Droplets As Liquid Robots

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Abstract Liquid droplets are very simple objects present in our everyday life. They are extremely important for many natural phenomena as well as for a broad variety of industrial processes. The conventional research areas in which the droplets are studied include physical chemistry, fluid mechanics, chemical engineering, materials science, and micro- and nanotechnology. Typical studies include phenomena such as condensation and droplet formation, evaporation of droplets, or wetting of surfaces. The present article reviews the recent literature that employs droplets as animated soft matter. It is argued that droplets can be considered as liquid robots possessing some characteristics of living systems, and such properties can be applied to unconventional computing through maze solving or operation in logic gates. In particular, the lifelike properties and behavior of liquid robots, namely (i) movement, (ii) self-division, and (iii) group dynamics, will be discussed.

Keywords
Robot, droplet, movement, self-division, group dynamics

1 Introduction

The word "robot" was first introduced in 1920 in a famous Czech play *R.U.R.* (Rossum's Universal Robots) [22], where robots are not clanking metal constructions, but humanlike beings made of soft matter. The author of the play, Karel Čapek, describes them as being made of a protoplasm—a substantive essence of living matter. It is described by Domin in the first act as "a blob of some kind of colloidal jelly that even a dog wouldn't eat." At the time the similarities between colloidal materials and the living protoplasm inside cells was already being investigated [27, 37].

Today robots are typically thought of as dynamic electromechanical objects. In contrast, Čapek's robots did not have wheels, electric power, or computer systems to control them. They were based only on chemical principles and consisted of fluidic colloidal substances. Thus we can consider a droplet based on chemical principles and activated through fluid dynamics to be an embodiment of robotics more sympathetic to Čapek's original conception. Such soft-bodied robots might be made from a variety of substances, including liquid droplets [56] and gels [68]. Such chemical and liquid robots could perform autonomous movement through the exploitation of chemical potential without using predefined mechanical parts, but rather using self-organized fluid dynamics.

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The play *R.U.R.* is famous not only because of the invention of the word "robot"; it was a controversial play that was ahead of its time. Briefly, it was about a mad scientist, Rossum, who discovers how to create artificial life and starts creating artificial human beings. What follows is a factory for making robots, a robot rebellion, and the extinction of the human race. Although the play is almost one hundred years old, it provokes many contemporary questions. In a way, *R.U.R.* also predicted biological engineering, which is now taking halting steps toward creating artificial life. In addition the play used the term "robotka" for female robot, even without gender equality requirements in its time. Only the masculine form "robot" found its way into many languages; the word "robotka" is not used, even in Czech.

The term "robot" derives from the Czech word "robota," which means *forced labor*. In the context of robots in general this meaning still holds. In the context of droplets as liquid robots, we can argue that any force acting on the droplet would induce a response such as movement, division, or release of content. In this article we will develop the idea that forces shape the dynamics of droplets in many different liquid robot contexts.

In another view, droplet-based liquid robots can be considered as a physical embodiment of Braitenberg's *vehicles* [18]. These motile vehicles possess simple environmental sensors linked to actuators at the wheels for movement. In this way Braitenberg's vehicles were capable not only of motion and directed taxis, but also of complex behaviors. It can be argued that mobile droplets possess the basic attributes of vehicles (e.g., sensors, actuators, body), including sensory-motor coupling [46, 51, 57].

The present article is structured as follows. First we introduce droplets in general. Then a literature overview is given to summarize the context of droplet behavior: (i) movement, (ii) self-division, and (iii) group dynamics. This is followed by some examples of droplets moving in mazes or manipulated in logic gates. Finally, liquid marbles are presented as another potential embodiment of liquid-based robotics.

2 Droplets and Vesicles

Droplets are liquid entities for which a degree of immiscibility is required between at least two phases (gas-liquid or liquid-liquid), and the attractive and repulsive interactions between molecules at the interface can give rise to a surface tension, which defines among other things the shape of a droplet. Standard examples include water droplets in air [95], water droplets in oil [5], and oil droplets in water [24]. In addition, molecules can partition preferentially into the water or the oil phase, depending on their hydrophilic or hydrophobic properties. For example, oil-soluble dyes (e.g., Oil Red O, Sudan Black) are used for better visualization of oil phases, while inorganic salts (e.g., NaCl) dissolve preferentially in aqueous phases. However, surfactants, which are amphiphilic molecules containing both hydrophilic and hydrophobic groups, self-assemble on the phase boundary (Figure 1). Surfactants are surface-active compounds that can lower the interfacial tension between the two phases. Droplets can of course form also in the absence of surfactants, but surface-active molecules that self-assemble at the droplet boundary are useful in modulating the interfacial tension of the interface and therefore the properties and behavior of droplets. Another purpose of surfactants is to stabilize droplets by lowering in general the interfacial tension and suppressing droplet coalescence.

When an aqueous droplet is covered by a continuous lipid bilayer in a bulk aqueous phase, it is called a *vesicle* [11]. The self-assembled amphiphilic molecules on the vesicle surface define the vesicle. In principle a vesicle is a water-in-oil-in-water droplet with an aqueous core that can contain water-soluble molecules and a lipid bilayer membrane where oil-soluble molecules can be incorporated. Vesicles are dispersed in the continuous water phase and range in size from tens of nanometers to hundreds of micrometers. For artificially made vesicles using phospholipids or lipids derived from biomembranes, the term *liposomes* is often used, and applications for liposomes range from artificial cells [60] to drug delivery to microcontainers [98].

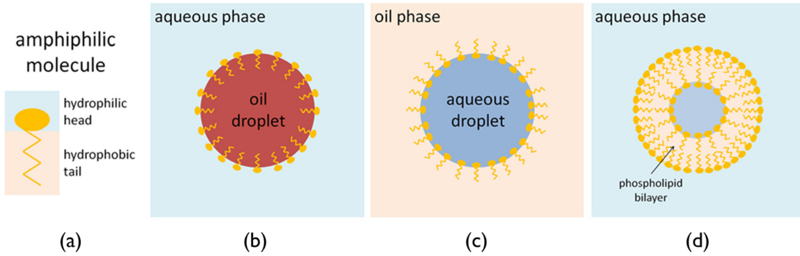


Figure 1. (a) A representation of an amphiphilic surfactant molecule consisting of a hydrophilic head that preferentially partitions in the aqueous phase and a hydrophobic tail that preferentially partitions in the oil phase. Different architectures of surfactants in differently arranged multiphase systems: (b) oil droplet in water phase, (c) aqueous droplet in oil phase, (d) vesicle consisting of a phospholipid bilayer.

Droplets can be produced in various ways. To produce a single droplet or a few droplets, simply dropping liquid from a micropipette or a syringe can be sufficient. Large quantities of droplets can be produced by a wide range of techniques including, for example, atomizers, nebulizers, and homogenizers of various designs. These techniques will produce thousands to millions of droplets dispersed in the continuous phase as emulsions. Typical architectures include oil in water (Figure 1b) or water in oil (Figure 1c) emulsions, but more complex organizations such as double emulsions also exist [36]. The implementation of robotic platforms and microfluidics for the generation and analysis of droplets has been demonstrated [43, 47, 49, 59, 74]. In general, droplets can be produced easily. However, long-term stability is typically achieved through the presence of surfactants, which increase the kinetic stability of the system.

3 Moving Droplets

Droplets can be designed to move and can be controlled by various external forces, and thus the droplets can mimic both the behavior of nonliving objects, such as rocks rolling down a hill, and also the behavior of living cells or small organisms that can move purposefully in response to various stimuli. There are several examples of motion due to applied forces or perceived stimuli: Gravitational force induces gravitaxis (geotaxis), a gradient of chemicals that are soluble in the fluid induces chemotaxis, movement in the gradient of cellular adhesion sites or substrate-bound chemoattractants is called haptotaxis, electrotaxis (or galvanotaxis) is directional movement in response to an electric field, magnetotaxis is movement in a magnetic field, phototaxis is the ability to respond to light, and thermotaxis is migration along a gradient of temperature. These kinds of natural movements are well known for biological objects that have locomotion organelles [23], and in the same way the movement of synthetic objects can be studied for orthologous dynamics. If droplets can become animated and follow one or more of these types of motion, then it would be justified to argue that they are liquid robots, as one of the primary characteristics of robotics is programmed movement. Although it is not common to term moving droplets as robots [56, 92], in the case of solid particles we commonly encounter terms such as swimming micro- or nano-robots [16, 65, 70, 78]. The different types of motion will be presented in the following subsections: Section 3.1 will describe artificial haptotaxis, Section 3.2 will summarize the movement of droplets mimicking chemotaxis, and Section 3.3 will present other examples of oriented movement (such as magnetotaxis or galvanotaxis of droplets).

Figure 2 shows several contexts in which a droplet can be placed and tasked for movement, viewed in vertical cross section. Droplets have been shown to move when placed on a solid surface in air [21] (a), surrounded fully by another liquid (b), or placed in a thin layer of a liquid in contact with both substrate and air [24] (c). When there is an interaction of droplet with solid substrate, the shape of the droplet can change as a result of change in contact angle. Another type of droplet

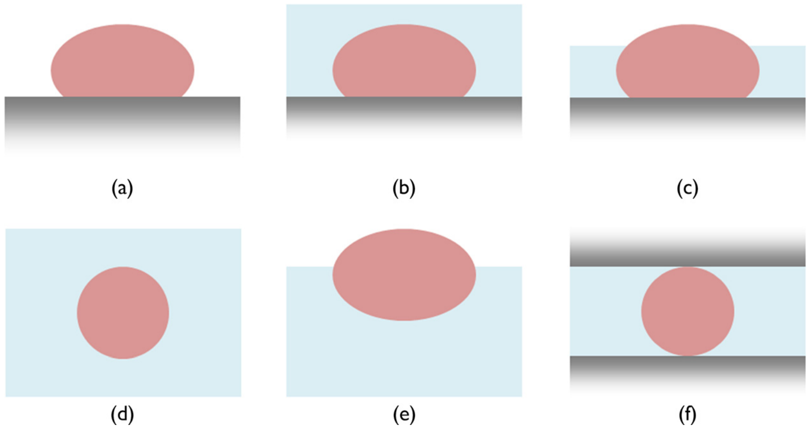


Figure 2. Configuration of droplet movement experiments in a side view: (a) droplet on a solid substrate surrounded by air, (b) droplet on a solid substrate surrounded fully by another liquid, (c) droplet on a solid substrate placed in a thin layer of another liquid, (d) droplet freely swimming in another liquid, (e) droplet floating on the surface of an another liquid, (f) droplet in a channel.

motion is swimming (d), in the case when the droplet and surrounding liquid have similar densities. This will require that viscosity dominate and the droplet move by creating friction with the surrounding fluid. The floating of a droplet on the surface of another liquid (e) happens if the droplet has a lower density than the continuous phase. Both internal droplet dynamics and proximal fluid dynamics in the surrounding fluid may govern droplet movement. Finally, in microfluidics the droplets can move within channels (f). The width of channels and the droplet diameters have similar magnitudes, and the channels are not open to the air. However there can be a configuration where the droplet moves in a channel that is open to the air [62]. Some atypical experimental setups have been used; for example, Sumino et al. have shown rotational motion within a circle normal to the horizontal plane and climbing motion on a stairlike substrate [90].

Studies on oil droplet movement can be performed in various geometrical configurations. Various arenas, shown from the top, are presented in Figure 3. Commonly a round petri dish is used with various depths of the continuous phase [94], where 2D trajectories of droplets are observed and recorded (a). Circular channels can be created, for example, by two rings attached to the glass substrate [76] (b). The space between the inner and outer rings (walls) forms in principle an endless channel ideal for self-propelled droplet experiments. Simple architectures are based on rectangular cells or wide channels (c). Some works deal with droplet movement in more complex systems such as mazes [24, 62] (d).

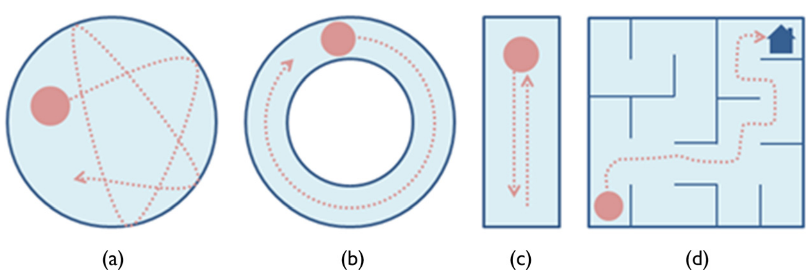


Figure 3. Configuration of droplet movement experiments in a top view: (a) round dish, (b) circular channel, (c) straight channel, and (d) maze.

The droplet movement can be characterized by various parameters; the most common ones are directionality and velocity. Other parameters include acceleration, pause duration, and turning angle [46, 51, 57]. In our article [24] on chemotactic decanol droplets we evaluated also the *induction time*, that is, the time needed for the response to the chemical signal. In the following text, we will summarize experiments according to the designed experimental setup.

3.1 Droplet Movement on Solid Surfaces

In nature, motion induced by an adhesion gradient is called haptotaxis. Droplets can move on solid surfaces without an additional continuous liquid phase if there is any difference in surface properties between the front and the rear of the droplet. This usually results in a difference in contact angle between different parts of the droplet and produces artificial haptotaxis. We present examples below that might be used for various targeted outcomes, such as reversible or irreversible movement.

The classic experiment by the Whitesides group showed how droplets of water can in fact move "uphill" against gravity if the solid surface is patterned with areas that affect the contact angle of the droplet [53]. Droplets consisting of *n*-alkanes and silane molecules behave as *self-runners* on hydrophilic glass or silicon substrates [32]. The mechanism is based on leaving a hydrophobic coating on the hydrophilic substrate, which shifts the center of mass and pushes the droplets towards the exposed hydrophilic area. The movement stops due to depletion of free hydrophilic substrate. It is noted that the droplet trajectories never cross. In another study, reversible self-propelled droplet movements of long-chain alkanes at solid-gas interfaces have been shown [63], with reversibility of movement modulated by temperature changes near the alkane bulk melting temperature.

Cira et al. [21] have shown that miscible liquids such as propylene glycol and water deposited on clean glass cause the motion of neighboring droplets over a distance, because these droplets are stabilized by evaporation-induced surface tension gradients. The droplets move in response to the vapor emitted by neighboring droplets. This kind of movement enables the crossing of droplet trajectories, and no permanent change of substrate surface occurs.

Sumino et al. [90] described oil droplet movement on a glass substrate that is based on a difference in surface tension between the front and the rear of the droplet. This mechanism also allows reversible movement. They have also studied self-running motion of an oil droplet on an acid-treated glass substrate [89]. Similarly, squalene droplets move on a hydrophobic solid substrate [44]. Thus, when using specific substrates and chemical droplets, haptotaxis can be artificially created and studied as long as the system can maintain a differential in surface energy along the droplet with the underlying substrate. This creation and maintenance of a differential in surface energy also underlies the mechanisms of droplet movement presented in the following subsections.

3.2 Chemotactic Droplet Movement

In nature, if a motile cell senses soluble molecules and follows a concentration gradient to the source, or if it moves away from a source of undesirable chemicals (e.g., repellent, toxin), it is displaying a directional movement called positive or negative chemotaxis, respectively [23]. This phenomenon is well known to biologists and intensively studied in living systems. Recently a few laboratories have started to focus on the movement properties of artificial constructs, including the directional movement of nonliving objects in chemical gradients, and such movement is usually called artificial chemotaxis.

Almost all observed movements of droplets in chemical gradients are in fact movements due to gradients of surface tension that are induced by chemical signals. These systems usually involve two immiscible liquids, with one liquid forming the droplet and the other forming the continuous phase (Figure 2b–f). When a surfactant is placed in an aqueous system, it self-assembles at the air-liquid or liquid-liquid interface and lowers the surface tension of the system. Kurup and Basu [35, 61] have used the term *tensiophoresis* for droplet movement due to a gradient of surface tension. When the surface tension of a liquid is altered, liquid and surfactants flow from areas of low surface tension to areas of high surface tension along an interface. This flow continues until the differential in interfacial tension is null, and this phenomenon is known as *Marangoni flow*.

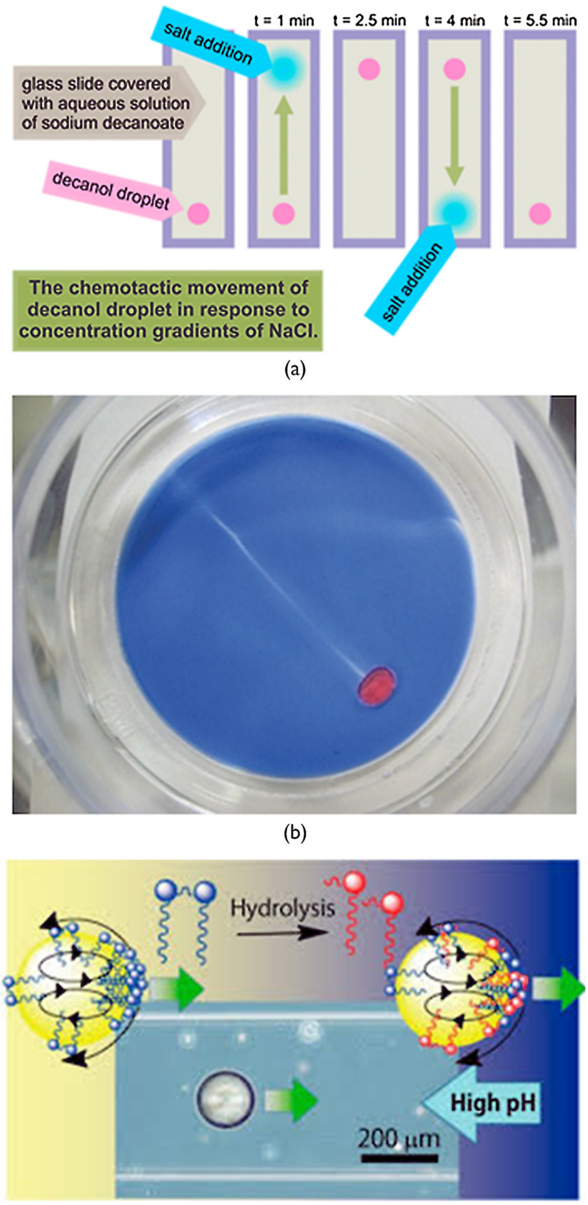
The Marangoni-type oil droplet movements are driven by thermal or chemical concentration gradients that affect the local interfacial tension. The properties of the movement are dependent on the size and shape of the droplets. Nagai et al. [73] have found that a pentanol droplet with a volume of less than 0.1 μl shows irregular translational motion, whereas intermediate-sized droplets of 0.1–200 μl show vectorial motion. This mode selection is interpreted in terms of competition between the droplet size and the critical wave number in the instability due to the Marangoni effect. In addition, Horibe et al. [51] showed mode-switching for oleic-anhydride-fueled oil droplets that again depended directly on the size (volume) of the droplets. For this system it was also argued that the self-moving oleic-anhydride-fueled oil droplets are an embodiment of homeostasis and therefore contain the basis for sensory-motor coupling. Later, possible memory effects in these self-moving droplets were reported, implying perhaps a limited degree of autonomy [46, 57].

We have studied the movement of 1-decanol droplets in the presence of sodium decanoate solution [24] (Figure 4a). Decanol droplets were able to follow salt additions and mimic the chemotactic behavior of living organisms [23]. This droplet system has also the ability to reverse the direction of movement repeatedly, to carry and release a chemically reactive cargo, to select a stronger concentration gradient from two options, and to initiate chemotaxis by an external temperature stimulus. Again here the interfacial tension between the decanol droplets and the surrounding aqueous solution is governed by the interaction of the decanoate surfactant with the added salt gradients.

A system of oil droplet movement based on fatty acid chemistry has been proposed by Hanczyc et al. [45, 48, 97] (Figure 4b). An oil phase containing oleic anhydride precursor was introduced into an aqueous environment that contained oleate micelles. The products of the precursor hydrolysis were coupled to the movement of the oil droplet and the production of waste vesicles. The oil droplet successfully moved away from this waste product into fresh unmodified solution, displaying a form of chemotaxis. It has been also shown how droplets can move in a pH gradient. In this case the droplets move as they consume the on-board fuel. The droplets move as they generate a local pH gradient through the chemical hydrolysis of the precursor. The self-generated pH gradient then affects the interfacial tension between the droplet and the aqueous environment. As verification of the mechanism, the autonomous motion can be overridden by large external pH gradients imposed on the aqueous environment, resulting in directed chemotaxis. The same chemistry was used by Suzuki et al. [92], who prepared an alginate gel capsule robot with an embedded droplet.

Ban and Nakata [8] have studied nitrobenzene droplets containing di-(2-ethylhexyl)phosphoric acid (DEHPA) in a phosphate buffer solution. In this system, gels containing various alkaline-earth metal ions induced movement of oriented droplets, mimicking chemotaxis. The directional movement was due to the metal ions creating asymmetric convection due to interfacial surface tension differences. In addition the same droplets are responsive to pH gradients [10]. pH-sensitive movement was shown also by Banno et al. [13]. They used *n*-heptyloxybenzaldehyde oil droplets that were self-propelled in the presence of ester-containing cationic surfactant. Later they studied the differences in droplet behavior dependent on surfactant concentration and type and also the phosphate concentration [14]. This group [72] also demonstrated the underwater self-propelled motion of micrometer-sized oil droplets controlled by using chemical reactions, namely pH-induced motion of 4-heptyloxybenzaldehyde droplets using a hydrolyzable gemini cationic surfactant. In this study the droplets moved towards higher pH, where the rate of hydrolysis was increased (Figure 4c).

In the previous examples, the importance of a chemical gradient, either self-generated or externally imposed, is noted for producing an imbalance in the interfacial tension around a droplet, resulting in chemotactic droplet movement. The formation of a chemical gradient that triggers droplet movement can also be controlled by light and is then termed photo-driven chemopropulsion (photo-chemopropulsion) [33]. Photoirradiation in the close proximity of a dichloromethane (DCM) droplet containing 2-hexyldecanoic acid (HDA) and chromoionophore I (CI) (molar ratio HDA : CI ≈ 170 : 1) initiates a rapid pH change in the aqueous channel fluid. This leads to a cascade of events involving, for example, protonation of the 2-hexyldecanoate ion and a change in surface



(c)

Figure 4. Examples of moving droplets. (a) Schematic representation of repeatable chemotactic decanol droplet movement in a salt gradient (reprinted with permission from [24]; © 2014 American Chemical Society). (b) Nitrobenzene droplet containing oleic anhydride and Oil Red O as colorant moving in a dish containing both oleate micelles and a pH indicator thymolphthalein (reprinted with permission from [45]; © 2011 The Royal Society). (c) pH-induced self-propelled motion of micrometer-sized oil droplets controlled by using chemical reactions (reprinted with permission from [72]; © 2014, American Chemical Society).

tension of the fluid surrounding the droplet, resulting in a fast movement of the droplet away from the light source.

Directed motion of a nitrobenzene droplet floating in an aqueous solution can be generated by using a laser beam, which causes a local increase of temperature leading to temperature-induced Marangoni convection [82]. With these laser-induced flows the droplet is able to move backward or forward, depending on whether the laser beam is focused on the top or the bottom part of the droplet. Dixit et al. [30] have shown that water droplets covered by a surfactant or a lipid monolayer immersed in an organic liquid (decanol or mineral oil) can be controlled using infrared light via both the thermocapillary effect and convection. Hu and Ohta [52] have shown the manipulation of aqueous droplets by optically induced Marangoni circulation. For more details about Marangoni-driven swimmers we recommend the recent review article of Maass et al. [67]. Table 1 in [67] summarizes the properties of different droplet systems, namely droplet size, droplet velocity, and active swimming period.

In these experimental systems, it is clear that when the physical mechanism of droplet motion is known, the droplets can be manipulated, resulting in various forms of directional taxis. The systems are typically compositionally very simple, and therefore external control is relatively easy to implement. Precise control may be exerted more efficiently using light/thermal gradients rather than purely dissipative chemical gradients. This type of artificial chemotaxis of droplets should be contrasted with biological systems, which are vastly more complex, and whose taxis mechanisms are complicated. Living cells responding to and then decoupling from external stimuli are common and result in a kind of autonomy. The liquid robots presented here are far less autonomous and perhaps more easily controlled. It is possible that as the degree of complexity in droplets is increased, so will their autonomy. The degree of external control necessary for directed motion can then be experimentally tested.

3.3 Other Types of Droplet Movement

A fully functioning electromagnetic actuation (EMA) system for the manipulation of liquid robots was proposed and fabricated by Zadražil et al. [100]. The system consisted of a custom-made experimental setup using a set of four solenoids and a control algorithm written in LabVIEW software with micro-droplets moving with two degrees of freedom on an air-water interface. The magnetic liquid robots were made from kerosene droplets (stabilized by Tween 65) containing iron oxide nanoparticles (size approximately 10 nm). The EMA system proved to be a robust system for manipulation and navigation of droplets of variable size (diameter 100 μm–1 mm). Furthermore, the LabVIEW-based algorithm was effective in performance and manipulation tasks. Using a video feedback loop to obtain information about the instantaneous droplet position and velocity, the algorithm calculates the currents required in each of the four solenoids such that the resulting magnetic force acting on the droplet drives it in the desired direction. The algorithm is optimized to achieve a "soft landing," that is, to smoothly decelerate the droplet as it approaches the target setpoint without overshooting it. The system allows the user to freely switch between locomotion tasks (user-defined target position, user-defined trajectory, or gamepad control), and so it provides the basis for a wide range of potential future applications involving the use of such liquid robots.

There are additional systems for the two-dimensional magnetic manipulation of droplets, such as manipulation of aqueous droplets suspended in silicone oil [64]. For example, water droplets can be coated with magnetic porous Si nanoparticles in dichloromethane [31] and manipulated with external control. The ability to control the magnetic droplets by external magnetic fields shares some similarities with remote control of traditional mechanoelectrical robots in that no contact between the robot and the operator is necessary.

Overall, most studies of droplet movement analyze lateral motion. There are only a few works that describe vertical motion. As an example, Phan [79] has demonstrated the vertical oscillation of a water droplet between two stationary water-oil interfaces. This mechanism of oscillatory motion is not due to magnetism, but rather to the electrostatic interaction of the droplet with either interface. When in proximity to one interface, the electrostatic potential of the droplet changes and the droplet then travels to the other interface, where the electostatic potential again changes, resulting in repeatable oscillations in the vertical dimension.

Velev et al. [99] have shown a liquid-liquid microfluidic system for manipulating freely suspended water or hydrocarbon droplets, which float on a denser perfluorinated oil and are driven by an alternating or constant applied electric field. Apart from the influence of applied magnetic or electric fields, the motion of droplets has been observed on a horizontal air-water interface purely due to surface tension effects. For example, it was recently shown how an oil droplet is repelled by a meniscus in pure water but shows the opposite behavior and is attracted to the wall when surfactant is added to the water [66]. The addition of surfactant changes the interfacial energy and therefore the macroscopic behavior of the system. That article also presented a very simple system consisting of drinking water, plant oil, and dishwashing detergent as surfactant. This is a good example of the fact that liquid robots are in principle already easily accessible and exploitable.

Motile droplets as in the examples above can be quite simple in composition. A more intricate system was developed by Sanchez et al. [84]. They observed self-sustained flows in *active gels* in the absence of external forces. Their active gel consisted of substances extracted from living cells; namely, the protein streptavidin served as a scaffold where clusters of kinesin motor proteins were assembled and mediated the bundling of microtubules. Such an active gel was introduced into water, forming water-in-oil emulsions, and autonomous droplet motility was observed due to self-sustained active flows of microtubule bundles at the inner surfaces of droplets. The dynamic properties of this material stemmed from the higher-order assembly of active molecules into emulsion droplets.

4 Droplet Division

The field of robotics continues to develop robots from new materials and with new functionalities. For example, stretchable and deformable electronic devices have been introduced, showing distinct advantages over standard rigid wafer-based systems [81]. Some target functionalities of new types of robots include self-healing, shape change (morphing), reconfiguration, and self-replication. For example, several studies in robotics demonstrate how a robot can replicate by moving, collecting, and assembling another copy of itself from provided parts [91].

With regard to liquid robots, Grzybowski's group has studied the self-division of macroscopic droplets [19]. A droplet of dichloromethane that contained 45–50% 2-hexyldecanoic acid (2-HDA) was placed in a solution of KOH (pH 12). The interfacial reaction between 2-HDA and the base led to the accumulation of the deprotonated 2-HDA at the interface and to the increase of the interfacial area (elongation of the droplet). The droplet divided into two smaller droplets, and they divided further in the same way, until nanometer size was reached. The droplets could divide indefinitely and thus dissolve, or division could be limited under the control of the pH.

Later, Caschera et al. [20] showed that nitrobenzene droplets loaded with cationic surfactant and added to anionic surfactant formed tori, followed by breaking into two or more smaller droplets (Figure 5a). The division event occurs through a temporary minimum in interfacial tension coupled with fluid dynamics as the catanionic system approaches equilibrium. Conditions that support spontaneous droplet fission were tested for several different surfactant pairs. Also, salt-induced droplet fusion in cationic surfactant has been shown, demonstrating a rudimentary fission-fusion cycle capable of the addition of new chemistries or refueling of the droplets.

In addition, Derenyi and Lagzi [28] have shown a self-division of millimeter-sized fatty acid droplets, again governed by surface tension effects. The division was controlled by an autonomous chemical reaction (a pH clock reaction). The pH change affected the protonation state of the fatty acid head groups; the change in fatty acids led to a change of surface tension followed by destabilization and expansion of the droplet. The resulting ringlike structure became unstable (Plateau–Rayleigh instability) followed by the coalescence of some connected protrusions and the division of the unstable droplet. Statistically, the most frequent outcome is the self-division of a droplet into two daughter droplets of the same size.

Both self-propelled motion and division of micrometer-sized oil droplets induced by chemical conversion of the oil components was studied by Banno and Toyota (Figure 5b [12]). Hydrolysis of the surfactant in the system produced a hydrophobic product that added to the mass of the oil droplet, and eventually this resulted in droplet division [15]. From a theoretical and modeling

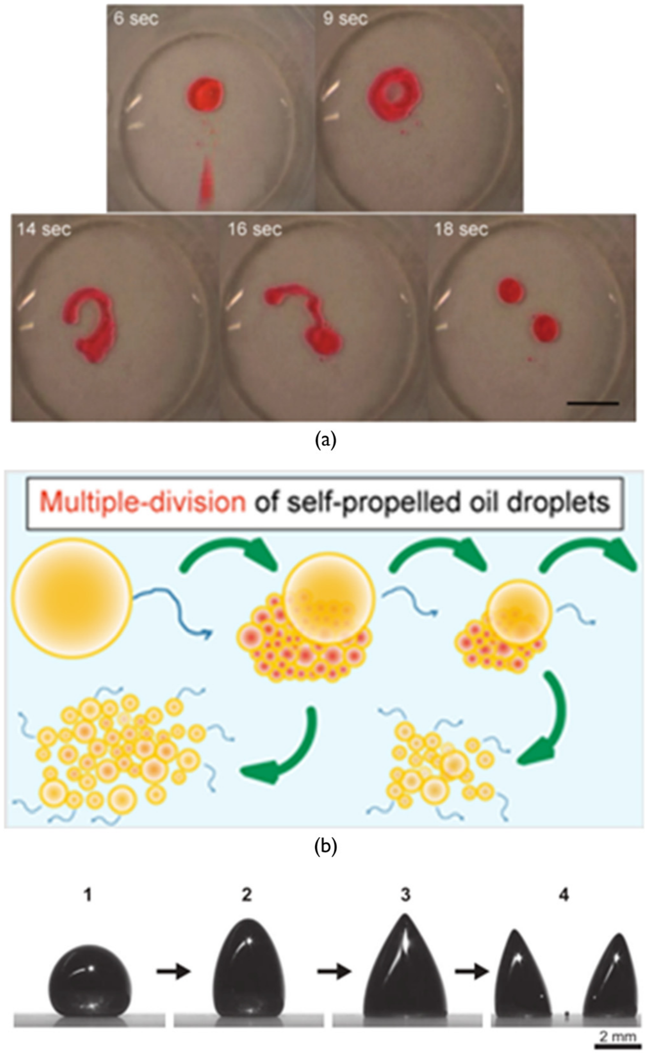


Figure 5. Examples of dividing droplets. (a) Spontaneous droplet division (reprinted with permission from [20]; © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (b) Schematic illustration of the proposed mechanism for multiple division of self-propelled oil droplets (from [12]; © The Royal Society of Chemistry 2015). (c) Magnetically triggered ferrofluid droplet division on a superhydrophobic surface (reprinted with permission from [95]; © 2013 American Association for the Advancement of Science).

perspective, Schwartz et al. discussed the analogy between cell division (and propulsion) and the division of droplets in the presence of surfactants and determined that the energies required to drive both motion and division are quite small [86]. Their hypotheses are based on the work of Greenspan [40, 41], who studied this problem in the 1970s.

Another self-dividing system was introduced by Sato et al., testing the influence of surface area on the state of the system [85]. Their assumption is that a synthetic cell will divide if the ratio of the surface area to volume increases. Their droplets (formed by a mixture of sorbitan monooleate (Span 80) and polyoxyethylene sorbitan monooleate (Tween 80) with alkaline phosphate buffer solution) were placed in a hydrophobic oil (mineral oil or liquid paraffin with *p*-nitrophenyl palmitate (pNPP)). The aqueous droplets increased their surface area through a hydrolysis reaction. Division occurred through the increase in surface area, and it was shown that the temperature and viscosity of the microenvironment influenced the division types (e.g., equal versus unequal divisions, and multiple buddings).

Armstrong and Hanczyc [5] revisited a dynamic water-in-oil system first described by Bütschli in 1892. In their experiments, sodium hydroxide was added to olive oil in a Petri dish, and lifelike behavior of aqueous droplets was observed, including droplet group dynamics. Various kinds of droplet division and other behavior modes (explosion, vibration, stardust, galaxies) were observed by Cronin's group when searching the compositional space of the droplets placed in an aqueous phase [43]. Song et al. [87] have shown the splitting of droplets by laser irradiation. It is notable that in [43] the behaviors of droplets were selected over time, resulting in the evolution of droplet composition. This demonstrates that the behavior of droplets is tied to their individual composition. From a robotics perspective, the chemical content of a droplet could be considered as its programming.

On the other hand, droplet division can be manipulated by externally imposed forces. Timonen et al. [95] have shown manipulation and division of magnetic aqueous ferrofluid droplets on a low-friction lotus-leaf–like superhydrophobic surface with an external magnetic field (Figure 5c). A ferrofluid droplet was subjected to increasing magnetic field from a cylindrical permanent magnet. This resulted in a division into numerous daughter droplets that formed different static self-assembled patterns to minimize their total energy. When the magnetic field decreased, the relaxation of conical daughter droplets into spherical ones occurred.

Recently, we have found that decanol droplets surrounded by a decanoate solution containing salt perform intriguing shape changes [26]. Depending on the initial system composition, interesting patterns (e.g., stars, tentacular structures) are observable during the evaporation of the aqueous phase. In addition, the division of droplets can occur. The interesting point is that when the evaporation is completed, the droplets usually return more or less to the original spherical shape. Such reproducible morphological changes in simple droplets, dependent on the initial state of the system, can be used to produce predictable temporal state changes in liquid robotics.

Much like the mechanisms of self-motion, droplet division appears to be achievable if the interfacial tension is reduced. This is often governed by the addition or production of surfactants. Under these conditions a small amount of energy in the form of internal or external fluid dynamics appears to be enough to trigger division events. The division may be noisy, producing several droplets of various dimensions, or well-controlled, transforming one droplet into two daughter droplets of the same size. In all examples provided here we can see the propensity for liquid droplets, either pushed from equilibrium or created far from equilibrium, to produce such dynamics. Such soft-material properties of droplets make them ideal for key aspects of soft robotics, namely self-healing, shape change (morphing), reconfiguration, and self-replication. Consider a robot tasked to pass through a small hole. The droplet can divide, go through in the form of smaller objects, and then coalesce to form the original liquid robot.

Although we have highlighted a few examples from the literature in which the controlled fusion and division of droplets was studied, the development of a functional liquid robot remains a challenging task.

5 Problem Solving by Droplets

5.1 Droplets in Mazes

Above we summarized diverse approaches to animating droplets for both motion and division. Several groups have applied such dynamic liquid robots to solve rudimentary tasks. For example, could a self-moving droplet solve a maze? Maze solving, and finding the shortest path or all paths in mazes, are computational problems that could be solved by using algorithms. There are several types of mazes that could be treated. Here we will consider only 2D perfect mazes (called also simply connected mazes), mazes without any loops or closed circuits and without any inaccessible areas. From each point, there is exactly one path to any other point, and the maze has exactly one solution.

There are several approaches a human might take toward maze solving [7]. Imagine a human being standing at the starting point of a huge perfect maze. Here we will introduce just three simplest options. First, the human can use the algorithm called *random mouse*, meaning to run randomly in the corridors and hope to find the way out. A disadvantage of this algorithm is that it is extremely slow and there is a probability that the human will never reach the exit. A better approach is to use the *wall-follower* algorithm, which is based on keeping one hand in contact with one wall of the maze and following that wall. The solver is guaranteed not to get lost and will eventually reach the exit. The time spent in the maze may depend on the choice of hands; sometimes a left-hand path may be much shorter than a right-hand path or vice versa. If the solver has a chalk, a Trémaux's algorithm can be implemented. In this method the solver makes a random decision where to go from the start point and draws lines on the floor to mark his path. If the solver reaches the endpoint of any corridor, he goes back to the closest crossroad where he chooses any corridor that he has not visited yet. The paths are either unlabeled (which means unvisited yet), marked once, or marked twice (meaning leading to the dead end). These approaches work also for traditional robots, programmed to behave similarly to people.

It is also possible for self-propelled droplets to solve mazes. The self-propelled droplets can implement the random mouse algorithm, with a low probability that the droplet will reach the exit; the time for solving the maze may be long. The wall-follower and Trémaux's algorithms are not applicable to liquid droplets without some further signal that could prompt the liquid robot towards the exit [38].

In all articles where it was shown how chemotactic droplets can solve a maze, the droplets have in fact followed the shortest path predefined by a concentration gradient in the channels of the maze. Therefore diffusion and Marangoni flows are the physical solvers of the maze in principle, and the droplet follows the gradients in order to minimize its free energy [2]. The chemoattractant (i.e., the chemical substance placed at the exit) diffuses and causes a surface tension gradient that a droplet can sense. If the liquid robot is placed anywhere in a perfect maze and follows the steepest gradient, it reaches the source of the chemical signal. The intelligence of liquid robots is not in the ability to find the target, but in the ability to follow the track leading to the target. Note that not all droplets have this ability and not all kinds of droplets can follow the gradient chemotactically.

We have shown that decanol droplets are able to solve a maze containing a thin layer of sodium decanoate solution and locomote to the position with the highest concentration of salt (Figure 6a

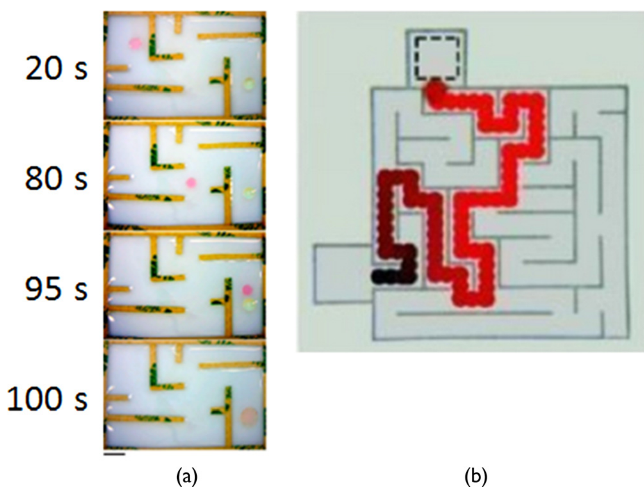


Figure 6. Examples of droplets in topologically complex systems. (a) Chemotactic decanol droplet following salt in a maze (reprinted with permission from [24]; © 2014, American Chemical Society). (b) Maze-solving HDA droplet following HCl gradient (reprinted with permission from [62]; © 2010, American Chemical Society).

[24]). In principle the path was indicated in advance as the salt spread from the source point by diffusion and Marangoni-induced flow along the liquid surface. The decanol droplet representing the liquid robot demonstrates the ability to follow this path without mistake and without exploring alternative paths. In the absence of the gradient of surface tension and determination of the shortest path, the droplet remains at the start point without any long-distance motion or exploratory behavior.

Lagzi et al. [62] have shown maze solving by chemotactic droplets, where oil droplets (mineral oil or dichlormethane) containing 2-hexyldecanoic acid (HDA) were able to move to the area with lowest pH (Figure 6b). As in the case described above, the pH gradient predefined the proper path, and the oil droplets with HDA followed this path. As a control, droplets without HDA have not shown chemotactic ability and have not followed the gradient. In principle, the H^+ ions from the target of the maze were the physical solvers of the maze, while the droplets enabled visualization of the shortest path [2].

Francis et al. [34] presented self-propelled chemotactic ionic liquid droplets that spontaneously travel along the liquid-air interface by release of surfactant-type ions when following HCl, similarly to Lagzi's system. The droplets were placed in any position within the fluidic network, and in every case they spontaneously traveled towards the chemoattractant source.

A further example of solving mazes by droplets is a recent article by Jin et al. [54]. They present self-propelling artificial swimmers in the form of oil droplets in an aqueous surfactant solution driven by interfacial Marangoni flows induced by micellar solubilization of the oil phase. The authors demonstrated that chemotaxis along micellar surfactant gradients can guide these swimmers through a microfluidic maze.

The intelligence of droplets consists in their ability to follow environmental signals; they are not able to solve the maze by themselves. This is not trivial, in that a droplet is able to sense its immediate environment and then link the environmental patterning to self-motion. Using ionic liquids for liquid robots instead of organic compounds will have advantages due to their negligible vapor pressure, low combustibility, and high thermal stability. Further, they are suitable solvents for numerous chemical species and can be used in a wide range of harsh reactions.

5.2 Droplets in Logic Gates

Research in unconventional computing includes analyzing new types of systems for their ability to perform basic logical operations. In some ways these unconventional systems mimic their electronic counterparts, but there are striking differences, including slow processing and high parallelism. It has been already shown that logical arguments could be performed by unconventional systems such as the slime mould *Physarum* [1, 3] or swarms of crabs [42]. A number of articles describe logic gates in chemical media, namely, those based on chemical wave propagation in excitable media (e.g., the Belousov-Zhabotinsky reaction) [88]. In past decades the research on logic gates has also focused on using droplets or bubbles.

Microfluidic computing elements, such as logic gates for logic operations, adders for arithmetic operations, and memory to store information, have been created [69]. Microfluidic chips with logic have been designed, where the presence or state of one droplet was influenced by the state of other droplets, or by the state of the chip. For example, pneumatic membrane valves have been used to open and close different channels and force droplets to execute a certain protocol depending on which valves were activated [29]. This allowed the creation of NOT, NAND, and NOR gates, flip-flops, oscillators, self-driven peristaltic pumps, and a 12-bit shift register. Cheow et al. [55] have demonstrated droplet-based microfluidic AND/OR and NOT logic gates. Logic operations were based on the nonlinear change in hydrodynamic resistance for channels containing droplets. Digital microfluidic logic gates were also shown, for example, by Toepke [96] and Zhao and Chakrabarty [105]. A universal microfluidic logic gate that is capable of conducting all 16 logic operations in one chip was presented by Zhang et al. [101].

The team of Prakash [80] has shown bubble logic processors implemented with nitrogen bubbles in water (with added surfactant 2%(w/w) Tween 20 to stabilize the interfaces) flowing through

PDMS microfluidic chips. Computational models related to bubble logic circuits were presented also by Anandan et al. [4]. Recently Prakash's group demonstrated synchronous water-based ferrofluid droplet generation and propagation in an oil-based carrier fluid between two parallel Teflon-coated glass surfaces [58]. A rotating magnetic field enables parallel manipulation of arbitrary numbers of ferrofluid droplets on permalloy tracks. The limits of synchronization were defined in dependence on frequency and droplet diameter.

Mertaniemi et al. [71] have demonstrated water droplets in air on superhydrophobic substrates, either coalescing or rebounding, depending on the Weber number and impact parameter. Under conditions when droplets rebound (not coalesce), experiments were performed on droplet logic gates (NOT/FANOUT and AND/OR). A toggle flip-flop memory based on controlled droplet collisions was successfully demonstrated, as well as a basis for programmable encapsulated chemistry.

Therefore certain logical operations, also associated with traditional programmed robots, can be implemented with droplet-based liquid robots. So far a substantial amount of external structure—for example, in the construction and architecture of microfluidic channels—is necessary for computing with input and output droplets, with the operations performed by droplets playing a key role in much larger systems. It has not yet been shown that individual droplets regardless of context can execute logical operations of note. Thus we consider the collective behavior and potential interactions of multiple droplets in the next section.

6 Multi-droplet Interactions

Since single droplets are able to demonstrate dynamic properties from self-motion to self-division to maze solving, it is intriguing to ask what types of behaviors can be demonstrated by multiple droplets, including swarms. Some works focus on the behavior of two or more droplets that either touch each other (and form a matrix of "artificial tissue") or are distributed in the environment independently and are able to mimic intracellular communication by means of chemical signals. In the same way as in the populations of living objects or robots, the collective behavior and swarming of liquid robots can be investigated. As Aristotle pointed out, "the whole is more than the sum of its parts"[1]—in terms of droplet behavior a swarm of liquid robots may display more useful properties than individual droplets; a swarm could perhaps perform targeted tasks better, faster, more robustly, or more efficiently.

For a start, we can ask whether two or more droplets influence each other in a measurable way. In [51], we studied in detail the motion of single and multiple self-propelled droplets over the course of minutes. In our experiments we studied the behavior of two droplets placed in one petri dish, and as a control experiment we observed two droplets separately in two petri dishes. We found that in the early part of the experiment (the first 20 minutes) two droplets tended to move close to one another, resulting in a circling effect. Compared to controls, we found that the two droplets influence each other and this influence depended on droplet size (volume).

Multiple droplet behavior may be influenced by attraction or repulsion, but a droplet may change its state through coalescence. Cira et al. [21] have shown that droplets consisting of propylene glycol and water mixtures fuse only if they have the same composition; otherwise they repel each other. In their device, droplets moved down a ramp by gravity. Along the way, a droplet merged only with a container of matched composition (and thus surface tension); otherwise the droplet moved along until it met a container with the appropriate mixture. In such a way the droplets sort themselves through surface tension (Figure 7).

These are examples where the behavior of the systems changes due to the presence of more than one droplet. Perhaps the droplets show some kind of "intelligence," or at least selectivity based on composition. Such purely intrinsic behavior of multiple droplets has great potential for applications

1 "In the case of all things which have several parts and in which the totality is not, as it were, a mere heap, but the whole is something beside the parts,...." (Aristotle, *Metaphysics*, Book 8, part 6).

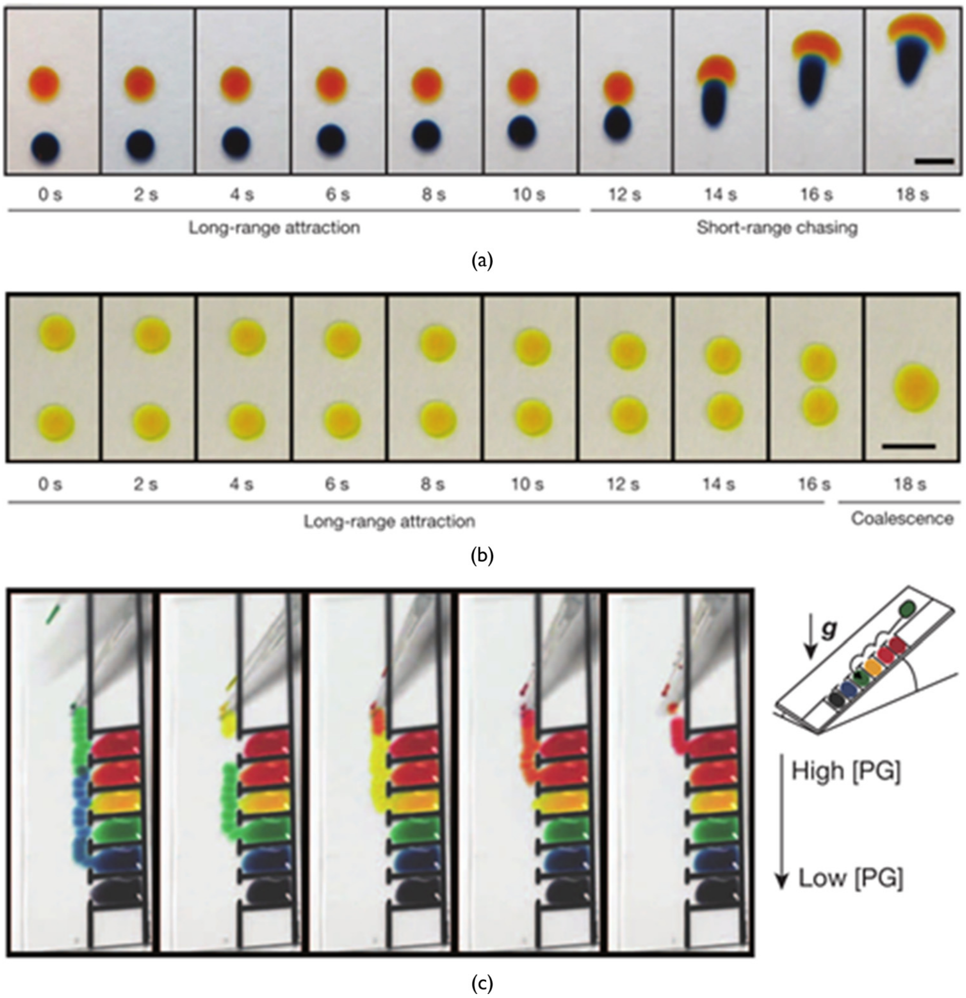


Figure 7. Interaction of two-component droplets consisting of water and propylene glycol mixture. (a) Repulsion of droplets with different compositions. (b) Coalescence of droplets with the same composition. (c) Surface tension sorter. (Reprinted from [21] by permission of Nature Publishing Group.)

of liquid robots where identical droplets may be tasked to work together or specialized droplets may form a working consortium. In this way the system may become more robust and also suitable for diverse targeted outcomes.

7 Liquid Marbles

A special category of droplets, distinct from the liquid-liquid systems depicted in Figure 2, are so-called liquid marbles as defined by Aussillous and Quéré in 2001 [6]. A liquid marble is a liquid droplet encapsulated in a hydrophobic powder that adheres to its surface (Figure 8). Preparation of liquid marbles is a very simple operation—a small amount of liquid is rolled on a layer of hydrophobic powder consisting of nano- or microparticles, which spread spontaneously at the liquid-air interface. This process results in a liquid marble that has some of the properties of a liquid droplet and at the same time behaves as a soft solid. Liquid marbles are an alternative to superhydrophobic surfaces, because particles at the interface prevent the liquid in the marble from

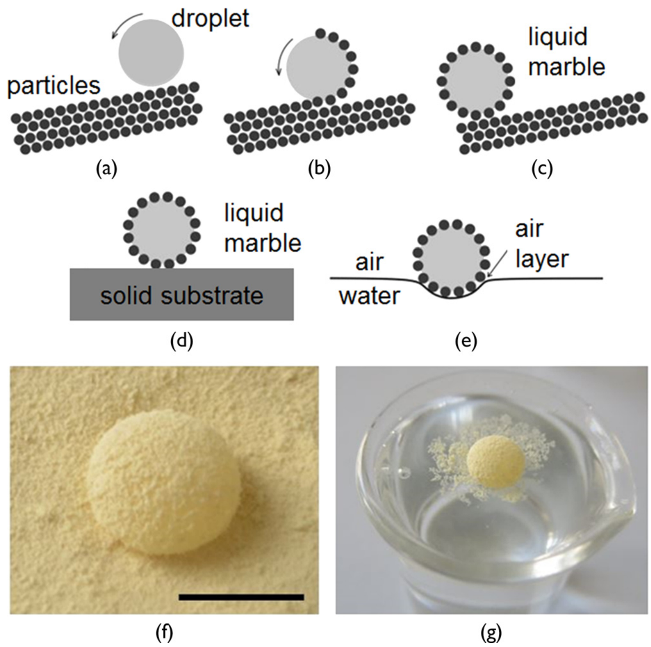


Figure 8. Liquid marbles. (a)–(c) Scheme of liquid-marble preparation process. (d) Scheme of liquid marble on a solid substrate. (e) Scheme of liquid marble floating on the water surface. (f) Photograph of liquid marble (100 μl of water covered by *Lycopodium*). Scale bar corresponds to 5 mm. (g) Photograph of liquid marble from (f) floating on water surface (reprinted with permission from [25]).

wetting the carrier surface. The substrate on which the liquid marble moves can be a solid or even a liquid surface. Liquid marbles can serve, for example, to transport of small volumes of liquids or powders [25, 83].

Like with simple droplets, liquid marbles can be moved using external forces. Ooi [75] summarized methods for manipulation of liquid marbles, mainly by electrostatic and magnetic forces, with other options mentioned (e.g., mechanical, gravitational, irradiation, changes in temperature or pH). Magnetic force could be used for both the manipulation [103] and also for controlled fusion of two liquid marbles [104]. Bormashenko et al. have shown self-propulsion of liquid marbles filled with aqueous alcohol solutions and placed on a water surface [17]. Recently Paven et al. introduced a system whereby laser-driven liquid marbles can push 150 times their own weight [77]. This type of droplet thus also shows potential to be used as a liquid robot and is attracting further interest.

8 Conclusions and Outlook

It is widely accepted that robots are artificial objects that can in some contexts make human life easier. However, the idea of electromechanical robots dominates. In the present review we have described how simple droplets can be an embodiment of liquid robots. These droplet-based robots have the ability to sense gradients and even each other, resulting in directional chemotactic motion and also group dynamics. The composition of individual robots also influences their behavior. Even with such rudimentary abilities, the droplets are able to sense chemical gradients in complex environments and thereby to solve mazes. In addition, droplet-based liquid robots are soft and can deform [9], sometimes to such an extent that the droplets divide into daughter droplets. Moreover, they can change their own shape [26]. Along with fusion, this forms the basis of self-replication and perhaps even evolution. Although multiple droplets in an experiment can perform logical operations, it remains to be seen how individual droplets can also perform logic based on their chemistry.

Like Braitenberg's vehicles, droplet-based liquid robots can be semi-autonomous and self-propelled. And like billiard balls, droplet-based robots can be deterministically controlled by external forces. It is this potential for both external and embedded control that makes liquid robots intriguing and useful as a branch of robotics.

Due to the ability of droplets to change state (e.g., by fission or fusion), the link between chemical composition and function, and the link between environmental information and self-movement, it is possible to design liquid robots that not only perform targeted delivery but also process complex input information—for example, to distinguish the inside from the outside of a tumor and provide controlled doses of therapeutic substances in a manner not available with current theranostics. Beyond medicine, liquid robots as smart materials may allow for the prolonged proper function of machines, organisms, and infrastructure [46, 57].

With regard to potential engineering applications, the area of environmental sensing and remediation is one where droplet-based devices could prove to be valuable and technically feasible. For example, it has been recently demonstrated that droplets can encapsulate chemical species and perform oriented motion in microchip channels, where they can induce phenomena such as the flocculation of a dispersed model pollutant [102]. At the same time, it has to be kept in mind that droplet movement in an actual real-world environment without well-defined channels, in a fluid of uncontrolled composition, and in the presence of macroscopic convective transport is a rather different task.

Although droplets as liquid robots are promising tools for performing various tasks, there is still a long way to go before we can use them in real life. All droplet studies presented in this article were performed in well-defined laboratory conditions, and nobody has yet focused on robustness of droplet systems. For practical application of liquid droplets in biological or environmental use, one must consider the influence of ambient noise on the dynamics of droplets. To transfer liquid robots in the form of droplets from laboratories to real-world conditions is a challenging task in the area of liquid robotics.

A possible way of increasing the robustness of robotic devices in a real-world environment is to proceed from individual robots to robotic swarms [39]. In nature, this is a successful survival strategy used by collective organisms such as swarms of insects, schools of fish, and flocks of birds. Collective phenomena are observable also in cells, as in the multicellular development of *Dictyostelium* cells [50, 93]. The main benefit is that even if a number of individuals are lost, the majority can still complete the mission, thanks to a combination of the statistics of large numbers and mutual communication that leads to the so-called swarm intelligence. Thus, the collective motion of interacting droplet swarms is an area of research that can improve the practical application potential of droplet-based liquid robots.

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