Oscillating sessile liquid marble - A tool to assess effective surface tension

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A long-standing problem of liquid-marble based technology is the inconsistency of the effective surface tension values. This inconsistency could be due to particle size, particle type, volume of the liquid marble or the preparation method. The prevailing liquid marble preparation method is to roll a droplet on a powder bed. The lack of control of rolling duration or revolution speed could contribute to the inconsistent effective surface tension values. We hypothesize that a systematic preparation approach could improve the consistency of the effective surface tension values. In this work, we (i) determine the effective surface tension using the natural oscillation of a sessile liquid marble and (ii) investigate the effects of liquid marble preparation methods on the effective surface tension for the first time. We find that the effective surface tension values of a liquid marble prepared manually are inconsistent. In comparison, a systematic preparation method improves the consistency of the measured effective surface tension values. Interestingly, the systematic preparation at higher revolution speed causes interfacial jamming at the liquid marble shell which decreases the consistency. The results from this work can provide a deeper understanding of the fundamental characteristics of liquid marbles.

1. Introduction

Microfluidic devices have been attracting enormous research interests owing to their ability to handle liquid in the microscale, particularly in sensing and controlling liquid flow [1–3]. Liquid marble, a digital microfluidic platform has recently become a hot research topic due to the superior advantages [4–6], particularly in the emerging field of micro-elastofluidics [7]. Fundamental research on liquid marble has been focused on understanding its stability [8–18], effective surface tension [19–22], and evaporation rate [23–25]. These crucial properties are inherently related to the structure and properties of the liquid marble shell. A liquid marble shell consists of encapsulating particles and air pockets. The structure and the properties of the shell largely depend on the preparation method and properties of the encapsulating particles. Therefore, it is important to identify and understand the factors that affect the effective surface tension of a liquid marble. This paper investigates the effect of the preparation method on the effective surface tension of a liquid marble oscillating at its natural frequency.

Oscillating drop is a popular method for measuring the surface tension of a droplet [26–33]. Surface oscillation of a free-falling droplet was
observed and analyzed to measure the surface tension [34]. To obtain a spherical shape of the free-falling droplet, a zero-gravity environment, magnetic [35] or acoustic levitation [36] is required. As these methods need complex setups, we consider the approach of levitation-free vibration of a non-wetting sessile droplet on a solid surface to analyze the natural oscillation of a liquid marble [27,37]. We used a non-uniform DC electric field to generate dielectrophoresis (DEP) to momentarily actuate the liquid marble and produce free oscillation. DEP arises from the particle movement by a non-uniform electric field, which exerts a dielectrophoretic force. [38]. DEP is convenient to operate and can be applied on liquid marbles with any type of coating [39]. Subsequent analysis of the oscillation provides the effective surface tension. Our approach eliminates the need for measuring the contact angle of a liquid marble which is troublesome because of its non-wetting characteristics.

The coating particles encapsulate the droplet to form a liquid marble. The capillary interaction between these particles affects the force balance at the droplet surface and results in the so-called effective surface tension [40]. Researchers attempted to measure the effective surface tension of a liquid marble using techniques established for bare droplets. These droplet-based techniques can be classified as static or dynamic methods. Static methods include capillary rise [41] and shape analysis [40,42], whereas dynamic methods include vibration analysis [26,43] and spinning drop tensiometry [44]. To date, effective surface tension values determined with these different techniques and for different volume of liquid marbles are inconsistent [20,45]. The inconsistency could be caused by the particle size, particle type, particles agglomeration, and volume of the liquid marble [13,46]. Moreover, the irregular shape and fuzzy appearance of the liquid marble shell reduces the consistency of the effective surface tension values [47]. We hypothesize that the shape and the structure of the shell are affected by the liquid marble preparation method. Therefore, the preparation method should be one of the major contributors to the inconsistent effective surface tension values. To the best of our knowledge, we are the first in (i) determining the effective surface tension using the natural oscillation of a sessile liquid marble and (ii) investigating the effects of liquid marble preparation methods on the effective surface tension. The most popular liquid marble preparation method is rolling a liquid droplet on a hydrophobic powder bed. This method is faster than many other preparation methods [48,49]. Researchers prefer rolling the droplet manually as this method only requires simple tools. Nonetheless, manual preparation does not consider rolling parameters such as the revolution speed and duration, resulting in poor repeatability. This could in turn affect the fundamental properties of the liquid marble. Conversely, the systematic approach addresses this issue by keeping the rolling parameters constant. In this paper, we compared the effective surface tension of liquid marbles systematically prepared using a vortex mixer to those prepared manually. We found that the effective surface tension values of a liquid marble prepared manually are inconsistent as reported previously in literature [20,45]. The consistency improved significantly with our systematic preparation method as hypothesized. Our findings provide further insights into the characterization of a liquid marble. The effective surface tension values affect the robustness, elasticity, and lifetime of a liquid marble. With the enhanced consistency of the effective surface tension values, the liquid marble characterization could be more accurate.

2. Theory

2.1. Principle of liquid marble formation

A liquid marble consists of a core liquid droplet and a shell of encapsulating particles. The encapsulating particles attach to the droplet surface during liquid marble preparation [50]. The distribution and the amount of the encapsulating particles in the liquid marble shell depend on the preparation method. The manual preparation method does not consider the revolution speed and the duration. A short rolling duration results in a partially covered liquid marble. On the other hand, rolling a droplet at a higher revolution speed causes interfacial jamming at the liquid marble shell [9]. Interfacial jamming is a phenomenon where the encapsulating particles are adsorbed at a sufficiently high concentration to the droplet surface. Consequently, the liquid marble loses mobility and exhibits solid-like features [51,52]. Therefore, the manual preparation method produces liquid marbles with inconsistent coverage. We hypothesize that the inconsistent coverage leads to poor repeatability of effective surface tension results. A systematic preparation method could solve this problem.

2.2. Measurement of the effective surface tension using natural frequency

We consider the oscillating drop method for the analysis of effective surface tension. In this method, surface oscillation of a free-falling droplet is observed and analyzed to determine the surface tension of the droplet [31,34]. This method is a non-contact approach that offers contamination-free surface tension measurement. The basic equation to measure the surface tension of a freely oscillating droplet is given as:

\[ \gamma = \frac{3\pi M f_n^2}{n(n-1)(n+2)} \]  

(1)

where \( \gamma \) is the surface tension of the droplet, \( M \) is the mass of the droplet, \( n \) is the mode of oscillation, and \( f_n \) is the oscillating frequency.

Here, we consider the approach of a sessile droplet oscillating on a solid substrate. This analysis is more complicated since a portion of the free droplet is constrained by the underlying substrate. Noblin et al. reported that the vibration of a droplet on a solid substrate depends on the state of the three-phase contact line [27]. They proposed two models, namely Type I for droplets with an immobile contact line and Type II for droplets with a mobile contact line.

A sessile liquid marble adopts the shape of a sessile droplet, which leads to the existence of an apparent contact angle between the liquid marble and the underlying substrate. The porous shell isolates the core liquid from its surroundings and makes it non-wetting. Hence, the contact angle hysteresis of a liquid marble to its underlying solid substrate is negligible. The contact line of the liquid marble consists of solid-solid interface instead of the conventional solid-liquid line for the droplet. Therefore, we consider measuring the ‘effective’ surface tension using Noblin’s model as proposed by Mchale et al. [37]. Since, the contact line of the liquid marble is highly mobile [50], we consider Noblin’s Type II model: [27,37].

\[ f_n^2 = \frac{\pi k \gamma}{4 \mu p^2} \]  

(2)

where \( k \) is the number of nodes of the standing wave on the surface of the oscillating liquid marble, \( \rho \) is the effective density of the liquid marble, and \( p \) is the perimeter of the liquid marble profile. This equation enables the determination of the effective surface tension of a liquid marble by measuring its oscillating frequency.

3. Materials and methods

3.1. Preparation of liquid marbles

Liquid marbles were prepared both manually and systematically. The manual process starts with dispensing deionized (DI) water droplets of 20 \( \mu \)l and 30 \( \mu \)l onto a powder bed and, then followed by rolling them around vigorously by hand for 5–6 s to achieve complete coverage of the droplets. Polytetrafluoroethylene (PTFE) (Sigma Aldrich, 1-\( \mu \)m average diameter) and polyvinylidene fluoride powder (PVDF) (Sigma Aldrich, 25-\( \mu \)m average diameter) were used as coating materials. For the systematic preparation of liquid marbles, we placed the powder beds over a microplate vortex mixer (RATEK, model MPS1) and rolled the droplets at various rpm between 100 and 500 rpm for the same duration.
Prepared liquid marbles were then transferred onto a flat metal substrate directly under an electrode using a spatula.

3.2. Experimental setup

The electrode was a cylindrical metal pin with a diameter of approximately 0.8 mm. The electrode was housed in a PMMA block with the end exposed towards the substrate. The exposed end was adjusted at a fixed distance of 1 mm to the top of the liquid marble. The top end of the electrode was connected to a DC high-voltage power supply, Fig. 1. The output voltage was set at 2.4 kV. Once the liquid marble was in position on the substrate, the electrode was energized. The induced DEP force elongated the liquid marble in the vertical direction [39,53]. An abrupt removal of the electric field caused the liquid marble to retract to its original shape. The stored energy from the deformation caused the liquid marble to oscillate at its natural frequency. We used a high-speed camera (Photron FastCam SA3) to capture the oscillation of the liquid marble, Fig. 1. Suitable lighting was set up to allow the camera to record at 1000 frames per second.

3.3. Determination of natural frequency

The captured images were analyzed in MATLAB (MathWorks). A bounding box was fit around the liquid marble to record its change in height over time. The liquid marble height was then analyzed using Fast Fourier Transform (FFT) to determine its natural frequency. Fig. 2 shows the time signal of a 30-µl PTFE liquid marble prepared systematically. The inset shows the corresponding frequency spectrum with the natural frequency peak at 29 Hz.

4. Results and discussions

The images of the oscillating liquid marbles were sharp with high contrast. Fig. 3a shows three overlapping images during the oscillation. Due to the requirement of FFT, we considered 1024 (2^10) frames for all trials. There are two main systematic errors in the calculation of the natural frequencies. The first error \( e_1 \) arose from the systematic error of the experimental trials. The second error \( e_2 \) is the bin size of the FFT, which is 1.0 Hz for all trials. We considered the combined errors \( (\sqrt{e_1^2 + e_2^2}) \) to estimate the uncertainty of the final value of the natural frequencies. For example, the natural frequency of a 20-µl PTFE liquid marble prepared manually is 34.5 ± 1.6 Hz.

Next, we consider Noblin’s model to determine the effective surface tension of the liquid marbles [27]. We observed that the contact radius of an oscillating liquid marble is time dependent. Moreover, the liquid marbles could easily be displaced with a mild air flow. These observations indicate that the liquid marbles possessed mobile contact lines, confirming our above-mentioned hypothesis. To calculate the effective surface tension, we determined the number of nodes, \( k \) at the liquid marble surface and the static perimeter of the free surface of the liquid marble profile, \( p \). The nodes are generated due to the stationary surface waves of the oscillating liquid marble [37].

These nodes define the pseudo-wavelength, \( \lambda \) in terms of the perimeter of the liquid marble profile. The perimeter of the liquid marble profile and the pseudo-wavelength are related as: [37].

\[
p = \frac{\lambda}{2}
\]

For a liquid marble with a mobile contact line, the contact points of the liquid marble with the underlying substrate are antinodes. Image analysis of the oscillating liquid marble provides the location of the nodes. We observed two nodes \( (k = 2) \) at the liquid marble surface while oscillating at its natural frequency. The two nodes at the surface of an oscillating 30-µl PTFE liquid marble are shown in Fig. 3b. Therefore, the perimeter of the liquid marble profile is equal to a full wavelength...
according to Eq. (3) there is a half wavelength distance between the two nodes and a quarter wavelength distance between a node and the antinode at the contact point on each side of the liquid marble. We measured the perimeter of the liquid marble profile using ImageJ (National Institutes of Health, U.S.A.) [54].

We considered both the errors of the natural frequency, $e_1$ and $e_2$ to yield the effective surface tension of a liquid marble. For example, the effective surface tension of a 20-µl PTFE liquid marble prepared manually is $70.7 \pm 6.4 \text{ mN/m}$, Fig. 4a. Each data points in the Fig. 4 represents an average of 4 individual measurements with the combined systematic error deviation as an error bar. The obtained result agrees with the observation by Ooi et al. who also used 20-µl PTFE liquid marble [55].

The natural frequency and the effective surface tension of a 20-µl PTFE liquid marble prepared manually is $34.5 \pm 1.6 \text{ Hz}$ and $70.7 \pm 6.4 \text{ mN/m}$ respectively, Fig. 4a. The repeatability and uniformity of the particles packing at its shell might be impeded due to manual preparation, which produced inconsistent results. To confirm our hypothesis of improving the consistency, we controlled the rolling parameters using the vortex mixer running at a revolution speed of 100 rpm. The natural frequency and effective surface tension of the liquid marble at this revolution speed is $34.2 \pm 1.3 \text{ Hz}$ and $69.5 \pm 5.2 \text{ mN/m}$ respectively. The result shows an improved consistency, though the surface packing of the liquid marble is sparse and non-uniform, Fig. 4b. We observed that the dispensed droplet does not roll smoothly on the powder bed at 100 rpm. It could be due to the insufficient revolution speed for the droplet to overcome its adhesion to the powder. We increased the revolution speed to 175 rpm for further observations. The rolling of the dispensed droplet at 175 rpm was smooth and produced the liquid marble shell with more even distribution of particles. The natural frequency and the effective surface tension of a 20-µl PTFE liquid marble prepared at 175 rpm is $33.2 \pm 1.0 \text{ Hz}$ and $65.5 \pm 3.9 \text{ mN/m}$ respectively. We observed that the systematic preparation method improves the consistency of the natural frequency and effective surface tension values. We obtained similar results for the liquid marbles prepared systematically at 250 rpm. We hypothesize that the systematic preparation method enhances the repeatability and uniformity of the particles packing at the liquid marble shell, producing substantially consistent results.

We performed identical experiments for 30-µl PTFE liquid marbles to Fig. 4. (a) Natural frequency and effective surface tension of 20-µl PTFE liquid marbles, prepared manually (M), systematically at a revolution speed of 100 (S100), 175 (S175), 250 (S250), and 500 (S500) rpm. Uncertainty due to bin sizes are not shown in (a), microscopic images of surface coverage of liquid marbles prepared at a revolution speed of (b) 100 rpm, (c) 175 rpm, and (d) 500 rpm.
understand the volumetric effect on the inconsistencies produced from the preparation method. The natural frequencies of a 30-µl PTFE liquid marble prepared manually and systematically were 29.8 ± 1.6 Hz and 29.3 ± 1 Hz, respectively, Fig. 5a. These frequencies correspond to effective surface tension values of 67.2 ± 7.3 mN/m and 65.0 ± 4.4 mN/m, respectively. As expected, liquid marbles prepared systematically have more consistent effective surface tension values. The improved consistency was observed for both 20-µl and 30-µl PTFE liquid marbles (Fig. 5).

Next, we increased the revolution speed of the vortex mixer to 500 rpm to investigate the effect of the preparation parameters on the effective surface tension. The natural frequency and effective surface tension of a 20-µl PTFE liquid marble prepared at a relatively high revolution speed of 500 rpm is 34.7 ± 2.1 Hz and 71.6 ± 8.8 mN/m respectively, which are substantially inconsistent and do not agree with liquid marbles prepared at a lower speed. This large error could be attributed to the interfacial jamming of the encapsulating particles at higher speeds. A higher revolution speed deforms the droplet more and generated an enlarged contact area during coating, Fig. 6. Once the rotation is stopped, the droplet retracts to its equilibrium shape, increasing the packing density of encapsulating particles. Interfaceal jamming occurs when the surface area of the equilibrium state is comparable to that of the dense packing of the encapsulating particles [56, 57]. Interfacial jamming arrests the retraction and retains morphological coarsening [58]. Therefore, the encapsulating particles overlap with each other after retraction. We believe that interfacial jamming and the random overlapping of the encapsulating particles increase the irregularity of the liquid marble shell.

We compared the time signal of an oscillating 20-µl PTFE liquid marble prepared at a revolution speed of 175 rpm and 500 rpm, Fig. 7. The results indicate that the liquid marble prepared at the revolution speed of 175 rpm damped within 0.7 s, whereas the liquid marble prepared at the revolution speed of 500 rpm damped within 0.37 s. The faster damping of the liquid marble prepared at 500 rpm could be due to interfacial jamming of the encapsulating particles. Interfaceal jamming causes shear thickening and stabilizes two-phase morphological coarsening, which increases the viscosity of the liquid marble [59–61]. As a result, the liquid marble prepared at the revolution speed of 500 rpm damped faster than that prepared at 150 rpm. Insets in Fig. 7b shows interfaceal jamming of the encapsulating particles at the liquid marble shell. Such non-uniformity at the liquid marble shell increases the inconsistencies of the effective surface tension value.

Next, we performed experiments with PVDF powder to understand the effect of powder type on the consistency of natural frequency and effective surface tension. The natural frequency of a 30-µl PVDF liquid marble prepared manually and systematically is 30.8 ± 1.4 Hz and 29.3 ± 1.0 Hz respectively. The effective surface tension of the liquid marble is 74.4 ± 6.8 mN/m and 67.5 ± 4.6 mN/m, respectively. We observed a similar trend as PTFE liquid marbles. The systematic preparation method produced substantially more consistent natural frequency and effective surface tension values. Nonetheless, excessive rolling speed during the preparation process caused interfaceal jamming and reduced the consistency. The natural frequency and effective surface tension of a 30-µl PVDF liquid marble prepared at a revolution speed of 500 rpm is 33.2 ± 2.6 Hz and 86.7 ± 13.5 mN/m, respectively.

5. Conclusion

We reported for the first time the measurement of the effective surface tension of a levitation-free naturally oscillating liquid marble. We used high non-uniform DC electric field to generate DEP force which caused the liquid marble to oscillate at its natural frequency. Our method does not require contact angle measurement and does not assume a spherical shape for the liquid marble. With this method, we investigated the effect of the preparation method on the effective surface tension of liquid marbles. We found that the effective surface tension values of manually prepared liquid marbles were inconsistent as reported in literature. Such inconsistencies could be attributed to the lack of control over rolling parameters during the preparation process such as revolution speed and duration. Liquid marbles prepared systematically using a vortex mixer at a constant revolution speed produced significantly more consistent effective surface tension values. The systematic preparation method enabled more uniform encapsulation than the manual preparation method. Nevertheless, excessive revolution speed reduces the uniformity of the shell. We observed interfacial jamming of the encapsulating particles at such speeds which contributed to the inconsistencies of effective surface tension values. We believe that our findings could provide new insights towards understanding the causes of inconsistencies of the effective surface tension values. Further work could be conducted to understand the effect of the preparation method on the additional fundamental properties such as elasticity, robustness and viscosity.

CRediT authorship contribution statement

Fig. 7. Comparison of damping of a 20-μl PTFE liquid marble prepared at a revolution speed of (a) 175 rpm and (b) 500 rpm. Scale bar is 200 μm.

Nguyen: Supervision, Visualization, Writing – review & editing. Chin Hong Ooi: Project administration, Validation, Methodology, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

CHO acknowledges funding support from the Australian Research Council (ARC) Discovery Early Career Research Award (DECRA) DE200100119. NTN acknowledges funding support from the ARC Discovery Project DP170100277. PS acknowledges funding support from Griffith University International Postgraduate Research Scholarship and Griffith University Postgraduate Research Scholarship. The authors thank Utkarsh Jadli for helping with MATLAB analysis.

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