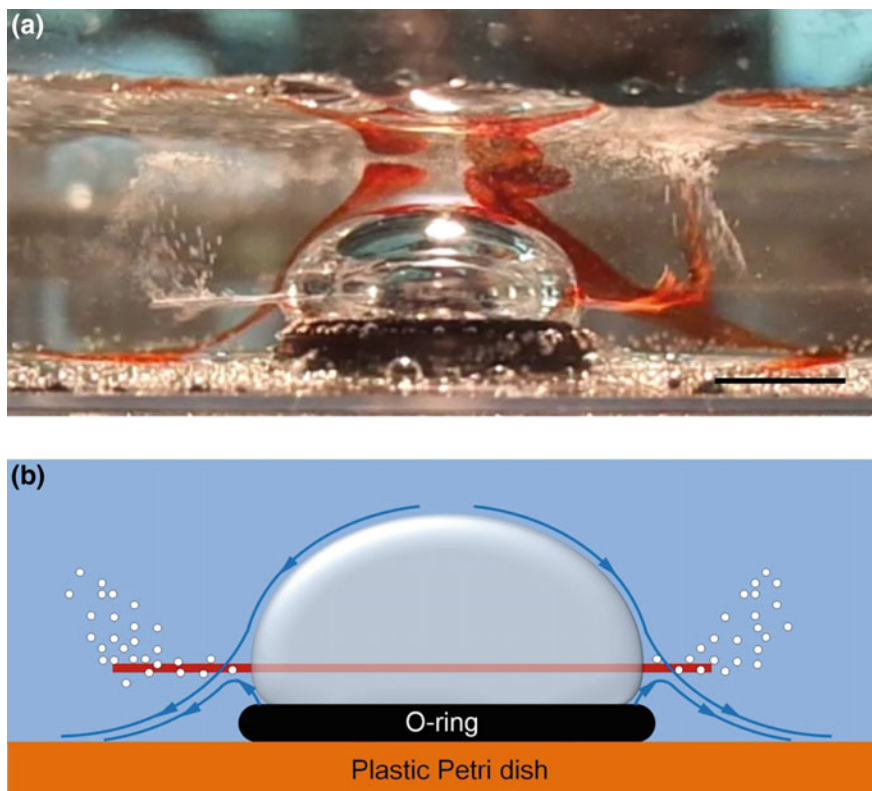


Fig. 15.5 Pausing state of the copper wire [10]. **a** Side view (scale bar, 5 mm), red ink was dropped to reveal the flow field. **b** The streamline on liquid metal surface. All pictures are reproduced with permission

$$\cos \theta_{\text{in}} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (15.3)$$

$$\cos \theta_{\text{out}} = f_1^* \cos \theta_1 + f_3 \cos \theta_3 \quad (15.4)$$

respectively, with material 1 as solid wire, material 2 as alkaline solution, and material 3 as hydrogen. Since the generated hydrogen volume was 1000 times more than reacted alkaline solution (calculated from chemical reaction), the total area of solid contacting liquid metal per unit projected area on the right part f_1^* was smaller than left part f_1 . Thus, $f_1 \cos \theta_1$ is larger than $f_1^* \cos \theta_1$. Besides, it is obvious that f_2 was smaller than f_3 . Since the surface tension of liquid metal was almost ten times higher than alkaline solution, one could assume θ_2, θ_3 to be π . Thus, $f_2 \cos \theta_2$ is larger than $f_3 \cos \theta_3$. As a result, $\cos \theta_{\text{in}}$ is larger than $\cos \theta_{\text{out}}$. Since the contact angle is the same along the contact line region between wetted copper wire and liquid metal [18], the dragging forces on the two edges can be expressed as follows [13]:

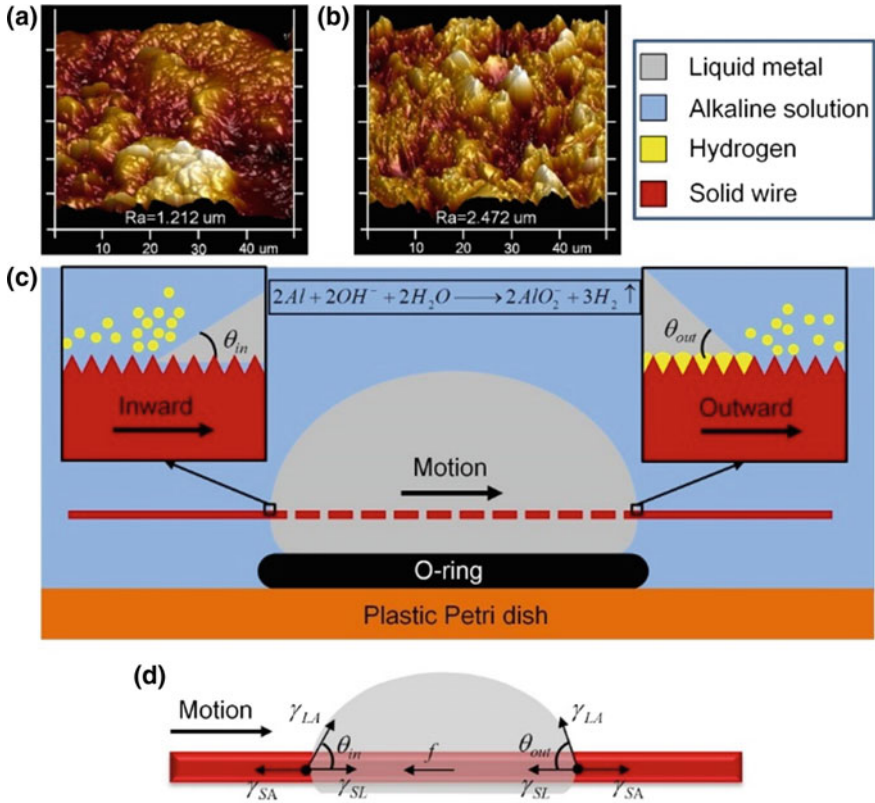


Fig. 15.6 Interaction between copper wire, liquid metal, and alkaline solution [10]. **a** Surface structure of bare copper wire measured by atomic force microscope (AFM). The roughness is 1.212 μm . **b** Surface structure of wetted copper wire measured by AFM. The roughness is 2.472 μm . **c** Chemical reaction nearing contact lines. **d** Force analysis of the copper wire. All pictures are reproduced with permission

$$F_{in} = \pi D_{in}(\gamma_{LA} \cos \theta_{in} + \gamma_{SL} - \gamma_{SA}) \quad (15.5)$$

$$F_{out} = \pi D_{out}(-\gamma_{LA} \cos \theta_{out} + \gamma_{SA} - \gamma_{SL}) \quad (15.6)$$

where D represents the diameter of solid wire.

Assuming that the diameter on the left and right was almost the same, then the total driving force acting on the copper wire can be expressed as

$$F_{drive} = \pi D \gamma_{LA} (\cos \theta_{in} - \cos \theta_{out}) \quad (15.7)$$

For liquid metal without Al granules, the average adhesion force between liquid metal and wetted copper wire can be as high as 0.27 mN (Fig. 15.7) [10]. The force enabled the wetted copper wire shooting through the liquid metal drop once

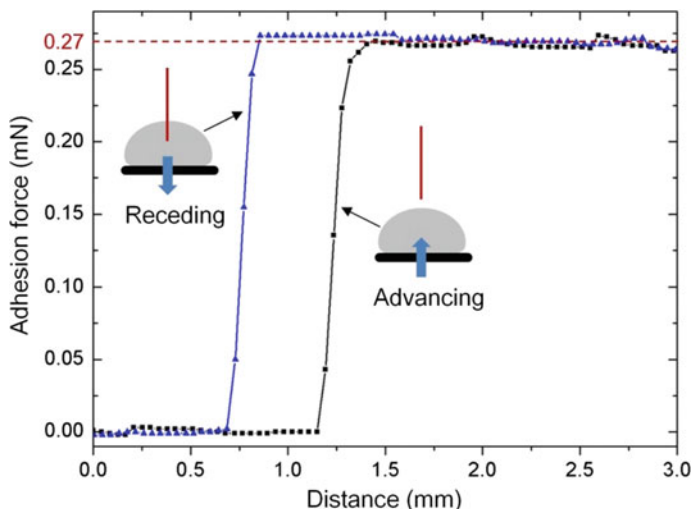


Fig. 15.7 Adhesion force between the wetted copper wire and liquid metal GaIn₁₀. The adhesion force was measured by dynamic contact angle meter and tension meter [10]. All pictures are reproduced with permission

it contacted the drop surface within 60 ms (Fig. 15.8). The mass of wetted copper wire was 0.2 mg, and thus according to Newton second law, i.e., $F = ma$, one got the initial transient acceleration as high as 1.35 m/s^2 . After the copper wire ran through the liquid metal drop, the wetting force balanced on two edges and the wire stopped gradually due to friction force, i.e., the viscous force between copper wire and surrounding liquids.

For liquid metal with Al granules, the imbalance of dragging force due to contact angle difference provides the driving force F_{drive} . At the same time, the solution brought inside liquid metal would react with Al fiercely, producing H_2 . The H_2 also functioned as a lubricating film between liquid metal and wire, reducing the friction force greatly. For the pausing stage, it might be resulted from the delay of reaction. When the wire moved to one side, the solution brought inside liquid metal would take some time before reacting with Al granules. Before enough H_2 was produced, the dragging force was unable to overpass the dragging force on the other side.

15.4 Controlling Oscillation Process of Hybrid Liquid Metal Machine

Apart from the above phenomenon, it disclosed further interesting effect that by touching a steel needle on the liquid metal surface [10], the oscillation period can be shortened significantly (Fig. 15.9). H_2 would be generated on the steel needle

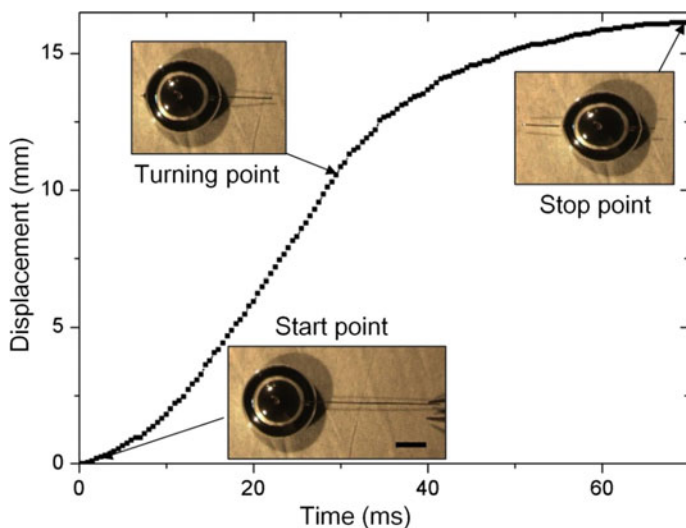


Fig. 15.8 Time evolution of a wetted copper wire swallowed by liquid metal GaIn₁₀ [10]. The start point refers to the wetted copper wire contacting the liquid metal, turning point as the copper wire runs out on the other side, and stop point as the copper wire stops (scale bar, 5 mm). All pictures are reproduced with permission

fiercely due to the primary battery formed between steel and Al [19]. Statistical analysis showed that the period shortened was mainly the pausing time (Fig. 15.9b). This might be that the accelerated reaction speed reduced the time for the solution on the wire to react with Al. The moving time was shortened slightly as well. Copper wires with different lengths (15, 25 mm) were also investigated for the same process (Fig. 15.10).

Overall, as it was displayed, liquid metal contains amazing capabilities never realized before. The above findings offer a unique strategy toward fabricating self-fueled oscillator machines with no rigid bodies. The whole autonomous oscillation system was easily fabricated and reliable. The oscillation period can be regulated by simply contacting a steel needle to the surface of the liquid metal machine [10]. These revealed fundamental phenomena and the mechanisms disclosed refresh the basic knowledge of classical oscillation and wetting effects and provide insight into further exploration. Given appropriate designing, such autonomous oscillator composed of hybrid solid and liquid elements can work as a switch device in periodically regulating fluidic, electrical, mechanical, and optical signals. It also suggested important platform for developing future complex hybrid machine made of soft and liquid mechanical systems together.

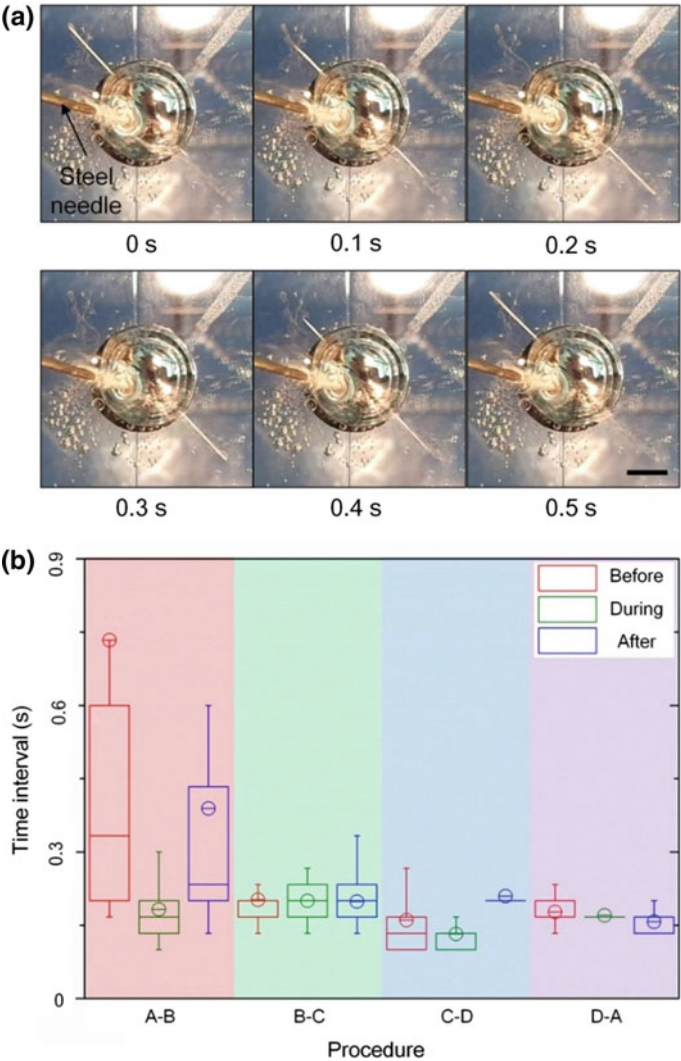


Fig. 15.9 Oscillation period regulated by touching a steel needle on liquid metal surface [10]. **a** Top-down view of oscillation with a steel needle contacting the liquid metal surface (scale bar, 5 mm). **b** Comparison of time interval between the four states (Fig. 15.4a) before, during, and after the needle contacting the liquid metal surface. All pictures are reproduced with permission

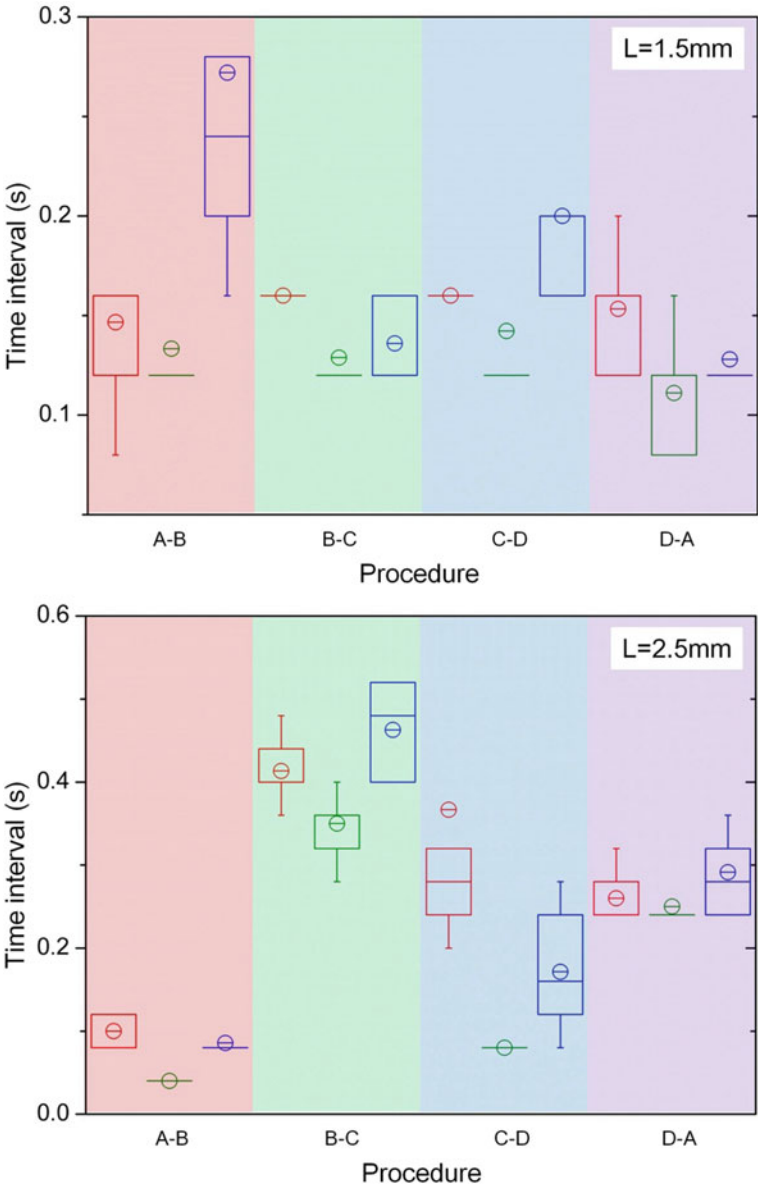


Fig. 15.10 Comparison of oscillation behavior before and after contacting steel needle for copper wire with different lengths [10]. All pictures are reproduced with permission

15.5 Graphite-Induced Periodical Self-actuation of Liquid Metal

Different hybrid material systems or configurations would generate very different liquid metal actuation behaviors. This lab demonstrated self-actuation phenomena of liquid metal sphere in NaOH solution including oscillating and stretching induced by graphite alone [20]. When a liquid metal sphere was leaned against the side of a piece of graphite, it could oscillate periodically. As the sphere contacted the graphite, it rapidly collapsed while the curvature radius of the sphere at the contact point became smaller. And as the capillary force imposed on the sphere was larger than the friction force, the sphere recovered to its original spherical shape. The surface tension of the liquid metal sphere acted as the restoring force of the oscillatory movement. Further, a phenomenon of resonance could be observed when two spheres were laid, respectively, on the top and the side of the graphite. The vibration of the top sphere was induced by the vibration of the side one. Such finding provides a novel supplement for making future liquid metal beating heart system and graphite/liquid metal-based batteries or machines.

Figure 15.11 gives the basic pictures of the periodic oscillation behavior of the liquid metal [20]. Here, galinstan (68.5% gallium, 21.5% indium, and 10% tin by weight) was used as the test object and laid on the side of the graphite. The substrate is tilted slightly to ensure that the liquid metal sphere could roll toward the graphite spontaneously. The top view snapshots of a liquid metal sphere with 1.2 g are shown in Fig. 15.11a, while the side view snapshots of a sphere with 0.9 g are shown in Fig. 15.11b. Relative variations of the frontal projected area of the 1.2 g sphere and the height of the 0.9 g sphere during oscillation process are shown in Fig. 15.11c. The green dashed lines represent the departure of the spheres from the graphite. It can be seen that at the beginning of the oscillation, the liquid metal spheres are in the shape of approximate spheroid with the minimum frontal projected area A_0 and the maximum height H_0 . As they are in contact with graphite, the area becomes larger rapidly and the height becomes smaller simultaneously. This is due to the reduced surface tension of the spheres caused by the graphite/liquid metal galvanic cell. Then the area decreases gradually and the height increases simultaneously. When the spheres leave from the graphite, they recover to their original shapes rapidly which is attributed to the surface tension of their own. Therefore, the surface tension acts as the restoring force of the oscillatory movement of a liquid metal sphere.

Figure 15.12a presents the deformation schematic diagrams (images 1, 3, and 5) and the corresponding snapshots (images 2, 4, and 6) of liquid metal spheres in contact with graphite in NaOH solution viewed from the top [20]. The horizontal force diagram of the sphere is shown in the image 1. As the sphere contacts the graphite, it is subjected to the capillary force F_s directed rightward and the friction force F_f directed toward the graphite. The magnitude of F_s which is caused by the surface tension gradient of the liquid metal can be expressed as [21]

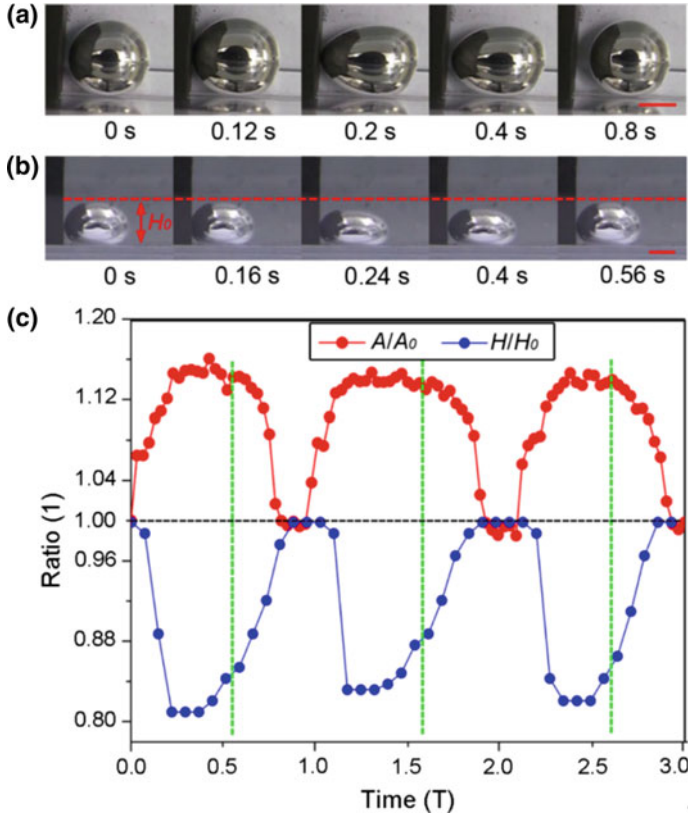


Fig. 15.11 Oscillation movement of the liquid metal on the graphite substrate immersed in the NaOH solution [20]. **a** Top view snapshots of liquid metal sphere 1 with 1.2 g. **b** Side view snapshots of liquid metal sphere 2 with 0.9 g. **c** Relative variations of the frontal projected area of the sphere 1 and the height of the sphere 2 during the oscillation process. Symbol A denotes the frontal projected area of the liquid metal viewed from the top and A_0 denotes the area when $t = 0$. Symbol H denotes the height of the sphere viewed from the side and H_0 denotes the height when $t = 0$. The horizontal coordinate unit T represents the oscillation period of the liquid metal sphere. Scale bars are all 3 mm in length. All pictures are reproduced with permission

$$F_s \sim \frac{\varepsilon V E_{gl}}{\lambda_D} \quad (15.8)$$

where E_{gl} is the electric field strength induced by the graphite/liquid metal galvanic cell, V is the potential difference across the liquid metal/electrolyte EDL, and ε and λ_D are the electric permittivity and the Debye screening length of the electrolyte, respectively. The friction force F_f includes the viscous force between the sphere and the NaOH solution as well as the frictional force between the sphere and the substrate. $F_s > F_f$ is a necessary condition for pushing the sphere off the graphite and oscillating (see image 1 and 3). Let r represent the curvature radius on the contact point between

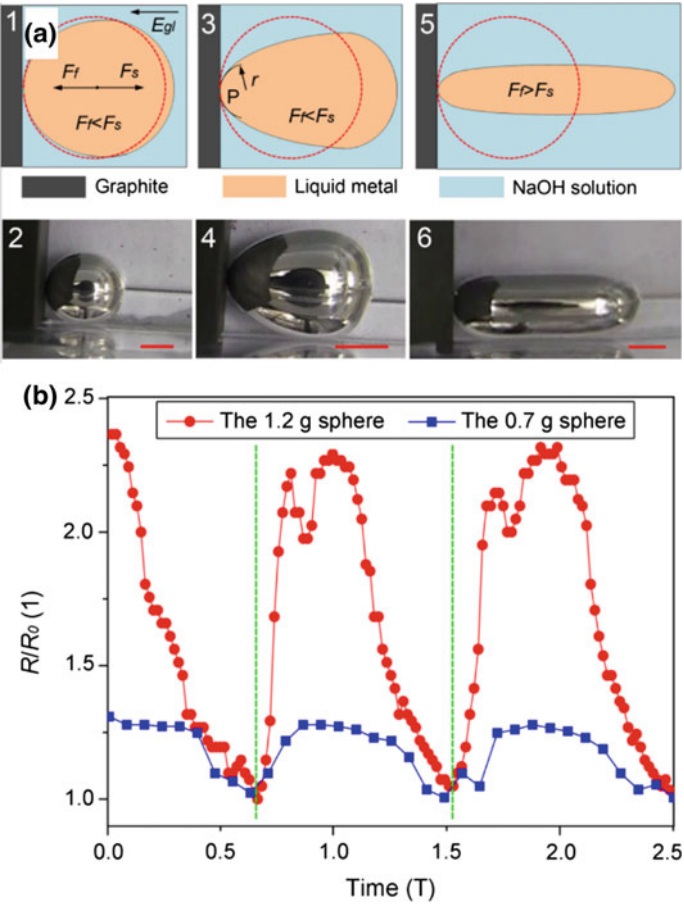


Fig. 15.12 **a** Deformation schematic diagrams and snapshots of liquid metal in contact with graphite in NaOH solution viewed from the top. The red dashed-line circles represent the outline of the liquid metal before deformation. **b** Relative variation of the curvature radius at the contact point P between the liquid metal spheres and the graphite. Symbol R denotes the curvature radius of the contact point viewed from the top and R_0 denotes the minimum value. The horizontal coordinate unit T represents the oscillation period of the liquid metal spheres. Scale bars are all 3 mm in length. [20] All pictures are reproduced with permission

graphite and liquid metal which is denoted by P. As the surface tension on the left hemisphere is larger than that on the right side, the liquid metal will flow rightward inside the sphere. As a result, r becomes smaller due to the pressure comes from the sphere's surface surrounding the point P. Relative variation of the curvature radius at the contact point P of the spheres with 0.7 and 1.2 g is presented in Fig. 15.12b. The green dashed lines represent the departure of the spheres from the graphite. It can be seen that whatever the mass of the sphere, it detaches away from the graphite when the curvature radius reaches the minimum value. The ratio of the maximum value to

the minimum value is 1.30 to the sphere of 0.7 g (images 1 and 2), compared to that of 2.36 to the sphere of 1.2 g (images 3 and 4). This indicates that the sphere with larger mass has larger deformation degree, and it shows a shape of melon seed at the maximum deformation. When $F_s < F_f$, the capillary force imposed is too small to push the sphere away from the graphite. And the sphere (1.2 g) will be elongated to a wormlike cylinder without oscillation as shown in images 5 and 6.

The variation of the oscillation period–time relationship of the liquid metal sphere is investigated, and the result is shown in Fig. 15.13a. It can be seen that the oscillation period becomes increasingly larger with the time and presents the form of ladder as shown as the blue dashed lines [20]. In the interval of each step, there occasionally appear periods with longer time which indicates a slowing down trend of the oscillation movement. The sphere ultimately stops oscillating with slightly but continuously deformation after about ten minutes. However, it oscillates again after the surface layer of the graphite is scraped off. To find the reason, a comparison is performed between the surface of a piece of graphite after oscillation experiment and that of a pure one without experiment. Their scanning electron microscope (SEM) images obtained in the same condition are presented in Fig. 15.13b and c, respectively. It can be seen that the experimented graphite shines brightly and unevenly which indicates the poor conductive of the surface. Energy-dispersive X-ray (EDX) is performed to analyze the surface element composition for the graphite after oscillation experiment, and the result is shown in Fig. 15.13d. There is Na element with 3.18% by weight on the surface which indicates that some Na^+ ions in NaOH solution are adsorbed on the graphite surface. It may be the absorbed ions that destroy the graphite/liquid metal EDL and further weaken the induced electric field strength E_{gl} . The driving force F_s imposed on the sphere is thus reduced to a value lower than the friction force F_f and ultimately results in the termination of oscillating.

15.6 Resonance Phenomenon of Two Liquid Metal Spheres Contacting with Graphite

As two liquid metal spheres are, respectively, laid on the top and the side of the graphite, an interesting phenomenon of resonance can be observed [20]. The vibration of the side sphere denoted as LM2 with 1.0 g can induce the vibration of the top one which is denoted as LM1 with 0.2 g. The schematic diagram and snapshot of the liquid metal double-sphere resonance oscillation experiment are, respectively, shown in Fig. 15.14a, b. As the side sphere contacts the graphite, its height decreases with the increase of the top one. As the side sphere leaves from the graphite, however, its height increases with the decrease of the top one. This can be seen from the height–time relationship curves of the two spheres presented in Fig. 15.14c. The curve crest of LM1 and the curve trough of LM2 correspond to each other which are marked by the green dashed lines. And LM2 is detached away from the graphite at the time corresponds to these lines. Let V_{gl1} and V_{gl2} represent the potential differences

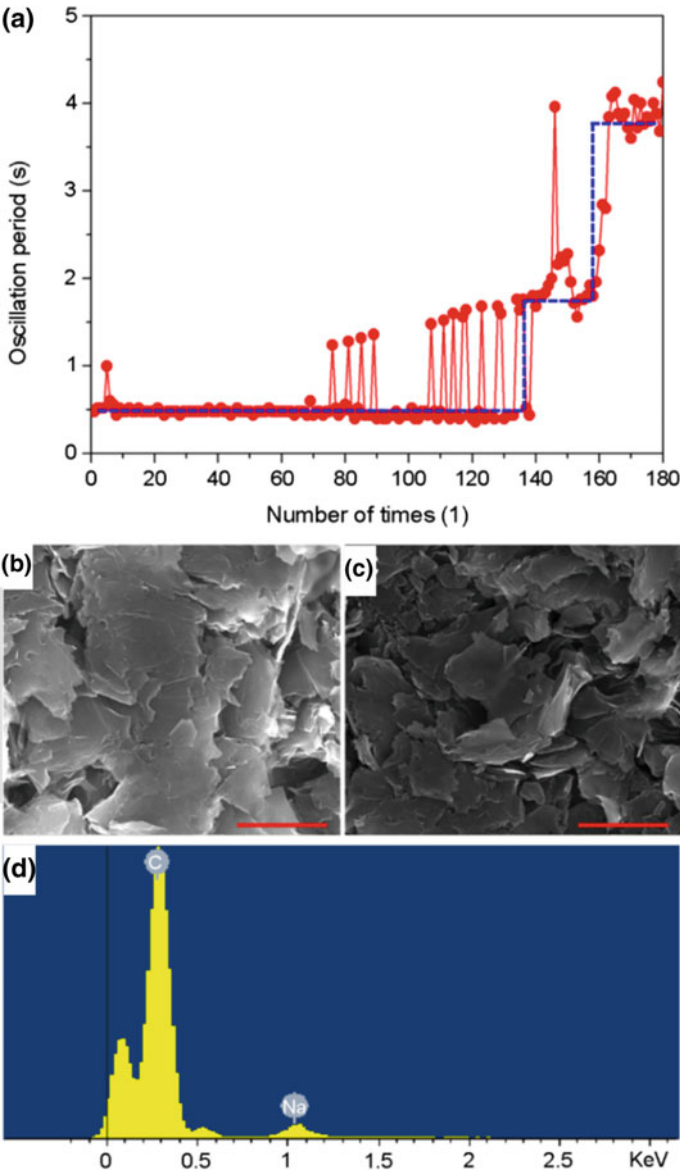


Fig. 15.13 **a** Variation of the oscillation period of the liquid metal sphere with the number of times. **b** SEM image of the graphite after the liquid metal sphere oscillation experiment. **c** SEM image of the pure graphite. **d** EDX elemental analysis of the graphite after the liquid metal sphere oscillation experiment. Scale bars are all 2 μm in length [20]. All pictures are reproduced with permission

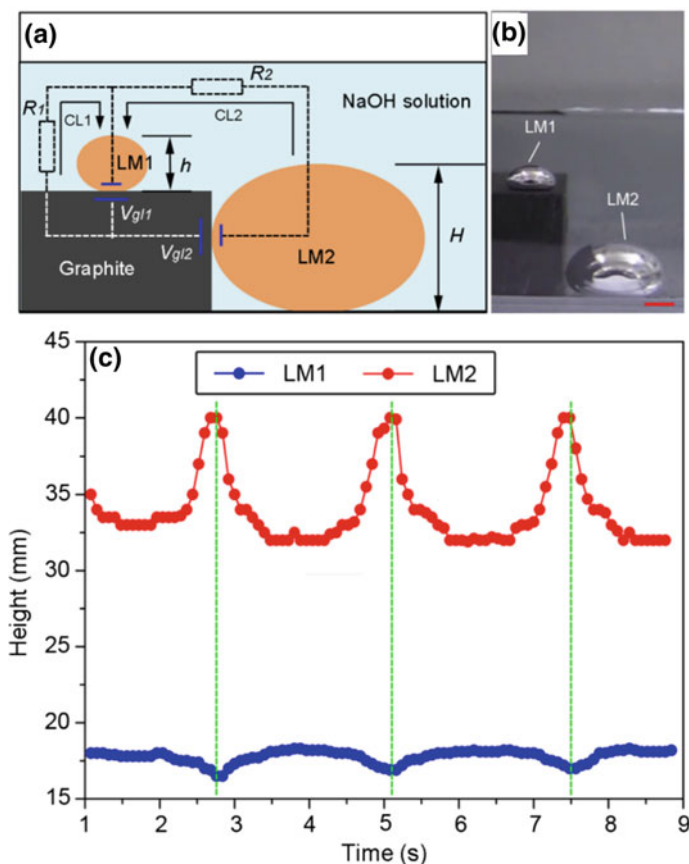
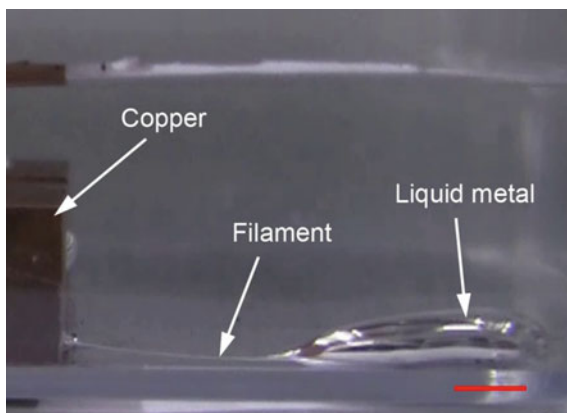


Fig. 15.14 **a** Schematic diagram and **b** Snapshot of the liquid metal double-sphere resonance oscillation experiment. Scale bar is 3 mm in length. **c** Variation of the heights of the top sphere LM1 and the side sphere LM2 with the time in oscillation state viewed from the side [20]. All pictures are reproduced with permission

across the graphite/LM1 and the graphite/LM2 galvanic cells, respectively. As LM2 is not in contact with the graphite, a loop circuit CL1 is formed which comprises LM1, the graphite, and the electrolyte whose equivalent resistance is R_1 . The voltage imposed on LM1 is V_{gl1} directed downward, which actuates LM1 to spread. As LM2 contacts the graphite, a loop circuit CL2 is formed which comprises LM1, LM2, the graphite, and the electrolyte whose equivalent resistance is R_2 . The voltage imposed on LM2 is $V_{gl1} + V_{gl2}$ directed leftward, which actuates LM2 to spread. However, the voltage imposed on LM1 is $V_{gl1} - V_{gl2}$, which is smaller than V_{gl1} and LM1 retains its spherical shape.

As a kind of nonmetal conductor, graphite owns more stable chemical properties than common metals such as copper. It cannot fuse or react with the liquid metal

Fig. 15.15 The adhesion of the liquid metal to the copper [20]. Scale bar is 10 mm in length. All pictures are reproduced with permission



to ensure the maintenance of oscillation movement [20]. As to copper, however, a filament will be formed as shown in Fig. 15.15 when the liquid metal is detached away from it. The self-actuation of liquid metal is driven by the surface tension gradient which is induced by the graphite/liquid metal galvanic cell. Such mechanism is different from that of traditional mercury beating heat system induced by the oxidation–reduction chemical reaction which has obtained abundant research. Based on the actuation of graphite/liquid metal system, oscillator with complex structure including series–parallel connection can be developed. In addition, graphite/liquid metal-based batteries can also be conceived with a vast application prospect.

Overall, when a liquid metal sphere was laid on the surface of the graphite, it may become collapse rapidly [20]. This is due to that a graphite/liquid metal galvanic cell was formed and provided the sphere with a potential directed downward. When a liquid metal sphere was put against the side of the graphite, it would oscillate periodically. Once the sphere was in contact with the graphite, an electric capillary force F_s was induced by the graphite/liquid metal galvanic effect and imposed on the sphere. As F_s was larger than the friction force F_f , the sphere would be detached away from the graphite and the oscillation movement was triggered. And as F_s was lower than F_f , the sphere would be elongated to a wormlike cylinder without oscillating. When two liquid metal spheres were, respectively, laid on the top and the side of the graphite, a phenomenon of resonance was observed. They oscillated in opposite directions, and the vibration of the top sphere was induced by the vibration of the side one. The mechanism of such self-actuation of liquid metal is quite different from that of traditional mercury beating heat system which is ascribed to oxidation–reduction chemical reaction. This oscillating method provides a novel idea for investigating graphite/liquid metal-based oscillators and batteries, as well as hydrogen production strategy.

15.7 Galvanic Corrosion Couple Induced Marangoni Flow of Liquid Metal

Except for the above hybrid structure, through coupling with certain special matching material and ambient conditions, global flow of liquid metal can even be induced. A special case is to generate Marangoni flow on the liquid metal [22]. As is known to all, Marangoni effect is a surface tension driven flow at the interface between two fluids. Its driving mechanisms are multiple which can generally be classified as concentration gradient, pH gradient, surfactant-induced flow, and so on. Among these origins, temperature gradient especially received tremendous attentions and researches. To most liquids, there is a negative relationship between surface tension and temperature, namely, $d\gamma/dT < 0$, resulting in that the flow direction on fluid surface is from the hot side to the cold one, or a droplet moving in the direction along temperature decreasing on a plate.

So far, most of the methods to induce actuation of liquid metal are limited to the external electric field. From an alternative, Tan et al. [22] disclosed a new Marangoni flow phenomenon of liquid gallium induced by the gallium–copper Galvanic corrosion couple. Meanwhile, the temperature condition is also found to affect the region of Marangoni flow. This finding broadens the classical understanding of liquid metal surface flow, which also suggests a new way for the application of soft machine.

The experimental setup is displayed in Fig. 15.16a, where an open rectangular slot with size of 80 mm × 10 mm × 7 mm was fabricated in a PMMA sheet. A copper bulk was fixed at one end of the slot and liquid metal was filled in other space. Here, pure gallium was chosen as the test liquid metal. Above the copper bulk, a semiconductor cooling plate was stuck and on the other end of the channel, a semiconductor plate with heating side was stuck at the bottom. Therefore, a temperature gradient could be generated along the liquid gallium. Hydrochloric acid solution with concentration of 3 mol/L was injected to remove the oxide layer of gallium due to reaction $\text{Ga}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Ga}^{3+} + 3\text{H}_2\text{O}$.

As gallium can amalgamate metals such as copper, liquid gallium shows good wettability on copper surface [22]. When the semiconductor cooling plate placed above the copper bulk worked properly, the gallium at the section near the copper bulk started to solidify. And at the other end, the gallium was heated to a high temperature via the reverse side of another semiconductor plate. When the temperature field reached equilibrium state, a rapid flow of the HCl solution overlays the liquid gallium that can be observed, whose direction runs away from the cold side to the hot side at the region near the copper.

Because the surface of liquid gallium was very smooth like a mirror, the flow of liquid metal cannot be observed directly [22]. The surface current of HCl solution could be known by analyzing the motion of bubbles which was generated by the reaction between HCl and liquid gallium. Figure 15.16b demonstrated a global picture of the superficial solution streamline. The flow on liquid gallium surface distributed in two regions, including the forward flow region attached with the copper and the counter flow region at the far end. By tracing the H_2 bubbles at the central axes (y

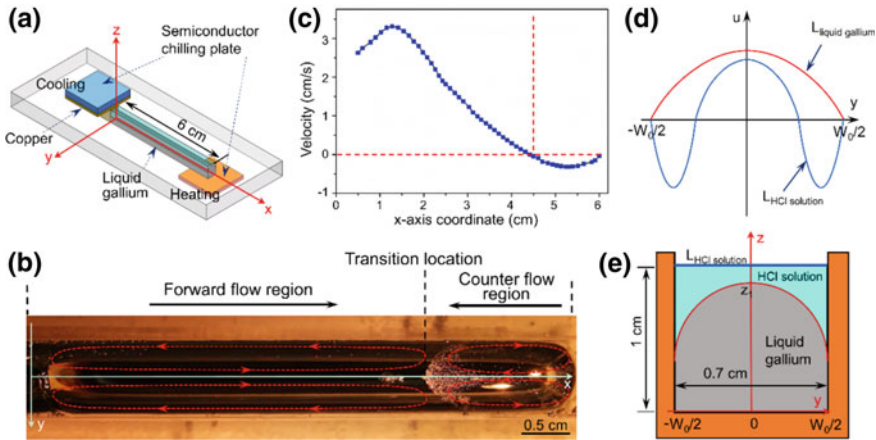


Fig. 15.16 Marangoni flow phenomenon of liquid gallium when it touches with copper bulk under influence of the temperature gradient [22]. **a** Schematic of the experimental setup showing a slot fabricated in a PMMA sheet. A copper bulk was fixed at one end and contacted with liquid gallium. Two semiconductor cooling plates were adopted to generate a thermal gradient; **b** Global picture of the superficial solution streamline, showing the flow region to be divided into two parts; **c** Velocity distribution along x -axis coordinate at the central axes ($y = 0$); **d** Schematic diagram of velocity distribution on the liquid gallium–solution interface and the solution–air interface in the forward flow region; **e** yz plane view of the liquid gallium and acid solution in the channel. All pictures are reproduced with permission

= 0) of liquid metal surface, Fig. 15.16c about the velocity distribution along x -axis coordinate was acquired, which indicated that the velocity increased at first and then dropped to zero at transition point. While in the counter flow region, the velocity turned negative and was lower in absolute value than that in the forward flow region.

Focusing on the forward flow region, the solution located on the central axis flowed along the positive x -axis and the solution near both sides of the channel flowed along negative x -axis [22]. Because the interface shape of liquid metal in channel presented an arc shape with central bulge, the HCl solution in the central of channel was thin and easily kept the same flow direction with the liquid gallium–solution interface, while the HCl solution on both sides was not. According to the conservation of mass in the yz plane, the velocity distribution of HCl solution meets the following formula:

$$\int_{-\frac{w_0}{2}}^{\frac{w_0}{2}} \int_{z(y)}^{z_0} u dy dz = 0 \quad (15.9)$$

where u is the fluid velocity in x direction, w_0 is the width of the channel in y direction, and $z(y)$ is the height coordinate of liquid metal surface on yz plane. Therefore, when the velocity on the central axis was set as the positive value which was along positive x -axis, there must be reverse velocity on both sides. Besides, due to

the boundary condition on channel surface fulfilling no-slip boundary conditions, namely, $u(\pm \frac{w_0}{2}, z) = 0$, the velocity distribution of HCl solution on the height of $z = z_0$ could be depicted qualitatively as the blue curve in Fig. 15.16e, corresponding to the observation in Fig. 15.16d.

Then, it turned to the flow analysis of liquid gallium. Based on the no-slip condition at the interface, the flow situation of upper surface of liquid gallium could be reflected indirectly by that of HCl solution [22]. Furthermore, it was determined as one-way flow due to the unidirectional surface tension gradient on the surface of liquid gallium. Coupled with the zero velocity on the contact surface with channel walls on both sides, the velocity distribution of upper surface of liquid gallium could be depicted qualitatively as the red curve in Fig. 15.16e.

In order to calculate the flow inside the liquid gallium, an effect should be taken into account: the Rayleigh–Bénard convection induced by the temperature gradient along the direction of increasing x . Tan et al. [22] made a numerical simulation with no surface tension gradient on liquid gallium–HCl solution interface. Consider the two-dimensional flow in xz plane of liquid gallium with density ρ under the Boussinesq approximation. The temperatures were set to 29.6 °C (gallium melting point) for cooling surface. And the heating zone was set to 53.0 °C which is equal to the experimental value measured on the heating plate. The governing equations can be given as follows:

Momentum equations (N–S equation):

$$(u \cdot \nabla)u = -\frac{1}{\rho_0} \nabla p - \beta(T - T_m)g + \nu \Delta u \quad (15.10)$$

Mass conversation equation:

$$\nabla \cdot (\rho u) = 0 \quad (15.11)$$

Energy equation:

$$(\nabla \cdot u)T = \lambda \Delta T \quad (15.12)$$

With the boundary condition:

$$\frac{du}{dz}|_{z=H} = 0, \quad u|_{z=0} = 0 \quad (15.13)$$

where $u(x, z)$, $T(x, z)$, and $p(x, z)$ are the velocity, temperature, and pressure fields inside liquid metal, respectively. g is the acceleration of gravity. β , ν , λ , and T_m are the volume thermal expansivity, kinematic viscosity, thermal diffusivity, and melting point of the liquid gallium. ρ_0 references density at T_m . H is the height of liquid gallium in the slot.

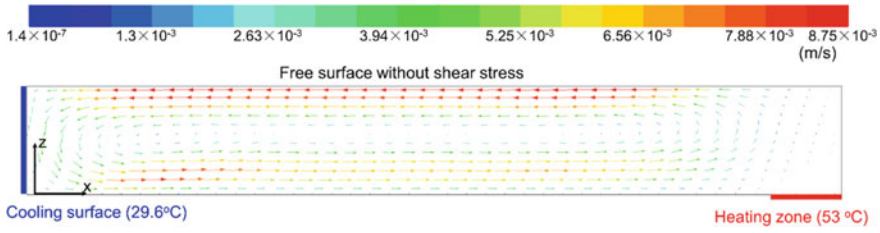


Fig. 15.17 Velocity field distribution under the Rayleigh-Bénard convection [22]. All pictures are reproduced with permission

Figure 15.17 shows the simulation velocity fields distribution [22]. The up surface velocity of liquid gallium was negative in x direction which was contrary to the experimental observation and the maximum value was 8.75×10^{-3} m/s which was about 3 times smaller than the experiment. Thus, one can make a conclusion that the Rayleigh-Bénard convection was insignificant in this problem.

To the real situation, the surface gradient $d\gamma/dx$ on gallium-solution interface was not constant which makes it difficult to calculate the whole field velocity. Nevertheless, the velocity in x direction far away from the boundary can still be obtained. First, regardless of Rayleigh-Bénard convection (eliminate $-\beta(T - T_m)g$) and y direction, Eq. (15.10) can be simplified as follows:

Momentum equations (N-S equation):

x direction:

$$u \frac{\partial u}{\partial x} + w \frac{\partial u}{\partial z} = -\frac{1}{\rho_0} \frac{\partial p}{\partial x} + \nu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial z^2} \right) \quad (15.14)$$

z direction:

$$u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} = -\frac{1}{\rho_0} \frac{\partial p}{\partial z} - g + \nu \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial z^2} \right) \quad (15.15)$$

Due to the incompressibility of liquid gallium, the mass conservation equation is

$$\nabla \cdot \mathbf{u} = 0 \quad (15.16)$$

where u and w are the velocities in x and z directions, respectively.

Then considering the region far away from the boundary, the velocity can be approximately simplified as

$$u = u(z), \quad w = 0 \quad (15.17)$$

According to Eq. (15.16):

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0 \quad (15.18)$$

Thus, it can be concluded:

$$\frac{\partial u}{\partial x} = \frac{\partial w}{\partial z} = \frac{\partial w}{\partial x} = 0 \quad (15.19)$$

Equations (15.14) and (15.15) can be further simplified as

$$0 = -\frac{1}{\rho_0} \frac{\partial p}{\partial x} + \nu \frac{\partial^2 u}{\partial z^2} \quad (15.20)$$

$$0 = -\frac{1}{\rho_0} \frac{\partial p}{\partial z} - g \quad (15.21)$$

After making a subtraction, the Eqs. (15.20)–(15.21) can be further simplified as

$$\frac{\partial^3 u}{\partial z^3} = 0 \quad (15.22)$$

and Eq. (15.16) was converted to

$$\int_0^H u dz = 0 \quad (15.23)$$

with the boundary condition

$$\frac{du}{dz}|_{z=H} = \frac{1}{\rho\nu} \frac{d\gamma}{dx}, \quad u|_{z=0} = 0 \quad (15.24)$$

The solution (15.18) satisfying the constraints in Eqs. (15.19) and (15.20) is obtained as

$$u = \frac{1}{\rho\nu} \frac{d\gamma}{dx} \left(\frac{3}{4H} z^2 - \frac{1}{2} z \right) \quad (15.25)$$

Figure 15.18 shows the profile of the velocity. After plugging the average velocity whose value was about 2 cm/s (Fig. 15.16c) in the forward flow region into Eq. (15.25), it could be calculated that the surface tension gradient $d\gamma/dx$ was equal to 0.014 N/m².

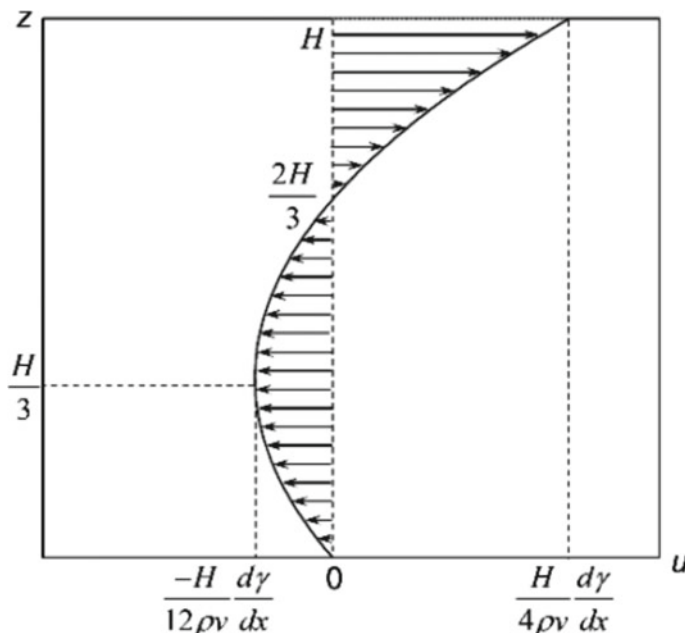


Fig. 15.18 Velocity profile inside liquid gallium which is far away from the boundary in the forward flow region [22]. All pictures are reproduced with permission

15.8 Temperature Effect on Galvanic Couple Induced Marangoni Flow of Liquid Metal

With the elimination of the Rayleigh–Bénard convection influence, Tan et al. [22] analyzed the contribution of another factor: the surface tension gradient caused by temperature drop. In general, the relationship between surface tension and temperature was linear and negative: $d\gamma/dT < 0$. This surface tension gradient would drive the flow at the interface toward higher surface tension region (lower temperature region), which was contrary to the experimental result. Therefore, a supplementary experiment was conducted for further exploration. The copper bulk was removed, and the semiconductor cooling plate was transferred to the bottom. No obvious Marangoni flow could be observed when the temperature field of liquid gallium gets stabilized. This indicated that the surface gradient which was directly generated by the temperature difference (below 20 °C) was too small to drive the liquid gallium surface flow. In a word, the temperature determined surface tension difference was very small and was not the primary reason here.

After further analysis, the reason for the Marangoni flow was attributed to the kinetic behavior caused by electrochemical reaction. When the metal gallium alone was immersed in HCl solution, metal oxidation occurs through an anodic reaction and hydrogen reduction is through a cathodic reaction as shown below:



Consequently, both anodic and cathodic reactions are coupled in a corrosion process. The potential of the isolated gallium electrode (E_c), which was also called the corrosion potential, could be acquired through mixed potential diagrams. The corrosion potential E_c was higher than $E_c(\text{Ga}/\text{Ga}^{3+})$, but lower than $E_c(\text{H}/\text{H}^+)$, where $E_c(\text{Ga}/\text{Ga}^{3+})$ and $E_c(\text{H}/\text{H}^+)$ were the equilibrium potential of anodic and cathodic reactions, respectively.

Then, engaging copper in this interaction, a copper–gallium corrosion couple would form (Fig. 15.19). Thus, the essence of this phenomenon was a galvanic corrosion problem, which was similar to some common corrosion couple like steel–carbon couple, copper–zinc couple, and titanium–zinc couple. In this copper–gallium corrosion couple, due to the higher equilibrium potential of copper ($E_c(\text{Cu}/\text{Cu}^{2+})$) relative to $E_c(\text{H}/\text{H}^+)$, the copper would not dissolve and play the cathode of reaction (15.27). There would be current flow from copper to gallium. For the gallium electrode, reactions (15.26) and (15.27) were happened simultaneously. However, there is only reduction reaction (15.27) on the copper electrode. Therefore, in terms of the dissolution of gallium, it was mainly caused and accelerated by the galvanic corrosion couple which was formed by contact with the copper, besides the reason of coupled reactions (15.26) and (15.27). The inserted small figure of Fig. 15.19b showed the schematic diagram of the electrode potential distribution in solution across the surface of a galvanic corrosion couple. The potential distribution was between $E_{\text{corr}-A}$ and $E_{\text{corr}-B}$ and varied with the distance from the A–B junction. $E_{\text{corr}-A}$ and $E_{\text{corr}-B}$ were the free corrosion potential of element A and B in solution, respectively.

To obtain a quantitative data here, one could measure the potential distribution of the Cu–Ga corrosion couple on gallium surface [22]. The experimental arrangement is shown schematically in Fig. 15.19a. The positive pole of electrometer was connected with the copper bulk, and the negative pole was connected with a saturated calomel reference electrode (SCE). The measurement result indicated that the potential distribution was really regular. The potential reached maximum value at the position of Cu–Ga junction and then decreased with increase of the distance from this junction. There was a pattern that the minimum point of the potential corresponded to the transition point of Marangoni flow. In the range of Cu–Ga junction to transition point, the potential drops and the Marangoni flow go forward along the x-axis. In the range of transition point to the far end, the potential rose and the Marangoni flow reversed.

The relationship between the surface tension and potential across the liquid metal–solution interface can be depicted by the Lippman equation:

$$\gamma = \gamma_0 - \frac{1}{2}c(E - E_{\text{PZC}})^2 \quad (15.28)$$

where γ is the value of surface tension, γ_0 is the maximum value, c is the capacitance per unit area, E is the potential across the liquid metal–solution interface, and E_{PZC}

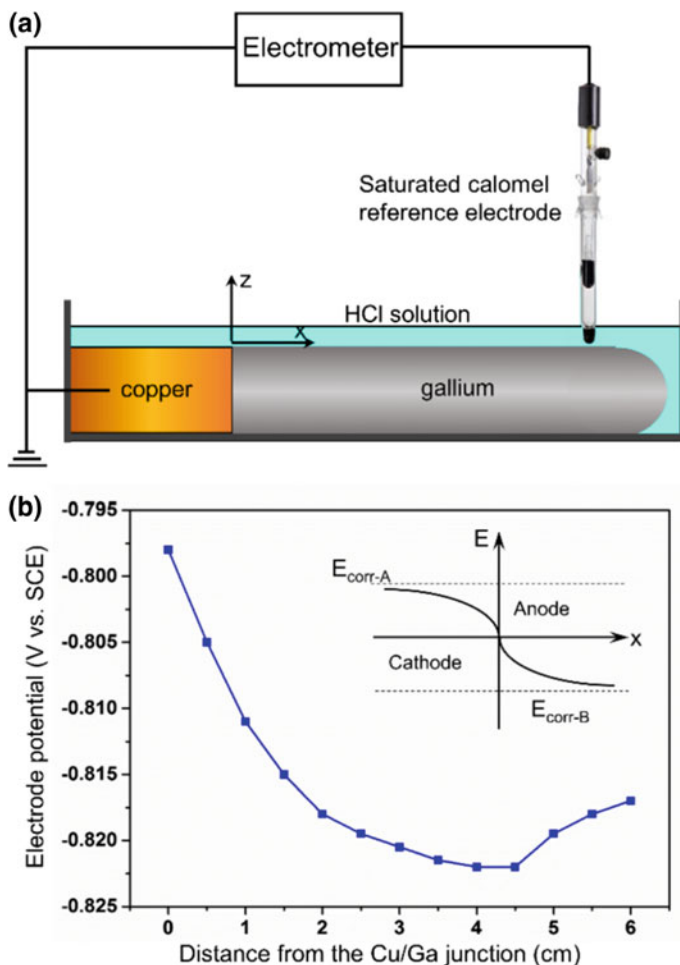


Fig. 15.19 **a** Schematic diagram showing the experimental arrangement for measurement of gallium potential distribution of the Cu–Ga corrosion couple; **b** Experimental points showing the gallium potential distribution. The inserted figure was a theoretical schematic diagram of the electrode potential distribution in solution of a galvanic corrosion couple [22]. All pictures are reproduced with permission

is the potential of zero charge (PZC). According to the literature [23, 24], E_{PZC} is -0.91 V (vs. SCE) and the surface tension of gallium is at its maximum value on this potential condition. Because the potential range of measurement values was on the positive side of the electrocapillary maximum (E_{pzc}), the surface tension of gallium would increase with the reduction of the potential across the liquid gallium–solution interface. Thus, it could be concluded that the position with the highest surface tension on liquid gallium surface was the transition point. Under the effect of surface tension gradient, the Marangoni flow of liquid gallium on both sides of transition

location was pointed to this position. What is more, in absolute terms the derivative of the potential with respect to x -axis coordinate in the forward flow region was higher than that of the counter flow region, which corresponds to the higher surface tension gradient and a faster velocity along liquid gallium surface (Fig. 15.16c). Plugging the potential value of Fig. 15.19b into Eq. (15.28), one derived that the surface tension drop was equal to 4.08×10^{-4} N/m in the range of 0–4 cm. The capacitance per unit area on gallium surface was taken as $18 \mu\text{F}/\text{cm}^2$ according to the reference [24]. Thus, the surface tension gradient $d\gamma/dx$ was equal to 0.0102 N/m^2 , which was of the same order as that calculated in Sect. 15.7.

According to the abovementioned analysis result, the Marangoni flow on liquid gallium here was mainly caused by the nonuniform potential distribution owing to copper–gallium corrosion couple [22]. However, temperature gradient also played an important role. Figure 15.20a shows the variation of transition point when the two ends of the gallium strip's upper surface were at different temperatures. The result indicated that the length of forward flow region shrank obviously when the temperature rose at Cu–Ga junction but reduced at the far end. To further explore the influence of temperature, we measured the gallium potential distribution when the Cu–Ga junction ($x = 0$) was at 50°C and at the far end ($x = 6 \text{ cm}$) was at 29.6°C as shown in Fig. 15.20b.

Combining Fig. 15.20a, b, one can reach the following conclusions [22]: (a) The result further proved that the transition location was the lowest point of potential distribution along the gallium surface; (b) When the temperature of Cu–Ga junction was at 29.6 and 50°C , respectively, the two corresponding potential distribution curves approximately coincided in the region near Cu–Ga junction; (c) At the region near the far end, the lower the temperature, the higher the potential. Therefore, it could be inferred that the potential distribution was dominated by the corrosion couple in the forward region, while the temperature has a small impact. However, the corrosion couple effect on potential distribution was weakened with the increase of the distance from the Cu–Ga junction. Thus, at low temperature, the potential was higher than at high temperature in the far end, resulting in enlarging for the counterflow region. From the experiments, one can also find that the Marangoni flow in the forward flow region was still faster due to a higher gradient of potential distribution rather than the slow one of the counter flow regions.

Overall, the liquid gallium in channel would have obvious Marangoni flow when it was contacted with copper bulk and formed a Cu–Ga corrosion couple [22]. Control experiments and numerical simulations indicate that, even natural convection and temperature gradient were excluded, the kinetic behavior caused by the galvanic corrosion couple would serve as the main cause to lead to the nonuniform potential distribution and even the formation of surface tension gradient on liquid gallium's surface. And this conclusion was further confirmed by combining the experimental measurement of liquid gallium surface potential and the thermocapillary effect. Further, experiments on the variation of the Marangoni flow under different temperature conditions show that a higher potential in the far end at low temperature would lead to

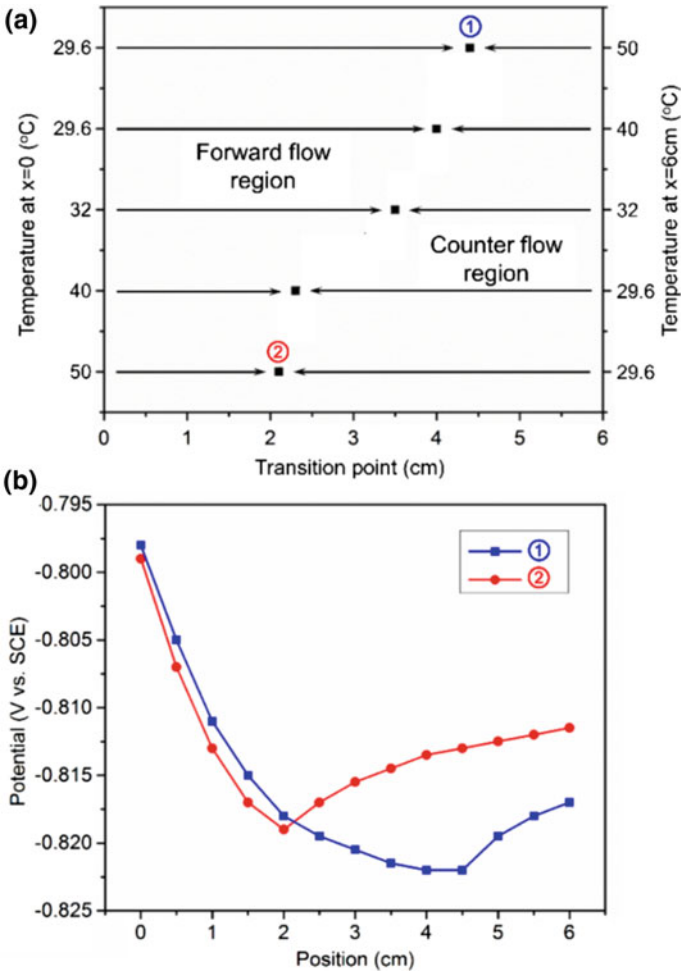


Fig. 15.20 **a** The variation of transition point when the two ends of the gallium strip's upper surface were at different temperatures; **b** Comparison of the gallium potential distribution under two temperature conditions [22]. All pictures are reproduced with permission

the enlarging of the counter flow region. All these phenomena suggest given specific designs on the configurations, structures, and materials between liquid metal and surrounding structures, a group of self-actuated liquid metal machines can possibly be made in the coming time.

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Chapter 16

Liquid Metal Wheeled 3D-Printed Vehicle



Abstract Liquid metal as smart soft material can serve as powerful core elements in innovating unconventional dynamic system. For illustrating purpose, this chapter presents a basic strategy to develop the liquid metal driven vehicle and the related soft machines it may involve. Miniaturized vehicles are witnessing an increasing demand in many areas such as lab-on-chip, flexible fabrication, microfluidics, and small object manipulation. Lots of efforts had therefore been made to build a small-scale, controllable, robust, and adaptable carrying vehicle. To explore an alternative way, this lab (Yao and Liu in RSC Adv 6:56482–56488 [1]) demonstrated a new conceptual vehicle driven by liquid metal droplet “wheels” with geometric size in millimeter scale. Unlike former trials, this vehicle is a movable structure composed of soft wheels and rigid body. Such a hybrid construction could adapt to multiple electrolytes especially NaOH solution. Under variable conditions of electrical voltages and channels, the vehicle can be controlled precisely to achieve progressing, steering, and more complex locomotion. With a boat-like core body, the vehicle can take burdens up to 0.4 g at a speed of about 25 mm/s. More sophisticated vehicles with integrated manipulators and power supply could still be built based on such attempt. This kind of vehicle design realizes complex and accurate controlling as well as driving of miniaturized robotic structure. The finding may shed light for the construction of further complex miniaturized machine or robot in the coming time.

Keywords Liquid metal wheel · 3D printing · Miniaturized vehicle
Hybrid construction

16.1 About Liquid Metal Wheeled Vehicle

During the long years’ process in developing microrobot devices, vast structures and manufacture methods have been carried out by way of the latest technologies such as MEMS, biomedical chip, molecular self-assembly, etc. [2–8]. Miniaturized motor is one of the hottest research spots in small-device area, as power supply is a key factor among them during their delivery, transport, assembly, and mixing process.

Previous efforts to build small-scale motors generally fall into two main categories. One is catalytic chemical reactions [2, 7] which generate gas bubbles among the surface of rod or sphere-shaped motors dipping in fuel chemical solutions. The other one is to implement exterior physical fields such as electric field or magnetic field [9–13]. Electric field can break up the symmetry of surface energy of motors via gas generation or uneven electric double layer, while magnetic field can exert directional mechanical forces on granular motors with magnets attached upon the surfaces or inside the bodies. Either strategy has attracted lots of attention and has been experimentally investigated so far.

Based on these motors, functional devices or carrying vehicles can be further developed. An intuitive idea is to attach target objects onto motors through electroplate or incubate techniques. Researchers in biomedical and pharmaceutical areas tend to work on this way since it can deliver drugs or modified biomolecules with microscale maneuverability. In most cases, vehicles and burdens are closely integrated with no distinct interfaces, while the whole systems are powered by catalytic chemical reaction which can lead to consumption of metal electrodes. A relatively larger vessel was also devised. Diller and Sitti [3] proposed magnetic robotic small grippers of a customized U-shape which is manufactured by rubber molding. External magnetic field is needed in this particular example which can control the position, orientation, and opening/closing state of grippers. In view of associating and aligning these different types of small vehicles, one can further depict a vision of micro-factory concept. Differing from its counterpart in real industry, micro-factories have much smaller transporters, manipulators, and grippers. Comprised of basic elements such as power supply, transportation, manufacture, and assembly, miniaturized factory can perform significant roles in many fields such as medicine test, cell culture, lab-on-chip, and so on.

Yao et al. [1] proposed and demonstrated a new kind of millimeter-scale boat-like vehicles driven by soft liquid metal wheels immersed in aqueous solutions and powered by exterior electric fields. Eutectic gallium–indium (EGaIn) liquid metal is a metal material which has a room temperature melting point and is basically composed of gallium and indium elements. Previous works have shown that liquid metal droplets can swim, swirl, and deform in electrolytes based on Marangoni effect and surface tension asymmetry [14–16]. Regarding liquid metal droplets as variable motors [17, 18], they can be exploited as soft and compliant wheels of the miniaturized vehicles. Such assembly will accommodate the design of complex body structures as the power source can be switched from external electric field to interior button cells. In the fabrication approach, 3D printing technology is implemented to fabricate the rigid body of the vehicle. Carrying capability can be up to 0.4 g with overall dimensions of 10–20 mm. Both fabrication and actuation methods can be improved in order to build vehicles of different sizes to meet varied tasks.

16.2 Fabrication of Liquid Metal Vehicle

The aforementioned liquid metal vehicle is a millimeter- to centimeter-scale carrier with a rigid body and several soft liquid metal wheels [1]. In previous research, it has been found that liquid metal droplet can move with exterior electric stimuli in multiple conductive liquors such as alkaline, acid, and NaCl solution where the droplet submerged (Fig. 16.1a). Thus, a rigid body can be assembled with soft liquid metal droplets to form a vehicle. The EGaIn eutectic alloy was here chosen as room-temperature liquid metal due to its high surface tension and fine conductivity [19]. The body can be designed and fabricated into various shapes combined with different numbers of soft wheels. In the following, three representative structures with one, three, and four wheels are presented, respectively. The body structure slightly floats upon the aqueous solution in order to reduce friction retardation force. Theoretically, plenty of vehicles could be driven and controlled simultaneously.

Regarding the assembly of the vehicles, for solo-wheel liquid metal vehicle, a droplet of liquid metal is first injected into the Petri dish, then a 3D-printed shell can

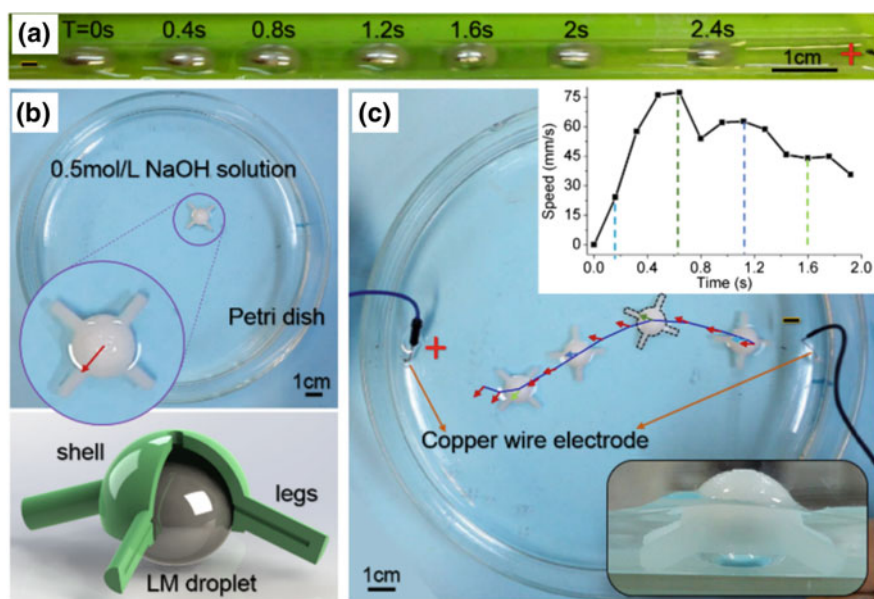


Fig. 16.1 Solo-wheel liquid metal vehicle [1]. **a** Liquid metal drop rushing toward anode in an open-top channel. Red “+” represents anodic electrode while black “-” represents cathode. Successive snapshots are overlapped on the same picture. Applied voltage is 23 V. **b** A 3D-printed body shelters a liquid metal droplet and forms a solo-wheel vehicle. Inner structure can be seen from the sectional view of the vehicle below. **c** Solo-wheel liquid metal vehicle can travel across the Petri dish with applied voltage of 26 V. Chromatic short arrows represent the orientations of the vehicle every 0.32 s, and the positions are recorded to form the trajectory. The lower half of the vehicle is submerged in 0.5 mol/L NaOH solution, which is shown at lower right corner and the instantaneous speeds are plotted at upper right. All pictures are reproduced with permission

be applied to cover the sphere droplet [1]. Water level is at the waist of droplet in case of that the solution might drift the shell away. For four-wheel and boat-like liquid metal vehicles, first the copper rods are stuck to the solid body structures, which is plastic sheet or 3D-printed triangular boat-like vehicle, then the partial assembled structure was put into electrolyte and let to float upon the surface. The water level here should allow the bottom end point of copper rods to be not far away from the vessel bottom. Thus, the liquid metal wheels could bridge the distance. After that, liquid metal droplets/wheels are injected at the end points of the copper rods, contacting with the rods and the whole vehicle is finally assembled.

On the activation of locomotion, two copper electrodes are implemented at the opposite sides of basic solution [1]. The shape of electrodes may affect the locomotion, because it influences the electric field distribution. Over the experiments, wire electrodes are used for solo-wheel and four-wheel liquid metal vehicles, and copper sheet electrodes for boat-like liquid metal vehicle. Electrodes are connected to a constant voltage source (ZhaoXin KXN3030D) with the applied voltage ranging from 15 to 26 V.

For the fabrication of the channels, the virtual 3D model of channels was designed by software Solidworks 2013. The PMMA transparent channel is CNC machined, while the channel with three grooves is SLA 3D printed. The lengths of both channels are 100 mm, and the widths are 37 and 25 mm, respectively. Grooves of the 3D-printed channel have widths and depths of 5 mm.

16.3 Solo-Wheel Liquid Metal Vehicle

At the first step, to prove the feasibility of the concept, a 3D-printed coat covering a liquid metal droplet was designed [1], which can be regarded as a solo-wheel liquid metal vehicle. The solo-wheel vehicle is a hemisphere shell with four uniformly distributed legs stick out at four extreme ends of the shell. The rod legs would support the shell structure and prevent it from overturn. A mono-venthole is arranged at the top center of the hemisphere in case of hydrogen gas accumulation which may split the vehicle and liquid metal wheel. A demi-semi-sectional view of the solo-wheel vehicle is illustrated at the bottom of Fig. 16.1b, of which the green part represents the 3D-printed shell and legs, with gray-colored liquid metal droplet coated in the center. A glass Petri dish is implemented as experimental container in which liquid metal vehicle can swim in electrolyte. Meantime, an external 26 V electric potential is applied at the two opposite ends of Petri dish (anode at left side while cathode at right side in Fig. 16.1c). The diameter of dish is about 16 cm from which we can infer that the electric field intensity is ~ 173.3 V/m. Liquid metal droplet had a volume of about 0.1 ml (the same as in Fig. 16.1a). Vehicle shell structure wraps the upper parts of droplets and would synchronize with the movement of droplet by physical contact. The electrodes are the tips of two copper wires with diameters of 0.5 mm. Half of the solo-wheel vehicle is immersed in the electrolyte of 0.5 mol/L NaOH, which is shown at the bottom right side of Fig. 16.1c.

According to previous research [14], when an external electric field is applied to the electrolyte, liquid metal droplet dipping in the solution can be driven by asymmetry of surface tension. On the basis of Lippmann's equation, one has

$$\gamma = \gamma_0 - \frac{1}{2}cV^2 \quad (16.1)$$

where γ is the surface tension, c is the capacitance of electric double layer (EDL) per unit area, V is the potential difference across the EDL, and γ_0 is the maximum surface tension when potential difference is zero. Electric potential would increase the V at the cathodic pole of liquid metal droplet and decrease the V at the anodic pole at the same time. Thus, the surface tension at two opposite sides would decrease and increase, respectively; meanwhile, a surface tension gradient would appear simultaneously. On account of Marangoni effect, the gradient would lead to a fluxion along the surface of liquid metal droplets from cathodic pole to anodic pole. Impelled by this surface flow, liquid metal droplets can move toward the anodic electrode at a speed ranging from 10 mm/s to 80 mm/s, approximately.

Figure 16.1c exhibits the locomotion trajectory with a fixed time interval of 0.2 s, from which it can be noticed that the vehicle orientation would veer accordingly (orientation is labeled by red arrows along with trajectory [1], which is shown in the up-down zoom-in view of vehicle, Fig. 16.1b. Instantaneous speed ranges from 0 to 77 mm/s, which is spotted in upper right of Fig. 16.1c. The distortion of the trajectory can be interpreted by slight unevenness of viscous friction between different legs and aqueous solution, frictional resistance between legs and Petri dish, along with irregular glass bottom. The shape of the trajectory varies within repeated experiments.

16.4 Four-Wheel Liquid Metal Vehicle

Considering that solo-wheel liquid metal vehicle cannot veer and take burdens, a four-wheel liquid metal vehicle is further presented [1], which was composed of four EGaIn droplets and a square plastic sheet. Four copper rods are adhered onto the square plastic sheet (15 mm $\times$ 30 mm) at four extremities with cyanoacrylates super glue (502 instant adhesive). The rods are curved into L-shaped structures with upper parts parallel to plastic sheet to facilitate fixation and stickup. Due to surface tension of aqueous solution and hydrophobic property of polyethylene plastic, the plastic sheet would float upon the electrolyte surface along with four L-shaped copper rods. Four EGaIn liquid metal droplets are adhered to lower parts of copper rods through wetting mechanism while the volume of each droplet is about 0.1 ml. The whole apparatus is accommodated in a polymethyl methacrylate (PMMA) open-top channel and submerged in aqueous solution. The channel is a square ditch, of which the length is 100 mm, the width is 25 mm, and the depth is 8 mm. On account of buoyancy generated by aqueous solution surface tension, the end points of copper rods have a distance of ~ 2 mm away from the bottom of PMMA ditch. Therefore,

liquid metal droplets can bridge the space with their sphere form by contacting the bottom of channel and the copper rods simultaneously.

When droplets attach and wet copper rods surface, after applying an exterior electric potential, aforementioned liquid metal locomotion can be delivered to the rods through a dragging force [1]. For current liquid metal vehicle, with four rods and four liquid metal droplets, the whole structure can be uniformly propelled by such locomotion. To investigate the critical characteristics of vehicle locomotion and propulsion, a series of comparative experiments are conducted. First, incremental voltages are applied starting from 15 to 23 V with a step of 4 V. While the electrolyte is 0.5 mol/L NaOH solution, the electrodes are placed at two extreme ends of PMMA channel. Power supply is a constant voltage source which can provide a highest voltage up to 30 V. To better demonstrate the locomotive velocity and direction, a black letter Y signature is drawn at the upper surface of transparent plastic sheet.

Before applying the step voltage, non-wheel structure is gently placed on the surface of water solution with a tweezer [1]. The structure would be floated by solution surface tension just like gerridae standing on water surface. At the edge of sheet, an obtuse contact angle (θ) can be observed, as is illustrated in Fig. 16.2a. When the structure is immersed in aqueous solution, a syringe is used to inject liquid metal toward four copper rods, respectively. Liquid metal would wet the surface of copper and adhered to it stably. After four times of injection, the four-wheel liquid metal vehicle would be assembled completely and capable to voyage Fig. 16.2b). Figure 16.2c demonstrated the continuous motion process of four-wheel vehicle when applied with a 19 V electric potential. Center point of signature Y is utilized as the reference point to calculate horizontal displacement and velocity. There are three different forces affecting the vehicle structure [20], which are electric potential induced liquid metal propelling force, viscous friction between the structure and the basic solution, as well as friction between soft liquid metal wheels and PMMA substrate, respectively. For every single wheel, its propelling force is determined by liquid metal volume and adjacent electric field intensity. Considering that the precise size of each wheel cannot be strictly equivalent, and the electric field intensity is not uniformly distributed, the propelling forces of different wheels are thus unequal. Meantime, due to machining error, the friction between liquid metal wheel and PMMA channel bottom also varies according to the positions of contacting points. Taking above factors into account, the locomotive speeds of different wheels would be different, and thus the vehicle would rotate and oscillate within open-top channel. For instance, the upper two wheels have a higher speed compared with their lower counterparts, as shown in Fig. 16.2c. As a result, the letter Y signature yaws clockwise along with the plastic body and then becomes restricted by channel sidewall. Such deflection happens occasionally and is dominated by the precise volumes of injected liquid metal wheels.

To depict the locomotive characteristics of liquid metal wheeled vehicle, displacements and instantaneous velocities are charted in Fig. 16.3a, b with applied voltages of 15, 19, and 23 V, respectively [1]. The positions and velocities are recorded every 0.08 s. From Fig. 16.3a, we can see that the displacement of vehicle ascends gradually in any case, whereas the red line (19 V) and blue line (23 V) are much closer

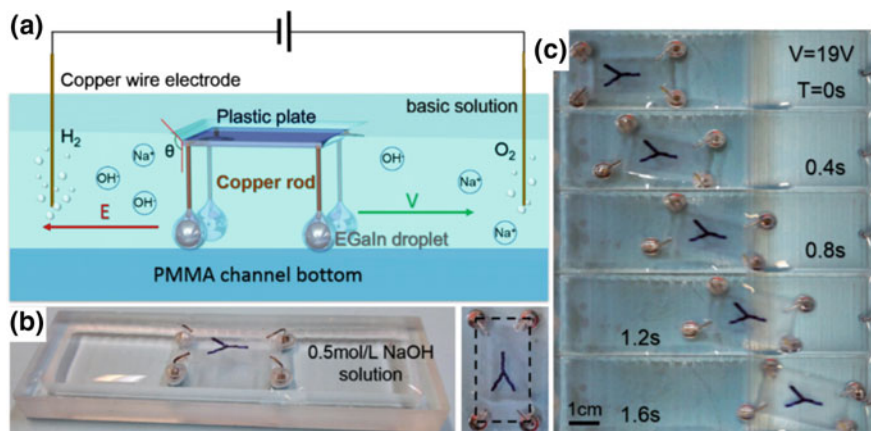


Fig. 16.2 Four-wheel liquid metal vehicle [1]. **a** Schematic diagram of experimental setup and ambient environment. Transparent plastic sheet floats upon the surface of basic solution. At four extremities, there are four copper rods adhered to the sheet with four liquid metal droplet “wheels” attached to their feet, separately. θ represents the contact angle between plastic sheet and aqueous solution. Green V represents motion direction and red E represents electric field orientation. **b** Vehicle and open-top channel apparatus. The transparent plastic sheet is outlined by dashed lines, with a Y signature written on it to show the position and orientation of the vehicle. **c** Continuous captures of vehicle locomotion at every 0.4 s. Applied voltage is 19 V. All pictures are reproduced with permission

to each other when compared to the black line (15 V). When the conducted voltage is lower than 15 V, the vehicle moves too slow to accomplish the entire distance of about 60 mm. It is obvious that the average speeds are not linearly related to voltage increases. To confirm such a dependency and eliminate the impact from stochastic factors, experiments are repeated with different voltage steps of 5 and 3 V, respectively. There exists a quite similar phenomenon that displacement increase rates of 20 and 25 V are much closer than the counterpart rates with 15 V (Fig. 16.4a, b). When applying a smaller voltage interval of 3 V, such regularity still remains (Fig. 16.4c, d). To further elucidate the phenomenon, instantaneous velocity diagram is shown in Fig. 16.3b, from which it can be clearly noticed that the speeds of 15 and 19 V are much closer and would intersect with each other at several points.

Displacement and instantaneous velocity diagrams with voltage intervals of 5 and 3 V are shown in Fig. 16.4b, d. As a comparative result, displacements and instantaneous speeds data of a single liquid metal droplet locomotion are also illustrated in Fig. 16.4e, f, from which the volume of droplet is 0.1 ml and the voltage increment is 3 V. Here is a tentative further explanation of the phenomenon [21, 22]. The relation between propelling force and locomotive velocity, as well as the fluidic resistance force, needs to be clarified. First, we need to evaluate the Reynolds number of solid vehicle structure swimming in the pool, which is the ratio of liquid inertia force and viscous force. It can be calculated by expression

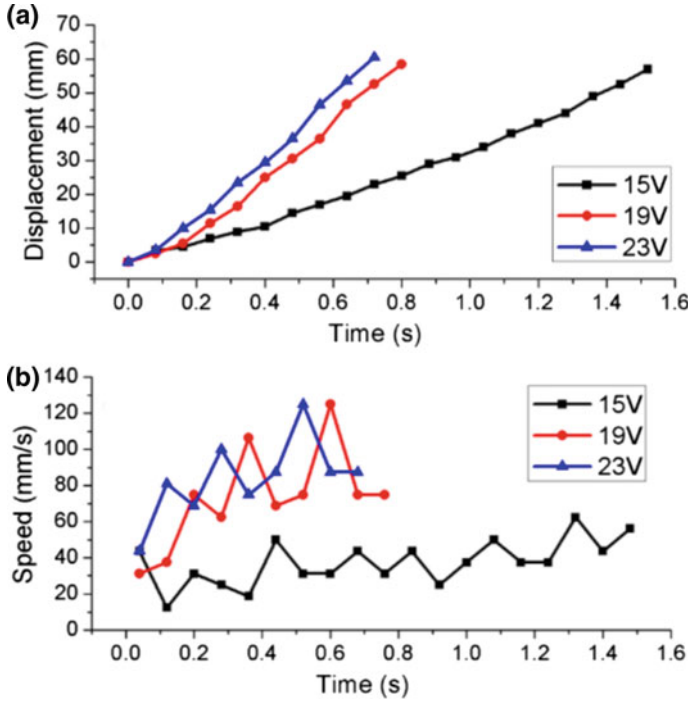


Fig. 16.3 **a** Displacements of the locomotion with different applied electrical potentials. **b** Instantaneous speeds of locomotion under different voltage conditions [1]. All pictures are reproduced with permission

$$R = \frac{\rho V D}{\mu} \quad (16.2)$$

where ρ is the solution density, V is the flow velocity, D is the characteristic length, and μ is the dynamic viscosity of the fluid. To simplify the computational model, the whole structure is regarded as a single plastic plate, and thus the characteristic distance is 30 mm. The ρ and μ values of 0.5 mol/L NaOH solution are approximately $1 \times 10^3 \text{ kg/m}^3$ and $1 \times 10^{-3} \text{ Pa s}$, respectively, while the motion velocity is assigned with the lowest average speed, which is about 40 mm/s. Then one can get that the Reynolds number of the system is about 1200.

For each liquid metal soft wheel, its propelling force varies with the distances between the wheel and the electrodes, and thus a controllable steering can be achieved by placing copper electrodes at asymmetrical positions of vehicle in a free space [1], as shown in Fig. 16.5a. The four-wheel liquid metal vehicle stays still in a large glass Petri dish; the filled solution is 0.5 mol/L NaOH alkaline solution while the diameter of Petri dish is 10 cm.

The orientation of vehicle is defined as the pointing direction of the lower part of character “Y”. If one wishes to turn the direction of vehicle, for example, right-hand

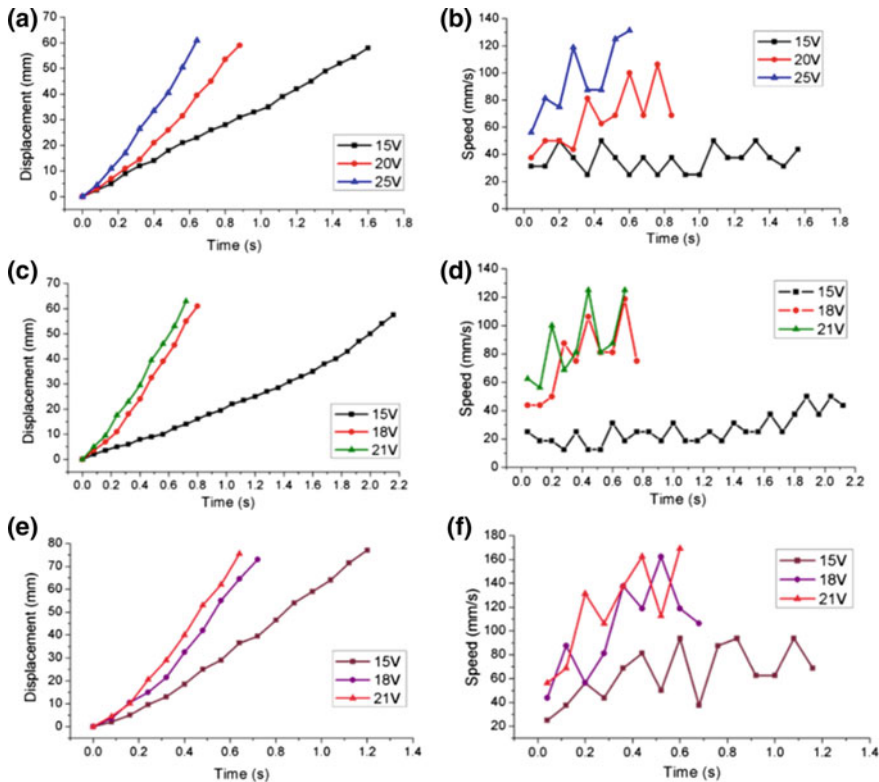


Fig. 16.4 Displacements and instantaneous speeds of locomotion under different conditions. **a** and **b** Diagrams with the applied voltage interval 5 V. **c** and **d** The voltage interval is 3 V. **e** and **f** Diagrams of a single liquid metal droplet with no affiliated solid structure. The voltage interval is 3 V [1]. All pictures are reproduced with permission

rotation, he or she can put the anodic electrode at the right side of the front part of vehicle, while the cathode at the left side of the front part of vehicle. Obviously, the front part is closer to copper electrodes and therefore has a stronger electric field intensity. Accordingly, the front two wheels would display a higher rightward directional propulsion and then the whole vehicle would rotate clockwise [1]. Apparently, left-hand rotation can also be achieved in a similar way via exchanging the anode and cathode. Another way to approach directional rotation is to place electrodes closer to the rear part of the liquid metal vehicle, while in this case, anode needs to be put at the right side of rear part of vehicle to turn it left, and left side of rear part to turn it right, contrarily. From Fig. 16.5a, one can calculate that the entire average angular speed is ~ 0.73 rad/s.

Besides, analogying to the real manned sedan, liquid metal vehicle can move backwardly [1], as is shown in Fig. 16.5b. The anodic electrode is placed at the tail side of vehicle and the cathode in front of the vehicle. With a 19 V voltage

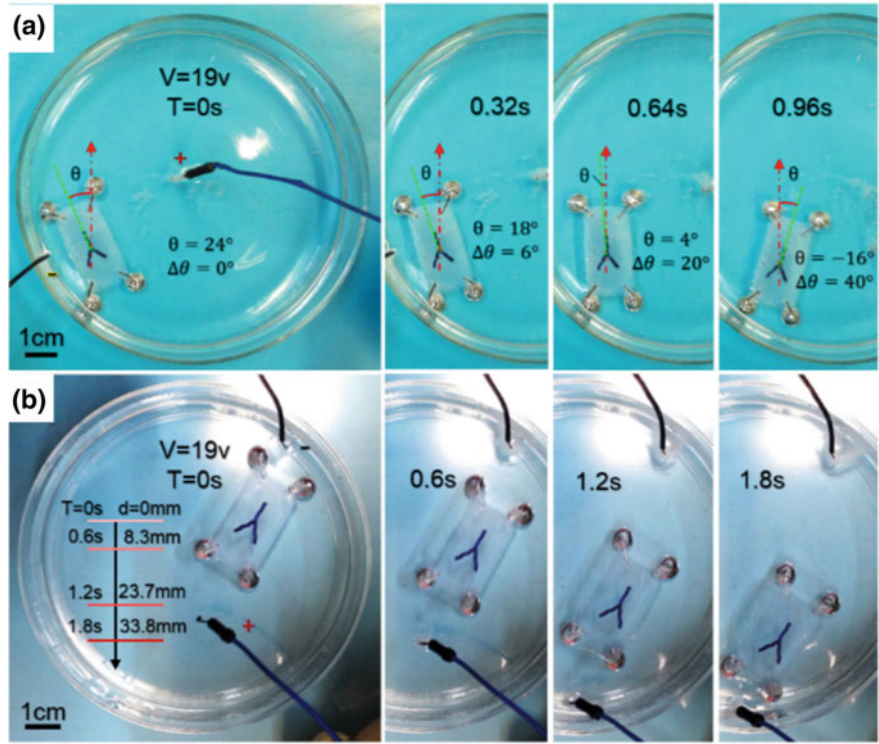


Fig. 16.5 Steering and reversing [1]. **a** Steering of the vehicle. θ represents the absolute angle of the vehicle, while $\Delta\theta$ represents relative steering angle from which we can calculate the angular velocities. **b** Reverse of the vehicle. The coordinate at left shows the displacements along the arrow direction at every moment. All pictures are reproduced with permission

implementation, the vehicle would back down with an average speed of ~ 18.8 mm/s. The displacement and speed here depend on the traveled distance along the downward coordinate (black arrow), while the distance numbers are labeled above red stripes with different shades.

With an overview of above experiments, it is feasible to achieve a more complex and comprehensive locomotion through combining all these individual manipulations [1]. Compared with manned car in daily life, the presented liquid metal vehicle is much more flexible and compliant. For instance, the vehicle can move omnidirectionally and spin around if the electrodes are appropriately placed. Besides, the soft liquid metal wheels can play a role of bumper when the vehicle collides with other rigid objects, and hence the solid structure of vehicle would be protected. When the vehicle runs along the edge of the Petri dish, liquid wheel would contact the glass wall and add a recoil force to the vehicle, in which the liquid metal would act as guide pulley and driving wheel simultaneously.

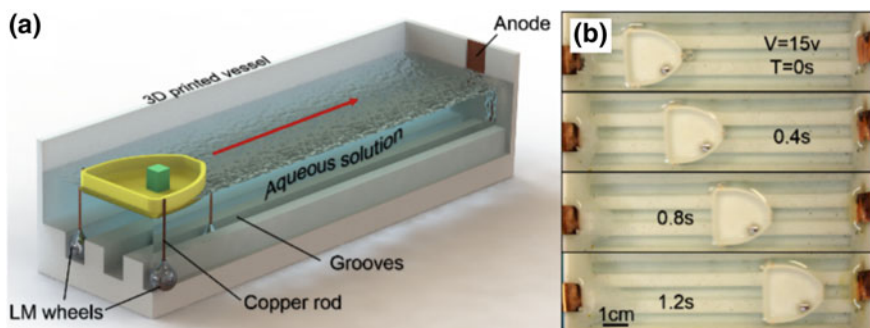


Fig. 16.6 Boat-like liquid metal vehicle running on railway [1]. **a** Experimental setup of the boat-like liquid metal vehicle design. Yellow triangular structure represents the body which can take loads (the green cube). Wheels along with the copper rods are confined within three orbital grooves, corresponding to their positions. The vehicle floats upon the aqueous solution and moves in the direction of red arrow. **b** Continuous snapshots of liquid metal vehicle carrying another liquid metal droplet with a volume of 0.03 ml. Time interval is 0.2 s. All pictures are reproduced with permission

In most application situations, only a movable plastic sheet is not practical to achieve complicated tasks. To broaden the vehicle's ability, the body structure is redesigned utilizing stereolithographic (SLA) 3D printing technology [1]. As preliminary attempts, a triangular boat-like shaped body is fabricated, as shown in Fig. 16.6a. The rest of the parts of structure are quite similar to the four-wheel liquid metal vehicle. Three thin copper rods are stuck to the 3D-printed body. The length of rods is about 20 mm, while the glue is 502 instant adhesive. Regarding the vehicle as a transporter of micro-factory, more accurate trajectory would be needed. A channel with three parallel grooves can thus be designed at the bottom, which can be seen in the partial section view of Fig. 16.6a, b. The channel would be filled with aqueous electrolyte; meanwhile, the body of the vehicle would float upon the solution surface. Liquid metal wheels are injected to the downward end point of the thin copper rods by syringe. Afterward, the liquid metal drops would wet the rods and embed into the grooves, separately. The diameters of wheels are 5 mm, the same as widths of the grooves. For the wheels are well confined in the groove tracks, the whole vehicle structure would follow a quite straight pathway (Fig. 16.6b). With a concave belly upon the body structure, it would be easier to carry loads as well as more complex modules, such as power source or manipulators [23, 24].

16.5 Boat-like Liquid Metal Vehicle

To demonstrate the cargo carrying capability of the vehicle and the relationship between the masses of loads and the velocities of locomotion, further experiment is conducted in which the vehicle carried different volumes of liquid metal droplet, in particular, empty, 0.03 and 0.05 ml EGaIn liquid metal [1]. Motion processes

are recorded accordingly. Displacements and instantaneous speeds are shown in Fig. 16.7a, b. Applied voltage is 15 V, while the concentration of NaOH is about 0.8 mol/L. From the diagrams, we can notice that the vehicle has a highest average velocity (~ 40 mm/s) when taking a 0.03 ml droplet cargo. After a few more repetitive experiments, it is found that the order of velocities is not consistent, which means that the effect of accidental disturbance from turbulence and friction overwhelms the influence of carried loads. If more experiments are conducted with other variables being precisely controlled, the exact relation between the mass of cargo and motion velocity could be further identified.

Anyhow, it can be proven that such a boat-like structure design does own the carrying ability up to hundreds of milligrams. So long as the vehicle would not sink, more cargos can still be loaded. The size of the vehicle could be enlarged to increase its carrying capability. More complex tasks could be done if several customized vehicles cooperate with each other [1]. Furthermore, if equipping the vehicle with grippers or manipulators, a desktop-level miniaturized factory could be accomplished. Another way to improve the vehicle is to mount the vehicle with untethered power source such as button cell, and employ chips and circuits to control

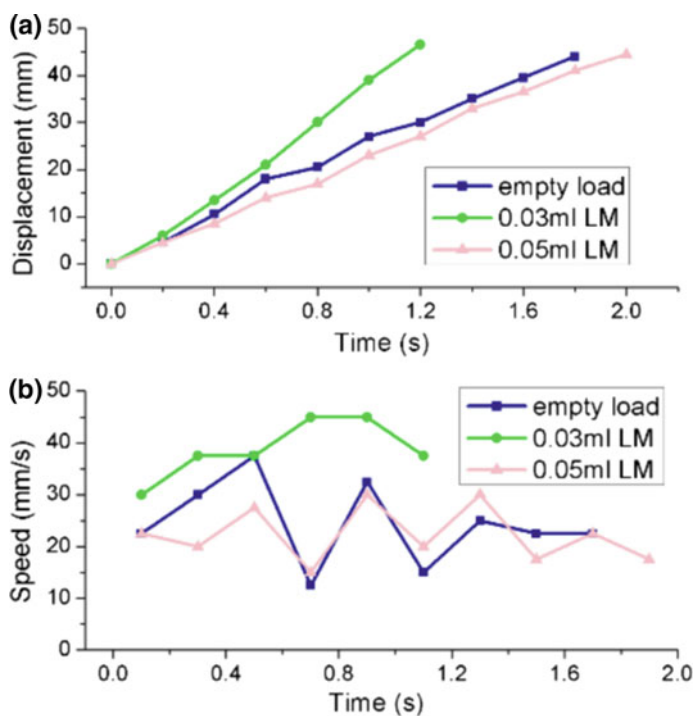


Fig. 16.7 Displacements and instantaneous speeds of three-wheel liquid metal vehicle with different amounts of loads, which are empty, 0.03 ml liquid metal droplet and 0.05 ml liquid metal droplet, respectively [1]. All pictures are reproduced with permission

the motion of wheels individually. As liquid metal wheel is affected by local electric field, putting electrodes close to wheels separately can reduce reciprocal interference and control the wheels precisely.

16.6 Perspective of Future Liquid Metal Vehicle

In the above vehicle based on EGaIn liquid metal droplets, its principal idea is to integrate the liquid metal droplets with a solid body, with the body floating upon aqueous solution to reduce the friction of contact [1]. When applying an exterior electric potential to the vehicle, liquid metal wheels would be propelled by the induced unbalance of surface tension, which would further result in flow along the droplet surface. Here, physical wetting as well as Van der Waals' force connects liquid metal wheels to the body. Thus, when the wheels tend to move, the solid body would be dragged to move forward. The motion characteristics are affected by many factors, in which the dominant one is the applied voltage magnitude. With a higher voltage, the vehicle would move faster, though the speed is not linearly proportional to the voltage according to hydromechanics.

Such a small vehicle can be utilized in many practical fields like small-scale transporter, miniaturized valve, as well as micro-factory [25, 26]. Since the vehicle is controlled by electric potential, which is very easy to modulate, it can have a higher control precision compared with some flagellum propelled swimmers. Another advantage of the current design is that the body structure can be arbitrarily customized so long as it can float upon liquid surface. Such flexibility can bring it more consolidated capabilities, along with its carrying capability. The propulsion force can be adjusted by increasing the number of wheels or voltage magnitude. To improve the design, microcontrollers and built-in power source can be implemented. It is expected that such work can inspire future researches in related areas to build more powerful and flexible miniaturized robots [27, 28], as well as helping to advance the fields of microfluidic systems, programmable intelligent machines, and so on in the years to come.

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