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Manipulation of Liquid Marbles – A Review

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Abstract

A liquid marble is a liquid droplet coated with hydrophobic powder which enables the marble to be manipulated like a soft solid. Recently, liquid marbles have been used in applications such as micro bioreactors for three-dimensional cell cultures and could be a new platform for digital microfluidics. Despite its potential significance, there is a lack of a systematic, thorough review and discussion on the manipulation schemes for liquid marbles. This paper presents past and recent manipulation schemes for liquid marbles. This paper discusses the major working principles, their advantages and drawbacks. Finally, the paper concludes with recent applications and the challenges of this research area.

1 Introduction

If a liquid droplet is placed on a solid surface, the bottom of the droplet wets the surface. As the sessile droplet moves, the liquid usually leaves a trail on the surface resulting in a loss in droplet volume and its content. Due to the viscous force a liquid droplet is resistant to any form of movement. This phenomenon prevents small quantities of liquid to be transported efficiently on a planar surface as relatively large forces are required for actuation and manipulation. The problem is even more serious as the droplet volume continuously decreases due to evaporation and liquid trail loss. In the past two decades, a variety of solutions have been proposed for inhibiting the wetting of liquid droplets on a solid surface. These solutions can be broadly classified into two categories, namely superhydrophobic surfaces and liquid marbles. By studying one of the best examples of naturally hydrophobic surfaces – the lotus leaf, the relationship of surface microstructures and superhydrophobicity was well understood (Barthlott

and Neinhuis 1997). Numerous techniques are available for creating superhydrophobic surfaces. Another approach to anti wetting is engineering the liquid droplet instead of the surface, leading to the development of liquid marbles. The scope of this paper is the manipulation schemes of liquid marbles, hydrophobic surfaces will not be discussed further.

A liquid marble is a liquid droplet coated with particles preventing the liquid to wet the carrier surface which can be a solid or liquid surface. Due to the non-wetting property, a liquid marble exhibits very low friction with its carrier surface. This characteristics allows liquid marbles to move easily without leaving behind any trail. A liquid marble can roll around on solid surfaces, float (Gao and McCarthy 2007; Lee and Kim 2008; Bormashenko, Bormashenko et al. 2009; Bormashenko, Bormashenko et al. 2009; Bormashenko and Musin 2009; Dupin, Armes et al. 2009; Zhang, Cha et al. 2012) or even sink (Bormashenko, Pogreb et al. 2012; Mele, Bayer et al. 2014) in liquids and still maintain its integrity. In the nature, insects such as aphids manipulate liquid marbles for their survival (Pike, Richard et al. 2002). In the lab, simply rolling a liquid droplet over a bed of hydrophobic powder can create a liquid marble. The powder coats and assembles itself on the droplet, effectively creating a protective coat (McHale, Shirtcliffe et al. 2007; McHale and Newton 2011). Although various coating materials have been successfully used to create liquid marbles, a majority of them are hydrophobic particles with diameters in the micro scale ($\leq 100\mu\text{m}$). Many types of liquids have been encapsulated as liquid marbles, and the selection of the coating-liquid pair will ultimately determine its properties and possible manipulation schemes. The coating ability of some powders has been studied quantitatively and independently by McEleney et al. (2009) and Zang et al. (2013). Table 1 lists the various liquid-coating pairs reported in literature:

Table 1 Composition of liquid marbles

Coating material	Liquid content	Particle diameter (μm)	Water affinity
Lycopodium	Mixture of water and glycerol (Aussillous and Quere 2006; Bormashenko, Pogreb et al. 2012), water (Newton, Herbertson et al. 2007; Bormashenko, Balter et al. 2010; Hashmi, Strauss et al. 2012)	17-30	Hydrophobic

Polytetrafluoroethylene (PTFE)	Water (Tosun and Erbil 2009; Bormashenko, Bormashenko et al. 2010; Eshtiaghi, Liu et al. 2010; Tian, Arbatan et al. 2010; Eshtiaghi and Hapgood 2012; Cengiz and Erbil 2013), hydroxyl propyl cellulose (HPC), ferrofluid (Nguyen 2013), liquid containing cell culture (Arbatan, Al-Abboodi et al. 2012; Sarvi, Jain et al. 2014), ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF ₄) (Yang, Halvorsen et al. 2012), phenolphthalein (Tian, Arbatan et al. 2010), cobalt chloride (Tian, Arbatan et al. 2010)	0.1-200	Hydrophobic
Perfluorinated oligomeric tetrafluoroethylene (OTFE) (Gao and McCarthy 2007)	Water, ionic liquids	<1	Hydrophobic
Polyethylene (PE) (Bormashenko, Pogreb et al. 2012)	Mixture of water and glycerol	2	Hydrophobic
Silica powder (SiO ₂)	Water (Inoue, Fujii et al. 2011), mixture of water and glycerol (Aussillous and Quere 2006), mercury (Zeng and Zhao 2010)	~0.01	Hydrophobised
Hydrophobised copper (McEleney, Walker et al. 2009)	Water	9-320	Hydrophobised
Iron oxide nanoparticles (Fe ₃ O ₄) (Zhao, Fang et al. 2010; Zhang, Cha et al. 2012; Zhao, Xu et al. 2012)	Water	0.01-0.45	Hydrophobic
Iron oxide nanoparticles combined with fluorinated decyl polyhedral oligomeric silsesquioxane (FD POSS) (Xue, Wang et al. 2010)		<70 (aggregate)	Hydrophobic
Polyvinylidene fluoride (PVDF)	Mixture of water and glycerol (Bormashenko, Pogreb et al. 2012),	0.1-0.13	Hydrophilic

	water (2009; Bormashenko, Balter et al. 2010) , ferrofluid (Bormashenko, Pogreb et al. 2008)		
Graphite micropowder (Doganci, Sesli et al. 2011)	Aqueous sodium dodecyl sulfate (SDS)	5-30	Hydrophobic
Carbon black	Mixture of water and glycerol (Bormashenko, Pogreb et al. 2012), water (Bormashenko, Bormashenko et al. 2010; 2010)	0.03 (particle) ~100 (aggregate)	Hydrophilic
Hydrophobic glass beads	Water (Eshtiaghi, Liu et al. 2010; Eshtiaghi and Hapgood 2012), mixture of water and alcohol (Whitby, Bian et al. 2012; 2013)	65-106	Hydrophobised
Hydrophobised fumed silica	Poly(diallyldimethylammonium chloride) (PDDA) (Bhosale and Panchagnula 2010), water (Bhosale, Panchagnula et al. 2008)	<0.01 (particle) 0.2-5 (aggregate)	Hydrophobised
Hydrophobised titanium dioxide (TiO ₂) (Tan, Ahsan et al. 2014)	Water and various organic solutions	0.021	Hydrophobised
Tungsten trioxide (WO ₃) (Sivan, Tang et al. 2013)	Galinstan (liquid metal)	0.08	Hydrophobic
Latex (Dupin, Armes et al. 2009; Fujii, Suzaki et al. 2011)	Water	<1	Hydrophobic
Poly(methyl methacrylate) (PMMA) (McEleney, Walker et al. 2009)	Water	42	Hydrophobic
Spiropyran (Nakai, Fujii et al. 2013)	Water	N/A	Hydrophobic
Alumina	Water (Chin, Reithofer et al. 2013), galinstan (Sivan, Tang et al. 2013)	40	Hydrophobised
Poly(perfluoroalkyl ethyl acrylate) (Cengiz and Erbil 2013)	Water	8-60	Hydrophobic
Poly(N-isopropylacrylamide) (PNIPAM) (Yusa, Morihara et al. 2014)	Water	N/A	Hydrophobised
Poly(lactic acid) microparticles (Matsukuma, Watanabe et al.	Water	1-10	Hydrophobic

2013)			
Poly(methylsilsesquioxane) (Ogawa, Watanabe et al. 2014)	Water	4.4	Hydrophobic
Molybdenite (Whitby, Bian et al. 2013)	Mixture of water and alcohol	1-20	Hydrophobic
Fluoroacrylic copolymer and cellulose acetate nanofibers (Mele, Bayer et al. 2014)	Water	<1	Hydrophobised
Perfluorodecanethiol-grafted silver nanowires (Miao, Lee et al. 2014)	Methylene blue solution	0.065 >10 (length)	Hydrophobised

Liquid marbles have been drawing much attention from the research community due to its many interesting and useful properties. As mentioned above, a liquid marble is inherently non-wetting. This feature enables the transport of liquid through large distances without mass loss and utilizing a minimum amount of energy. For digital microfluidics, samples in liquid marbles can be transported with minimal effort and practically zero contamination, a major advantage compared to sessile droplets. Miniature electric generators (Yang, Halvorsen et al. 2012), ferrofluidic bearing (Bormashenko, Pogreb et al. 2008) and even an accelerometer (Zeng and Zhao 2010) based on liquid marbles have been proposed. A liquid marble is relatively robust as it behaves like a soft solid. A liquid marble can survive impacts and even be handled with tweezers (Zhao, Fang et al. 2010). The ease of handling increases the chance of survival of a liquid marble in lab processes and hence its efficacy. As the coating material is porous, gas exchange between the liquid and the surrounding can still occur. The liquid content of a marble could evaporate like its uncoated counterpart (Dandan and Erbil 2009; Tosun and Erbil 2009; Doganci, Sesli et al. 2011) at a rate that depends on its coating condition (Laborie, Lachaussee et al. 2013). Recently, these two features have been exploited by biomedical researchers for a new cell culture platform (Arbatan, Al-Abboodi et al. 2012; Arbatan, Li et al. 2012; Tian, Fu et al. 2013; Sarvi, Jain et al. 2014) and sensors for detecting gas pollution (Tian, Arbatan et al. 2010; Tian, Arbatan et al. 2010). Liquid marbles can even be coalesced to form a larger marble via impact (Dorvee, Derfus et al. 2004; Planchette, Biance et al. 2013). A larger marble can be formed by direct liquid addition (Bormashenko, Balter et al. 2010; Xue, Wang et al. 2010).

Merging ability demonstrates the suitability of a liquid marble as a micromixer or a microreactor (Xue, Wang et al. 2010; Zhao, Xu et al. 2012).

Several excellent review papers have discussed the various properties and applications of liquid marbles (Aussillous and Quere 2001; Aussillous and Quere 2006; Bormashenko 2011; McHale and Newton 2011; Yan, Li et al. 2011; Bormashenko 2012). These reviews mainly focus on the fundamental physics, properties and applications of liquid marbles. We present here a systematic review of the manipulation schemes for liquid marbles. These schemes are classified according to the nature of the actuating energy as electromagnetic, mechanical and others. Within the electromagnetic category, the liquid marble can be manipulated via the electrostatic or magnetic force. The mechanical category covers manipulation concepts using the gravitational force and pressure gradient. Finally, the other category involves the pH change, surfactant concentration, ultraviolet (UV) irradiation and temperature change. Figure 1 shows an overview of the various schemes, methods, associated functions and applications.

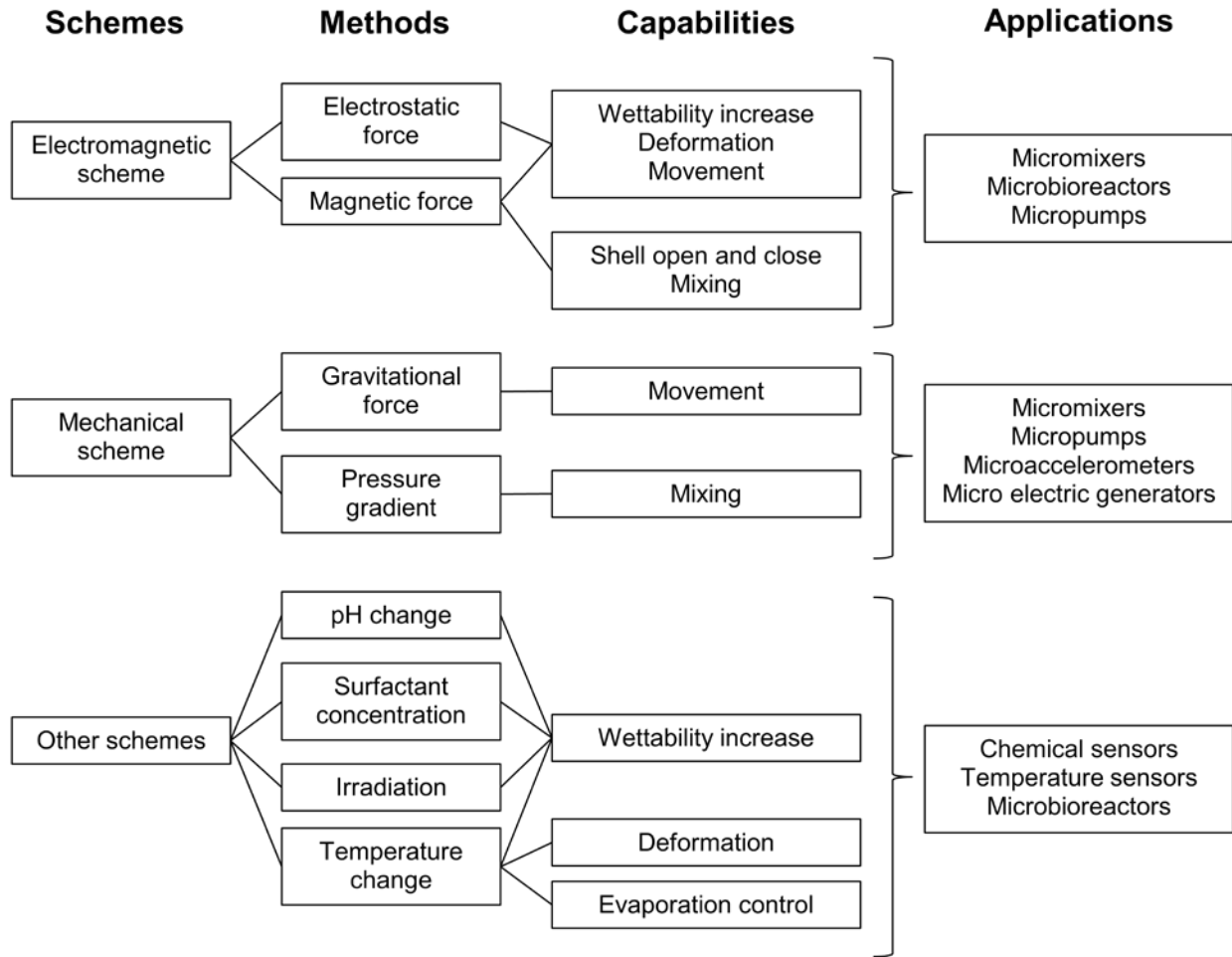


Fig. 1 An overview of different manipulation schemes. Each scheme consists of several methods with their capabilities shown. These capabilities lead to applications which are listed accordingly

2 Manipulation schemes

2.1 Electromagnetic schemes

2.1.1 Electrostatic force

An electric field can deform, move or change the wettability of a liquid marble. If the liquid marble is stationary, the additional electrostatic energy applied to the marble causes an increase in surface energy that deforms the marble. A simple experiment was conducted by Aussillous and Quere (2006) to demonstrate the electrostatic effect by using a charged Teflon stick to lift a liquid marble against gravity. Bormashenko et al. (2012) applied an electric field on a liquid

marble. The electrostatic force deforms the marble such that its contact area with the solid surface is reduced. The applied electric field generates an upward force that opposes gravity, such that $F \propto E^2$ where F is the force opposing gravity and E is the applied electric field. This investigation was extended by the introduction of composite marbles consisting of different polar liquids. Bormashenko et al. (2012) demonstrated that if two marbles are placed in contact with each other in an electric field, one of the marbles climbed on top of the other so that the dipole moments are aligned with the direction of the external electric field, Figure 2 (a). This effect is possible because the energy provided by the external electric field exceeds that of the gain in gravitational potential energy through the climb.

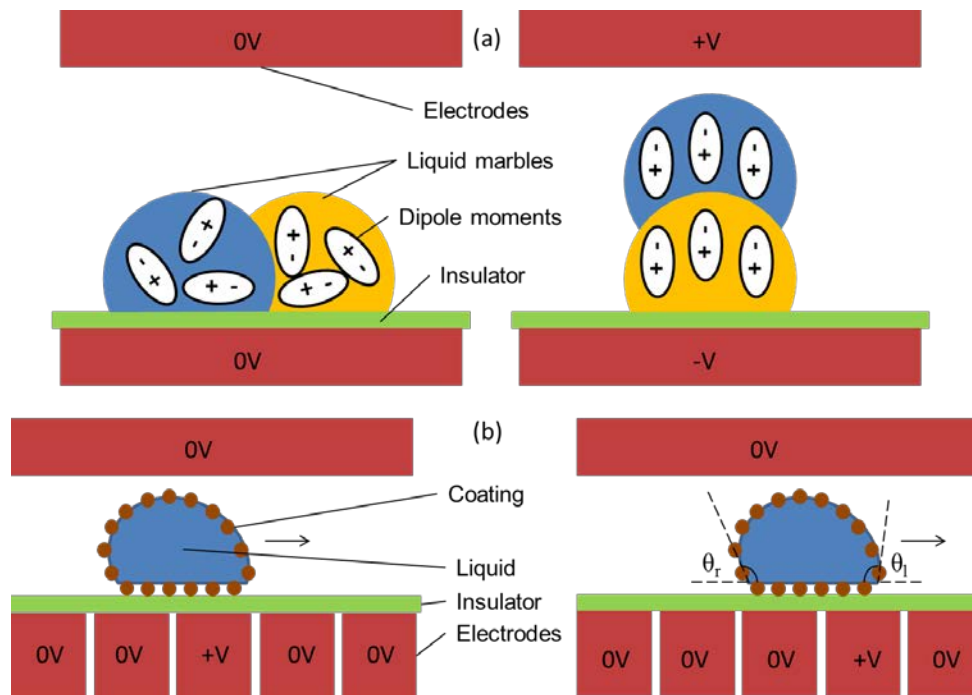


Fig. 2 Electrostatic manipulation: **(a)** The climbing phenomenon of different liquid marbles under an electric field. The dipole moments within the liquid marbles align with the electric field. Note that the coating material is not illustrated. **(b)** Motion caused by the electrowetting effect. A liquid marble with difference between the receding and advancing apparent contact angles. The arrow indicates the direction of movement.

The wettability of a liquid droplet is changed under an applied electric field. This phenomenon has been known as the electrowetting and the increase in wettability is due to a decrease in interfacial energy as shown by Vallet et al. (1996):

$$E(V) = E(0) - \frac{\varepsilon}{2d} V^2 \quad (1)$$

where E is the interfacial energy, V is the applied voltage, ε is the permittivity and d is the thickness of the insulator. When there is a difference in interfacial energy or wettability between the two ends of a droplet, droplet movement can be induced. For a sustained and directional movement, electrode fingers were used to apply the electric field to the marble, Figure 2 (b). Newton et al. (2007) used a finger electrode setup to move liquid marbles coated with lycopodium powder.

Using the electric field as a means to manipulate a liquid marble is attractive because there is no need for a physical contact between the electrodes and the liquid. Also, accurate control can be easily achieved by varying the applied voltage. However, the main drawback of this scheme is the required high voltage, ranging from hundreds to thousands of volts. Furthermore, Newton et al. (2007) observed that some of the coating material was inevitably charged and ejected from the liquid marble during transport.

2.1.2 Magnetic force

Using magnetism is one of the most popular manipulation schemes of liquid marbles due to its simplicity. Magnetism is effective at a relatively long range and requires no physical contact. Small permanent magnets are available off the shelf and can be incorporated into miniature devices and do not require external power supply. However, magnetism can only be utilised if the liquid marble consists of a magnetic coating or has a magnetic content. Magnetite is a common material for this application because it can either be used as the coating or suspended as micro- or nanoparticles to form a magnetic liquid.

Applying a magnetic field can change the shape and wettability of a liquid marble. This effect was studied and known as magnetowetting (Nguyen 2012; 2013). For a sessile ferrofluid marble coated with PTFE, the liquid marble deforms under the influence of a permanent magnet. The magnetic Bond number was used as an independent variable to characterise the height h and the contact radius of the marble l , Figure 3. The dimensionless height and contact radius are normalised by the undeformed radius R : $h^* = h/R$, $l^* = l/R$.

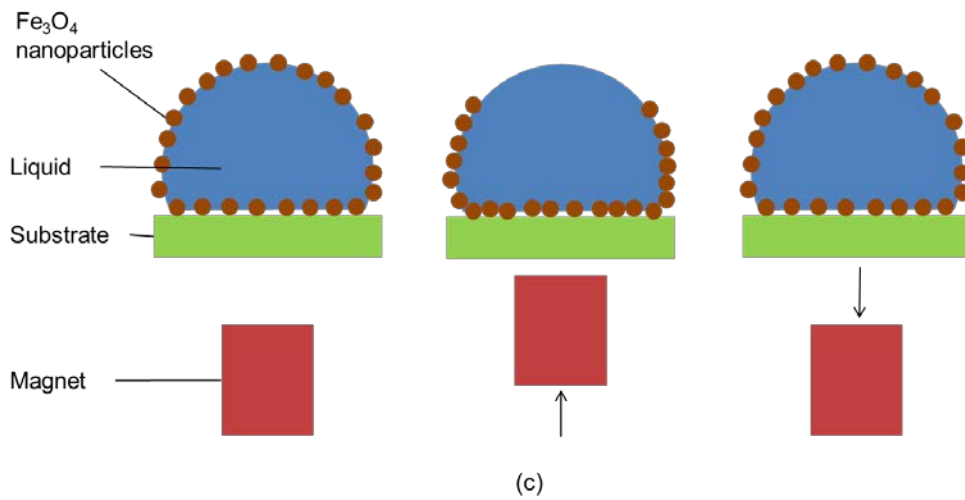
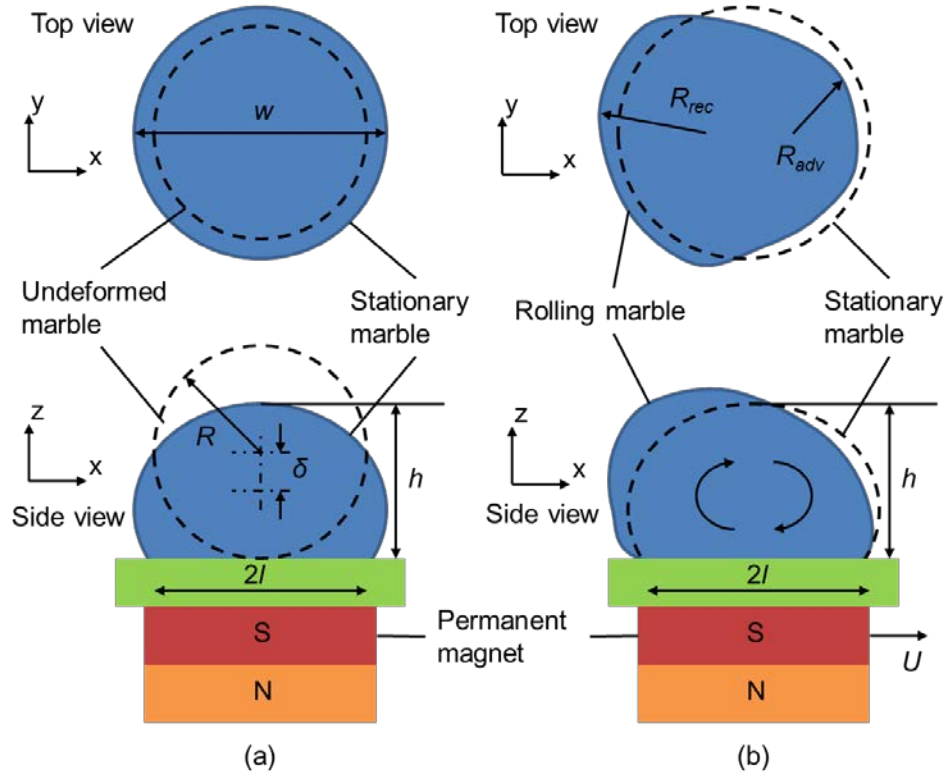


Fig. 3 Magnetic manipulation: **(a)** , **(b)** Various parameters used to characterise the deformation of a liquid marble under the influence of magnetic field for both the static and dynamic cases (Nguyen 2013). **(c)** Manipulation of liquid marble using the magnetic field. From left to right, the iron oxide nanoparticles are concentrated downwards when a magnet is brought into proximity. The process is reversible as the nanoparticles reassembled themselves after the magnet is removed

Assuming that the magnetic force is much larger than the weight of the marble and the magnetic flux density imparted onto the liquid marble is much larger than the critical magnetic flux density, the scaling relationships can be obtained as $l^* \sim Bm^{1/4}$, $h^* \approx 2$ for small, spherical marble and $l^* \sim Bm^{1/4}$, $h^* \approx Bm^{-1/2}$ for larger, puddle-shaped marble, where Bm is the magnetic Bond number, $Bm = RMB/\sigma$, M is the magnetisation density of the ferrofluid, B is the magnetic flux density and σ is the apparent surface tension of the marble (Nguyen 2013). Relationships are derived from the increase in surface energy due to the above deformation and the gained magnetic energy.

The threshold magnetic field needed to induce droplet movement has been experimentally investigated by Zhao et al. (2012) using a magnetite coating and Bormashenko et al. (2008) using a ferrofluid droplet. Both reported that the threshold magnetic force is equal to the frictional force between the marble and its carrier surface. Magnetic mixing of liquid marbles have been demonstrated by Dorvee et al. (2004) and Zhao et al. (2010).

The deformation of the rolling liquid marble was studied in detail by Nguyen and the relationship between the magnetic field, movement speed and the marble shape were derived as (Nguyen 2013):

$$R\left(\frac{1}{R_{adv}} - \frac{1}{R_{rec}}\right) \sim CaBm^{\frac{1}{4}} \text{ for small, spherical marble} \quad (2)$$

$$R\left(\frac{1}{R_{adv}} - \frac{1}{R_{rec}}\right) \sim CaBm^{\frac{5}{4}} \text{ for larger, puddle-shaped marble} \quad (3)$$

Where R_{adv} and R_{rec} are the advancing and receding radius respectively, Ca is the capillary number $Ca = \mu U / \sigma$, where μ is the dynamic viscosity and U is the movement speed of the marble. The left side of the equations yields a dimensionless number for the deformation of the marble while the right side takes into account the external magnetic field, ferrofluid magnetisation (from the Bond number) as well as the speed, viscosity and surface tension of the marble (from the capillary number).

The ability of the magnet to “open” and “close” the hydrophobised iron oxide-coated liquid marble was reported by Zhao et al. (2010; 2012) and Xue et al. (2010). The mechanism of the rearrangement of surface particles was described and is simplified in Figure 3(c). The magnetic field strength required to open the marble was determined experimentally. Moreover, the liquid content can be accessed from the top without rupturing the marble. Liquid exchange can be conducted conveniently and optical probing is possible too. This feature allows the liquid marble to be used as a reactor. Droplet deposition into liquid marbles was demonstrated by Xue et al. (2010), making the liquid marble a viable option as a microreactor.

2.2 Mechanical schemes

2.2.1 Gravitational force

One of the simplest ways to initiate the movement of a liquid marble is allowing it to roll down an inclined plane. Gravitational potential energy is converted into kinetic energy leading to a downward movement. Mahadevan and Pomeau (1999) established a model of a rolling droplet on a superhydrophobic surface, which also applies to a liquid marble, as verified by Aussillous and Quere (2004). For a steady rolling motion down a plane, droplet velocity can be determined by balancing viscous dissipation and the decrease in gravitational potential energy (Mahadevan and Pomeau 1999):

$$UR^3 \rho g \sin \alpha \sim \mu \int_{V_d} (\nabla u)^2 dV \quad (4)$$

where U is the velocity of the centre of the mass of the marble; u is the velocity field in the droplet; V_d is the volume which viscous dissipation occurs; and μ is the dynamic viscosity of the liquid.

Considering the local viscous dissipation to height l (Fig. 4), the magnitude of fluid velocity in this region can be written as $|\nabla u| \sim U/R$ and $V_d \sim l^3$. Substituting these relationships into equation (4) and solving for steady-state velocity, the marble velocity can be determined as (Mahadevan and Pomeau 1999):

$$U \sim \frac{R^5 \rho g \sin \alpha}{\mu l^3} = \frac{\sigma^{\frac{3}{2}} \sin \alpha}{\mu R (\rho g)^{\frac{1}{2}}} \sim \frac{\sigma Bo^{\frac{1}{2}} \sin \alpha}{\mu} \quad (5)$$

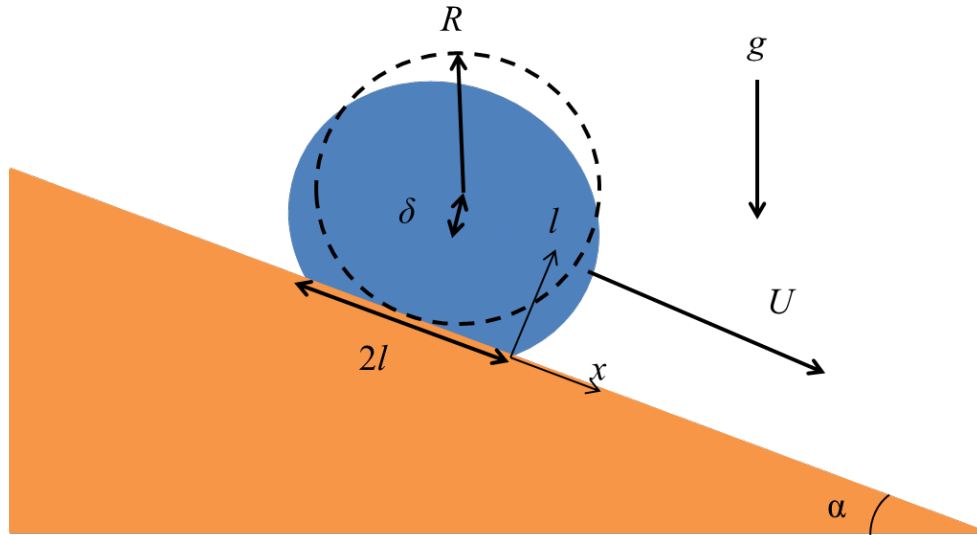


Fig. 4 A droplet rolling down an inclined plane under the influence of gravity

This relationship shows that the speed of the marble is determined by the angle of inclination, dynamic viscosity, surface tension and Bond number. Furthermore, smaller droplets roll faster than their larger counterpart, which is in good agreement with Richard and Quere's (1999) experimental results. The degree of control provided by moving a droplet using only gravity is limited, as loss of potential energy is non-reversible and droplet movement is uni-directional. Yang et al. (2012) demonstrated that it is possible to generate small amounts of electricity by rolling an ionic liquid marble down an inclined layer of interdigitated electrodes. A simple liquid marble-based accelerometer was created by Zeng and Zhao (2010) by utilising gravitational force. Planchette et al. (2013) utilised gravity to control the speed of droplets to be merged with liquid marbles.

2.2.2 Pressure gradient

A micropump based on liquid marbles has been demonstrated by Bormashenko et al. (2010), by utilising the concept of difference in Laplace pressure. The Laplace pressure of a water droplet can be found as (Finn 1986):

$$P = P_0 + \frac{2\sigma}{R} \quad (6)$$

Where P is the pressure inside the droplet and P_0 is the atmospheric pressure.

By coating a liquid marble with different materials, the difference in surface tension σ results in a difference in Laplace pressure. Bormashenko et al. (2010) connected the two marbles with a polyethylene (PE) tube as shown in Figure 5, allowing liquid transport from one marble to another until the pressures were equalised.

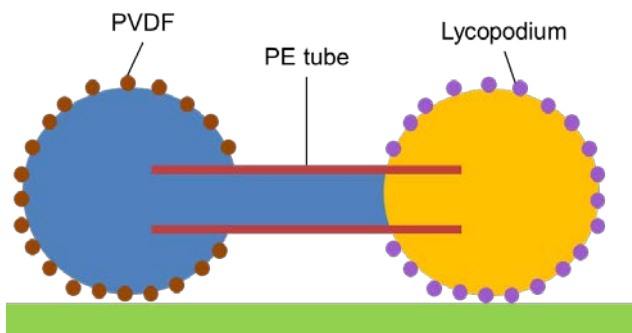


Fig. 5 Two marbles with different coating and water dyed with different colours. Fluid from the PVDF-coated marble is flowing into the other marble

The advantage of this method is that no external energy supply is required. The pressure difference provided the energy for the liquid transport. Instead of surface tension, the marble radii could be varied to produce the different Laplace pressures. Nevertheless, a means to sustain the pressure difference is needed before this concept could be incorporated into a microfluidic device. Also, as the marble at the receiving end grows, the coating material to liquid volume ratio will decrease. If the amount of injected liquid exceeds a critical value, the marble might rupture.

2.3 Other schemes

Instead of treating the coating material of a marble as just an inert protective layer, a number of reported studies attempted to chemically change the properties of the coating particles or to engineer new coating materials with specific properties. The reviews encompassed thus far have all featured the change in wettability of the coating material via chemical scheme. Since the integrity of the liquid marble depends on the hydrophobicity of the coating material, decreasing the hydrophobicity would eventually lead to the destruction of the liquid marble. Most of the research efforts involving chemically manipulating the coating material were conducted with liquid marbles floating on a solution. The chemical composition of the solution can be more precisely controlled and the destruction of the liquid marble is more visible. Controlling the

coating properties enables a liquid marble to be used as a chemical sensor. In the presence of a chemical substance, the marble generates a response visible to the naked eye.

2.3.1 Temperature change

It is well-known that the coating material of the liquid marble acts like a porous shell that allows gas exchange without direct fluid contact (Bormashenko, Bormashenko et al. 2009). In fact, a liquid marble evaporates, shrinks, deforms and eventually collapses over time. This phenomenon has been reported by many authors and the evaporation rates have been studied in detail for various coating materials (Dandan and Erbil 2009; Tosun and Erbil 2009; Doganci, Sesli et al. 2011). The lifetime of a liquid marble can be estimated by controlling the temperature, humidity and the volume of the marble. In high humidity, a liquid marble could last for days (Tosun and Erbil 2009; Nakai, Fujii et al. 2013). The evaporation rate of a liquid marble has been established and can be described as (Erbil, McHale et al. 2002; Dandan and Erbil 2009; Tosun and Erbil 2009; Doganci, Sesli et al. 2011):

$$-\frac{\partial V}{\partial t} = \left(\frac{4DM_w P_{vs}}{RT\rho} \right) \left(\frac{3\pi^2 V}{2 - \cos\theta + \cos^3\theta} \right)^{\frac{1}{3}} (1 - RH) f(\theta) \quad (7)$$

Where t is time, V is the marble volume, D is the vapour diffusion coefficient, θ is the contact angle in radians, M_w is the molecular weight of water, P_{vs} is the saturation vapour pressure at temperature T , R is the gas constant, RH is the relative humidity and finally $f(\theta)$ is given by:

$$f(\theta) = (4.4785 \times 10^{-5}) + (0.31665)\theta + (5.8 \times 10^{-2})\theta^2 - (4.439 \times 10^{-2})\theta^3 + (5.165 \times 10^{-3})\theta^4 \quad (8)$$

In a recent detailed investigation, Laborie et al. (2013) concluded that the evaporation rate of a liquid marble is higher than that of an uncoated water droplet, provided that the liquid marble coating consists of a monolayer of particles. The main reason is that particle monolayer incompressibility forces a constant evaporation rate as opposed to a decreasing one for its uncoated counterpart. Nevertheless, this finding does not contradict previous works as it determined that the evaporation rate was significantly lowered for liquid marbles with multilayered coatings due to porous media effect. Previous studies on evaporation rate indicated

that coating particles formed multiple layers on liquid marble surface (Dandan and Erbil 2009; Tosun and Erbil 2009; Cengiz and Erbil 2013).

The long lifetime of a liquid marble is needed for biomedical applications where cell cultures usually require extended periods of storage time. Shen's group grew various cell types inside a liquid marble (Arbatan, Al-Abboodi et al. 2012; Tian, Fu et al. 2013; Sarvi, Jain et al. 2014), demonstrating the importance of prolonging the marble lifetime.

On the other hand, a liquid marble can be deformed by freezing. Both Zang et al. (2014) and Hashmi et al. (2012) reported that the spherical liquid marble could be reversibly flattened into a the shape of a flying saucer at low temperatures due to the Marangoni convection within the marble. For a sessile liquid marble placed on a cold substrate, ice formation starts at the bottom of the marble. Hashmi et al. (2012) postulated that due to the warmer coating particles, the liquid in the vicinity impede ice formation at the bottom edge of the marble. This results in a thermal and surface tension gradient in the liquid which drives the Marangoni convection as shown in Figure 6.

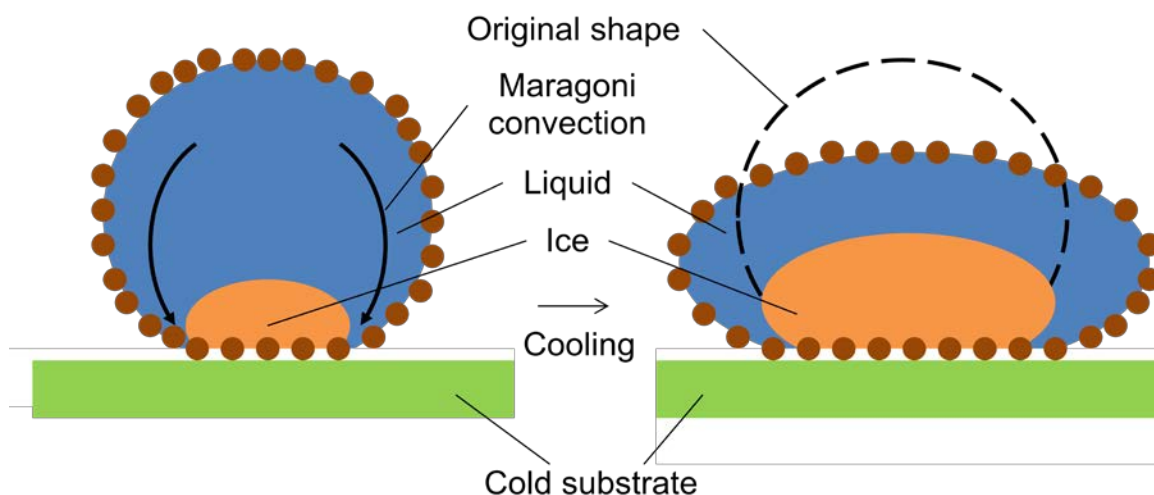


Fig. 6 Deformation of a cooled liquid marble. As ice starts to form inside the liquid marble, Marangoni convection forces liquid movement to the bottom edge of the marble. Eventually, the marble deforms enough to adopt a “flattened” shape.

The detailed study by Zang et al. also concluded that the hydrophobicity of the coating material determines the shape of the frozen marble since the Gibbs free energy barrier is

influenced by the wettability of the coating material. A frozen liquid marble can be transported much easier compared to its liquid counterpart as it is much more robust. Also, the reversible deformation suggests that the frozen marble can be thawed and studied subsequently. Yusa et al. (2014) destroyed a liquid marble by lowering the temperature utilising the thermally reversible phase separation properties of Poly(N-isopropylacrylamide) (PNIPAm) (Fujishige, Kubota et al. 1989). A liquid marble coated with PNIPAm was destroyed when the temperature dropped below its lower critical solution temperature.

2.3.2 Irradiation

The wettability of some specially coated liquid marbles can be changed without any physical contact by optical irradiation. Currently, only the UV spectrum has been used. Using a photoresponsive material as the coating material makes this scheme possible. UV radiation induces surface structural changes of the coating material, resulting in a significant increase in wettability of the liquid marble to the point of rupture. Tan et al. (2014) used hydrophobised titanium dioxide as the photoresponsive coating material. Charge carriers were created when titanium oxide was irradiated with UV. The charge carriers migrated to the material surface which then facilitated the formation of hydrophilic hydroxyl groups. Zhang et al. (2012) created liquid marbles coated with stimuli-responsive magnetic particles (RMP) whose hydrophilicity increases when protonated. The RMPs were in turn coated with silica loaded with photoacid generator (PAG). When irradiated with UV, the photoacid generator protonated the RMP and caused the coating particles to become hydrophilic. Another UV responsive liquid marble was created by Nakai et al. (2013). Spiropyran (SP) powder was used as the coating material with UV irradiation-assisted isomerisation. The process yielded merocyanine (MC), which is more hydrophilic than SP, Figure 7. This change was verified with the rupture of the liquid marble which would otherwise have remained stable for more than a week in dark and humid conditions (Nakai, Fujii et al. 2013). The method of UV irradiation provides remote control capability to liquid marble manipulation, but might not be suitable for marbles containing sensitive biological samples.

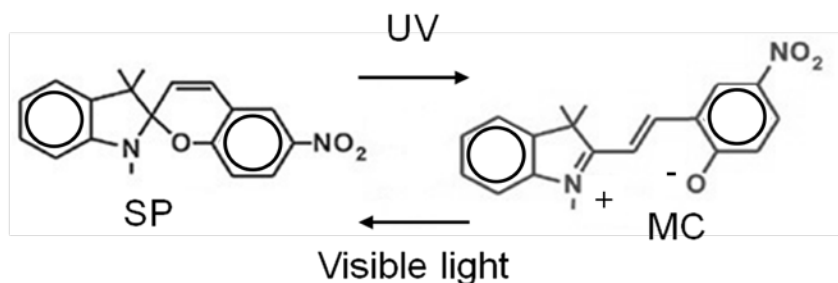


Fig. 7 Chemical structure of the reversible isomerisation of SP and MC. UV irradiation changes SP into MC while visible light irradiation reverses the effects

2.3.3 Surfactant concentration

Bormashenko and Musin (2009) demonstrated that the integrity of a liquid marble floating on water can be altered by changing the surface tension of the carrier liquid, in this case water with the presence of silicon oil or kerosene. The qualitative study concluded that surface tension of the carrier liquid must be higher than that of the liquid marble to maintain its integrity. The argument is that it is more energetically favourable for the coating particles to adhere to the fluid with lower surface tension, Figure 8. This phenomenon allows a liquid marble to work as a sensor of pollutants on water surface.

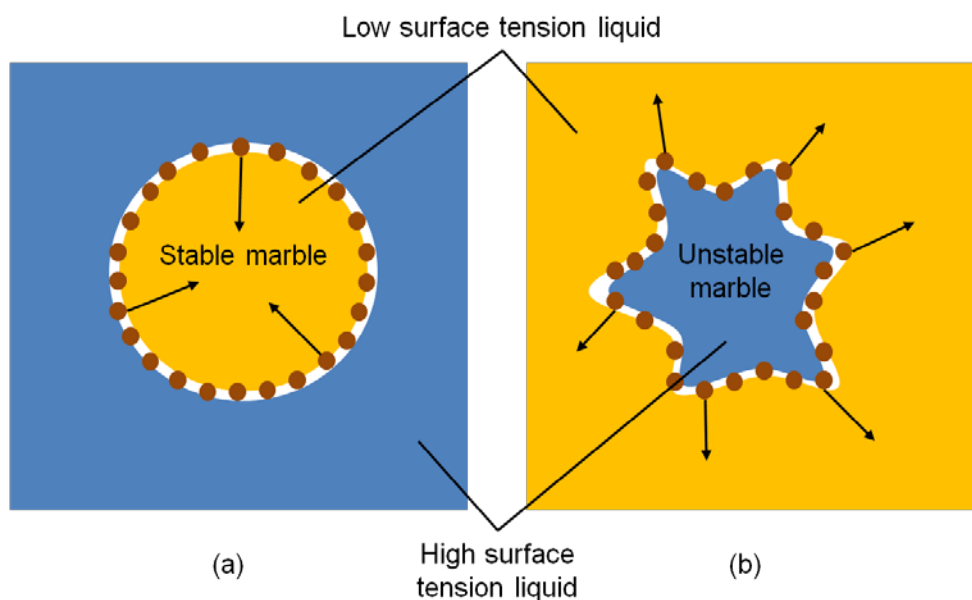


Fig. 8 Effect of liquid surface tensions on the integrity of liquid marbles: (a) Stable liquid marble condition. The coating particles tend to adhere to the liquid marble and form a stable shell. (b) Unstable

liquid marble condition. The coating particles tend to adhere to the carrier liquid and destroy the liquid marble

2.3.4 Change of pH

Besides detection of pollutants, Fujii et al. (2010; 2011) and Inoue et al. (2011) both developed liquid marble coatings that are responsive to pH changes. Styrene terminated poly (2-(diethylamino) ethyl methacrylate) latex coating that is neutrally charged and hydrophobic in alkaline environment. If the liquid marble is floated on an alkaline solution, it is stable for a long time. As the pH decreases, the coating material of the liquid marble becomes hydrophilic and hence destroyed it. When the pH of the carrier liquid drops below 7, the latex rapidly changes into a hydrophilic material and destabilises the liquid marble.

The liquid marble reported by Inoue et al. behaves in an opposite manner as it is stable in an acidic environment and responds to alkaline instead. The coating material is poly(6-(acrylamido) hexanoic acid)-grafted silica particles which becomes hydrophilic at pH 10 (Inoue, Fujii et al. 2011).

3 Applications

A liquid marble can be deformed using magnetic force (Newton, Herbertson et al. 2007; Bormashenko, Pogreb et al. 2012) or temperature change (Hashmi, Strauss et al. 2012; Zang, Lin et al. 2014). In the presence of external stimuli the marble deforms. The input energy is converted to surface energy of the marble. Consequently, the marble adopts a more stable shape through energy conservation. Deformation is usually visible and measureable, which makes it potentially useful as a visual sensor.

The motion of liquid marbles under magnetic (Newton, Herbertson et al. 2007) or gravitational force (Aussillous and Quere 2004; 2006) is potentially useful for digital microfluidics. Miniature accelerometers and electric generators have been developed based on liquid marble motion (Zeng and Zhao 2010). Liquid marbles coated with magnetic particles can be opened and closed reversibly. The liquid content can then be partially exposed for convenient

liquid addition or removal. This feature enables a liquid marble to be used as a microreactor or a micromixer. Since only marble shell is manipulated, any liquid content can be used.

If liquid marbles are impacted together with a sufficient momentum, they merge and form a single larger marble. Dorvee et al. (2004) have used magnetic force to merge two marbles and mix their liquid contents. A quantitative study by Planchette et al. (2013) determined that the impact velocity, marble and coating particle diameters affect the ability of the marbles to coalesce. Large liquid marble volume, small coating particles and large impact speed facilitate the merging process (Planchette, Biance et al. 2013). After merging, the coating material rapidly reassembles itself at the outer shell of the marble as deduced by both Dorvee et al. and Planchette et al.. Bormashenko et al. (2010) achieved mixing of liquid marbles by connecting two of them with a miniature bridge that allows liquid passage. This function enables a liquid marble to be used as an efficient and precise micromixer, as the volume of the constituent liquids can be accurately controlled.

One of the unique features of a liquid marble compared to a droplet is the limited evaporation. As gas exchange across the marble shell is inevitable, the marble volume can be stabilised by changing the temperature and humidity of its surroundings. Reducing the evaporation rate causes a liquid marble to last for several days, making it an excellent cell culture platform. Furthermore, large liquid marbles can be formed with suitable coating material. Cengiz and Erbil (2013) produced a liquid marble up to 1 ml using a stabilised coating material. Massive liquid marbles such as these can contain large amount of nutrients needed by the cells, potentially rendering nutrient addition and waste removal unnecessary. On the other hand, accelerating evaporation causes the liquid to be removed with the coating shell left behind. Usually, the shell is too weak to support itself and collapses. Eshtiaghi et al. (2009; 2010) stabilised the dried shell and created a hollow sphere. These shells have large surface areas which can act as a scaffold for cell growth.

Tian et al.'s (2013) demonstrated cell culture in liquid marbles placed on a petri dish. The concept can be further extended to submerged liquid marbles. As shown by Bormashenko et al. (2012), liquid marbles can be submerged to form a Pickering emulsion. Once the liquid marbles are submerged in an organic liquid, gas exchange is prohibited. This creates a condition which is favourable for anaerobic cell growth or monitoring aerobic cells in an anaerobic environment.

Another important aspect in cell growth is real-time imaging and monitoring. Bhosale et al. (2008) created a transparent coating material based on fumed silica nanoparticles. This allows researchers to have constant tracking of cell growth. Real-time imaging in liquid marble would allow researchers to study cell behaviour in a true three-dimensional environment.

In Miao, Lee et al.'s (2014) recent work, a liquid marble coated with silver nanowires was used as a miniature, rate-controllable catalytic reactor. The high surface area of the catalytic nanowires facilitates reaction while the liquid marble volume controls the reaction rate. The authors reported high reaction efficiency with their low-cost solution. This could drastically reduce the amount of reactant required since the catalytic reaction can take place in microliter-sized liquid marbles.

4 Conclusion and perspectives

Many aspects of research on liquid marble have been advanced within the past two decades. Liquid marbles can be produced easily with a wide range of materials. Numerous manipulation schemes arose from a better understanding of the fundamental properties of a liquid marble. Various applications have been explored for liquid marbles, including but not limited to sensors, cell culture and micromixers. Despite the recent advances, some important issues have yet to be addressed.

From the reviewed literatures, production of the liquid marble almost invariably involves rolling a liquid droplet on a powder bed. This is either achieved manually or using a laboratory granulator, which utilise the same concept discovered decades ago. There is a need for a method that can produce liquid marbles that have consistent volumes automatically and on a larger scale. The Pickering emulsion polymerisation method seems to be a promising lead (Guan, Meng et al. 2014).

Furthermore, although a liquid marble is known to be relatively more robust compared to an uncoated liquid droplet, special care is still required in terms of handling and transport. Recently, several works attempted to address this issue by engineering a stabilized liquid marble shell to enhance its integrity and to reduce evaporation rates (Fujii and Murakami 2008; Braun

and Cardoso 2012; Chin, Reithofer et al. 2013; Matsukuma, Watanabe et al. 2013; Wu, Watanabe et al. 2013; Ueno, Hamasaki et al. 2014). More recently, nanofibers have been used as the coating material for enhanced mechanical strength. It is reported that nanofibers can form a networked, three-dimensional coating which has superior strength compared to its conventional loose powder-based counterpart (Mele, Bayer et al. 2014). This departure from conventional coating materials could generate renewed interests and radical discoveries. More progress in this aspect is speculated within the next few years.

As liquid marbles have very low coefficient of friction with its solid or liquid carrier, they can easily move with just a slight disturbance. Since many of the above mentioned applications involve the in situ manipulation of the liquid marble, precise delivery to a target site is still a major challenge. Manipulation using magnetic schemes is a straightforward solution, but the challenge remains unaddressed for non-magnetic liquid marbles.

Except for deformation, all the manipulation schemes discussed here involve a non-reversible destruction of a liquid marble. This can be used as a delivery system to transport a liquid sample to a location and to manipulate it if there is a need. Upon manipulation however, not only the liquid content is delivered but also the coating material. The problem arises if a clean and uncontaminated location is required. A further complication is the possible reaction between the coating material and the carrier liquid. Surprisingly, none of the reviewed references proposed an efficient and effective method to remove the unwanted coating material. A removal method would be a significant benefit for application of liquid marbles.

From the review, liquid marble manipulation schemes seem to be extensive. Nonetheless we would like to discuss several viable options worth exploring. The irradiation method currently only involves UV irradiation chemically changing the liquid marble coating material. Manipulation using the electrokinetic forces has not been exploited for liquid marble mixing. Two liquid marbles can be charged up and then merged by the attractive electric force. Subsequently, mixing of the liquid content can be accelerated with electrophoresis. Many previous studies have explored the dynamics of particles floating on water (Kralchevsky and Nagayama 2000; Singh and Joseph 2005; Vassileva, van den Ende et al. 2005; Dalbe, Cosic et al. 2011). Since small liquid marbles adopt spherical shapes, these studies are expected to be applicable to floating marbles as well. Besides capillary forces, the Marangoni effect can be

exploited to propel the liquid marble floating on a liquid. A temperature gradient can be generated on different regions of the liquid which in turn creates a surface tension gradient needed for the Marangoni effect.

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