Spreading, encapsulation and transition to arrested shapes during drop impact onto hydrophobic powders

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**Graphical Abstract**

Arrested shape formed during the impact of a 2 mm water droplet onto hydrophobic 25 μm particles.

**Abstract**

We present findings from an experimental study of the impact of liquid droplets onto powder surfaces, where the particulates are hydrophobic. We vary both the size of the drop and impact speed coupled with the size range of the powder in order to assess the critical conditions for the formation of liquid marbles, where the drop becomes completely encapsulated by the powder, and arrested shapes where the drop cannot regain its spherical shape.

By using different hydrophobization agents we find that a lower particle mobility may aid in promoting liquid marble formation at lower impact kinetic energies. From observations of the arrested shape formations, we propose that simple surface tensions may be inadequate to describe deformation dynamics in liquid marbles.

**1. Introduction**

Superhydrophobicity has been an exciting topic of research for many years and many different techniques, typically incorporating both micro-texturing and vapor deposition, have been developed in order to render surfaces in such a state [1,2]. When water comes into contact with such a surface, it will exhibit a high contact angle and low degree of hysteresis. In particular, Water droplets resting on hydrophobic textured surfaces are typically in the Cassie–Baxter state [3] meaning that the bottom surface of the droplet is supported only by the tops of the surface asperities (pillars). This ultra-low contact area yields a very low-friction state whereby droplets can roll easily across a surface.

A liquid marble, which is a liquid droplet encapsulated with solid particulate matter [4–7] essentially mimics this principle, whereby the marbles can roll and be transported in a very low-friction state [8–10]. In essence liquid marbles create a Cassie–Baxter state by having “pillars” (i.e. particles) embedded across the entire free-surface of the droplet.

Given their mobility and robustness, liquid marbles have been studied and tested for a variety of potential applications, such as...
for gas sensing [11], synthesis of compounds/composites [13], blood typing and cell culture [12], and miniature chemical and biological reactors [10].

The mechanisms and conditions for liquid marble formation have been investigated previously [14–18] with the aim of quantifying the dependence on various parameters such as surface tension, viscosity, and droplet kinetic energy. Post-production, various phenomena such as evaporation [17], condensation [19] and freezing [20] have been observed. In all of these studies, the key parameters studied are shape and size of the individual particles encapsulating the liquid droplets.

More generally, liquid marbles are a specific class of particle-laden interfaces, where solid particles lie at an interface [22] and induce interfacial mechanical properties beyond a simple surface tension [23]. In particular, particle-laden interfaces exhibit visco-elasticity and diminishing surface tension as they transition to a jammed state [25–28] and can form aggregates or “rafts” [24]. To date, only two studies [29,30] have reported jammed interfaces during liquid marble formations, which provides significant motivation for the present study; Given that liquid marbles are designed to be low friction transportable micro-reservoirs, their shape and mobility are key properties and understanding the transition towards a jammed interface is paramount.

In the context of liquid marble formation, cratering [31,32,21,33–35] could be an important consideration as the compliance of the powder bed will influence the spreading dynamics and ultimately, the final coverage of powder on the surface of the drop.

The spreading stage of a droplet during impact is typically quantified by the maximum spread, \( D_{\text{max}} \) (e.g. [36–42]), often scaled in terms of initial drop diameter, \( D_0 \), and impact Weber number, \( \text{We} = \rho D_0 V^2/\sigma \). For the inviscid case, two primary scaling laws have been proposed: Firstly, where the kinetic energy at impact is completely transferred to surface energy at maximum deformation, whereby it can be derived that \( D_{\text{max}}/D_0 \sim \text{We}^{1/2} \) [36]. Secondly, when considering that the impact itself induces an acceleration term \( V^2/D_0 \) and assuming a roughly cylindrical shape at maximum deformation, applying volume conservation leads to the scaling \( D_{\text{max}}/D_0 \sim \text{We}^{1/3} \) [37].

For powders, where the target surface can be deformed, the compliance of the powder bed has been incorporated through the bulk density, \( \rho_{\text{p}} \), of the bed to render the scaling law \( D_{\text{max}}/D_0 \sim V^2 \rho_{\text{p}}^{1/4} \) [33,34], where \( D_{\text{c}} \) is the crater diameter (equivalent to the maximum spread diameter). For low viscosity and low surface tension drops it was found [21,43] that the maximum spread \( D_{\text{max}}/D_0 \) scaled as \( \text{We}^{1/5} \) onto dry, wettable powders for \( \text{We} \approx 10–100 \), which decreased to \( \text{We}^{1/10–1/5} \) for pre-wetted powders, but for hydrophobic powders, the scaling \( \text{We}^{2/5} \) was observed [29] for \( \text{We} \approx 30–100 \). A summary of these observed scaling laws is presented in Table 1. Thus from previous theoretical arguments and empirical observations, the normalized maximum spread during impact onto hydrophobic powder beds should be described by the Weber number raised to some exponent \( x = 0.2–0.5 \). However, there is no widely accepted scaling law for the impact of liquid drops onto loose, hydrophobic powder surfaces. This is an important aspect as it is pertinent to the formation of liquid marbles. As such, one focal area in this work was to conduct an experimental campaign to provide empirical evidence for a scaling law.

To achieve this, we have complemented, and extended, previous works by performing liquid marble formation experiments across a broad range of parameters, including the contact angle, \( \theta \), between the droplet and the particles, particle diameter, \( d_p \), initial droplet diameter, \( D_0 \), and impact speed, \( V_0 \). We have also examined grain mobility on the liquid droplet surface, which in turn affects the encapsulation of the liquid droplet with the particles. In doing so, we have expounded upon the threshold conditions for the formation of fully covered (spherical) and deformed (non-spherical) liquid marbles, originally reported in [29,30].

### 2. Materials and methods

The experimental setup, shown schematically in Fig. 1, consists of a small container filled with fine glass beads. We release a drop of pure water from heights \( h \approx 7.5 \text{ cm} \) up to 40 cm using hydrophobic glass capillaries to achieve highly repeatable droplet sizes, \( D_0 = 0.8–3 \text{ mm} \). The falling drops thus impact vertically with speed \( V_0 \approx \sqrt{2gh} \), which varies from 0.61 to 2.6 m/s in our case. The impact, spreading and rebound of the impinging droplets are all captured in a single video sequence using a high-speed video camera (Phantom V711, Vision Research Inc.) equipped with a Nikon 60 mm micro-lens, which yielded a range of effective pixel sizes of 29–41 μm/pixel. Frames rates of up to 10,000 fps were used.

#### 2.1. Powder preparation and properties

The primary particles used in this study were glass beads (Potters Industries Inc.), with a total particle diameter range of \( d_p = 25–500 \mu\text{m} \). A summary of the powder properties is given in Table 2. The untreated glass beads exhibit a contact angle of approximately 60° (e.g. [44,45]). As such, the glass beads were subject to hydrophobization using commercial agents – namely – Glaco mirror coat ‘zero’ (Soft 99 Co.) and Ultra every dry (UltraTech International Inc.). The former is an alcohol-based suspension of silica nanoparticles, which form micron and sub-micron sized roughness elements when heat-cured [29]. The Ultra ever dry is a two layer
coating. The bottom layer binds to the surface where the coating is applied, and another layer binds to the base layer and has an exposed layer that displays superhydrophobicity and oleophobicity, due to the formation of nano-pillar structures. To prepare the beads, we first wash them by immersing in a water–ethanol mixture and placing in an ultrasonic cleaner for at least 15 min. The beads are then immersed in the hydrophobizing agent and sonicated again for a further 15 min before drying for several hours on a hot plate.

Particle sizing was performed on an API Aerosizer (TSI Inc.), where the particle diameter is calculated based on the time of flight of the particles. The particle size distributions allowed us to extract the mean size, $d_{50}$, as well as corresponding upper and lower percentiles $d_{10}$ and $d_{90}$. The particle shape was characterized by a circularity parameter based on two-dimensional projections using microscopy imaging, and subsequent image analysis, an example of which is shown in Fig. 2. The expression for circularity is given by $C = 4A/P^2$, where $A$ is the projected area and $P$ is the perimeter of the glass beads. In all cases we found $C > 0.9$, indicating a high degree of sphericity.

The contact angle was measured using the sessile drop method, which was critically evaluated previously by [46]. The glass beads were firmly attached to a microscope slide using double-sided adhesive tape. A water droplet is then gently placed over the glass slide. Using a Nikon D90 camera equipped with a microscope objective, the apparent contact angle between the water droplet and the beads attached on the glass-slide can be estimated, as shown in images in Fig. 3. The contact angle of a water droplet placed on the adhesive tape is $57^\circ$, which increased to between $96^\circ$ and $150^\circ$ when the hydrophobized glass beads were attached. The full range of contact angles is shown in Table 2.

### 2.2. Dimensionless groups for drop impact

The main dimensionless parameter used to characterize the impact is the Weber number, $We = \rho D_0 V_0^2 / \sigma$, whilst the deformation due to gravity can be expressed by the Bond number, $Bo = \rho g D_0^2 / \sigma$ and the role of viscosity can be evaluated by the Ohnesorge number, $Oh = \mu / \sqrt{\rho \sigma D_0}$. Note that the largest drop size of approximately 3 mm exceeds the capillary length for water, $\sqrt{\sigma/\rho g} = 2.7$ mm, however, given that all Bond numbers herein are $Bo = O(0.1) - O(1)$, and that $We > O(1)$, we assume the impact dynamics to be inertia dominated and thus we neglect gravitational deformation. Furthermore, in the absence of viscous forces, the shapes during impact are determined by the competition between inertia and surface tension, i.e. the Weber number. Therefore, we expect a priori that impact kinetic energy plays a dominant role in the formation of liquid marbles.

Previously it was shown [18] that the impinging droplet survives impact without shattering onto the powder bed if $We < 1000$ and $Oh > 0.05$. For our experiments, we used pure water with $\mu \approx 0.001$ Pa s, whereby $Oh < 0.05$ for all cases as indicated in Table 3. In this regime, the droplets survived impact only for $We < 100$. This critical weber number holds for the range of the liquid droplet diameters in our experiment for (a) $D_0 \approx 1$ mm, (b) $D_0 = 2$ mm and (c) $D_0 = 3$ mm. The role of the packing fraction of...
the bed on droplet shattering has already been investigated by [21]. However the effect of other key factors on droplet splashing like the nature of coating of the glass beads and the ratio $D_b/d_p$ has yet to be studied.

As shown in Table 3, for $D_b \approx 1$ mm the value of Bond number is around 0.13 which would imply a spherical shape. Still in some cases, as shown herein we found that the shape of the liquid marble formed is not spherical. This naturally poses the question: what determines the final shape of the liquid marble formed if not the Bond number (i.e. surface tension) of the impinging liquid droplets?

3. Results

3.1. Overview of impact dynamics

Figs. 4 and 5 show images from high-speed video sequences of the impact of water droplets of diameters $D_0 \approx 1, 2$ and 3 mm onto powder beds of hydrophobic glass beads with $d_p = 25 \mu m$ for a range of impact Weber numbers and Bond numbers (see captions for details). In Fig. 4, the droplets are fully encapsulated and all regain their spherical shape after the initial impact with the powder bed, i.e. they form liquid marbles. In contrast, Fig. 5 shows the same size droplets impacting at higher speed whereby the surface of the droplets become jammed with particles and do not regain a spherical shape. This observation of deformed marbles was first reported by [29,30] and it is precisely this stark difference in the resulting form of the liquid marble that is a key motivation for this study. As such, we have discussed the impact dynamics and different observed features pertaining to liquid marble formation in detail in the next subsections.

3.2. Maximum spread

Fig. 4 provides example images of droplets at their maximum spread (see image 3, image 2 and image 2 in Fig. 4a, b and c, respectively). The maximum spread provides us with a single quantitative measure of the impact dynamics which, as per previous arguments [36,37], should be reconciled with the impact Weber number via an appropriate scaling law. As such, in Fig. 6, we have presented the full results of the maximum spread determined by high-speed video observations. Given that each data point is the average of several repeat trials, this data incorporates over 1100 experimental trials. Across nearly three orders of magnitude in the Weber number, we find that the single-valued exponent which best describes the entire data range is approximately 0.32, i.e. $D_{max}/D_0 \sim We^{0.32}$, represented by the red line. Noting that this data comprises droplet diameters of 1, 2 and 3 mm and a large range of particle diameters, this single scaling is remarkably universal.

We now consider an energy-based argument to describe the spreading and compare this to our empirical scaling law. An expression for the maximum spread in the inviscid case can be found by simply balancing the surface and kinetic energies of the drop both prior to the impact and at the time of maximum spread. Since the contact angle of the impinging drop with the powder bed is generally high, we make the overly simplistic assumption of negligible contact between the particle bed and the drop, thereby assuming that surface tension acts on both the top side and underside of the drop and around the periphery. Note also that several authors have determined surface tensions of particle-laden interfaces to be very similar to that of the pure liquid [47–49], so that this assumption appears justified. As a first approximation we neglect the influence of the compliance of the powder bed. Finally, we approximate the shape of the maximally deformed droplet as a cylinder, where the height, $h$, can be found by volume conservation as $h = \frac{\pi D_0^2}{12 q_{max}}$. We can thus write the balance of surface and kinetic energies as:

$$\frac{1}{12} \pi D_0^2 \mu V_0^2 + \pi D_0^2 \sigma = \left(\frac{1}{2} \pi D_{max}^2 + \pi D_{max} h\right) \sigma$$

Which, upon substitution for $h$ and some rearranging, yields the following equation for the normalized maximum spread:

$$\left(\frac{D_{max}}{D_0}\right)^3 - 2 + \frac{We}{6} \left(\frac{D_{max}}{D_0}\right)^4 + \frac{4}{3} = 0$$

Solving Eq. (2), we thus find the maximum spread scales as $D_{max}/D_0 \sim We^{1.3}$ for low Weber numbers with $We \lesssim 10$. In the high Weber number limit, neglecting the constant term, we find the trivial solution $D_{max}/D_0 = \sqrt{2} + (We/6)$, i.e. we recover the $We^{1/2}$ scaling for high Weber numbers ($We \gtrsim 100$). This high-Weber number approximation simply recovers the original $We^{1/2}$ scaling by [36] in the limit of negligible surface energy prior to impact.

The data in Fig. 6 with the power-law exponent of 0.32 certainly gives support to our simple energy-based model for the low-Weber number regime ($We < 100$) but does not follow the model in the high-Weber number range ($We > 100$). We attribute this to two principal causes – namely – bed compliance [33–35] and kinetic energy. Examining the data sets for 1 mm, 2 mm and 3 mm droplets independently, we find a slightly weaker dependence on the Weber number for larger droplets, which may be partly explained by the larger energy dissipation through crater formation, i.e. the larger the impact kinetic energy, the larger the crater that will be formed. Thus the initial assumptions in the energy balance, where all other forms of dissipation, including crater formation are neglected, are only likely to hold for smaller droplets, i.e. low Weber numbers, where indeed the best agreement is found.

Since our data in Fig. 6 covers the full range of particle properties shown in Table 2, we conclude that if the powder is hydrophobic, i.e. contact angle $\theta > 90^\circ$, the maximum spread is independent of both particle size and contact angle.

3.3. Marble formation

Criteria for complete marble formation have been reported previously [14,18], where it was found that the principal prerequisite for complete particle coverage on the original droplet is that the ratio of droplet-to-particle diameter, $D_0/d_p$, must exceed a threshold of 25. However, our findings of liquid marble formation, summarized in Table 4, indicate that liquid marbles can be formed with ratios as low as 6.8, i.e. $D_0/d_p \geq 6.8$. The total size ratio tested herein was from $D_0/d_p = 2$ to 120. We highlight the fact that different hydrophobization techniques and particle size distributions could lead to differences in contact angle and particle mobility, which may be the cause of the discrepancy in terms of the critical ratio $D_0/d_p$ between our study and those of [14,18].

Fig. 7 plots the maximum spread diameter against the impact speed for water droplets of diameter 1 mm, 2 mm and 3 mm, respectively. As shown in Fig. 7, monotonic increase in maximum spread with impact speed is observed until the onset of splashing with the ejecta being lifted off the surface (e.g. Fig. 5b and c). The different symbols in the Fig. 7 correspond to different observed features: (Squares) not fully encapsulated, (Circles) Full and mobile spherical liquid marble, (Diamonds) frozen marble. In light of these three different states, we now elucidate to the factors which control the particle encapsulation over the liquid droplet.

Whilst the kinetic energy has previously been given significant attention [14], we infer that this effect is more neatly summarized by the relationship between the maximum spread and impact Weber number, noting that the Weber number can be thought of
as the balance between impact kinetic energy, $KE \sim \rho D_0^2 V_0^2$, and surface energy $SE \sim D_0^2 \sigma$. As such, with this influence being evident from the data in Fig. 7, we now proceed to evaluate factors specific to the particle which may influence the formation of liquid marbles and arrested shapes. In particular, particle mobility on the surface of the droplets.

3.4. Particle mobility

One key factor in determining whether liquid marbles can be formed with such low size ratios is particle aggregation on the surface. An example of this is shown in Fig. 8(a) where we observe that particles form aggregates or “rafts” [24]. This particular fea-
ture itself is a manifestation of the hydrophobization, evident upon comparison of Fig. 8(a) and (b) both for the same particle diameter. In Fig. 8(a), the particles were hydrophobized with Ultra Ever dry and we observe the formation of particle rafts, which essentially stabilize networks of particles against gravity, with patches of free-surface still visible. Such particle rafts are known to induce elasticity and, furthermore, interfacial rheology [22,23,50]. By contrast, in Fig. 8(b) the particles were coated with Glaco MCZ and we do not observe the formation of such rafts, rather the particles appear to move independently of each other and settle under gravity around the periphery of the drop. Thus the particles coated with Glaco MCZ, exhibit a higher apparent mobility on the surface, meaning that particles will move more freely over the free surface, as seen in Fig. 8(b).

To extend the raw observations of raft formation, we plot the formation of liquid marbles for these two coatings for both 2 and 3 mm droplets most clearly manifested in the $D_{\text{max}}$ vs. $V_0$ parameter space, shown in Fig. 9. The particles coated with Ultra every dry form complete liquid marbles at impact speeds of approximately 0.9 m/s for both 2 and 3 mm droplets, whereas those coated with Glaco MCZ do not form marbles until impact speeds of approximately 1.35 and 1.85 m/s for 3 mm and 2 mm drops respectively. The fact that liquid marbles form at lower speeds for one particular hydrophobization treatment is therefore due to the aggregation of particles into elastic rafts. We postulate that this is due to micro-scale interactions between the surface structures formed during the hydrophobization, but this is yet to be conclusively determined. Note that the contact angle measured with the sessile drop method is lower for the Ultra ever dry coating which, following previous observations [51], should lead to increased propensity for raft formation. Therefore, cohesive forces between particles due to the specific treatment could be a significant factor in deter-
mining individual particle mobility, the mesostructure of the interface, and ultimately whether a liquid marble will form or not.

To further quantify particle mobility, we tracked individual grains located at the interface of the partially coated droplets. An example image sequence highlighting this tracking process is shown in Fig. 10(a) and the corresponding digitized particle locations are shown in Fig. 10(b). Whilst the drop is still undergoing small oscillations, the drop shape in Fig. 10(b) is represented as a perfect sphere for ease of display.

By performing such tracking for different droplet diameters and calculating the displacement frame by frame, the derived average velocities of the beads around the droplets were 13.7 μm/s for \( D_0 = 3 \) mm, 23.4 μm/s for \( D_0 = 2 \) mm, and a maximum of about 37.5 μm/s for \( D_0 = 1 \) mm. We can rationalize these increasing velocities simply with the ratio \( D_0/d_p \). The larger the drop, the lower the curvature and the more planar-like the surface becomes. A higher curvature (i.e. smaller drop diameter) renders particles relatively more mobile. To our knowledge, the only study to date examining the effect of liquid interfacial curvature on particle contact angles is that in [52], where it was found that higher curvature resulted in lower receding contact angles whilst the advancing...
angle was unaffected. Thus, based on a higher contact angle hysteresis, this would imply that higher curvature results in a lower degree of mobility, which would therefore seem at odds with our observations. We note, however, that the sign of curvature relative to the particle could be a factor that has not been considered, see Fig. 11.

In our experiments, where we have a positive curvature (based on the convention shown in Fig. 11) we estimate the particle contact angle by examining images of particles at the interface, such as that shown in Fig. 12. Based on the protrusion length, $l = r_p(1 - \cos \theta)$, we find $\theta \approx 120^\circ$, in reasonable quantitative agreement with the contact angle measurements using the sessile drop method. We have not observed or measured the advancing or receding (i.e. dynamic) contact angles for these particles and while study of dynamic contact angles of hydrophobic particles moving across the droplet surface would certainly complement our work herein and [52], it is considered beyond the scope of the present study.

3.5. Transition to a jammed interface

Prior observations of “frozen” droplet shapes upon rebound from a hydrophobic powder surface [29,30] found a critical impact speed $V_0 \approx 1.6$ m/s for $D_0 \approx 2$ mm. Herein, we have also observed a critical impact speed above which the droplets do not regain a spherical shape. As evident from the data in Fig. 7, the critical impact speed is dependent primarily on the drop diameter and does not exhibit any quantifiable dependence on the particle size. For our experiments, we find critical impact speeds of $V_0 \approx 2.1$, 1.5 and 1.3 m/s for drop diameters of $D_0 = 1$, 2 and 3 mm, respectively. This means that we can describe the transition to a jammed interface in terms of a critical Weber number with $We^\approx 60–70$. One important factor to bear in mind when discussing the formation of jammed interfaces is the onset of splashing: The vertical dashed lines in these plots represent the threshold in terms of impact speed for the onset of the deformed marbles and splashing, respectively. These two thresholds largely coincide, which is not unexpected as the detachment of satellite drops leaves a smaller volume to encapsulate. Based on the total detached volume of all satellite drops, we estimate the surface area of the remaining vol-

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**Fig. 8.** Impact of 2.1 mm water droplets onto glass beads with mean diameter $d_p = 170$ µm coated with (a) Ultra ever dry and (b) Glaco MCZ. The impact speed in both cases is $V_0 = 0.94$ m/s with $We = 25$. Images in (a) are taken 10 ms apart, whilst in (b) images are taken at $t = 0, 10, 40, 55, 70, 115, 145$ and 200 ms from impact. The scale bars are 2 mm long.

**Fig. 9.** Plot of maximum spread versus impact speed, with arrows indicating the onset of complete marble formation for different hydrophobization agents (red = Glaco MCZ, black = Ultra ever dry). Square symbols indicate incomplete coverage, circles indicate formation of full liquid marbles and diamonds indicate arrested shapes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
If we further assume the total contact area of the drop during the spreading phase to be \( \pi D_{\text{max}}^2 / 4 \), we can then derive a critical condition \( D_{\text{max}} > 1.67D_0 \) to fully cover the droplet. Thus, with reference to Fig. 7, given that the maximum spread beyond the splashing threshold is typically \( D_{\text{max}} \geq 2D_0 - 3D_0 \), the drop attains more than enough powder to become fully encapsulated, thus increasing the propensity to yield a jammed interface. Precisely how much powder is required to yield a jammed interface for liquid marbles remains an open question, however, we assert that the liquid free surface must vanish entirely \([30]\), which is consistent with measurements of effective surface tensions \([49]\) for liquid marbles where the surface tension was observed to decrease as the surface coverage of particles increased.

\[
\frac{1}{r_1} > 0 \quad \frac{1}{r_2} < 0
\]

Fig. 11. Sign of curvature relative to particle.
3.6. The most deformed shapes

We end our analysis by examining the most deformed shapes, which were given by the smallest particle sizes used $d_p = 25 \mu m$. Fig. 13 presents the reader with three example sequences of jammed interfaces, which result in arrested shapes that are clearly far from a spherical equilibrium that would normally be observed under the influence of surface tension. What these shapes clearly demonstrate is that a simple interfacial (surface) tension is no longer adequate to describe the properties of the interface and that we should instead seek both mechanical and rheological properties \[22–24,50\] to characterize deformation of liquid marbles. Such work is currently underway and will be addressed in future publication. One final observation is that the arrested shapes result from higher impact speeds, leading to higher speeds of retraction from maximum spread in the horizontal direction and in the vertical axis upon rebound (e.g. image 3 in Fig. 13(a)). As such, it appears that the rate of change of surface coverage could influence the formation of arrested shapes.

4. Concluding remarks

We have conducted an experimental investigation of the spreading of water droplets and subsequent formation of liquid marbles during impact onto hydrophobic powder surfaces. Both the maximum spread and marble formation were subject to detailed analysis, with specific emphasis on the role of droplet-to-particle diameter ratio and resulting particle mobility.

We have shown that, in addition to impact kinetic energy of the droplet, the degree of cohesive forces between the particles as well as the droplet-to-particle diameter ratio both influence the marble formation in terms of minimum impact speed required to form a fully encapsulated marble and the transition towards a jammed interface or “deformed” marble.

We found that the maximum spread of the liquid droplets onto the powder bed is independent of the size of the particles and the degree of inter-particle cohesive force and can be described by the scaling law $D_{\text{max}}/D_0 \sim We^{0.32}$ with $We \in (1, 100)$ for $D_0 \approx 1–3 \text{ mm}$. This is in relatively good quantitative agreement with a 1/3 exponent found by a simple energy balance approach. However, for larger droplets, $D_0 \gtrsim 2 \text{ mm}$, a slightly weaker dependence was observed and is thought to be due to energy losses during to the crater formation, i.e. the compliance of the powder bed. We observed that droplets remained intact only for $We < 100$ and propose future studies to investigate the influence of packing fraction in this phenomena, as previously indicated \[21\] as well as the role of other key factors like the nature of coating of the glass beads which affects the inter-particle cohesive forces.

In addition we have observed the transition between different regimes in the liquid marble formation process – namely – (i) partial coverage, (ii) full encapsulation with spherical liquid marble, and (iii) frozen deformed shape across a broad range of parameters. We found that the transition to a deformed (arrested) shape is characterized by a critical impact speed, $V^*$, consistent with previous results \[29,30\], leading to a critical impact Weber number $We^* = 60–70$ and maximum spread $D_{\text{max}} < 2D_0$. We note that the arrested shapes occur during the retraction-rebound phase, which may imply that the rate of change of surface area and therefore surface coverage plays a dominant role in this phenomenon. Interfacial properties beyond a simple surface tension need to be explored for liquid marbles and are the subject of an ongoing investigation.

Acknowledgements

The authors would like to thank Eric Aston for useful discussion on this work, Erqiang Li for assistance with preliminary experiments, and Abhishek Kumar for measurement of contact angles.

Appendix A

In deriving Eq. (2), the following steps were taken. Starting from the original energy balance \(1\):

$$\frac{1}{12} \pi D_0^3 \rho V^2_0 + \pi D_0^2 \sigma = \left(\frac{1}{2} \pi D_{\text{max}}^2 + \pi D_{\text{max}} h\right) \sigma$$

we substitute in for $h = \frac{2D_{\text{max}}}{D_{\text{max}}}$ and divide by $\pi$ to give

$$\frac{1}{12} \pi D_0^3 \rho V^2_0 + \pi D_0^2 \sigma = \left(\frac{1}{2} \frac{2}{3} \pi D_{\text{max}}^3 + \frac{2}{3} \pi D_{\text{max}} \frac{2D_{\text{max}}}{D_{\text{max}}}\right) \sigma$$

Fig. 13. Arrested shapes formed during the impact of 2 mm water droplets with beds of hydrophobic 25 $\mu m$ particles.
\[
\frac{1}{12} D_0^2 q V_0 + D_0^2 \sigma - \frac{1}{2} D_{\text{max}}^2 \sigma + \frac{2}{3} \frac{D_0^3}{\alpha R} \sigma
\]

One final division by \( \frac{\alpha R}{D_{\text{max}}} \) renders Eq. (2).

References
