Liquid marbles with in-flows and out-flows: characteristics and performance limits

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We characterized the breaking, buckling and deformation of a liquid marble upon liquid exchange via external inflow and outflow. During liquid addition, the breaking of liquid marbles was affected by the existence of a swirl flow pattern. During liquid removal, the liquid marbles buckled and their morphology was controlled using penetrating pins. During a zero-net-flow perfusion process, the shapes of liquid marbles were controlled by the arrangement of the inlets and outlets.

Liquid droplets have been widely used in many microfluidic applications.4,5 A new type of droplet called liquid marbles has gained a lot of popularity ever since Aussillous and Quéré first brought them into the limelight in 2001.7 In liquid marbles, a liquid core is fully coated with micro- or nano-particles; these particles prevent the liquid core from wetting its supporting substrates, whether solid or liquid, thus creating a unique liquid container.8–11 Depending on the nature of the coating and the size of the droplets, similar structures have also been studied in the past such as colloidosomes,12 vesicles,13 particle-stabilized emulsions14–16 and dry waters.17 Liquid marbles, specifically, are usually a few millimeters in size. They can be merged, divided, manipulated (e.g. via gravitational force,18 electrostatic force,19 and magnetic force20), and their contents can be mixed, which makes them an ideal candidate for performing chemical and biological experiments.21–24 For example, liquid marble micro-bioreactors can be used to determine the blood type effectively and cheaply21 and culture cancer cells with better performances than traditional methods.22 One critical aspect of using liquid marble bioreactors is that the reagents need to be added or removed from the liquid core, and if long-term culture is performed, constant perfusion of the liquid marble is needed. Moreover, several other applications of liquid marbles, such as liquid marble micropumps25 and liquid marble surface tension calculators,26 also rely on the removal or addition of liquids. Although important, to the best of our knowledge, the behavior of liquid marbles during liquid exchange processes has not yet been systematically studied. Therefore, in this study, we characterize the properties of liquid marbles and explore their limits during liquid exchange.

We used a hydrophobic lycopodium powder (27.5 ± 5 μm, Fisher Scientific) – a popular liquid marble coating27,28 – and de-ionized (DI) water to manufacture our liquid marbles. The marbles were prepared by dropping controlled volumes of DI water using a syringe on a heap of lycopodium powder, and then rolling the droplet on the powder until an even sheath of particles adhered and enveloped the liquid. Fuji et al.29 have shown that this particle layer does not necessarily have to be a mono-layer, and the particles can exist as flocs and agglomerates. The marbles were then placed on various substrates, such as silicon wafers (Universitywafer.com, P/B (100), contact angle 30°), glass slides (Fisherbrand, contact angle ~0°), or PDMS (contact angle 90°), for the experimentation. A fairly simple experimental setup was adopted: DI water was injected and/or removed from the liquid marble core via needles with controlled volumes and flow rates using programmable syringe pumps (KDS 210 and Fusion 200). A high speed camera (PixeLink, PL-B771U) was used to record the side views and the top views of the liquid marbles during the experiments.

For the first series of experiments, we pumped water into the liquid marble, causing it to swell and break. For a low injection flow rate (e.g. 0.25 mL min⁻¹), the particle coating was observed to crack with the passage of time – the cracks originated from the top of the marble (Fig. 1(b)), and kept growing (Fig. 1(c)), until the rupture of the marble (Fig. 1(d)). For a high injection flow rate (e.g. 2 mL min⁻¹), the particles were observed to spread apart evenly at first, followed by a swirl motion that occurred due to the incoming water flow (Fig. 1(g)). The swirling motion ensures homogeneous spreading of the particles on the marble surface and thus prevents significant exposure of the liquid surface to the air. Even after a significant increase in the inter-particle spacing we noticed that the marble...
maintained its non-wetting nature. However, once this spacing crossed a certain limit, rupture ensued and the marble wetted the substrate. We have called this state the stationary rupture point. Note that in theory if the injection needle is perfectly vertical and positioned at the very centre of the marble, there would be no rotational flow inside the marble due to the axisymmetric flow condition. However, in reality, such a condition is difficult to achieve. Therefore, a rotational flow inside the marble may always exist. Such rotational flow induces a shear force to the inner wall of the particle shell. This force is balanced by resistive forces in the particle shell, possibly due to the inter-particle cohesive forces and frictional forces. For a fixed needle size with fixed injection location and direction, the shear force increases with increasing injection flow rate, while the resistive forces decrease with increasing marble volume due to the decrease in particle density in the shell. Therefore, the observed swirl motion on the marble surface will occur when the driving shear force becomes greater than the resistive forces. Indeed, our observation matches a previous study performed by Stancik et al. who studied the structure and dynamics of particle monolayers at a liquid–liquid interface subjected to shear flow. They reported that particles tend to move either at low particle concentrations or at high shear rates.

The swirl motion of the particles depends on various parameters. To avoid complication, in all the following experiments, we fixed the needle insertion point at 1 mm off the marble center with a 20° insertion angle and an insertion depth of 0.5 mm with the aid of a micromanipulator. For the first set of experiments, we measured the marble contact length with respect to time and marble volume from high-resolution images, and compared with existing theories. Fig. 2(a) shows the measured contact length variation of liquid marbles with various initial sizes, growing at different rates up to the stationary rupture point (crosses). As expected from intuition, for similar initial-sized marbles, the greater the flow rate of water being pumped into the marble the lower the survival time of the marble. On the other hand, for a constant pumping flow rate, larger-sized marbles generally survive longer. The same data have been plotted in Fig. 2(b) so that they can be compared to the shape equations suggested by Quéré and Aussillous:

\[
 l = \sqrt{2/3} R_0 \kappa \quad (R_0 < \kappa^{-1})
\]

\[
 l = \sqrt{2/3} R_0^{3/2} \kappa^{1/2} \quad (R_0 > \kappa^{-1})
\]

where \( l \) is the contact length, \( R_0 \) is the radius of the marble considered to be spherical, and \( \kappa^{-1} \) is the capillary length (\( \sqrt{\gamma/\rho g} \approx 2.5 \text{ mm} \)). Eqn (1) applies to spherical marbles and eqn (2) applies to puddle-shaped marbles. Our measurements match the theoretical curves to a certain extent.

Although it is extremely important to quantify the stationary rupture points of liquid marbles, a marble that has not yet reached the stationary rupture point may have already lost its ability to roll – a key feature of liquid marbles used in many practical applications. Therefore, we performed further experiments to examine the rolling abilities of enlarged liquid marbles. Marbles with an initial size of 0.05 mL were allowed to grow by pumping in controlled volumes of water at a controlled flow rate and then were tipped to roll on the substrate. In Fig. 3, the marbles which successfully completed an upside-down rotation without breaking were labeled “rolling marble” and the marbles which ruptured upon rolling were labeled “rolling rupture” (Fig. 3). In Fig. 3, we can identify two zones for rolling marbles: zone 1 and 2 – they represent two different mechanisms to obtain a rolling marble. In zone 1 the expansion of a marble was minimal, and therefore did not affect the rolling stability of the marble. In zone 2, the swirl motion of the particles was observed, which helped homogenise the particle coating of a marble and in turn enhanced the rolling stability of the marble. Note that the crosses in Fig. 3 represent the stationary rupture states.

Fig. 2 (a) Liquid marble contact length variation over time. (b) Liquid marble contact length as a function of marble volume. Legends list the initial marble sizes and injection flow rates. Crosses mark the stationary rupture points for each liquid marble.

Fig. 3 Effect of flow rate and the amount of water addition on the rolling abilities of enlarged liquid marbles. Each point represents one experimental case. Besides stationary rupture states, rolling rupture state and rolling marble state are also identified. Results with different sizes of marbles are summarized and compared in the insets.
From our observations we have reached the conclusion that the robustness of the marble is greatly affected by the swirl motion of the particles. Generally speaking, moderate levels of swirl within the marble enhance the robustness of the marble despite the growth which predominantly acts to make the marble less robust, while high swirl rates prove detrimental for marble strength. Similar phase diagrams were also made for marbles with different initial sizes. These diagrams are compared in the inset of Fig. 3. We can see that larger marbles can take more water before rupture compared to smaller marbles. It should be noted that the type of particle coating is also an important factor to the robustness of a liquid marble due to the effects of various physical and chemical properties of the coating powder. For example, Bhosale et al.\textsuperscript{33} showed that liquid marbles made from nano-sized coating particles (fumed silica) are up to 80% more robust than those having a micro-sized powder (lycopodium) coating. Liquid marbles with nano-sized particles are capable of accepting more compressive and tensile loads prior to rupture, probably due to the enhanced uniformity of the coating. In addition, the Hamaker constant,\textsuperscript{34–35} hydrophobicity,\textsuperscript{36–38} shape\textsuperscript{39,40} and electrical charge\textsuperscript{35,41–43} of the particles also play important roles by affecting the inter-particle cohesive forces.

In our second set of experiments, we tested the behaviour of liquid marbles upon water removal. In these experiments the syringe was used in reverse to suck water out of the marble. As the experiments progressed the liquid marble was observed to shrink. Initially the reduction in the marble size was isotropic and the marble maintained its spherical morphology; however, after a certain point the upper surface of the marble was observed to suddenly buckle. This abrupt onset of buckling has been called the buckling point, and all of our readings in Fig. 4 have been based upon this point. Fig. 4 delineates that a marble collapses when approximately 65% of the water has been removed from it. Experiments have shown that this factor does not change much with the flow rate of the liquid. Tsapis et al.\textsuperscript{44} studied buckling of drops with colloidal suspensions and attributed the abrupt onset of buckling to a sudden transition in the properties of the shell from viscous to elastic. They also observed that the particle monolayer on the drop surface folded and corrugated when the drops were deflated beyond collapse; however, no particles were expelled from the solid–liquid interface. Our experiments show that these observations can also be extended to liquid marbles.

Unlike earlier results from other experiments\textsuperscript{44–47} wherein liquid escaped from evaporation through the particle coating, in our experiments – with the liquid drawn out at a specific location – a pattern (Fig. 5) was observed around the location of drainage. The formation of the pattern indicates the steric jamming of the interfacially trapped particles\textsuperscript{48} due to compression\textsuperscript{49–51} during the water removal process. The insertion of the needle through the marble coating primarily provides a source of inhomogeneity of the particle coating, which has been found to be responsible for the folding pathway during a buckling event.\textsuperscript{52} Note that the buckled particle coating has the ability to retain its shape/form even after the removal of the external force (needle insertion), acting like a clumped up solid mass.

We also used a PDMS substrate to puncture the marble at its base and remove water from the bottom. The marble was observed from the top (Fig. 6). The radial ridges – characteristically found in the previous collapsing marbles – were not observed in this case; rather the marble top just collapsed and showed no observable warping patterns, indicating that a needle was needed to induce the ridge formation. To further verify this, the same experiment was repeated, except now the top of the marble was pierced with a needle. The water was again removed from the base; however, this time the radial ridges (Fig. 7) appeared, thus suggesting that the needle induced inhomogeneity is critical to the formation of the ridge pattern.

Another interesting observation of liquid marbles was that when water which was previously evacuated was re-supplied to the marble, the marble regained its spherical geometry while maintaining its non-wetting nature. Nevertheless, each water evacuation-pumping cycle left the marble more fragile and susceptible to failure; we were able to repeat these cycles a maximum of three times prior to failure.
In the third set of experiments, we tested the marble behavior under constant perfusion using both inflow and outflow. Fig. 8 characterizes the marble shape with respect to the needle angle and flow rate. The marble shape was defined by two parameters, which are indicated in Fig. 8. We had two observations for this experiment: the first was that the marbles broke easily under a high flow rate (higher than 9 mL min⁻¹, indicated by the dashed line in Fig. 8). Our second observation was based on the relation between the marble shape and the needle angles at low flow rates. The liquid marbles experienced a remarkable deformation at relatively low and high needle angles (i.e. 20° and 150°). However, the marble deformation was not significant for needle angles in the range from 45° to 125°. For example, for a needle angle within the aforementioned range and a flow rate under 6 mL min⁻¹, the marble deformation was observed to be within 15%. A possible reason for this phenomenon could be the competition between the surface tension and the dynamic pressure in the internal flow. Our results suggest that future perfusion experiments should be performed at low flow rates, within a certain permissible range of needle angles between the inlets and the outlets to ensure enhanced marble performance.

In summary, we studied the behaviour and properties of liquid marbles upon liquid exchange via external inflow and outflow. We also explored the operational limits during liquid addition, removal and constant perfusion. Our observations include the stabilization effect of swirl flow during liquid addition, the effects of penetrating needles on the buckling behavior of marbles during liquid removal, and the morphological change during controlled perfusion processes with various flow rates as well as in/outlets arrangement. These observations will provide basic operating principles for future use of liquid marbles in a variety of chemical and biological applications.

References