Capillarity-revisiting the fundamentals of liquid marbles

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Abstract

Liquid marble, an emerging platform for digital microfluidics, has shown its potential in biomedical applications, cosmetics, and chemical industries. Recently, the manipulation and fundamental aspects of liquid marbles have been reported and attracted attention from the microfluidics community. Insights into their physical and chemical properties allow liquid marbles to be utilised in practical applications. This review summarises and revisits the effect of capillarity on the formation of liquid marbles and how it affects the surface tension as well as their robustness. The paper also systematically discusses the applied aspect of capillarity of the carrier liquid for transporting floating liquid marbles.

Keywords- liquid marble, surface tension, capillarity, digital microfluidics

1 Introduction

Microfluidics is the science and technology dealing with the manipulation of fluid in sub-millimeter/micrometer scale. Microfluidics enables the implementation of liquid handling process on a single device (Whitesides 2006). Microfluidics has a broad range of applications from lab on a chip for point of care diagnostics to cell culture organ on a chip. It is well known that the liquid flow may behave differently in the microscale. For instance, in most cases liquid flow is laminar in the microscale and body forces such as weight are negligible compared to the dominant surface tension. The unique microscale behaviors open up subtopics in microfluidics, leading to applications in chemical engineering, biomedicines, and cosmetics (Bormashenko 2011; McHale and Newton 2011; Nguyen et al. 2019; Nguyen and Wu 2004; Oliveira et al. 2017; Ooi and Nguyen 2015). Recently, digital microfluidics (DMF) has been emerging as a liquid handling technology that manipulates discrete droplets (Choi et al. 2012). This technology offers several advantages over the conventional continuous flow microfluidics such as minimum reagent requirement, fast response, and the ability to scale up through parallelisation (Nguyen et al. 2017; Samiei et al. 2016). Droplets can be manipulated with active approaches such as electrowetting, (Teng et al. 2020) dielectrophoresis, (Velev et al. 2003) thermocapillary effect, (Chen et al. 2005) acoustic vibration, (Chen et al. 2017; Zang et al. 2015) and magneto-wetting (Nguyen et al. 2010a). However, evaporation, handling, contamination and surface modification remain current challenges. Liquid-marble based DMF has been utilised as a novel microfluidic platform to address the abovementioned issues.

A liquid marble is a non-wetting liquid droplet encapsulated by micro- or nanoscale hydrophobic particles. The concept of liquid marble exists in nature in the form of waste disposal of galling aphids. The insects could get trapped in their own honey dew waste, but the little aphids tackle this problem in a smart way. During defecation, powdered wax from the anus encapsulates the honey dew droplets. These encapsulated droplets can roll rapidly and efficiently without sticking anywhere. In this way, aphids save themselves from drowning in their own sticky waste (Pike et al. 2002). Aussillous and Quere were among the first to initiate the study of liquid marbles (Aussillous and Quéré 2001). A liquid marble serves as a standalone liquid system, as the liquid is physically

isolated from the surrounding. A liquid marble is robust (Bhosale et al. 2008; Liu et al. 2015) and elastic (Asare-Asher et al. 2015; Bormashenko et al. 2015b; Whyman and Bormashenko 2015). Furthermore, a liquid marble has low friction, controllable evaporation rate, (Dandan and Erbil 2009; Sreejith et al. 2018a) better stability, (Bormashenko et al. 2012; Cengiz and Erbil 2013) and unsusceptible to contamination (Aussillous and Quéré 2006). An existing issue in microfluidics is the lack of control over wetting, which causes contamination and affects performance. Conventional microfluidic systems overcome such problem by physical and/or chemical modifying device surfaces. Surface topography is one of the physical parameters for wetting control. For example, replication of lotus leaf surface structures through soft lithography enables a substrate to achieve Cassie-Baxter wetting (Sun et al. 2005). Surface modification with physical vapour deposition have also been widely used to manipulate the wetting (Lugscheider and Bobzin 2001). On the other hand, chemical vapour deposition and surface functionalisation modify the chemical properties of the surface to tune the contact angle (Moseke and Gbureck 2019). The coating of a liquid marble makes it perfectly non-wetting. While surface modification requires complex fabrication processes, liquid marbles are simple and already find applications such as gas sensors, (Tian et al. 2010a; Tian et al. 2010b) micro reactors, (Arbatan et al. 2012; Bormashenko 2017; Sato et al. 2015; Nguyen et al. 2020) and chemical/biological assays (Arbatan et al. 2012). Extensive research have been carried out on tuning the properties of liquid marbles, (Aussillous and Quéré 2006; Bormashenko et al. 2009c) forming Janus liquid marbles, (Bormashenko et al. 2011b; Xu et al. 2014) transport, (Kavokine et al. 2016; Paven et al. 2016) and floating liquid marbles (Bormashenko et al. 2010a; Bormashenko et al. 2011a; Bormashenko et al. 2009a; Bormashenko et al. 2009b; Gao and McCarthy 2007; Jin et al. 2019; Jin et al. 2020; Ooi et al. 2018; Rao et al. 2005; Tosun and Erbil 2009; Xue et al. 2010). Although there are many previous reviews on the fundamental and applied aspects of liquid marbles, (Jin et al. 2017; Ooi and Nguyen 2015; Sreejith et al. 2018b) none particularly focuses on the effect of the capillarity. The present paper aims to revisit the fundamental and applied aspects of capillarity in liquid marbles.

Capillarity or capillary action signifies the ability of a liquid to be raised or depressed at the contact line between the liquid and the container. Capillarity is determined by (i) the surface tension of the liquid γ , (ii) the gravitational force, and (iii) the contact angle between the liquid and the solid surface. The capillary length $l_c = \sqrt{\gamma/\rho g}$ correlates the former two factors. Capillary length is a scaling variable reflecting the balance between the surface tension force and the gravitational force. The capillary length plays an important role in determining the shape of a liquid marble, which is usually quasi-spherical or puddle-like depending on its volume (De Gennes et al. 2013). Conversely, capillarity is vital for the formation and stability of a liquid marble, because particles at the liquid-air interface introduce an additional meniscus on the surface of the droplet. The size and properties of the particles affect the surface energy of the droplet (Nguyen et al. 2010b). These particles trap air, allowing a liquid marble to float on the free surface of another liquid. The capillary interaction between the particles affects the force balance within the coating of a liquid marble and modifies its surface tension. The modified surface tension is termed as the effective surface tension of a liquid marble (Arbatan and Shen 2011; Bormashenko et al. 2009c). The effective surface tension determines the compressibility and lifetime of a liquid marble. The lifetime of a floating liquid marble depends also on the surface tension of the carrier liquid. A floating liquid marble has high mobility due to its non-wetting behavior and the lower friction with the carrier liquid surface. The surface tension of the carrier liquid can direct the movement of a floating liquid marble, which could be utilised as a vehicle for targeted drug delivery (Kavokine et al. 2016; Paven et al. 2016). On the other hand, a floating liquid marble induces a negative meniscus on the carrier liquid surface. This meniscus depression enables capillarity-based self-assembly (Singha et al. 2019). The meniscus angle

depends on the size of the liquid marble, (Ooi et al. 2016) and the surface tension of the carrier liquid (Singha et al. 2019). Very few works were reported on the effect of carrier liquid surface tension on liquid marble. The following sections discuss in details the effect of the capillarity on properties and behavior of liquid marbles.

2 Effect of surface tension on the formation of a liquid marble

A liquid marble consists of a liquid droplet and a coating of micro- or nanosized hydrophobic particles. The surface tension of the liquid and the surface energy of the particles interact to minimise the energy of the system. If a solid particle is attached to the liquid-air interface, the surface free energy G of the particle is: (Aussillous and Qur 2006; Tyowua 2018)

$$G = \gamma_{la}(A_{la} - \pi R_p^2) + \gamma_{sl}A_{sl} + \gamma_{sa}A_{sa} \quad (1)$$

where, $R_1 = R_p (1 - \cos\theta)/2$, A_{ij} and γ_{ij} is the interfacial area and the interfacial tension at the i - j interface respectively, R_p is the radius of the particle, and θ is the three-phase contact angle.

If the particle is fully immersed into the liquid or freely released into the air, the surface energy will be G_1 or G_2 respectively,

$$G_1 = \gamma_{la}A_{la} + \gamma_{sl}(A_{sl} + A_{sa}) \quad (2)$$

$$G_2 = \gamma_{la}A_{la} + \gamma_{sa}(A_{sl} + A_{sa}) \quad (3)$$

The energy for particle detachment is found by subtracting Equation (1) from Equation (2) and (3), such that: (Aussillous and Qur 2006; McHale and Newton 2011)

$$\Delta G_{1,2} = \pi R_p^2 \gamma_{la} (1 - |\cos\theta|)^2 \quad (4)$$

The energy required for the detachment of a particle from the liquid-air interface is usually higher than the energy released during the adsorption of the particle at the interface. Therefore, the adsorbed particle does not move out from the liquid-air interface without an additional effort.

Fig 1: Primary step towards the formation of a liquid marble

The interfacial energy also explains the formation and stabilisation mechanism of a liquid marble. Figure 1 depicts the attachment of a particle at the liquid-air interface. The attachment of the particle onto the liquid surface changes the interfacial area. The interfacial area between solid-liquid (A_{sl}) and solid-air (A_{sa}) is same when contact angle of the particle with the liquid is 90° . Hydrophilic particle penetrates more into the liquid than hydrophobic particle. The change in the interfacial energy after the particle attachment is determined by Equation (5).

$$\Delta f = A_{sa}(\gamma_{sl} - \gamma_{sa}) - A_{la}\gamma_{la} \quad (5)$$

According to Young's law:

$$\cos\theta = \frac{\gamma_{sa}-\gamma_{sl}}{\gamma_{la}} \quad (6)$$

γ_{ij} is the interfacial tension between i and j phase, θ is the contact angle of the droplet with respect to the solid. Combining (5) and (6) results in:

$$\Delta f = -A_{sa}\gamma_{la}(\cos\theta + \frac{A_{la}}{A_{sa}}) \quad (7)$$

The ratio A_{la}/A_{sa} is always greater or equal to zero. Hence, Equation (7) indicates clearly that the surface free energy always reduces after particle attachment, thus stabilising the system (Laborie et al. 2013). This hypothesis is always true except for the special case of the contact angle of 180° . The mechanism is explained by considering the formation of a monolayer. In practice, monolayer formation of particles around a droplet requires special treatments (Laborie et al. 2013; Li et al. 2017; Ogawa et al. 2014). The conventional technique to fabricate a liquid marble relies on rolling a liquid droplet over a bed of particles. The droplet wets the particles during the rolling process. The wetting transition at the interface depends on the contact angle of the liquid with the particles bed. In the case of high-degree wetting, the liquid advances sufficiently to cross over the first layer of particles on the bed. The liquid then collects the second layer of particles as a result of menisci effect (Hamlett et al. 2011; Shirtcliffe et al. 2006). Thus, the rolling process forms multilayered liquid marbles. Wang et al. utilised this primary concept of wetting transition to demonstrate the disintegration of a liquid marble (Wang and He 2018). The core liquid consisted of non-ionic surfactant Triton X-100, whereas the coating consisted of silica nanoparticles. The surfactant molecules sat on the surface of the droplet and reduced the surface tension of the core liquid. Adsorbed silica particles at the droplet surface became more hydrophilic after interacting with the surfactant (Binks et al. 2010; Doganci et al. 2011). Therefore, silica particles started to immerse into the solution. The air pockets trapped within the particles layer between the core liquid and the substrate became thinner. Further increase in surfactant concentration in the core liquid forced a portion of innermost silica particles to be engulfed into the solution. Thus, the particle coating started to be partially cleared and the liquid marble collapsed. Thus, a liquid marble with a low surfactant concentration in its core liquid has a longer lifetime.

Fig 2: Liquid marble formation as a capillary origami process: (a) particles climbing up the droplet surface, (b) particles encapsulate the droplet.

On the other hand, the conventional process to produce the liquid marble facilitates the so-called capillary origami process. Liquid marble coating is an example of origami assembly. When an elastic substrate is thin enough so that it can be bent or folded around the droplet sitting over it, the capillarity of the droplet shapes the substrate rather than the substrate shapes the droplet. This effect is called 'capillary origami' which produces a 3D shape from a flat surface (Py et al. 2007). As mentioned in the previous paragraph, liquid marble production starts with depositing a liquid droplet over a bed of hydrophobic particles, Figure 2. Immediately after the deposition, the adjacent particles start to adhere onto the droplet surface, Figure 2(a). As a result, the particles gradually climb up and cover the droplet surface. A conventional capillary origami process requires bending energy, stretching energy for the surface for wrapping around the droplet. Liquid marble provides an effective platform for capillary origami without the cost of bending energy or stretching energy, hence eliminates the elasto-capillary effect (McHale et al. 2011). Surface chemistry of the particle determines the adhesiveness. Contact angle measurement with the help of Young's equation provides indirect information about the surface chemistry of the particles.

3 Surface tension of a liquid marble

Surface tension at a liquid-air interface is caused by the unbalanced force at the interface, where the molecules experience a pulling force towards the bulk liquid. In a liquid marble, the liquid-solid interface substitutes the liquid-air interface, where the shell of hydrophobic particles partially wet the core liquid. Microscopic observation reveals that these particles deviate the curvature of the liquid (Nguyen et al. 2010c). Therefore, the capillary interaction between the particles are likely to affect the force balance at the liquid surface and modifies the surface tension of a liquid marble. The modified surface tension of a liquid marble is popularly termed as the 'effective surface tension' of the liquid marble, (Arbatan and Shen 2011; Bormashenko et al. 2009c) which is formulated as: (Aussillous and Qur 2004)

$$\gamma_{\text{eff}} = \gamma_{\text{la}} + \gamma_{\text{int}} \quad (8)$$

where, γ_{eff} is the effective surface tension of the liquid marble, γ_{la} is the surface tension at the liquid-air interface, and γ_{int} is the contribution to the effective surface tension due to capillary and electrostatic interactions (Arbatan and Shen 2011; Bormashenko et al. 2009c). The magnitude of the contribution γ_{int} may be either positive or negative which represents the net attractive or repulsive forces respectively. This is the reason why the effective surface tension of a liquid marble differs from the surface tension of a bare droplet.

Surface tension plays a significant role on the lifetime (Cengiz and Erbil 2013) and robustness (Liu et al. 2015) of liquid marbles. Cengiz et al. investigated the role of particle size and hydrophobicity of encapsulating particles on the effective surface tension of a liquid marble and how it affects the lifetime of the liquid marble (Cengiz and Erbil 2013). The authors used P-Zonyl-TAN powder of 8, 20 and 60 μm in diameter for the investigation. Smaller particles with diameters of less than 10 μm had negligible contribution to the capillary interaction as their weight was too small to create any deviation onto the liquid surface (Kralchevsky and Nagayama 1994; Kralchevsky and Nagayama 2000). Therefore, the capillary repulsion force decreases as the particle size decreases. Small particles contribute less to the capillary interaction. Moreover, the interaction between the particles at the liquid-air interface was repulsive, indicating that, γ_{int} is always negative in Equation (8). Consequently, the effective surface tension of the liquid marble should be lower than the surface tension of a bare droplet. Smaller particles cause less reduction in surface tension than large particles. Surface packing also attributes to the effective surface tension of a liquid marble. The defects and pores in the liquid marble layers reduces its effective surface tension. These defects and

the size of pores at the encapsulating layers increase with increasing particle size (Chen et al. 2013). That means, smaller coating particles will increase the lifetime of a liquid marble. Moreover, these smaller particles form a stronger inner network among themselves, opposing the compression of the liquid marble and hence enhancing the robustness (Forný et al. 2007; Mueggenburg et al. 2007). Evaporation of a liquid marble forms wrinkles on its surface (Vadivelu et al. 2015). These wrinkles are similar to the wrinkles of a particle raft in compression (Zuo et al. 2019). When a particle raft is compressed, the surface area decreases whereas the surface particle density increases. At a certain threshold, wrinkles form on the raft as it buckles.

Surface tension of a liquid marble opposes its deformation. If a liquid marble is compressed between two parallel flat plates, the deformation of the liquid marble is quasi-spherical. Therefore, the Laplace pressure of the liquid marble counters the mechanical compression. To determine the Laplace pressure P_L upon rupture, the Young-Laplace equation is used: (Liu et al. 2015)

$$P_L = \gamma_{\text{eff}} \left(\frac{1}{R_{\text{max}}} + \frac{2}{h} \right) \quad (9)$$

Where, γ_{eff} is the effective surface tension of the liquid marble, R_{max} is the radius of the liquid marble upon rupture, and h is the height of the liquid marble under compression. According to Equation (9), the surface tension enhances the robustness of a liquid marble. For instance, a liquid marble consisting of liquid paraffin and fumed fluorosilica-50% SiOH has a critical pressure of 93 ± 10 Pa. This pressure is compared to that of a water marble coated with identical particles at 157 ± 16 Pa (Liu et al. 2015).

Fig 3: Measurement method of the effective surface tension of liquid marbles (a) Wilhelmy plate method, (b) Capillary rise method, (c) Pendant drop method, (d) Puddle height method, and (e) Vibration analysis method

Several works reported on the measurement of the effective surface tension of a liquid marble (Arbatan and Shen 2011; Aussillous and Qur 2006; Bormashenko 2011; Bormashenko 2012; Bormashenko et al. 2013; Bormashenko et al. 2010b; Bormashenko et al. 2009c; Bormashenko et al. 2009d; Li et al. 2018a; McHale et al. 2007; McHale and Newton 2011; Newton et al. 2006). In practice, the methods which measure the surface tension of a liquid surface covered with hydrophobic particles, represents the effective surface tension of a liquid marble encapsulated with the same particles. In the following passage, we discuss the various methods to measure the effective surface tension of a liquid marble.

3.1 Wilhelmy plate method

The Wilhelmy plate method measures the surface tension of a liquid bed covered with hydrophobic particles, which is analogous to a droplet encapsulated with the same particles. Arbatan et al. proposed the Wilhelmy plate method to measure the effective surface tension of a liquid marble (Arbatan and Shen 2011). A surface-treated glass slide was immersed into a liquid bed that is covered with polytetrafluoroethylene (PTFE), Figure 3(a). The plate advances towards the liquid layer and touches the floating powder layer. Advancing the plate provides the reading in force measurement after touching the particle layer. The force increases with increasing particle size. Further insertion allowed the plate to pierce through the water level below the powder layer. A cycle consisting of advancing and receding phases gave the measured force, F . The magnitude of the force determined the effective surface tension such that:

$$\gamma_{\text{eff}} = \frac{F \cos \theta}{2(l+t)} \quad (10)$$

where, γ_{eff} is the effective surface tension of the liquid bed covered with PTFE, θ is the contact angle between the waterbed and the plate, l and t are the width and thickness of the plate respectively.

As mentioned above, the effective surface tension of a water marble is similar to the effective surface tension of the waterbed, which is covered with the same particles as the liquid marble (Arbatan and Shen 2011). The movement of the particles at the line of insertion of the plate depends on the capillary interaction between the plate and the particle size. Compared to large particles, small particles are pushed away more from the meniscus. The meniscus is higher with small particles. Therefore, small particles lead to a higher surface tension. This method largely relies on the size of the particles but does not consider the effect of multiple particle layers.

3.2 Capillary rise method

In the case of a liquid marble, encapsulating particles replace a significant portion of liquid-air interface with solid-air interface. These particles change the curvature of the droplet in the macroscopic scale. Capillary interaction between the particles affect the net balance of forces of the liquid marble shell (Nguyen et al. 2010b). These forces influence the surface tension of the droplet with powder encapsulation. Measurement of the effective surface tension of a liquid marble by capillary rise method utilises the theory that a quasi-spherical liquid-solid interface exerts a Laplace pressure. This pressure contributes to the capillary rise of the water column inside a tube and helps to determine the effective surface tension of the liquid marble.

Figure 3(b) shows the schematic of the capillary rise method to measure the effective surface tension of a liquid marble. A capillary tube with inner radius r is mounted rigidly over a plate and inserted into a flat-water surface. Capillary rise h_w is obtained with Equation (11).

$$\frac{2\gamma_w \cos\theta}{r} - \rho g h_w = 0 \quad (11)$$

where, γ_w is the liquid surface tension, θ is the contact angle between the liquid and the capillary wall, ρ is the density of the liquid, and g is the gravity.

The additional capillary rise of Δh_w is contributed by the curvature of a droplet, as described by Marmur's equation: (Marmur 1988)

$$\frac{2\gamma_w}{R_e} + \frac{2\gamma_w \cos\theta}{r} = \rho g h_w + \rho g \Delta h_w \quad (12)$$

where, R_e is the equilibrium radius of the droplet.

Capillary rise with a liquid marble is the combined effect of the water meniscus inside the tube and the liquid marble shell. The difference between the capillary rise of a flat-water surface and a liquid marble determines the effective surface tension of the liquid marble. Hence, Marmur's equation is modified with the additional capillary rise Δh_m due to the liquid marble to determine its effective surface tension γ_{eff} : (Arbatan and Shen 2011)

$$\frac{\gamma_{\text{eff}}}{m} + \frac{2\gamma_w \cos\theta}{r} = \rho g h_w + \rho g \Delta h_m \quad (13)$$

Combining equations (11) and (13) results in:

$$\gamma_{\text{eff}} = \rho g \Delta h_m m \quad (14)$$

where, $1/m$ is the hydraulic radius of the liquid marble which is considered as the same as a bare water droplet of identical volume.

3.3 Pendant drop and sessile drop method

The pendant drop method is a popular technique to measure the surface tension of liquids. When a liquid is suspended as a pendant drop from a tube with inner radius R , Figure 3(c), its shape is determined by the combined effect of capillarity and gravity. The surface tension of the droplet can be determined from its shape, based on the Young-Laplace equation: (Erbil ; Rotenberg et al. 1983)

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \rho g z \quad (15)$$

where, R_1 and R_2 are the principal radii of curvature, ρ is the density of the liquid, and g is the gravity.

Bormashenko et al. measured the effective surface tension of the liquid marble using the pendant drop method (Bormashenko et al. 2013). In this process, a solid substrate coated with hydrophobic powder was brought into contact with a droplet suspended from a needle. The substrate was moved slightly beneath droplet and the powders gradually encapsulated the droplet, forming a pendant liquid marble. A goniometer measured the effective surface tension of the imaged pendant liquid marble using the surface tension as a fitting parameter. This method is sensitive to the volume of liquid marble. Measured surface tension values vary with inflation and deflation. Inflation of the liquid marble increases its volume; hence the surface area and reduces the surface coverage by particles. Conversely, deflation as a result of subsequent evaporation of the liquid marble makes the surface covering denser.

The pendant drop method relies on the working accuracy of the image analysis software. Such software is designed to fit an axisymmetric drop with smooth profile, as obtained by a bare droplet. Fitting the rough surface of a liquid marble using the software can generate uncertainties

(Wang and Li 2020). A monolayer nanoparticle-covered (mNPc) liquid marble has a smoother surface than a multilayered liquid marble (Li et al. 2018b). Therefore, the pendant drop method is more suitable for a mNPc liquid marble than a multilayered liquid marble.

Another effective method to measure the surface tension of a liquid marble is the sessile drop method. Gravitational deformation of the axisymmetric droplet was analysed with the iterative fitting of Young-Laplace equation to measure the surface tension (Dorsey 1928; Stalder et al. 2010; Ziesing 1953). In the experiment, the image of the liquid marble was captured and analysed with a freely available plugin in ImageJ, called 'Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA) for measuring the effective surface tension of the liquid marble (Ooi et al. 2016; Rasband 2012; Stalder et al. 2010).

3.4 Puddle height method

A small liquid marble ($R < l_c$) is almost spherical. As the volume increases ($R > l_c$), the shape turns into a puddle due to the dominant gravitational effect over surface tension, Figure 3(d). The height of the puddle droplet h is estimated from Equation (16) assuming a contact angle of 180° (Bormashenko et al. 2009c).

$$h = 2l_c \quad (16)$$

where, l_c is the capillary length $= \sqrt{\frac{\gamma}{\rho g}}$, γ is the surface tension of liquid, ρ is the density of liquid, and θ is the apparent contact angle of the liquid with the substrate.

Therefore, the effective surface tension of the liquid marble can be calculated as:

$$\gamma_{\text{eff}} = \frac{\rho g h^2}{4} \quad (17)$$

For small liquid marbles ($R < l_c$), the height is the measurement of the radius, which is different from Equation (16). If we use Equation (17) to calculate the effective surface tension, the result will vary with the volume of the liquid marble. This is unexpected for smaller liquid marbles. Therefore, a puddle liquid marble is preferred rather than a spherical liquid marble for this measurement technique. Despite its convenience, the determination of puddle height of a liquid marble of infinite dimension is not possible. In addition, the exact position of the three-phase contact line and the liquid-particle interface are difficult to determine (Bormashenko 2011; Bormashenko et al. 2009c; McHale and Newton 2011). Moreover, the method for the accurate measurement of the apparent contact angle θ is yet to be established. The apparent contact angle is usually less than 180° . Collectively, these limitations contribute to the errors in the measurement of the effective surface tension. The consideration of an apparent contact angle minimises this error. Equation (16) and (17) can be modified with the apparent contact angle to Equation (18) and (19) respectively to determine the effective surface tension of the liquid marble (Bormashenko 2011; Bormashenko et al. 2009c; Gilles de Gennes et al. 2003).

$$h = 2l_c \sin \frac{\theta}{2} \quad (18)$$

$$\gamma_{\text{eff}} = \frac{\rho g h^2}{4 \sin^2(\frac{\theta}{2})} \quad (19)$$

It is necessary to consider the effect of surface packing density of the particles and the wettability of the substrate to determine θ . At lower particle density, the surface of the liquid marble is not fully covered. Therefore, the exposed liquid at the bottom of the liquid marble would

contact the substrate, which reduces θ . In addition, the wettability of the substrate contributes to the fluctuation of θ . The higher particle density at the surface of the liquid marble leads to the interfacial jamming, which deforms the liquid marble unpredictably. As a result, θ has different values for the right and left side of the liquid marble. On the other hand, the fluffy surface of the liquid marble is always problematic to locate the tangent to measure θ (Wang and Li 2020).

3.5 Vibration of liquid marbles

Surface tension measurement of a droplet using vibrations is a popular method in microfluidics (Bormashenko et al. 2007; Celestini and Kofman 2006; Chang and Franses 1994; Daniel and Chaudhury 2002; Della Volpe et al. 2002; Fujii et al. 2006; Matsumoto et al. 2002; Meiron et al. 2004; Vicente et al. 2002; Wilkes and Basaran 1997). Bormashenko et al. measured the effective surface tension of a liquid marble with vibration (Bormashenko et al. 2009c; Bormashenko et al. 2009d). A liquid marble placed on a superhydrophobic substrate is vibrated horizontally. The side profile of the vibrating liquid marble was obtained with the help of laser illumination, Figure 3(e). The lowest eigen frequency was kept constant for a liquid marble. The effective surface tension of a liquid marble can be determined using the resonant frequency: (Bormashenko et al. 2009c; Bormashenko et al. 2009d)

$$\gamma_{\text{eff}} = \frac{\rho V f^2}{2\pi h(\theta)(1-\cos\theta)} \quad (20)$$

where, γ_{eff} is the effective surface tension of the liquid marble, f is the resonance frequency, ρ is the water density, V is the volume of the liquid marble, θ is the apparent contact angle ($\tan \frac{\theta}{2} = \frac{2h}{d}$, h and d is the height and diameter of the droplet respectively), and $h(\theta)$ is a multiplier which depends on the apparent contact angle (Celestini and Kofman 2006).

To calculate the eigen frequencies, the liquid marble should be spherical and pinned to the substrate even after the vibration. This method needs precise arrangements of the substrate and the liquid marble. The liquid marble should be pinned on the surface to prevent rolling off. Moreover, its volume should be small enough to retain its spherical shape.

3.6 Analysis of liquid marble shape

The shape of a droplet is a resultant effect of surface tension and gravity. A liquid marble placed on a substrate always experiences a downward gravitational force which lowers its centre of mass. The surface tension force opposes the gravity and help to maintain the spherical shape. The Bond number ($Bo = \rho g R^2 / \gamma$) determines the shape of a droplet considering both surface tension and the gravity. When, $Bo \ll 1$, the effect of gravity is negligible, and the liquid marble remains as a sphere. Conversely, if $Bo \gg 1$, the liquid marble becomes a puddle (Aussillous and Qur 2006). The effective surface tension can be determined by analysing the liquid marble shape. A goniometer measures the contact angle and the shape of the liquid marble (Bormashenko et al. 2009c; Bormashenko et al. 2009d). In this method, a laser light is projected on the liquid marble in such a way that a magnified view of the liquid marble shape is imposed onto a screen. The shape of the liquid marble is considered as oblate spheroid after the deformation due to the gravity. The contact diameter and height of the droplet is measured from the captured images. These characteristic values are compared to the values calculated with oblate spheroid model of a droplet (Whyman and Bormashenko 2009). This method is also sensitive to the volume of the liquid marble. The axis ratio of the oblate spheroid reduces with the larger liquid marbles, affecting the effective surface tension (Bormashenko et al. 2009d).

Effective surface tension values of liquid marbles from the literatures have been tabulated below (Table 1). A thorough comparison between several measurement processes reveals that the effective surface tension values of the liquid marbles are not consistent. It varies with the measurement methods, particle sizes, particle types, and degree of agglomeration (Bormashenko et al. 2013; Li et al. 2018b). Moreover, there are accuracy issues due to the lack of particle homogeneity, the random distribution of the particles and particles jamming. These parameters affect the apparent contact angle, liquid marble height and shape. Current understanding of the effective surface tension of a liquid marble from the existing literatures only provides a macroscopic insight which reflects the property based on which the measurement has been conducted. Li et al. proposed the concept of equivalence quality to address the inconsistencies in the effective surface tension. It correlates various factors such as particle size, shape, and interfacial jamming to the effective surface tension of the liquid marble (Li et al. 2018b). Further investigations are required to understand the reasons behind the inconsistency and the contribution of interparticle forces to the effective surface tension.

Table 1: Effective surface tension of liquid marbles made of DI water

Particles	Particles size (μm)	Method	Volume of liquid marble (μL)	Surface tension value (mN/m)	Ref
PTFE	1	Capillary rise	30	71	(Arbatan and Shen 2011)
			50	71	
			100	70	
			200	69	
			300	71	
	35		30	70	
			50	70	
			100	70	
			200	68	
			300	70	
	100		30	69	
			50	68	
			100	69	
			200	69	
			300	70	
	1	Wilhelmy Plate		70.2±0.3	(Arbatan and Shen 2011)
	35			69.9±0.3	
	100			57.6±0.3	
100-200	Maximum height		60±6	(Bormashenko et al. 2009c)	
	Marble shape analysis		53±5		
	Vibration method		53±3		
0.13	Maximum height		70±7		(Bormashenko et al. 2009c)
	Marble shape analysis		79±5		
	Vibration method		75±3		
Lycopodium	30	Maximum height		50±5	(Bormashenko et al. 2009c)
		Marble shape analysis		62±5	
		Vibration method		43±3	
				55±3	

					et al. 2009d)
Polyethylene	2	Maximum height		66±5	(Bormashenko et al. 2009c)
		Marble shape analysis		63±3	
		Vibration method		60±4	
Silica	0.01	Maximum height		72	(Aussillous and Quéré 2006)

4 Capillarity driven movement of liquid marble

The previous sections discuss the effects of the surface tension of the core liquid on the stability of a liquid marble and on its properties. This section discusses the effect of capillarity of the carrier liquid on the liquid marble behavior. There are various means to adjust the surface tension of the carrier liquid and to create a surface tension gradient at the carrier liquid surface. We will systematically elucidate as follow.

4.1 Chemically induced movement

BORMASHENKO ET AL. REPORTED THE SELF-PROPULSION OF THE LIQUID MARBLE WITH SOLUTE MARANGONI FLOW (BORMASHENKO ET AL. 2015A). MARANGONI FLOW IS THE MASS TRANSFER AT AN INTERFACE BETWEEN TWO FLUIDS AS A RESULT OF A GRADIENT IN SURFACE TENSION. IN MOST CASES, THE FLOW FOLLOWED THE DIRECTION FROM THE REGION WITH A LOW SURFACE TENSION TO A REGION WITH A HIGH SURFACE TENSION. ETHANOL MARBLE WAS USED FOR THIS CONCEPT. ETHANOL IS VOLATILE AND CONDENSES ON THE CARRIER LIQUID NEAR THE LIQUID MARBLE (BORMASHENKO ET AL. 2015A). THE ABSORBED ETHANOL MOLECULES REDUCE THE SURFACE TENSION AT THE PROXIMITY OF THE CONTACT AREA OF CARRIER LIQUID AND PUSH THE LIQUID MARBLE TOWARDS THE REGION WITH A HIGHER SURFACE TENSION, FIGURE 4(A). LATER, OOI ET AL. ALSO REPORTED THE SELF-PROPULSION OF AN ETHANOL MARBLE WITH THIS SO-CALLED MARANGONI SOLUTOCAPILLARY EFFECT (OOI ET AL. 2015B). THE DURATION OF THE PROPULSION DEPENDS ON THE AMOUNT OF ETHANOL IN THE LIQUID MARBLE. THE LIQUID MARBLE MOVES FASTER WITH A HIGHER ETHANOL CONCENTRATION. THE SIZE OF THE LIQUID MARBLE IS ALSO AN IMPORTANT PARAMETER DETERMINING ITS MOTION. THE CONTACT AREA BETWEEN THE LIQUID MARBLE AND THE CARRIER LIQUID INCREASES WITH INCREASING SIZE OF THE LIQUID MARBLE. THE LARGER CONTACT AREA INCREASES THE FRICTION TO THE MOVEMENT OF THE LIQUID MARBLE. ON THE OTHER HAND, ETHANOL SUPPLY TO THE CARRIER LIQUID INCREASES WITH THE LARGE CONTACT AREA, RESULTING IN A HIGH SURFACE TENSION GRADIENT AND A STRONGER MARANGONI FORCE ACTING ON THE LIQUID MARBLE. THE CONTAINER SIZE PLAYED AN IMPORTANT ROLE FOR CONTROLLING THE MOVEMENT. A CONTAINER WHICH IS SMALLER THAN THE THRESHOLD SIZE CAUSES THE LIQUID MARBLE TO REMAIN IN THE MIDDLE OF THE CONTAINER DUE TO OVERDAMPING.

Fig 4: (a) Chemically induced, (b) thermally induced, and (c) optically induced Marangoni flow for the transport of liquid marble (T and γ denotes temperature and surface tension respectively).

4.2 Thermally induced movement

Frenkel et al. placed sulfuric acid inside the liquid marble to achieve self-propulsion (Frenkel et al. 2018). The absorption of water vapour from the carrier liquid into the core of the liquid marble through the pores of encapsulating layer induced an exothermic reaction. The absorption of water

vapour was asymmetric as the coating of the liquid marble was not uniform. Thus, the temperature rise at different locations within the liquid marble was also not uniform. The temperature gradient within the liquid marble induces Marangoni thermocapillary flow, which moved the liquid marble over the carrier liquid surface. Camphor was also used with liquid marble as an agent to create surface tension gradient to propulse it (Bormashenko et al. 2017).

Paven et al. generated a liquid marble with carbon black powder. The coating absorbs near infrared radiation and heats up the surrounding surface (Paven et al. 2016). The liquid marble was placed at the air-water interface. A manual NIR laser (800nm) irradiation at the three-phase contact line heated up the liquid marble. The temperature at the point of irradiation was higher than the temperature at the opposite side of the liquid marble. This temperature gradient induces a capillary force to push the liquid marble forward, Figure 4(b). The process is known as thermocapillary convection. This thermally driven concept enables the liquid marble to act as an engine that can pull or push with more than 150 times its own weight. Alternatively, a focused beam of sunlight can be used to actuate the liquid marble (Paven et al. 2016). The point of irradiation with respect to the liquid marble position was crucial and had to be precise to create the surface tension gradient.

4.3 Optically induced movement

Kavokine et al. reported the transport of a liquid marble using surface tension gradient generated by irradiating a photosensitive solution. Ultra-violet (UV) and blue light irradiation caused the photoreversible Marangoni flow at the surface of an AzoTAB solution (Kavokine et al. 2016). AzoTAB is a surfactant that makes a solution photosensitive. The surfactant reconfigures itself from trans to cis upon UV irradiation, and reversely from cis to trans upon blue light irradiation (Chevallier et al. 2011; Diguët et al. 2010). A cis structure resulted in a higher surface tension in the carried liquid than that with the trans structure. Illumination of UV light at the center of the container increased the surface tension zone in the region, whereas the boundary region remains unaffected. The surface tension gradient introduces Marangoni flow and pulls the liquid marble from the boundary towards the centre, Figure 4(c). Conversely, the reverse motion was observed with blue light such that the liquid marble was pushed away from the region of illumination. However, this observation was valid only for a thickness above a critical value. Below that value, both the UV and blue light exhibit a completely opposite behavior. Such phenomenon is known as anti-Marangoni flow. Converging Marangoni flow accumulated the liquid at the center of the container. Experimental analysis proved that the surface flow was the source of the difference in surface elevation between the boundary and the center of the container. The difference in the surface elevation from centre to boundary area, moves the liquid marble out of the centre, exhibiting the anti-Marangoni behavior.

4.4 Magnetically induced movement

Moses effect is the deformation of a diamagnetic liquid surface under the influence of an external magnetic field (Kitazawa et al. 2001). The depth of the deformation depends on the applied magnetic fields, magnetic susceptibility and the surface tension of the liquid (Gendelman et al. 2019). The surface tension of the liquid bed opposes this deformation. A liquid with a lower tension generates a deeper depression than that with a higher surface tension. Any floating entities within the range of depression is pulled to the depth of the well by gravity, Figure 5. Vialetto et al. demonstrated the transport of liquid marbles with Moses effect over liquid substrate (Vialetto et al. 2017).

Fig 5: Movement of the liquid marble due to (a) direct, and (b) reverse Moses effect.

Contribution of surface tension of water on the depression due to Moses effect is still a matter of debate. Water is diamagnetic and affected by the magnetic field. There are reports showing that the water surface tension varies with the magnetic treatment. The surface tension may decrease, (Cai et al. 2009) increase, (Fujimura and Iino 2009) and remains unaffected (Hayakawa et al. 2019) after the treatment.

4.5 Electrochemically induced movement

A liquid metal marble can be actuated by electrical (Eaker and Dickey 2016), magnetic (Jeon et al. 2016; Chen et al. 2019), photochemical (Tang et al. 2013b), and electrochemical (Tang et al. 2013a) triggers. Sivan et al. demonstrated the fabrication of a liquid metal marble with galinstan droplet coated with WO_3 nanoparticles and used them as an electrochemical-based metal ion sensor (Sivan et al. 2013). Such liquid metal marbles are further utilised by Tang et al. to exhibit electrochemically induced actuation in an electrolyte solution (Tang et al. 2013a). Under an externally applied voltage in a basic solution, a galinstan droplet moves due to Marangoni effect. The interface between the galinstan droplet and the electrolyte solution forms the electrical double layer (EDL). When a DC voltage is applied, a potential difference across the EDL along the droplet surface creates the surface tension gradient in the channel. Such behavior is an electrical analogue to the Marangoni effect (Jackel et al. 1983). Marangoni effect is also observed for a galinstan droplet coated with WO_3 nanoparticles. WO_3 nanoparticles produce a strong negative charge in a strong basic solution. When a low voltage ($\leq 7\text{V}$) is applied between the electrodes, there is a potential drop across both the coating particles and the surrounding EDL (Tang et al. 2013a). The anodic pole deforms more towards the cathode due to electrowetting which moves the liquid metal marble towards the cathode, Figure 6(b). At a higher voltage ($> 7\text{V}$), the liquid metal marble moves towards the anode, Figure 6(c). The speed of the liquid metal marble can be controlled with the voltage whereas the direction of movement can be controlled by changing the pH of the electrolyte (Tang et al. 2013a).

Fig 6: Surface charge distribution of a galinstan marble, coated with WO_3 nanoparticles in a basic solution when (a) no voltage is applied, (b) a voltage $\leq 7V$ is applied, and (c) a voltage $> 7V$ is applied.

Various research groups investigated floating liquid marbles (Bormashenko et al. 2010a; Bormashenko et al. 2011a; Bormashenko et al. 2009a; Bormashenko et al. 2009b; Gao and McCarthy 2007; Jin et al. 2019; Jin et al. 2020; Ooi et al. 2018; Rao et al. 2005; Tosun and Erbil 2009; Xue et al. 2010). The floating condition and stability are highly dependent on the surface tension of the carrier liquid. Bormashenko et al. demonstrated a liquid marble as a pollution indicator (Bormashenko and Musin 2009). A 10- μl polyvinylidene difluoride (PVDF) liquid marble floated on the water surface without any rupture. The liquid marble collapses at a surface tension of 61-62 mN/m in the presence of contaminants on the carrier liquid. Singha et al. investigated the effect of carrier liquid surface tension on the stability of liquid marbles of different volumes (Singha et al. 2019). Larger liquid marbles are less stable and require less reduction of carrier liquid surface tension to collapse. For example, a 10- μl PVDF water liquid marble was stable over a carrier liquid with a surface tension of 50 ± 1 mN/m, whereas a 6- μl PVDF liquid marble was stable at a surface tension of 35 ± 1 mN/m. Further reduction in the substrate surface tension causes the carrier liquid to penetrate the encapsulating particle layer. Thus, the reduction in substrate surface tension leads to the collapse of the floating liquid marble. In the same experiment, the authors demonstrated liquid marble induced

capillary assembly of micro-nano entities. The meniscus around the liquid marble provides a platform to the floating entities for capillary assembly, Figure 7. The meniscus deformation increases with increasing liquid marble volume, (Ooi et al. 2015a) which tuned the range of the self-assembly process. Most of the above-mentioned effects are highly dependent on the particle size and the liquid marble volume. Further investigation is required for the better understanding of the effect of particle size, liquid marble volume, surface covering and temperature.

Fig 7: Liquid marble mediated capillary assembly process: Before assembly (left) and after assembly (right)

5 Conclusion

Several research works on fundamental and applied aspects of liquid marbles were reported. The major research focus was on the manipulation of the properties, the transport and applications of liquid marbles. Most of these works utilise either capillarity of the core liquid or size of the liquid marbles or the properties of encapsulating powder. The capillarity of a liquid marble is not as straight forward as of a bare droplet. Surface tension of the core liquid helps to produce an energetically stable liquid marble. The surface tension of the system is changed after forming the liquid marble. The reported works lead to primary insight into the capillarity of liquid marbles and understanding of the effective surface tension. The effective surface tension of a liquid marble is commonly measured with vibration analysis, capillary rise, puddle height, pendant drop, sessile drop and liquid marble shape methods. Interestingly, the results obtained from these methods are not consistent. An approach for the accurate measurement of the effective surface tension is yet to be proposed. The effects of the apparent contact angle, particle size, particle shape, distribution of particles, jamming of particles at the liquid-air interface, agglomeration, number of encapsulating layers are to be investigated further in detail to answer the question of inconsistency.

Liquid marble behavior becomes interesting when the surface tension of the core liquid is varied. The core liquid wets the encapsulating particles more when its surface tension reduces. This reduction in surface tension enhances the wetting of encapsulating particles. Hence, the stability of the liquid marble reduces with the reduction of core liquid surface tension. There are only a few works which dealt with the core liquid surface tension. The detailed mechanism of penetration,

collapsing condition of liquid marbles of different volumes with core liquid of varied surface tension with different encapsulating particles are viable options for further investigation.

Transport is an important application of the liquid marble. Core liquid and the gradient in surface tension of the carrier liquid are the primary drivers for the movement of a floating liquid marble. External stimuli such as a UV light source or a NIR laser source enable the liquid marble to achieve a directional movement, which is yet to obtain precisely. Moreover, the movement of a floating liquid marble also depends on the size of the liquid marble and the meniscus angle, which are missing in the literature. It can be studied further in details.

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