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Observation of the liquid marble morphology using confocal microscopy

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ABSTRACT

The structure of the hydrophobic powder shell of a liquid marble is investigated in this study. Although the liquid marble morphology has been investigated using various forms of microscopy, the cross-sectional structure and the thickness variation of the shell have not been examined in detail due to the incapacity to view the cross-sectional plane of the liquid marble or low resolution images. In this work we employed a confocal microscopy approach to visually reveal and measure the shell structure of the liquid marble using confocal microscopy. The confocal microscopic imaging allows for the signal from out-of-focus planes to be eliminated and give a more in-depth view of the internal structure of a liquid marble from the in-focus plane. The 2D cross-sectional plane images or/and 3D images provide new visual insights of liquid marble shell morphology. Image reconstruction and analysis enables the measurement of the extent of particle penetration into the liquid core.

From the investigation, it was found that the liquid marble shell consists of mainly fine particle multi-layers which facilitate the liquid core in avoiding contact with a surface outside of the shell and increase the resistance of the liquid marble to deformation forces. The encapsulated liquid volume displays a fine balance between the hydrophobic interactions between the liquid and particles and the attractive particle–particle interactions. The particle–liquid core interaction is not the primary attribute to the liquid marble's integrity, rather it is speculated that the hydrophobic effect that forces the hydrophobic particles to aggregate on water surface is the dominating factor in keeping the integrity of the liquid marble.

1. Introduction

Liquid marbles are the encapsulation of a liquid mass with a hydrophobic powder casing. Liquid marbles appear to defy nature in that a stable structure comprising of a shell of hydrophobic particles surrounding a liquid mass would not appear to be possible. However, liquid marbles have already been created by Mother Nature as a means to clean dust off hydrophobic surfaces such as lotus leaves [1] and aphids use liquid marbles to remove their honeydew excrement [2]. Liquid marbles have also been exploited by man-kind as a novel way of transporting and delivering liquid medium in applications such as cosmetics and the indication of water surface pollution [3].

The interest in liquid marbles has arisen recently, particularly in the pharmaceutical industry where the formation and strength of the liquid marble are seen to be advantageous in drug delivery. Studies have shown that the particle size enlargement process, wet granulation, can produce liquid marbles [4–6]. The liquid marbles can act as the intermediate to produce hollow granules, which are able to withstand subsequent processing such as milling [5]. Liquid marbles in the pharmaceutical industry also offer the benefits of handling high drug loadings; simultaneous control of the size and structure of the granules; produce spherical granules with excellent flow; good compression properties; fast drying periods [5]. Hence the granulation of hydrophobic powders opens up a new branch of the wet granulation process and the research has expanded into this area. Research into the conventional wet granulation processes using hydrophilic formulations is relatively well established including the morphology of hydrophilic core-saturated granules. However, research into liquid marbles and liquid marble morphology may be considered to be at a relatively preliminary stage, especially knowledge of the liquid core–particle interface of the liquid encapsulated structures. This is the region of interest for this paper. What can the observation of the liquid core–particle interface of a liquid marble reveal to us in terms of the liquid marble structure and integrity?

1.1. Liquid marble imaging techniques

The structure of the liquid marble has been a focal point in several works [5–9] using theoretical models and microscopy

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techniques. However, the morphology of the liquid marble, in particular the liquid core–powder shell interface has not been studied in detail. This is due to the lack of effective experimental methods to make internal and cross-sectional observations of the liquid–powder interface of the liquid marble. Few studies have used specialised microscopy (other than optical microscopy) to view the liquid marble, which unfortunately did not provide images of the structure of liquid marble's shell with sufficiently high resolution [3,5,7,10,13]. In a more recent study of liquid marble, Fujii et al. [16] has used confocal microscopy to show the cross-section of a liquid marble. To our best knowledge, this may be the only study of the liquid marble where researchers have used the confocal method. However, the focus of this recent study [16] was not on the shell structure. In the present study we used the confocal microscopy to view the liquid marble, taking advantage of the microscope's capacity to remove the out-of-focus plane and give a more in-depth view of the liquid marble, particular of shell structure.

1.1.1. Optical microscopy

Optical microscopy is the basic and most common form of microscopy due to its simplicity; it has been used in several works for studying liquid marbles [6,8,10–12]. From the optical microscopy images, the overall morphology and surface of the liquid marble can be seen for liquid marbles with a liquid volume between 10 and 120 μL [6,8,10–12]. The disadvantage of the optical microscope is the low resolution of the image and inability to view the internal structure of the liquid marble. Therefore the observation of the solid–liquid interface is difficult unless a partial liquid marble is formed and the solid–liquid interface is viewed aerially [12]. After the formation of a partial liquid marble, a monolayer of particles are seen, but this layer may not reflect the actual structure of the liquid marble as the thin liquid marble shell may not be able to resist any deformation forces applied to the marble. Hence examining the solid–liquid interface for a complete or partial liquid marble is very difficult with optical microscopy.

1.1.2. Scanning electron microscopy

Scanning electron microscopy (SEM) studies of the liquid marble structure and surface have also been reported. Granulation work was used to produce liquid marbles [5], which were subsequently dried to form hollow granules. When the hollow granules were placed under SEM, the fine size fractions of hollow granules had a more spherical structure compared to the coarser hollow granules. The coarse hollow granule structure appeared to be less spherical with dents and holes present in the powder shell [5]. A detailed view of the particle–liquid core interface could not be viewed using SEM; the only detail that could be noted was that the powder shell appears to be composed with a multi-layer of particles [5]. In another study [7], the outer surface of hollow granules was viewed and the images obtained showed that the hollow granule is made up of aggregates of primary particles. This was supported by other liquid marble surface morphology works [3,10,13] using environmental scanning electron microscopy (ESEM). In these studies, it was revealed that the aggregates of primary particles on the liquid marble surface were separated by liquid region spacings [3,10,13]. This finding suggests that the liquid marble consists of a multi-layer powder shell in which the liquid region spacings were covered during the production of hollow granules. However, like the optical microscope, the SEM imaging technique cannot penetrate into the specimen to view the internal structure, which would be beneficial for understanding the liquid marble morphology.

1.1.3. X-ray tomography microscopy

X-ray tomography microscopy could potentially be used as another liquid marble imaging technique and was used to look at the cross-sectional plane of hollow granules [5,7]. Work carried out on hollow granules [5] using X-ray micro-tomography (μXT), discovered that the hollow granule size distribution was in the range of 100–300 μm with a wall thickness ranging between 25 and 50 μm. During the granulation process, agglomerates of liquid marbles were formed which produced larger granules containing clusters of hollow granules. A similar trend of multi-core granules was also found large size fractions [7]. The hollow granule shell structure in both studies showed that the hollow granule wall structure is composed of multiple layers of powders [5,7]. This was speculated to be formed by gradual layering of the primary powder [7], which would suggest that some form of kinetic forces are needed to develop the powder shell during the formation of liquid marbles. Although the X-ray tomography microscope has the capacity to capture cross-sectional planar images of hollow granules and enhance the understanding of the liquid marble structure, the use of X-ray tomography has not been used to view "wet" liquid marbles and particle–liquid core interface. The imaging of liquid marbles using X-ray tomography may not be possible due to the difficulty in accessing the microscope and to obtain a high-resolution image, the liquid marble is required to be mounted under the microscope for a long period of time. This makes capturing liquid marbles infeasible since the evaporation of the liquid core affects the results.

1.1.4. Confocal microscopy

Confocal microscopy provides an attractive alternative to capturing the liquid marble morphology. The confocal microscope is capable of capturing the internal structure of an optically transparent specimen and constructing a three-dimensional image of the specimen [14]. However, the specimen must be fluorescent under the microscope, in which the specimen can be excited by a laser to fluoresce and capture the image. This is advantageous in capturing the cross-sectional plane of the specimen of interest and can be applied to capture images across the plane of the liquid marble.

The confocal microscope mechanics is similar to that of a typical optical microscope; however, the microscope uses a raster mirror system, two confocal pin-holes and a laser beam to capture the fluorescence light emitted from the specimen to relay the image onto a computer monitor. With this microscope set-up, the second confocal pin-hole eliminates the out-of-focus regions of the image, which increases the clarity and provides an in-depth image of the specimen. Different regions of the specimen can be captured by adjusting the microscope focus plane in the z-direction, which provides the additional benefit of having the capacity to capture a stack of x–y plane images to be processed into a 3D image by a computer imaging software.

2. Materials and methods

2.1. Material characterization

The powder used to produce the liquid marbles for microscopy was hydrophobic silica powder (Aerosil, Degrusil, average particle size of 12 nm) grade R974. Silica powder is able to form a thin translucent powder shell, which gives the most optically transparent liquid marble for the microscope to collect the fluorescent light emitted by the liquid marble core.

The liquid core of the marble was made of aqueous rhodamine B (0.05 g in 20 mL water) (Ciba Limited Basle, Switzerland) which can emit orange/red fluorescence light under the laser to help capture the images.

2.2. Microscopy procedure

The liquid marble was captured using the confocal microscopes at *Monash Micro Imaging* (MMI) centre, taking images across the plane from the equator to the north or south-pole of the liquid

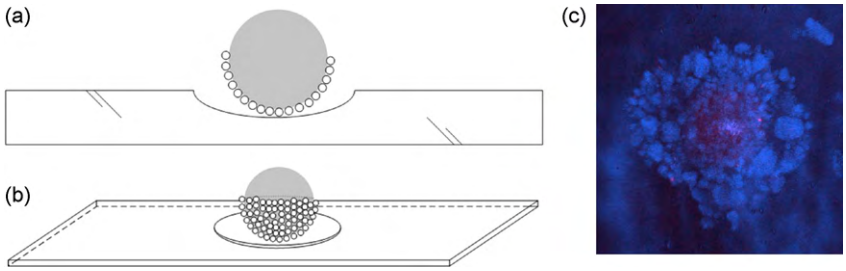

Fig. 1. Simplified diagram of partial liquid marble mounted on divot microscope slide: (a) cross-sectional view of mounting technique; (b) angled view of mounting technique; (c) confocal microscopy image looking into liquid marble shell, artificially high-lighted.

marble, or to focus on a particular region of the interface between the liquid core and the outer powder layer. The liquid marbles were taken using the up-right Leica TCS NT Krypton and inverted Leica SP5 confocal microscopes (Leica Microsystems, Heidelberg GmbH). The Krypton microscope was useful to see the extent of particle penetration into the liquid core, while the inverted SP5 microscope was useful to measure the liquid marble wall thickness. Magnifications of the objective lens that were used with the microscope were 5× and 10× as these gave the best resolution images.

The liquid marbles were produced in a watch glass with nano-silica powder, similar to the procedure carried out by McElenery et al. [12]. A fresh liquid marble was viewed and captured under the microscope, as the cohesiveness and/or the hydrophobicity of the silica powder in the watch glass appeared to have degraded over a period of time (observed to be over a period of approximately 1 h) when exposed to the air, consequently making a very weak liquid marble.

Several mounting techniques were employed to view the liquid marble under the microscope. For the up-right microscope, the microscope slide with a cavity for the microscope specimen was used to place the liquid marble securely. A partial liquid marble, where the powder partially wrapped around the droplet, was produced and placed in the microscope cavity. Care was taken to transfer the partial liquid marble from the watch glass to the microscope slide as the liquid marble was very susceptible to rupture. Viewing the liquid marble in this state was useful for observing the particle–liquid core interface. A schematic diagram of the mounting of the partial liquid marble on the microscope cavity is illustrated in Fig. 1.

For the inverted confocal microscope, a specially designed mounting plate, a fluoro dish, was used to mount the liquid marble specimen and view it under the microscope. The fluoro dish (World Precision Instruments, Inc.) looks similar to a mini petri dish but the top and bottom viewing areas of the dish are comprised of glass, as seen in Fig. 2.

Using this mounting technique, it was found that viewing of the complete liquid marble gave the best results for observing the arrangement of particles within the powder shell and measuring the powder shell thickness.

During the microscope imagining of the liquid marble, the TRITC filter was used to activate the green and red channels required to excite the rhodamine B. The confocal microscope was set to reflection mode such that the microscope captured the reflection light emitted by the liquid marble; the back-scattering light from the liquid core and through the solid particles. The powder shell is clearly seen with the presence of multi-layers within the powder shell and particles can be viewed on the liquid marble surface (see Fig. 3). For both types of confocal microscope (up-right and inverted types), the reflection mode was implemented as this gave the best imaging of the liquid marble.

The liquid marbles were captured as cross-sectional images or a series of x–y images varying in the z-direction for 3D construction, called z-stacks. The images were taken with either a resolution of 1024×1024 or 2042×2042 pixels. A line average of four lines per second was employed as a laser scanning frequency for image capturing. In capturing the z-stack images, the number of z-steps to capture the images ranged from 15 to 35 steps with a z-step increment varying from 2 to 5 μm.

A new model of the confocal microscope, the Leica TCS LSI (large-scale imaging), was trialled to view the liquid marble. This is a newly developed confocal microscope that is tailored for capturing large-scale specimens and this type of microscope has promise for future applications in viewing the liquid marble morphology. Because the LSI microscope was a demonstration model, extensive investigations were not carried out but leave a new potential technique for viewing liquid marbles.

2.3. Liquid marble 3D construction and measuring the extent of particle penetration into the liquid core

Once the images were captured, the stacked images were assembled together, using *Imaris Plus* (version 6.0.1), an imaging software, to produce a 3D image of liquid marble. To obtain a clearer view of the liquid marble, selected 3D images underwent a surface rendering process, in which the surface of the images (such as the liquid core or the solid particles) was artificially modified to make the surface look more solid and enhance the clarity of the image. The rendering of liquid marbles was limited by the strong emittance of fluorescent light from the liquid core which also transmits through the fine particle layer, as fine particles scatter light less than coarse particles. Therefore the rendering of the liquid marble core or the powder shell may have affected the particle–liquid core interface, and not as separate phase components. The modifying of the liquid marble surface was carried out such that the rendering of

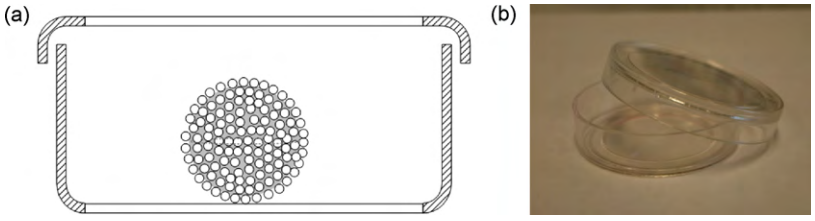

Fig. 2. Fluoro dish used for the inverted confocal microscope: (a) schematic diagram of a liquid marble in a fluoro dish and (b) close up of a fluoro dish.

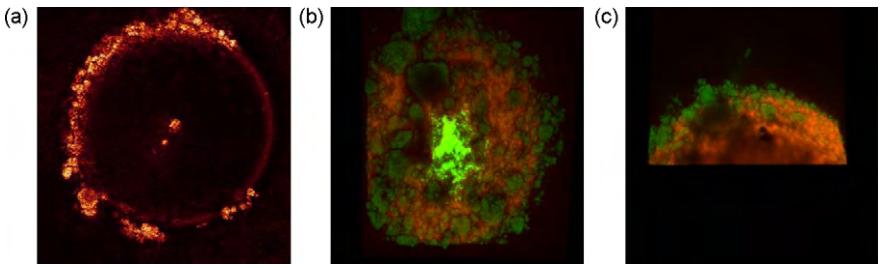

Fig. 3. A cross-section of liquid marble produced from silica R974 powder and rhodamine B liquid core. Image was captured using confocal TRITC filter (green laser channel) under reflection mode: (a) cross-sectional view of liquid marble; with the fluorescence artifically high-lighted (b) aerial view of liquid marble; (c) side view of liquid marble.

both phases in the particle–liquid core interface was minimised (as much as one phase of the interface was modified, for example the particles or the liquid core only). Animations of the rotating views of the liquid marbles were prepared to showcase the 3D image of the liquid marble.

The extent of particle penetration, κ_p (see Eq. (1)) into the liquid core was measured by using a combination of image cropping and analysis using a photo-editor software (*Microsoft Picture It!*) and *ImageJ*. The methodology began with taking the image of the solid–liquid interface of a partial liquid marble to view the cross-sectional area of the penetrating particles (see Fig. 4a), taken under the Krypton confocal microscopy. The photo-editor was used to draw an arc representing the liquid core surface. It was assumed in the definition of the liquid marble core that the outer surface of brightest ring represented the liquid core surface, as it is expected that the surface of the liquid core would emit the brightest fluorescence light. Such observation was also reported by Fujii et al. [16]. The particles that were seen to be penetrating into the liquid core were cropped out of the image (see Fig. 4c). The cropped particles then formed two new sets of images: (1) containing the complete morphology of the particles (see Fig. 4c) and (2) the penetrated portion of the particles in the liquid core (see Fig. 4e), ready for particle analysis. Imaging analysis software, *ImageJ*, was used to change the images to an 8-bit, black and white image (see Fig. 4f). Any white regions within the particle regions were filled in manually using the fill-in tool in *ImageJ*. The two images then underwent particle analysis in the *ImageJ* software to calculate the particle cross-sectional area (in μm^2) using the scaling factor conversion from pixels to μm, obtained from the microscope images and the pixel length from the *ImageJ* software.

The extent of particle penetration (κ_p) was calculated by dividing the wetted cross-sectional area of the particle by the total cross-sectional area of the particle:

$$\kappa_p = \frac{\text{wetted/penetrated cross-sectional area of particle}}{\text{total cross-sectional area of particle}} \quad (1)$$

An example of the extent of particle penetration is given in Fig. 5. From the extent of particle penetration obtained and the complete particle cross-sectional area, the relationship between the two variables was plotted as a function of each other to observe any trends.

3. Results

3.1. Liquid marble morphology

The overall structure of a segment or hemispherical liquid marble can be seen in Figs. 6–9 These figures demonstrate that the confocal microscope is a useful microscopy technique to give a detailed view of the liquid marble morphology. The packing of the particles can be seen on the liquid marble surface with the powder shell consisting of mono- and multi-layers of powder. Fig. 6 shows that the powder packs in a random nature around the droplet surface with the finer particles packing in-between the coarse particles.

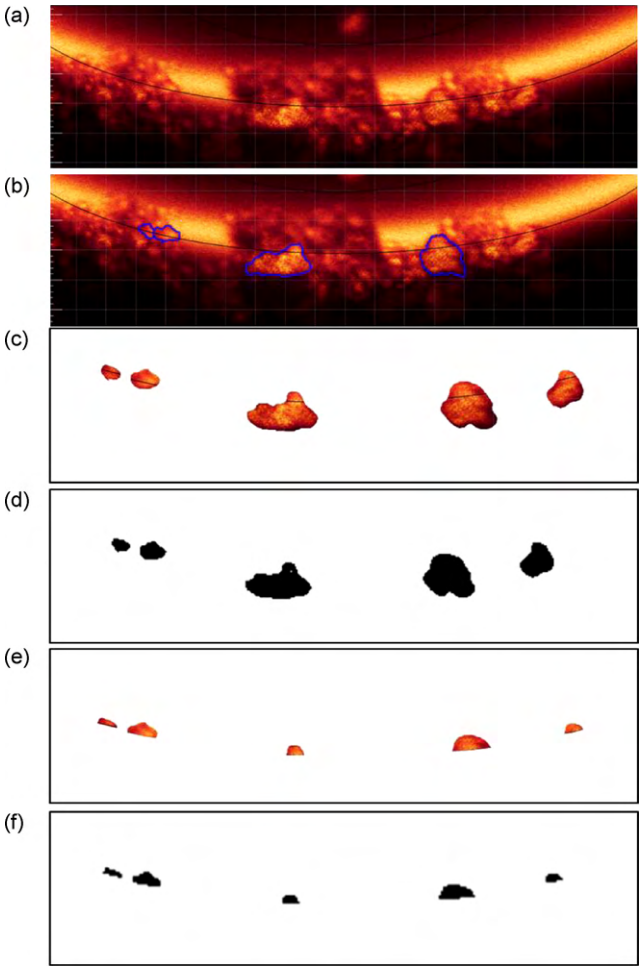

Fig. 4. Sequence in image modification for particle analysis in *ImageJ*. Each image represents (a) the original image with an arc drawn representing the liquid marble core surface; (b) the original image with the particles to be analyzed outlined in blue; (c) cropped images of the complete particles to be analyzed; (d) complete particles changed to 8-bit, black and white image; (e) cropped portion of penetrated particles; (f) penetrated portion of the particles changed to 8-bit, black and white image ready for particle analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

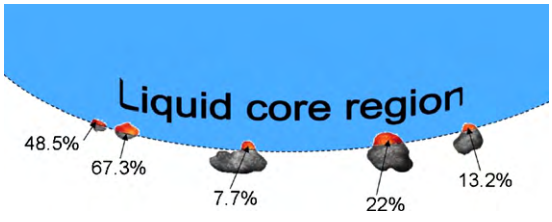

Fig. 5. Example of extent of particle penetration, κ_p, for particle of different sizes.

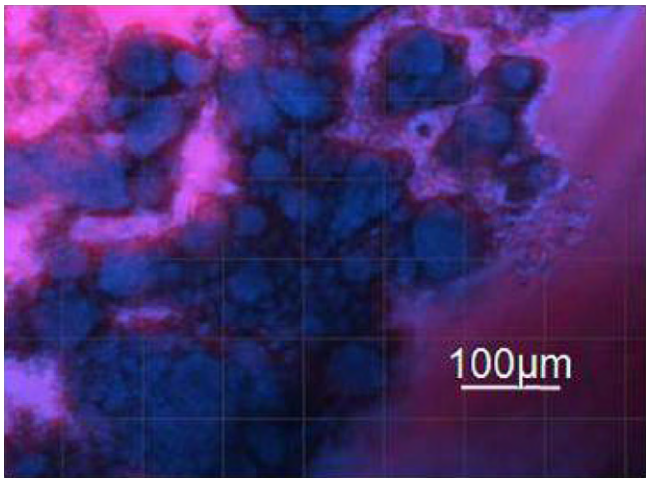

Fig. 6. Close-up of the silica particles (R974) on a partial liquid marble surface captured using the inverted SP5 confocal microscope with 100 times magnification.

Therefore the sections of monolayers are composed of coarse particles while the sections of multi-layers consist of fine particles. This makes the liquid marble surface rough in appearance and thus it can be reasoned that the liquid wall thickness would not be consistent.

Bormashenko et al. [13] noted that the powder shell is made up of aggregates separated by liquid region spacing. This observation is supported by the images in Fig. 7. The liquid region spacings are fine and the voids in between the particles act as torturous pores within the powder shell, in which the vapour of the liquid must diffuse through during the drying process of the liquid marble to form a hollow granule. Despite the existence of the liquid spacings, the particles pack in close proximity, possibly suggesting that the inter-particle attraction forces are responsible for the liquid marble stability. An interesting observation can be seen in Figs. 7 and 8 where the top of the liquid marble contains more fine particles compared to the rest of the liquid marble. This would be attributed to the weight of the particles, in which fine particles are transported more easily to the top of the liquid marble compared to the coarse particles.

Preliminary trials of viewing the liquid marble under the Leica TCS LSI (large-scale imaging) microscope showed that capturing an entire hemispherical liquid marble was easily achieved compared to the up-right confocal microscope. In the future it would be possible to capture an entire liquid marble using this microscope and this paves a way for potential research into liquid marbles in the near future. As noted before, from Fig. 8, it can be seen that the liquid marble contains more coarse particles around the equator of the marble compared to the top of the marble. Due to the low magnification of the objective lens, the individual particles cannot be seen in the images presented. However, under reflection mode, the liquid marble surface is rough, indicating the random packing of the particles.

The images captured using the LSI microscope were rendered using the *Imaris* software and is presented in Fig. 9 An overall view of the liquid marble can be seen from the image and the inside view of the powder shell shows that the particles have to penetrate into the liquid core to some degree to keep the integrity of the liquid marble. The heightened intensity of fluorescent emittance seen in the middle of the hemispherical powder shell in Fig. 9 is the concentrated reflectance of fluorescent emittance in the laser region.

3.2. Liquid marble wall

As mentioned previously, the thickness of the liquid marble wall is not uniform since the liquid marble wall is composed of a combination of mono- and multi-layers of particles. Fig. 10 provides examples of liquid marble walls. Particles which are approximately larger than 50 μm form the monolayers, while the

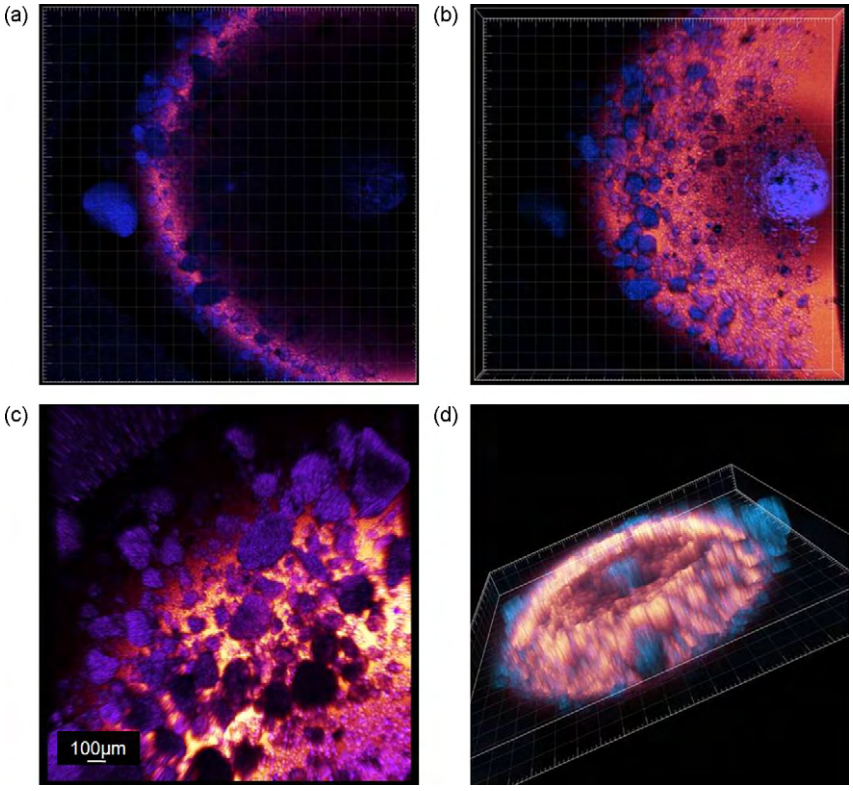

Fig. 7. Liquid marble morphology produced from silica R974 particle and aqueous rhodamine B liquid droplet. The liquid marble is seen in (a) cross-sectional view; (b) aerial view; (c) close-up view of the liquid marble surface; (d) angled view of the liquid marble, showing the coarse particles on the outer core surface.

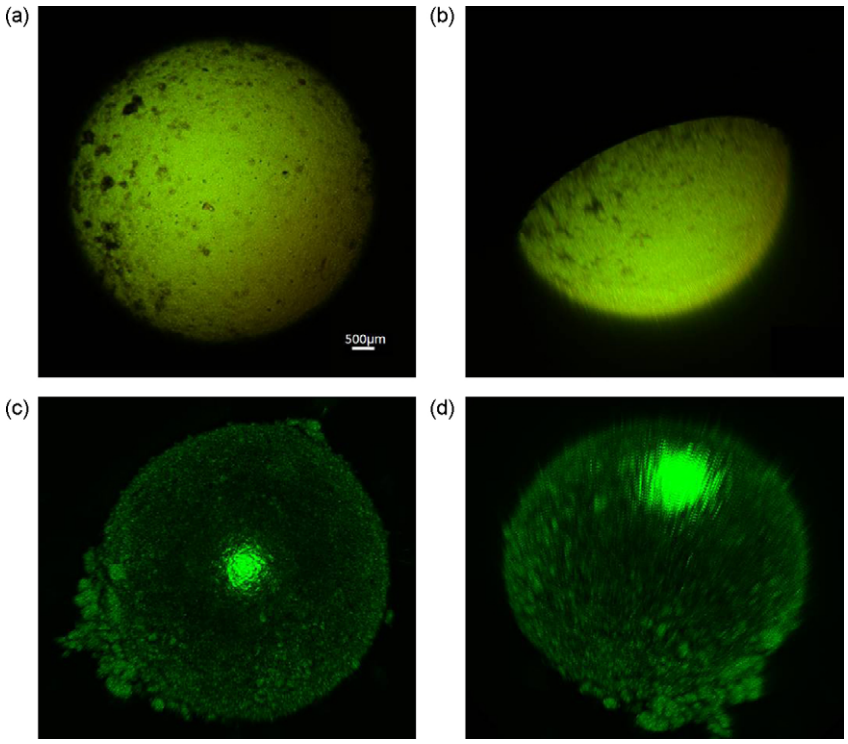

Fig. 8. Images of the liquid marble taken using the Leica TCS LSI confocal microscope under normal and reflective laser modes. The images show the liquid marble view under normal mode with (a) aerial and (b) angled view of the liquid marble; and reflective mode with (c) aerial; (d) angled view of the liquid marble.

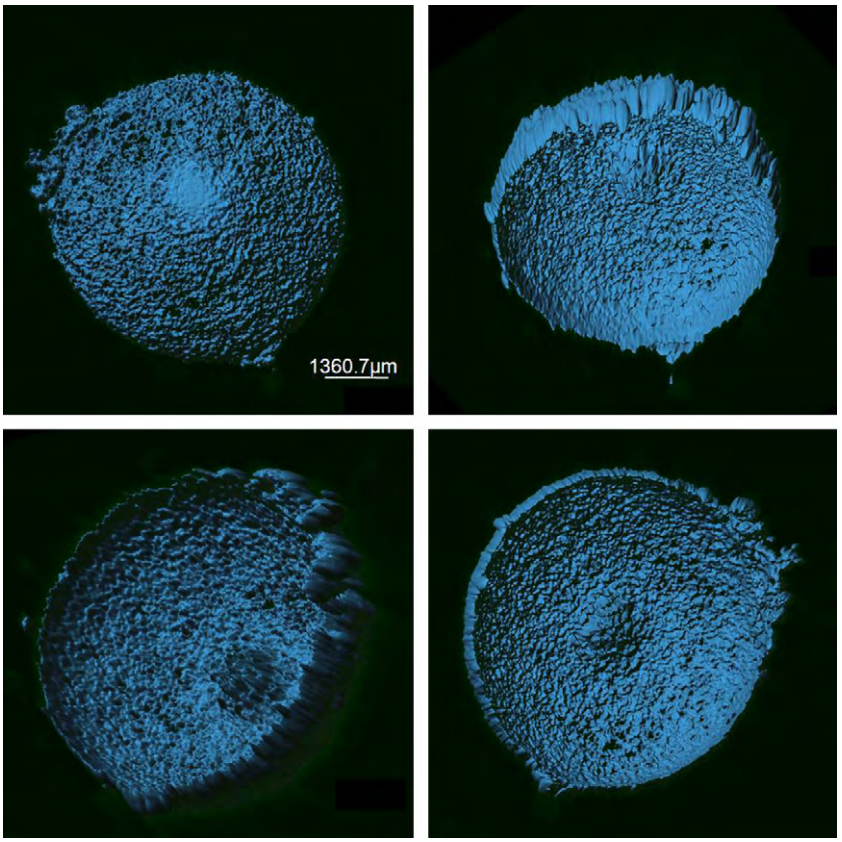

Fig. 9. Images of the liquid marble taken using the Leica TCS LSI confocal microscope under reflective laser mode and rendered using Imaris imaging software.

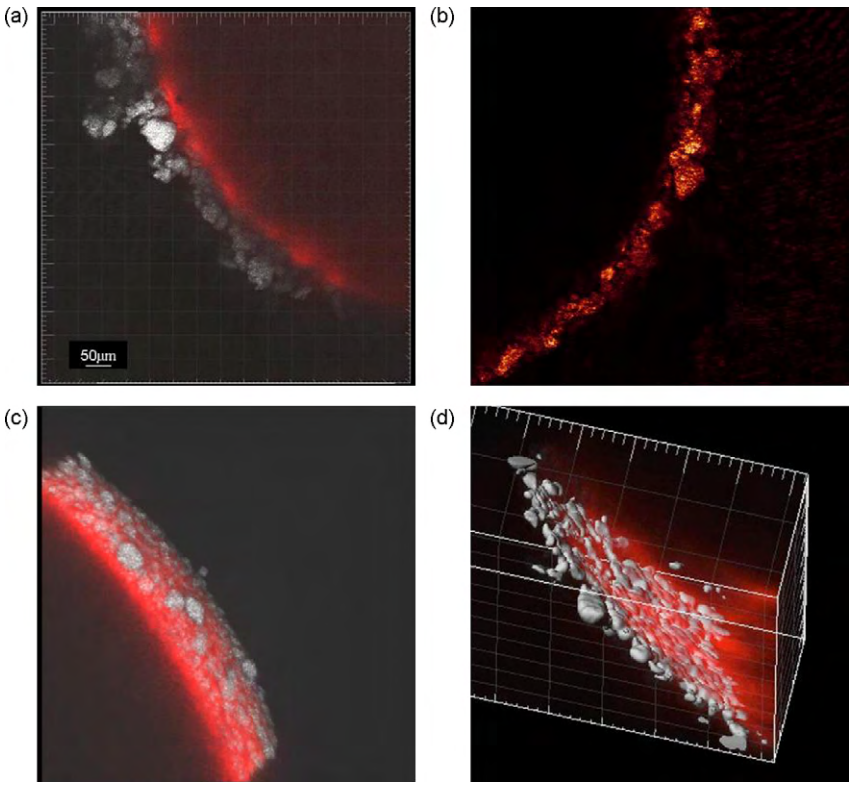

Fig. 10. Liquid marble wall (produced with silica R974 particles and aqueous rhodamine B) taken with (a) inverted SP5 confocal microscope and (b) Krypton confocal microscope. The figures show (c) side view of a liquid marble wall portion taken using the inverted SP5 confocal microscope and (d) angled view of the liquid marble wall, rendered by Imaris imaging software.

finer particles form multi-layers in the powder shell. Therefore the liquid marble wall covers a large range of thickness, varying from an average of 43–114 μm with a standard error of the mean ranging from 2.6 to 18.5 μm.

A side observation was made, during the capturing of the liquid marbles, where the silica powder quality deteriorates over a long period of time (approximately 1 h) which appeared to reduce the attractive interactions between the powder particles. This was evident in the increased sensitivity of the liquid marble to rupture during handling or when minor deformation forces are exerted on the marble. Therefore a new batch of silica powder was used for each liquid marble. A mechanically weak liquid marble made from a poor quality of powder was captured under the microscope and presented in Fig. 11, which shows the monolayer of particles in the liquid marble wall.

3.3. *Extent of particle penetration into the liquid core*

From the confocal images, the extent of particle penetration (κ_p) into the liquid core relative to the particle size was explored. Fig. 12 shows an example of a cross-sectional view of the liquid marble with the particles in the powder partially submerged into the liquid core. An image showing a consistent layer of particles partially submerged into the liquid core cannot be achieved using the present experimental set-up, as the particle position to capture the cross-section is dependent upon the focal plane of the microscope. The close-packing arrangement of the particles in Fig. 12, suggests that the liquid marble stability is dependent upon the particle–particle interactions. The majority of the particles within the powder shell are in contact with adjacent particle(s) which would play a factor in keeping the integrity of the liquid marble.

An assumption was made during the measurement of the extent of particle penetration that the outer brightest region of the liquid core ring is the solid–liquid interface, as it is expected that the bright ring corresponds to the emittance of fluorescent light from the rhodamine B liquid core. From the examination of the

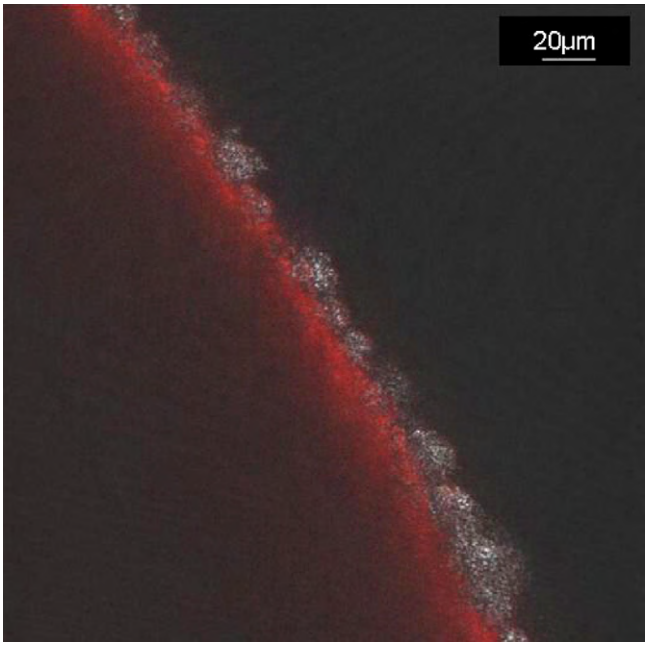

Fig. 11. Liquid marble wall of a liquid marble produced from a deteriorated quality of silica R974 powder and aqueous rhodamine B.

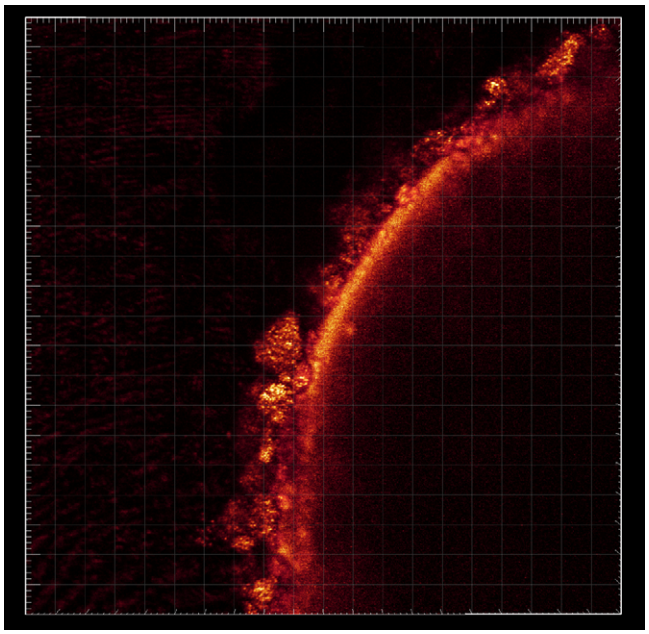

Fig. 12. Image of the liquid marble wall produced from silica R974 particles and aqueous rhodamine B droplet. The image was taken using the Krypton up-right microscope. The scale grid represents 50 μm.

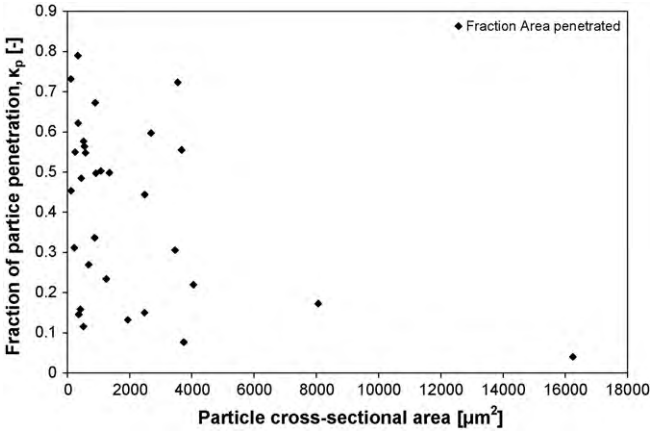

Fig. 13. Relationship between the cross-sectional area of a liquid marble particle and the degree of penetration into the liquid core.

solid–liquid interface, it was found that the extent of penetration of the particles into the liquid core was not strongly influenced by the particle size. Fig. 13 shows the results of the extent of particle penetration into the liquid core image analysis (as described in Section 2.3); the relationship between the percent of penetration of the particle into the liquid core and the particle cross-sectional area. The graph demonstrates that for a particle cross-sectional area of up to 4000 μm^2, the extent of particle penetration can vary in fraction from 0.1 to 0.8. This suggests that the penetration of the particle into the liquid core could be due to more dominant factors such as the weight of the particles sitting on top of the submerged particle. For much coarser particles (hence a larger particle cross-sectional area), the extent of penetration is much less, which would indicate that larger particles would tend to float on top of the liquid core rather than be submerged. Therefore the "floating" of the coarse particles correlates with the formation of a monolayer within the powder shell.

4. Discussions

4.1. Confocal microscopy for liquid marble shell morphology observation

From the results presented, it can be seen that the confocal microscope is a useful technique to examine the liquid marble morphology. However, using the confocal microscope to capture the liquid marble does pose some limitations, particularly in showing a clear image of the solid–liquid interface. During the imaging of the liquid marble, when the laser hits the powder shell, there is some scattering loss of the laser. But the laser that passes through the particle layer still has a strong intensity. The laser excites the rhodamine B dye in the liquid core and fluorescent light is emitted out of the liquid marble. However, the emitted fluorescent light encounters some scattering loss as it passes through the powder layer to reach the confocal lens. The scattering loss from the laser and emitted fluorescent light causes the image resolution and clarity to decrease in conjunction with dark regions registered in the solid–liquid interface images due to the decreased fluorescent light intensity. As a consequence, a clear boundary between the solid particles and the liquid core cannot be established for a complete liquid marble in this study. To overcome the scattering loss effects, an image of a partial liquid marble (where the north-pole is not covered by particles). However, it is difficult to capture an image in which there is an even distribution of particles around the liquid core perimeter.

The confocal microscope was originally designed to examine biological samples, which means that the specimens placed under the microscope are typically of cell-scale. For a liquid marble, this would be considered to be a large-scale specimen and the capturing of the entire liquid marble, from north-pole to south-pole is difficult to achieve using the TCS NT microscope. There is a trade-off between using a high magnification for obtaining good resolution images and the working plane height for the microscope. For high magnifications, the working plane height for the microscope is narrow, thus not allowing an opportunity to view the entire liquid marble. For low magnifications (for example 1.6 times magnification), reflection rings on the image appears, which are caused by the reflection of light from the large objective lens window. Placing a smaller liquid marble under the microscope is not feasible due to the high intensity of the laser bleaching (decreasing the fluorescent intensity) and evaporation of the liquid marble core within a short period of time and so a clear image of the whole liquid marble cannot be obtained. With the recent introduction of the Leica confocal TPS LSI, the viewing and capturing of a whole liquid marbles can be achieved and further examinations of the liquid marble can be carried out using this microscope.

Despite these short-comings of the confocal microscope, this technique of viewing the liquid marble provides an in-depth view of the liquid marble morphology and the application of the confocal microscope can be broadened from biological applications to examine granular products, including liquid marbles. The confocal microscope is relatively easy to access and a high-resolution image can be obtained quickly compared to other imaging techniques. This microscopy technique would offer many benefits in future liquid marble investigations.

4.2. Liquid marble wall morphology

As seen in Figs. 10–12, the liquid marble wall structure shows the combination of mono- and multi-layer of particles, with the most part of the powder shell being composed of multi-layers of particles. In order for the liquid marble to hold its structure, it is essential that the liquid core does not make contact with a wetting surface outside the marble. The particle multi-layer helps the liquid

core to avoid contact with wetting surface as this makes the powder shell dense.

The liquid marble powder shell can be considered to be a flexible super-hydrophobic surface, analogous to the super-hydrophobic surface explained by the Cassie–Baxter equation [15]. The hydrophobic surface described in Cassie and Baxter's study is of a rough surface in which the projected solid–liquid contact points help the liquid to avoid touching the surface, hence making the surface hydrophobic. The projected solid–liquid contact points need to be less than a critical separation distance from each other in order to be able to support the liquid interface and avoid making contact with the inner surface. This phenomenon is similar to the liquid marble powder shell, in which the hydrophobic particles make up the project solid–liquid contact points, and helps the liquid core to avoid making contact with a wetting surface. What makes the liquid marble powder shell interface more complicated than the Cassie–Baxter hydrophobic surface is that the powder shell is a flexible interface which can be stretched out and curve to fit around the liquid core; the Cassie–Baxter hydrophobic surface is considered to be a rigid surface. Therefore in order for the liquid marble to maintain its structure, the powder shell must be able to self-amend under deformation forces. When the liquid marble is subjected to deformation forces, the powder–liquid interface stretches out, and to keep the separation distance between the projected hydrophobic solid–liquid contact points below the critical separation distance, there needs to be a sufficient reserve of hydrophobic powder to amend the stretched powder–liquid interface. Therefore fine hydrophobic particles become critical in forming a multi-layer powder shell which helps to amend the powder–liquid interface when external forces are applied to the liquid marble.

Considering the previous explanation, this may help explain the reasoning for the tendency of fine particles to surround around the liquid core circumference. The fine particles help the liquid marble withstand any compression forces exerted on it. When the liquid marble is compressed, the fine particles are able to move easily around with the bulk liquid and can pack into the newly created voids within the powder shell to keep its integrity. It is also possible that the fine particles form a network of particles where the particles are entangled together [4]. The larger particles would be more rigid within the powder shell and would not provide the flexibility the powder shell requires to avoid liquid contact with the wetting surface. This finding is also supported by a separate study [10], which found that nano-sized particles produce a more stable liquid marble. This was attributed to the ease of the fine particle to fill any newly created voids during compression or deformation of the liquid marble.

Figs. 10 and 12 can help to reveal the number of particle layers that form the powder shell. From these figures, the number of particle layers can be estimated to vary between 1 and 4 layers. However, what should be pointed out here is that the micron-size particles that make up the particle layers are aggregates of silica particles (Aerosil R974 particles are approximately 12 nm in size). Comparing this finding to gravimetric analysis [12] on liquid marble morphology, the comparison demonstrates the weak function between the number of particle layers comprising the powder shell and the particle size. The gravimetric analysis involved determining the number of particle layers that make up the liquid marble using the mass of the particles in the powder shell, the particle size and the particle density. The powder shell structure was analyzed in terms of the number of monolayers on the drop surface. The number of layers varied between 0.3 for coarse copper powders (~320 μm) to 4.4 layers for fine PMMA powder (~45 μm). This study provides direct evidence of the presence of multiple monolayers of fine particles and independently supports the findings in studies by other workers [12]. Therefore the formation of multi-layers of particles around the droplet surface is essential for liquid marble stability.

4.3. Liquid marble integrity

The liquid marble appears to be a simplistic structure of liquid encapsulation, but a deeper examination into the morphology reveals a fine balance between non-wetting of the hydrophobic particles by the liquid core and intermolecular attractive (adhesive) interactions between the particles.

From the images of the liquid marble, the particles are hydrophobic as no immersion-wetting of the particles is occurring. With highly hydrophobic particles, the short range attractive van der Waals forces between the hydrophobic particles are the dominant forces to uphold the liquid marble structure. The greater the van der Waals forces between the particles (resulted from more contact areas between particles), the more likely the powder shell comprises of particle multi-layers which helps the liquid marble to withstand compression forces exerted on the liquid marble. Also, hydrophobic particles that are not wettable by water, but in particle contact with water has no hydrogen bonding interaction with water. The lack of hydrogen bonding between the hydrophobic particles and the strong hydrogen bonding between water molecules make the water to retreat from the inter-particle region [17]. This tendency enables a greater particle–particle contact area to be established, leading to stronger interactions between hydrophobic particles.

As shown in Section 3, the resistance of liquid marble to mechanical deformation decreases as the liquid marble wall thickness decreases, or when the particles become less hydrophobic and more wettable by water. This suggests that the stability of the liquid marble is dependent upon the hydrophobic interactions of the powder particles for reasons discussed above. When the hydrophobicity level of the powder deteriorates and the attractive van der Waals forces between particles are weakened by the presence of water between particles. Under this circumstance the inter-particles forces can be overcome more easily by the shell deformation under compression forces. Consequently, liquid spacings on the marble shell will increase, leading to potential rupture. In addition, from the macroscopic effect of liquid surface tension on particles, when the liquid surface tension and the solid particle surface free energy are such that wetting is allowed, then liquid will have capillary rise in the capillary channels defined by the particle layer. Such capillary rise is the result of positive Laplace pressure in the liquid penetrating front. The Laplace pressure also acts sideways on the capillary wall, pushing the particles away from each other. Conversely, for a non-wetting liquid and particles system, the Laplace pressure in capillary channels formed by hydrophobic particles is negative. There is, therefore, now force pushing the particles away from each other.

For fine particles, the short range van der Waals interaction appears to be stronger than coarse particles. This trend has been attributed to the large BET surface area and the sizes of the fine particles, both factors contribute to an increased particle–particle interaction [10]. This suggests that fine particles would be more favourable for producing stable liquid marbles and subsequently strong hollow granules.

5. Conclusions

From the investigation into the liquid marble morphology, it was found that confocal microscopy is a feasible method of viewing the liquid marble, including the internal of the liquid marble. However, some drawbacks apply when viewing the boundary between the particles and the liquid core; the whole liquid marble due to microscope limitations. Upon close examination of the liquid mar-

ble structure, the encapsulated liquid volume displays a balance between the hydrophobic particle–liquid core interactions and the attractive interactions between the particles. The liquid marble powder shell is composed of predominantly multi-layers of fine powders. These fine particles help the liquid core to avoid contact with a wetting surface and hence increase the flexibility of the liquid marble in withstanding compression forces. With the hydrophobic interaction between the particle and the liquid core playing little role in keeping the stability of the liquid marble, it is speculated that the hydrophobic powder attraction forces are the dominating factor in keeping the integrity of the liquid marble.

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