Properties of liquid marbles

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Liquid marbles are liquid drops made non-wetting by the use of a powder which coats them. Because of the absence of a contact line, quick motions without leak of small amounts of liquid are allowed, which can be of interest in microfluidic applications. After characterizing the static liquid marble, we focus on its properties: we study experimentally the viscous motion of liquid marbles. Then, we describe qualitatively possible ways for putting marbles into motion and quantify the robustness of this object.
I. INTRODUCTION

Liquid marbles are liquid drops coated with a hydrophobic powder [1]. This globule is observed to be in a non-wetting situation, and thus behaves as a micro-reservoir of liquid able to move quickly without any leak. This absence of contact with its substrate avoid contamination problems. In addition, the force needed to move these marbles is extremely small. This technique also allows to work with tiny quantities of liquid, and at low temperature, which permits to conserve biological samples.

Thus, these objects could be relevant in some microfluidic applications. We show here the conditions necessary for achieving liquid marbles; then, we study their static shape, and the laws of friction as they move on a solid substrate. Finally, we discuss how to manipulate these drops, and stress their relative robustness.

II. PRINCIPLES

Two water marbles are shown in Figure 1. Such objects are achieved by trying to mix a hydrophobic powder with water, or with a solution of water and glycerol. Because of their hydrophobicity, the grains cannot be mixed, and instead coat the surface of the drop. Similarly, a drop deposited at the top of a pile of hydrophobic grains runs down the pile, and gets coated during the descent. The grains can be natural substances such as soot or lycopodium grains, or artificial, as silica beads first treated using a fluorosilane (to make them hydrophobic). The size of the grain can be in the range 1-50 µm, much smaller than the drop size (typically millimetric).

Because of the grains, the marble adopts a pearl shape (figure 1a), which does not depend on the substrate. This marble is stable and does not evolve with time (except if it consists of a volatile liquid, in which case it evaporates).

Figure 1: Water marble on a solid (side view, left), or on a water pool (top view, right).
A water marble can even be transferred at the surface of a water pool on which it does not coalesce immediately (figure 1b). The drop can float for one minute (this lifetime is observed to depend on the liquid, but also on the way the drop is deposited on the bath, which is difficult to make in a reproducible way). It thus lasts much longer than a water drop on water (which can have a lifetime of about 0.3 second if surfactants are present) [8]. When the coalescence occurs, a small drop is often ejected, following a mechanism observed by Thorodsen [9]. If the marble is deposited on a pool of liquid in which the powder penetrates (as oil or alcohol), the destruction of the drop is immediate. This property can be used to destroy a liquid marble after its transportation.

A liquid marble can be manipulated with a solid without being destroyed and without sticking to it. There again, its “skin” allows it to resist shocks, and a marble impacting another one (at a reasonable speed) will deform during the shock, but not coalesce nor explode (Figure 2).

![Figure 2: Projection of a liquid marble on another one. 4 ms separate each image.](image)

The robustness of these objects can be exploited to vary their size. A millimetric marble can be divided in two smaller marbles by “cutting” it with a solid stick (or even with a finger) (figure 3). This operation cannot be achieved twice: as we increase the total surface at each separation, there is not enough powder to coat properly the drops and they spread on the solid.

![Figure 3: Division of a millimetric water marble. 4 ms separate each image.](image)
Looking at the marble surface with a microscope (Figure 4) reveals that the grains form less than one monolayer, with empty areas larger than the grain size. This is why these objects can be manipulated or divided, which imposes a dilution of the grains at the surface, without being destroyed.

![Figure 4: Surface of a liquid marble coated with lycopodium grains (of typical size 30 µm), as seen with a microscope (1 division = 5.6 µm).](image)

We can be more precise. If we deposit a hydrophobic powder on a plane water/air interface, each grain can find a position of equilibrium at the interface. The size of the grain being much smaller than the millimetric capillary length, gravity is dominated by capillary forces. We denote the contact angle between the grain and the liquid as $\theta_e$ (by definition, a material is hydrophobic if $\theta_e > 90^\circ$). We can evaluate the surface energy $\Delta E$ of the liquid/grain system at equilibrium, and compare it to the one of a grain tangent to the liquid surface (Figure 5), or fully immersed in the liquid. We consider the grain smooth and spherical, and denote the radius as $R$. $\Delta E$ can be calculated by using classical geometric relations together with Young’s relation $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_e$, which links the three surface tensions $\gamma_{SV}$, $\gamma_{SL}$ and $\gamma_{LV}$ (indices refer to solid, liquid and vapor) with the contact angle. We shall write simpler $\gamma_{LV} = \gamma$. In the first case (grain coming from the air), we find $\Delta E_1 = -\pi R^2 \gamma (1+\cos \theta_e)^2$, while we get in the second one (grain coming out of the liquid): $\Delta E_2 = -\pi R^2 \gamma (1-\cos \theta_e)^2$. In both cases, a particles lowers its energy by sticking to the interface whatever the contact angle, and the energy difference $\Delta E$ is all the larger since $\theta_e$ is large.

![Figure 5: Spherical hydrophobic grain deposited at a liquid/air interface, and finding its equilibrium position.](image)

In addition, using hydrophobic grains will maximise the distance between the liquid/vapor interface and the substrate, when depositing the marble on a solid (Figure 6). Note that the liquid/vapour interfaces are drawn planar, the grain being much smaller than the drop size.
We used two kinds of grains. The first ones were lycopodium grains treated with fluoro-decyl-trichlorosilane. The grains measure about 30 µm and are naturally textured (by micrometric cavities). These textures enhance the chemical hydrophobicity, and water contact angle measured on these beads stuck on a solid surface was found to be around 160 to 165°. The second powder was a silica powder (SiO$_2$), with a characteristic size of grain about 10 nm, yet likely to make clusters of micrometric size. There again, the grains were treated with dichloro-diméthyl-silane (SiCl$_2$(CH$_3$)$_2$) to make them hydrophobic. This key property is effective provided that liquids with high surface tension as polar liquids are used. We chose to work with mixtures of water and glycerol. Glycerol (1,2,3-pentan-3-ol) has properties close to the water ones (surface tension $\gamma = 63$ mN/m at 20°C and density $\rho = 1260$ kg/m$^3$; for water, $\gamma = 72$ mN/m and $\rho = 1000$ kg/m$^3$ at 20°C), but has a much higher viscosity ($\eta = 1200$ mPa s instead of 1 mPa s). Mixtures of water and glycerol are then particularly interesting to observe and quantify viscous effects. Small droplets are quasi-spherical, and we denote their radius as $R_0$. More generally, whatever the drop volume $\Omega$, we shall express our results as a function of $R_0$, the spherical drop of radius $R_0 = (3\Omega/4\pi)^{1/3}$.

III. STATICS

A. Static shapes of liquid marbles

Even if the internal liquid phase of a liquid marble does not contact its substrate, the solid presence influences the shape of the drop. These marbles are soft, and thus able to deform to minimise their potential energy. We define as a “contact” zone, the disk of radius $\ell$ parallel to the substrate. As first shown by Mahadevan-Pomeau [3], this zone does not restrict to a point, due to the drop weight: the drop tends to lower its center of gravity, which forces a contact. Of course, surface tension opposes the formation of this zone, which increases the drop area. The Bond number ($B_0 = \rho g R_0^2/\gamma$) compares the effects of gravity and surface tension. For $B_0 \ll 1$, which corresponds to $R_0 \ll \kappa^{-1}$ ($\kappa^{-1} = \sqrt{\gamma/\rho g}$ is the so-called capillary length), gravity is negligible and the drop looks like a sphere. Above the capillary length, the gravity predominates and the drop becomes a “puddle”. The capillary length is typically about 2.5 mm for our systems.
1. **Puddles** ($R_0 \gg \kappa^{-1}$)

If we deposit a large quantity of liquid on a surface in a non-wetting situation, it forms a puddle of constant thickness $h$. The surface tension acts on the upper and lower surfaces to reduce the puddle surface area, which yields as a total force (per unit length) $2\gamma$. This force is balanced by the gravitational pressure integrated over the thickness $h$, namely $\rho gh^2/2$. We thus find for the puddle thickness (in this non-wetting regime):

$$h = 2\kappa^{-1}$$

This formula is independent of the drop volume. Using the volume conservation ($\pi\ell^2 h \approx 4\pi R_0^3/3$), we deduce the size of the contact zone:

$$\ell \approx \sqrt[3]{\frac{2}{3}} R_0^{3/2} \kappa^{-1/2} \quad (1)$$

2. **Droplets** ($R_0 <\kappa^{-1}$)

A small drop is quasi-spherical, except at its basis where it is deformed by gravity, on a disk of radius $\ell$ (Figure 7).

![Figure 7: Sketch of a small non-wetting drop, below the capillary length.](image)

The pressure inside the drop is given by the Laplace law:

$$P = P_0 + \frac{2\gamma}{R_0}$$

where $P_0$ is the atmospheric pressure. The contact zone is planar, and crossing that interface must induce an overpressure $\Delta P = 2\gamma/R_0$. There is indeed an hydrostatic pressure acting at this point, on a zone of surface area $\pi\ell^2$. We deduce a formula for the equilibrium of the drop:

$$\Delta P \pi \ell^2 \approx \frac{4\pi}{3} \rho g R_0^3$$
from which we get as a radius for the contact zone:

$$\ell \approx \sqrt[3]{2} R_0^2 \kappa$$  \hspace{1cm} (2)

This law was first proposed by Mahadevan and Pomeau [3]. It shows that the contact radius increases as $R_0^2$, much quicker than for a drop in partial wetting, in which case the contact (which is then a real solid/liquid) contact increases as $R_0 (\ell = R_0 \sin \theta_e$, where $\theta_e$ is the contact angle). Note that Eqs. 1 and 2 logically give the same expression for $R_0 = \kappa^{-1}$.

3. Numerical calculation

We can finally calculate the shape of a non-wetting drop, by integrating numerically the Laplace equation. The Laplace pressure at a point P (below the interface) as defined in Figure 8 can be expressed as:

$$\Delta P = \gamma \left( \frac{1}{\delta} + \frac{1}{PQ} \right) = -\gamma \left( \frac{da}{ds} + \frac{\sin \alpha}{x} \right)$$\hspace{1cm} (3)

denoting $\delta$ as the radius of the meridian, and calculating the radius PQ along the normal ending on the axis in the case of an axisymmetric drop; $s$ is the curvilinear coordinate, and $\alpha$ is the angle between PQ and the axis of the drop.

![Figure 8: Shape of a drop in a non wetting situation: definition of the parameters.](image)

The hydrostatic pressure writes $P = P_0 - \rho g z$, where $P_0$ is the pressure inside the drop at $z = 0$ and depends on the volume of the drop. Balancing this pressure with the Laplace one, we get an equation for the drop profile:

$$\frac{da}{ds} \frac{\sin \alpha}{x} = 2a \frac{z}{a \kappa^2}$$\hspace{1cm} (4)

where $a = P_0 \gamma$ is the radius of curvature at the top of the drop (point O), which depends on the volume of the drop. Note also that we have $dv/ds = \cos \alpha$ and $dz/ds = \sin \alpha$. 

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The integration from the point O with the variable $\alpha$ gives the profiles of the Figure 9.

Figure 9: Numerical (half) profile of a non-wetting drop, for $R_0 = 0.5, 1, 2.4, 4.8$ and $8.8$ mm, and $\kappa^{-1} = 3$ mm.

From the numerical shapes, we measured the size of the contact zone and the height of the drop. As suggested by equations 1 and 2, we plot in Figure 10 these quantities as a function of the radius of the drop $R_0$, after normalizing all the lengths by the capillary length $\kappa^{-1}$.

Figure 10: Size of the contact zone and height of the drop as a function of the initial radius of the drop. Each length is normalised by the capillary length $\kappa^{-1}$. Points are deduced from the numerical integration of the Laplace equation, and the straight lines correspond to asymptotic behaviours described by Eqs 1 and 2.

The straight lines in Figure 10a (where the scales are logarithmic) successively indicate the slopes 2 and 1.5, with a numerical coefficient $(2/3)^{0.5} \sim 0.82$, as predicted by Eqs 1 and 2. The agreement is found to be excellent. We also report in Figure 10b the height of the drop as a function of its initial radius. As expected, we observe that the height tends towards $2 \kappa^{-1}$ for large volumes (puddles). Curiously, the thickest drop is not the largest puddle, but a drop of radius about $3.2 \kappa^{-1}$. This maximal thickness adopted by a drop in a non wetting situation is $2.1 \kappa^{-1}$. Note also that on the experimental point of view, the study of the drop height gives access to the surface tension – a non-trivial quantity for the liquid marbles where the interface consists of liquid and grains.
B. Measurements

Thanks to a microscope placed horizontally and displaced with micrometric screws, we measured the size of the contact zone and the height of various liquid marbles, as a function of the volume of the drop. We used two liquids (glycerol and water), two different substrates (glass and Teflon), and two kinds of powder (lycopodium and silica). The observed properties were found to be independent of the nature of both the substrate and the powder, as expected in a non-wetting situation.

The results are displayed in Figure 11. The observed height is compared with the numerical calculations, treating the capillary length as an adjustable parameter. An excellent agreement is observed, which yields for the surface tension of water and glycerol marbles with lycopodium: \( \gamma = 51 \text{ mN/m} \) and \( \gamma = 45 \text{ mN/m} \), respectively. The presence of lycopodium thus slightly affects the surface tension liquid/air of the system. For a drop of water coated with silica, the value of the surface tension stays the same as pure water (\( \gamma = 72 \text{ mN/m} \)).

![Figure 11: Height and size of the contact of liquid marbles, as a function of their radius before deposition. All the lengths are normalized by the capillary length. The dark symbols correspond to experiments with lycopodium, open symbols with silica; the triangles and circles are for water and glycerol on glass, and the stars for glycerol with lycopodium on Teflon. For the height, the full lines show the numerical calculation. For the size of contact, they represent Eqs 1 and 2, with a numerical coefficient of 0.9.](image)

It is observed in Figure 10b that the scaling laws for the size of the contact zone expected from Eqs 1 and 2 are indeed successively followed, which confirms the validity of the Mahadevan-Pomeau model. The fit with the data yields a numerical coefficient of 0.91, close to 0.82, the expected coefficient. The static description of the liquid marbles being completed, we now investigate their dynamics.
IV. VISCOUS MOTION OF LIQUID MARBLES

We report in this section a study on the mobility of viscous marbles running down inclines. We first study the case of puddles, before dealing with drops.

A) Viscous motion of puddles

1. Experimental results

Large puddles (all larger than the capillary length) are placed on substrates which are inclined by a small tilting angle (between 1 and $5^\circ$). Movies are taken from above, from which the descent velocity is measured. It is observed to reach quickly its asymptotic value $V_o$, which is reported in Figure 12 for various viscosities and drop sizes. The speed does not depend on the drop size, in this regime of puddles. On the other hand, it depends on the viscosity, and also on the tilt angle of the incline – it logically decreases as making the liquid more viscous, or the plane less inclined.

![Figure 12: Terminal speed of large viscous marbles ($\eta = 270, 450$ and $1150$ mPa s for the losanges, squares and triangles) running down planes inclined by $5^\circ$, or $1^\circ$ for $\eta = 270$ mPa s (open losanges).](image)

2. Analysis

The puddle thickness is independent of its volume when it is large enough (Figs 10b and 11a), and close to be $h = 2\kappa^{-1}$. Because of the very weak tilt angle $\alpha$, we can consider that the capillary length keeps its common value $(\gamma/\rho g)^{1/2}$, and we shall furthermore take as equal $\sin \alpha$, $\tan \alpha$ and $\alpha$. The driving force writes $\rho g \alpha$, and the viscous resistance $\eta V_o/\kappa^{-2}$ (inertia can be neglected in this limit of viscous puddles). Balancing these forces yields a velocity which (amusingly) does not depend on $g$:

$$V_o \approx \frac{\gamma \alpha}{\eta}$$

(5)
The numerical coefficient in this law is not so easy to predict. The velocity profile in the puddle can be calculated from integrating the Stokes equation, provided that we write two boundary conditions. The first one is a zero velocity for the liquid close to the substrate (we could refine by considering a slip on a grain size, but this does not affect the macroscopic law for the flow). The second boundary condition, which is written at the upper surface, is less clear. Because of the presence of the grains, this surface might behave in some intermediate fashion between a free surface and a solid surface. In the first case, we write a zero stress at the surface, while in the second one, the puddle behaves as a caterpillar with an upper surface going twice faster than the mean speed. We deduce a Poiseuille parabolic profile in the first case, and a linear Couette profile in the second one. The expression of the average speed of the puddle is easily deduced in both cases. It obeys the scaling behaviour of eq. 5, with a numerical coefficient of 4/3 or 1, considering a free or solid upper surface, respectively.

The boundary condition acting at the upper surface can be tested experimentally. We used drops of glycerol coated with lycopodium. The coating is relatively homogenous, close to a monolayer. The relative displacement of the grains is limited, and the motion of the drop should be close to the caterpillar one. If we follow the motion of a grain (used as a marker of the surface), it should spend the same time on the drop as below, and move (when visible) twice faster than the front of the drop. In Figure 13, we show top views of a large marble creeping on a plate inclined by xx°.

![Figure 13: Top view of large marbles of glycerol on a slightly inclined plane (a = xx°). The intervals between two lines (below the drop) are millimetric.](image)

We note that the puddle goes at a constant speed, and that it adopts an original shape, flattened at the rear. We report in Figure 14 the position $x$ of the front of the drop, together with the position of a grain, as a function of time. We also display the speed of different grains on the upper surface of the puddle as a function of the mean speed of the drop.
We observe that a grain placed at the top of the puddle moves about twice faster than the drop. Then, it disappears below the puddle (no data). The time the grain spends below the drop is found to be the same as the one spent at the top. In addition, the speed of the grain (measured when it is on the top surface) is observed to be slightly less than twice the average speed $V_0$ of the drop (we obtain $V_{\text{grain}} = 1.85 V_0$).

The value of this coefficient indicates an intermediate behaviour between a free surface (coefficient 1.5) and a caterpillar motion (coefficient 2). We suppose that the solid powder can move and rearrange to support a change of speed between the top and the bottom of the drop.

3. **Limits of the viscous puddle model**

Equation 5 shows that the speed $V_0$ of the viscous puddle varies as $\alpha \gamma/\eta$, with a numerical coefficient depending on the boundary condition at the top surface. To check this scaling law and its limits, we carried out a first series of experiments with pure glycerol and various angles of descent. The drop was made as large as possible (diameter between 1 and 2 centimeters), and the descent velocity was extracted from movies taken from above.

We report in Figure 15 the constant speed $V_0$ reached by the drop, and normalised by the quantity $\gamma/\eta$, as a function of the tilt angle $\alpha$. We observe a linear dependence, and deduce from the data a numerical coefficient of 1.5. The velocity is thus found to be slightly larger than expected (the numerical coefficient was supposed to be within the interval $[1, 4/3]$, which might be a finite size effect. (It is practically difficult to make coated puddles bigger than one centimetre of diameter.) Generally, the edges of the drop make it move slower (because of the special dissipation in such edges), but here the edges join the substrate with an angle of 180°, and the drop owns a rolling motion which can play a role in this observation.
Figure 15: Velocity of descent of a large glycerol puddle coated with lycopodium creeping down an incline (tilt angle $\alpha$), as a function of $\alpha$. The puddle velocity is normalized by the intrinsic velocity $\gamma/\eta$. A refaire en coordonnées normales. Arrêter la courbe à une valeur de $\alpha$ petite (entre 0.1 et 0.2) (comme actuellement).

This behaviour can be confirmed using mixtures of water and glycerol, which allows to vary the liquid viscosity. It is observed that deviations occur when the viscosity becomes smaller than typically 100 mPa s (then, the observed speed is found to be smaller than predicted by eq. 5). The model supposes a viscous dissipation in the whole thickness of the drop, which assumes a viscous boundary layer $\delta$ fully developed, i.e.:

$$\delta \sim \frac{\eta \ell}{\rho V_o \alpha > h}$$

where $\ell$ is the size of the zone of contact. The speed as $\alpha \gamma/\eta$ and $h$ as $2 \kappa^1$, which leads to the condition:

$$\eta^2 > \frac{\gamma^2}{\ell^2 \alpha}$$

For centimetric puddles and a slope of 5°, we find that the viscosity must be larger than about 50 mPa s, of the order of the viscosity below which deviations towards Eq. 5 were found.

An other possibility is that the air friction becomes predominant compares to viscous one. This condition can be written (ignoring numerical coefficients): $\rho_a V^2 \ell^2 > (\eta V/h)\ell^2$, where $\rho_a$ is the air density. On a plate tilted by 5°, the friction due to air should become dominant for liquid a viscosity smaller than about 5 mPa s, i.e. for liquids much less viscous than assumed in this section.
B) Viscous motion of small liquid marbles

Small, spherical liquid marbles placed on a slightly inclined plane follow a remarkable behaviour first discovered by Mahadevan and Pomeau [3]: the smaller the drop, the faster it runs. This property is particularly interesting practically, since it shows that these objects are all the more mobile since they are small, unlike usual droplets [1]. We describe more precisely this behaviour, and stress its natural limitations.

1. The Mahadevan-Pomeau regime

At a small Reynolds number, a viscous quasi-spherical drop adopts a solid-like rotation, in order to minimise the viscous friction. The viscous dissipation thus only takes place in the contact zone, whose size $\ell$ remains given by Eq. 2 if the velocity is not too large (that is, if the drop keeps a quasi-static shape). If the motion is stationary, the drop speed is determined by balancing the gain of gravitational energy by the viscous dissipation in the drop.

The energy dissipated per unit time by viscosity is $\eta \int_\Omega \left( \nabla \vec{u} \right)^2 d\Omega$, where the integral is calculated over the volume $\Omega$ (of the order of $\ell^3$) in which dissipation takes place. The velocity gradients in the contact zone are of order $V/R_0$, which yields a dissipated energy scaling as $\eta (V/R_0)^2 \ell^3$. Balancing this quantity with the gravitational energy gained by unit of time $mg\alpha$ yields the terminal velocity of the drop:

$$V \sim \frac{\rho g \alpha R_0^5}{\eta \ell^3}$$

If we assume in addition that the law for the contact remains given by its static expression (equation 2), we get:

$$V \sim V_o \frac{\kappa^{-1}}{R_o}$$

(6)

where $V_o$ is the puddle speed (given by equation 5). Both equations 5 and 6 should match for $R_o \sim \kappa^{-1}$, indicating that we expect a numerical coefficient of order unity in equation 6.

We report in Figure 16 the velocity of various viscous marbles running down inclines, as a function of the marble radius. The velocity is normalized by the puddle velocity $V_o$, and the radius by the capillary length $\kappa^{-1}$. The data are obtained using three viscosities (270, 450 and 1150 mPa s) and two slopes (4° and 8°). We observe that all the data collapse on the same curve, which is quite well fitted by Eq. 6 for small marbles ($R_o \ll \kappa^{-1}$). This suggests that the numerical coefficient in this equation is of order unity.
2. Limits of the Mahadevan-Pomeau regime

Viscous globules moving because of gravity generally follow a Stokes law, i.e. have a velocity which strongly increases with the globule size (as $R_o^2$). This is not the case of viscous non-wetting drops, for which the velocity increases (as $1/R_o$) as their size decreases, which is physically due to the quadratic dependence of the size of the contact zone with the drop radius (eq. 2). This remarkable behaviour is a signature of the Mahadevan-Pomeau regime, and we show here its limitations.

A first limitation concerns the liquid viscosity. Figure 17 shows that the speed of marbles of small viscosity ($\eta < 100$ mPa s) increases with their radius. For $\eta < 10$ mPa s, the law for the viscous puddle (eq. 5, dotted line in Figure 17) is not obeyed as well. Note in particular that the practically important case of water marbles ($\eta = 1$ mPa s) is concerned by these deviations.
A second limitation is the slope of the incline. Figure 18 shows the velocity of marbles (both puddles and drops) which are viscous (\(\eta = 1000\) mPa s), but run plates tilted by an angle larger than 10° (we display in the same graph the case of smaller tilting angles for a comparison).

![Figure 18: Terminal speed of glycerol marbles (\(\eta = 1000\) mPa s) normalised by the puddle speed as a function of the marble radius (normalised by the capillary length), for 4 tilting angles: 4° (circles), 8° (triangles), 14° (squares) and 24° (stars). Equation 5 (for \(R_0\kappa > 1\)) and equation 6 (for \(R_0\kappa < 1\)) are drawn in full line.](image)

For droplets (\(R_0\kappa < 1\)), the speed observed for the highest slopes (\(\alpha = 14\) and \(\alpha = 24°\)) are much larger (by a factor between 10 and 100) than expected from equation 6. Then, the terminal velocity is found to be of order 1 m/s, thus comparable with the terminal velocity of a drop falling in air (taking into account the fact that the gravity force is reduced by a factor \(\sin\alpha\) in our case). In addition, the drop is strongly deformed in these regimes, because of the centrifugation associated with the high rotational speed, and we reported in [1] the possible shapes of such rapid marbles, which resembles either a peanut or a doughnut (both shapes betray the existence of a strong centrifugation).

The Mahadevan-Pomeau regime concerns small spherical drops (\(R_0 < \kappa^{-1}\)). It assumes that most of the drop rotates as a solid body, because of a small Reynolds number:

\[
Re = \frac{\rho VR_0}{\eta} < 1
\]

Using eq. 6, we thus obtain a condition on both the viscosity and the tilting angle, which writes:

\[
\eta^2 > \rho\gamma\kappa^{-1}\alpha
\]  

(7)

For a slope of about 10°, this condition means that the liquid viscosity must be smaller than about 100 mPa s. For glycerol, it should be obeyed whatever the value of \(\alpha\) – while deviations were observed for \(\alpha > 10°\).

There are indeed other conditions to be satisfied. The Mahadevan-Pomeau regime assumes the drop
keeps its quasi-static shape, in spite of the motion. However, both inertia (centrifugation) and viscous forces are likely to deform the drop (and indeed dramatic modifications of the shapes were observed, as reported in [1]). Since surface tension tends to restore a spherical shape, the natural dimensionless number to be introduced are the Weber number, and the capillary number, both being assumed to be smaller than unity:

\[ \frac{\rho V^2 R}{\gamma} < 1 \quad \text{and} \quad \frac{\eta V}{\gamma} < 1 \]

Using condition 7, we thus obtain two lower limits for the drop radius. The condition on the capillary number appears to be the most restrictive, and we get as a final condition:

\[ R_0 > \alpha \kappa^{-1} \]  

(8)

This condition is easily satisfied for very small slopes ($\alpha$ close to zero), but is very restrictive as $\alpha$ becomes of order unity. Note that then, the gravity field itself must be corrected by a factor cos$\alpha$, which transforms this condition in: $R_0 > (\tan \alpha / \cos \alpha)^{1/2} \kappa^{-1}$. In Figure 18, it is observed that the velocity indeed deviates from the Mahadevan-Pomeau regime for drops smaller than some threshold $R^*$, as predicted by condition 8. Besides, the critical nature of the deviation allows a precise determination of $R^*$. This quantity is reported in Figure 19 as a function of $\tan \alpha / (\cos \alpha)^{1/2}$ (which reduces to $\alpha$ for $\alpha \ll 1$).

![Figure 19](image.png)

Figure 19: Radius of transition as a function of the slope for marbles of viscosity $\eta = 150, 300$ and $1150$ mPa s, corresponding to white, grey and black symbols. The line has a slope 2.3.

We indeed find that the radius at the transition $R^*$ is independent of the liquid viscosity, and varies linearly with small tilting angles (and for larger angles, as $(\tan \alpha / \cos \alpha)^{1/2}$), as expected from Eq. 8. The full line represents the slope 2.3. The fast regime observed for $R_0 < R^*$ remains to be understood, but we can stress that there again, marbles show a remarkable ability to be displaced very quickly, in spite of their small size (unlike usual droplets). We now qualitatively describe different ways to manipulate these objects.
V. MANIPULATIONS OF LIQUID MARBLES

A liquid marble is a micro-reservoir of liquid which can be conveniently manipulated. In the previous section, we performed the experiments using the gravity field as a driving force. Here we describe qualitatively how other fields can be used for driving the marbles. Then, we discuss the robustness of these objects.

A) Effects of fields

1. Electrostatic field

To check the possible effect of an electrostatic field, we approached a liquid marble with a stick of Teflon first charged by rubbing it on a fabric (Figure 20a).

![Figure 20: Water marble coated with lycopodium in an electrostatic field. The drop progresses between the substrate (here a metal plate) and a charged Teflon stick (in white, at the top of the photos). A detail of the shape of the drop close to the stick is shown in b. In c, the charged stick is displaced (to the right and then to the left), inducing a motion of the marble. There are respectively 6, 2 and 120 ms between each image, and the distance marble-stick is typically centimetric.](image)

When the charged cylinder approaches the liquid marble, we observe a motion with successive bouncing. Here, the drop is deposited on a metal plate, but the same phenomenon occurs whatever the substrate. During the motion, small droplets are ejected, (Figure 20b), as discussed by Taylor [10]-[12], who discussed the equilibrium shape of liquids submitted to an electric field. Placing a moving charged stick far enough from the drop, we can move the liquid marble without take off (Figure 20c).

We can imagine to use a controlled electric field to move the liquid marbles, as shown for water drops displaced on a hydrophobic substrate [13]-[14]. In these experiments, the authors reach a speed of about 0.4 mm/s with a field of 400 V in the first reference, and 1 cm/s with 124 V in the second one. Liquid marbles allows to reach larger speeds with smaller potential, and avoid the problems related to dust deposition, which eventually stops the classical drops [13]-[14].
2. **Magnetic field**

A magnetic field has no effect on a marble, but different tricks allow to induce such an effect. A first possibility consists in coating the drop with magnetic particles. In the first sequence of the Figure 21, the marble is coated by a mixture of an iron powder (made hydrophobic; diameter of each grain 4 µm) and lycopodium. If a magnet is approached, the drop takes off and sticks to the magnet.

![Figure 21: Water marble coated with a mixture of lycopodium and iron (a); water marble containing iron particles and coated with lycopodium (b). In both cases, a magnet is placed above the marble. 6 and 20 ms separate each image, respectively.](image)

We can also put the iron powder (not treated) inside the liquid, and coat it with lycopodium (second series in Figure 21). There again, the drop is attracted by the magnet. However, the sticking is short-lived: the iron particles are transferred to the magnet, so that the cleaned marble falls down (leaving a small cluster of iron grains). Note that the marble resists to the transfer and to the fall.

**B) Robustness**

We could see in different examples (such as reported in Figs. 2, 3, 20 and 21) that liquid marbles resist shocks and manipulation. We try here to describe more precisely the robustness of these objects. We performed two types of experiment. First, we observed what happens statically, when squeezing a marble in a press. Then, we looked at marbles impacting solid substrates.

1. **Squeezing marbles**

The experiment consists in placing a liquid marble between two transparent solid plates. Thanks to a micrometric screw, the upper plate can be moved with a precision of 10 µm. As we squeeze it, the drop adopts the shape of a non-wetting puddle of thickness $h$. For a thickness $h_{\text{min}}$, the envelope of the drop gets broken, and the liquid flows on the bottom plate. Figure 22 shows such a sequence, as seen from above through a microscope. Approaching the plates makes grow the contact zone, which appears as a disk more brilliant than the rest of the drop. The microscope is focused on the upper transparent solid plate and we can see the grains of lycopodium in contact with this plate.
The rupture (shown by an arrow in Figure 22) of the marble occurs on the edge of the drop. It corresponds to a zone where powder is lacking. The internal pressure at the rupture can be deduced from Figure 22: it writes \( \Delta P = \gamma \left( \frac{2}{h_{\text{min}}} + \frac{1}{R_{\text{max}}} \right) \), with \( R_{\text{max}} = \ell_{\text{max}} + h_{\text{min}}/2 \), and is typically 200 Pa.

We measured the minimum thickness \( h_{\text{min}} \) of the marble, as a function of its initial radius \( R_0 \), for different liquids (water or glycerol), powders (lycopodium or silica) or plates (plastic or Teflon). The rupture was found to be independent of all these parameters. When the drop is flattened, its surface area increases, keeping the powder coverage constant. In the edge, the ratio surface/volume is maximum, which makes this region more fragile: liquid contacts the solid in this region, which leads to the rupture of the marble. This explains why \( h_{\text{min}} \) does not depend on the surface properties of the press. Moreover, the characteristic size for the rupture zone is observed to be a fraction of a millimetre, large compared to the grain size, indicating why the powder characteristics do not influence the static robustness. We report in Figure 23 the maximal extension of the drop \( \xi = R_{\text{max}} - R_0 \), as a function of its initial radius.
The dashed line corresponds to the constant 0.38.

Within the experimental fluctuations, the maximum size of the drop does not depend on its initial size \( \frac{\xi}{R_0} \approx 0.38 \pm 0.15 \). This allows to evaluate the increase of surface area that a marble can endure: for an ellipsoidal final shape of major axis \( a \) and minor axis \( b \), and a small deformation (we note \( a = R_0 + \xi \), the surface area is given by \( S = 4\pi R_0^2 + (32\pi/5)\xi^2 \). This yields a relative increase of surface area \( \Delta S / S_0 \approx \left( \frac{8}{5} \right) \left( \frac{\xi}{R_0} \right)^2 \), which is about 25%. This explains why a drop could be shared once in two drops (see figure 3) (such a division makes the surface area increase by about 25%), but not twice.

2. **Impacting drops**

We let a liquid marble fall from a given height on a solid surface. Depending on the drop size, the liquid, the powder and the impact velocity, we observe that the drop can bounce or be stuck to the surface. We plotted in Figure 24 the coefficient of restitution (defined as the ratio between the velocity after the shock over the velocity before the shock), as a function of the impact speed for different coating powders (lycopodium or silica), drop radii (0.78 or 1.33 mm) and liquid viscosities (\( \eta = 1, 10, 78 \) and 220 mPa s).

![Restitution](image)

**Figure 24:** Coefficient of restitution of marbles impacting a solid, as a function of the impact speed \( V \), for \( R_0 = 1.33 \text{ mm} \), a lycopodium coating, and different viscosities: \( \eta = 1 \text{ mPa s} \) (black circles), \( \eta = 10 \text{ mPa s}, 78 \text{ mPa s} \) and 220 mPa s (triangles from white to black). For \( \eta = 1 \text{ mPa s} \), we also display the results for another drop size \( (R_0 = 0.78 \text{ mm}, \text{grey circles}) \) and another powder (silica, white circles).

In Figure 24, a zero restitution coefficient (no rebound) indicates that the marble ruptured during the impact. This occurs above a threshold velocity \( V^* \), below which the drop bounces. The shock is all the more elastic since the velocity is small, and we could not detect a sticking for very small impact velocity (unlike what can be observed with water drops bouncing on super-hydrophobic substrates). For water marbles (\( \eta = 1 \text{ mPa s} \)), the restitution coefficient seems independent of the drop size and of the powder coating it. On the other hand, the maximal speed of impact that a liquid marble can support without rupturing (that is, \( V^* \)) is sensitive to these parameters: the drop is more resistant if it
is small, or if the grains are large. For small viscosities (up to 10 mPa s) the curves superimpose. For large ones, the larger the viscosity, the less elastic the shock, and the more robust the marble. This defines an inertial regime, and a viscous one, respectively. Above 220 mPa s, the liquid marbles do not bounce, whatever the impact velocity.

These observations suggest that the dynamic robustness of the liquid marble is related to the spreading stage during the impact. The larger the drop viscosity, the larger the dissipation during the spreading-retraction phase, and the smaller the elasticity. Moreover, the maximal extension during the impact decreases with the size of the drops, small drops having a smaller kinetic energy than large ones. Then, and as suggested by the static experiments (previous section), we can assume that the marble robustness is related to the increase of surface during spreading. In our regime of small deformation, the bouncing can be seen as an oscillation of characteristic time $\tau$ [16]. At the maximum of the spreading, the drop takes the shape of an ellipsoid of major axis $a (a=Ro+\xi)$, and minor axis $b$. We consider that during the impact, the energy is dissipated by viscous friction close to the powder layer, on a boundary layer of thickness $\delta$ (assumed to be smaller than $Ro$). Hence we get:

$$E_{vis} \sim \eta \left( \frac{V^2}{\delta} \right) R_o^2 \delta \tau$$

The characteristic time of the shock is $\tau = \frac{\xi}{V}$, and the thickness $\delta$ of the boundary layer scales as $\sqrt{\eta \frac{\xi}{\rho V}}$, from which we get:

$$E_{vis} = \alpha \sqrt{\eta \rho R_o^4 \xi V^3}$$  \hspace{1cm} (9)

where $\alpha$ is a numerical coefficient. During the spreading, the kinetic energy $K$ of the drop is stored in surface energy and dissipated by the viscous friction. The energy balance can be written:

$$K + 4\pi R_o^2 \gamma = S + E_{vis}$$

with $S \approx 4\pi R_o^2 + (32\pi/5)\xi^2$. We thus obtain an equation for the maximum deformation $\xi$:

$$\left( \frac{\xi}{R_o} \right)^2 + \frac{\alpha}{12} \left( \frac{OhWe^3}{8} \right)^{1/4} \left( \frac{\xi}{R_o} \right)^{1/2} = \frac{5}{48} We$$  \hspace{1cm} (10)

where $We = \rho V^2 R_o^4 \gamma$ is the Weber number related to the shock, and $Oh$ is the Ohnesorge number (a characteristic of the drop):
\[ \text{Oh} = \left( \frac{\eta^2}{\rho R_0 \gamma} \right)^{1/2} \]  

(11)

We deduce:

\[ \frac{\xi}{R_0} = a \left( \frac{\text{We}}{2} \right)^{1/2} \text{ with } a^2 + \frac{\alpha}{12} \sqrt{\text{Oh} \alpha} = \frac{5}{24} \]  

(12)

For a millimetric glycerol drop, this number is typically around 5 and for water \(5 \times 10^{-3}\). The condition \(\delta \ll R_0\) assumed above can be rewritten \(a \text{Oh} \ll 1\), and thus should be easily fulfilled for liquids of low viscosity.

We deduce from Eq. 12 that the extension of the drop should vary as the square root of the Weber number, with a numerical coefficient depending on the properties of the drop. We can compare this scaling law with our data. The experiment consists in filming from below the impact of liquid marbles with a high speed camera (1000 images per second). We worked with a constant size \((R_0 = 1.33 \text{ mm})\), and we measured the maximum radius of spreading \(R_{\text{max}}\), from which we deduced the maximal extension \(\xi = R_{\text{max}} - R_0\). We report our results in Figure 25, by plotting this extension as a function of the Weber number for different viscosities \((\eta = 1, 9, 41 \text{ and } 220 \text{ mPa s})\).

![Figure 25: Maximal extension of impacting marbles (normalised by their radius), as a function of the Weber number for different viscosities \((\eta = 1, 9, 41 \text{ and } 220 \text{ mPa s})\) from the white squares to the black ones. The lines correspond to square root functions with different coefficients \(a\), which are plotted as a function of the Ohnesorge number. The line in the second figure corresponds to the resolution of the equation 12 with \(\alpha = 6.5\)].

We observe that the extension of the drop always remains smaller than the drop radius, and that we can fit the data by a power law 1/2, as expected from Eq. 12. The coefficient \(a\) in the law is indeed observed to depend on the liquid viscosity, especially for large \(\eta\). The value deduced from the fit can be plotted as a function of the Ohnesorge number (Figure 25b), and the data are in fair agreement with the values deduced from the resolution of Eq. 12, provided that we take \(\alpha = 6.5\) for the numerical coefficient.
3. Fatal jumps

We saw in Figure 24 that the restitution coefficient of a liquid marble impacting a solid could fall to zero, which corresponds to the destruction of the marble during the shock. We call fatal such a jump, which does not preserve the integrity of the object, and which transforms it in a common drop. Such a jump is observed above a given falling height (i.e. above a threshold in impact velocity), which can be easily measured. We report in Figure 26 the maximal extension of the drop during impact for an impact velocity just below the threshold (this extension is thus the maximum that a liquid marble can endure without breaking), as a function of the liquid viscosity.

![Figure 26: Maximal radius taken without breaking by a liquid marble of initial radius $R_0 = 1.33$ mm, as a function of its viscosity.](image)

The maximum value of the radius that a liquid marble of initial radius $R_0 = 1.33$ mm and coated with lycopodium can have is $R^* = 2.22$ mm, whatever its viscosity. This corresponds to a relative extension $\xi/R_0 = 0.67$. This value is constant, as for the static experiment (section VB1), but larger than in the former case where it was about 0.4. In both these experiments, the robustness of a liquid marble seems to be related to a maximal endurable increase of surface, but the sensitivity is different.

In a second series of experiment, we measured the maximal height from which a liquid marble can fall without breaking, as a function of the liquid, the powder, the size of the drop or the solid on which the drop impacts.

![Figure 27: Critical height of rebound for water marbles impacting different substrates (glass: black circles, metal: white circles, surface B: triangles, teflon: white squares and superhydrophobic surface: black squares), or glass for different powders (lycopodium: circles and silica: squares) as a function of the radius of the drop.](image)
The surface B is a product called Lotusan, on which water makes a large advancing angle yet a small receding angle. The superhydrophobic surface is made with lycopodium stuck on a solid surface [16]. Both the critical height and drop radius are normalised by the capillary length, and the lines represent hyperbola.

One can see that the smaller the drop, the larger the robustness. The data are quite well described by an hyperbolic law \( h = p\kappa^2/R_o \), where the numerical coefficient \( p \) depends on the nature of the solid or of the powder. On partially wetted surfaces with a contact angle below 90° (on glass \( \theta_e = 38° \) and on metal \( \theta_e = 60° \)), data can be superimposed, and we get \( p = 5 \). On Teflon or superhydrophobic surfaces (\( \theta_e \gg 90° \)), the drop is much more resistant, and we find \( p = 25 \). Let us stress that unlike all we established up to now, the behaviour observed here depends on the substrate. During the spreading stage, the drop exposes its liquid surface to the substrate, so that it is logical that non-wetting substrates (for which bouncing of liquid drops is possible) favours rebounds much more than wetting substrates. An important parameter seems to be the receding angle as the surface B shows the same behaviour than wetting surface whereas its advancing angle is high (above 90°) and its receding angle small (below 90°). We can suppose that for large receding angles, the drop will have enough inertia during the retraction to recompose after dewetting.

We can also briefly comment the effect of the powder: the thinner the powder, the weaker the marble. This is logical: for thinner powders, solid/liquid contacts are more likely to occur. Nevertheless, there is only a factor 3 between the numerical coefficients, whereas there is a factor 1000 in the size of the grains.

We can finally study how the liquid viscosity influences the robustness (Figure 28).

![Figure 28: Critical height of rebound for different viscosities (9 mPa s: black triangles, 38 mPa s: white triangles, 78 mPa s: black squares, 370 mPa s: white squares), as a function of the radius of the drop. Both lengths are normalised by the capillary length. The straight lines have the slope -1.](image)

The liquid marbles are all more resistant since they are viscous. There again, we can fit the curves by common hyperbola \( h = p\kappa^2/R_o \), where \( p \) depends on the viscosity. We can try to analyze these different features.
As suggested above, we suppose that the liquid marbles break for a given relative extension \( \beta = \xi/R_0 \), independent of the liquid viscosity. From the equation 12, we deduce that the maximal height of fall depends on the inverse of the drop radius:

\[
h = \left( \frac{\beta}{a} \right)^2 \left( \frac{\kappa^{-2}}{R_0} \right)
\]

(13)

where \( a \) may depend on the drop properties, according to the value of the Ohnesorge number (Eq. 11): For small \( Oh \), we deduce from Eq. 12 that \( a \) is a constant \( (a = \sqrt{5/24}) \); for large ones, it varies as \( 1/Oh \). In both cases, the dependence on the drop radius is very weak.

Experimentally, we saw that the data can indeed be fitted by hyperbola, plotting \( hk \) as a function of \( \kappa R_0 \). We denoted the experimental coefficient as \( p \), and determined it for each experiment. We display in Figure 29 its value as a function of the Ohnesorge number. In the same figure, we compare our data with Eq. 13, taking \( \beta = 0.67 \), as found in the bouncing experiments, and determining \( a \) by solving Eq. 11 with \( \alpha = 6.5 \) (full line) or using directly the experimental data of the bouncing (black triangles).

The model describes quite well the data, showing that the hypothesis of a maximum extension (of \( \beta = 0.67 \)) at the rupture is reasonable. Note that \( p \) is directly (half) the Weber number at the rupture, showing what kind of shock velocity a liquid marble can resist. Figure 29 finally allows to design a marble, for a given set of experimental conditions. The effect of the viscosity for strengthening them is particularly visible (since the Ohnesorge is mainly set by the value of this parameter, see Eq. 11). Conversely, Fig. 29 can be used to control how to break a marble, using a shock.
VI. CONCLUSION

We described in this work some properties of liquid marbles, which are liquid drops coated with a hydrophobic powder which isolates the liquid from its substrate. The main properties of these objects can be summarized as follows:

1. Unlike an usual droplet, a liquid marble is an object which has a minimum adhesion with its substrate. Thus, very weak fields allows its motion, which is observed to be independent of the nature of the substrate.

2. A liquid marble is mobile: because of a very small contact with the substrate, its speed is much larger than what can be observed with usual drops – typically 100 to 1000 times higher. This is particularly true in the limit of viscous droplets where the mobility has the property to increase as the size of the drop decreases, in agreement with predictions due to Mahadevan and Pomeau.

3. It is an integer object: even at high speed, the powder protects the drop, and prevents leaks. Here again, marbles behave differently from usual drops, which leave a film of liquid behind them when they move fast enough. Even in an impact situation, if the speed is smaller than (typically) one meter per second, the drops keep their integrity, absorbing the shock in internal deformations, and bouncing back.

4. It is an object easy to manipulate: it is relatively robust, and it can be transported using different fields (gravity, electric, magnetic). So it can be moved in a directed way.

On the whole, these systems present interesting properties for microfluidic, in cases where we want to drive a liquid without contacting solids or other liquids. If the powder which covers them can be a drawback in some cases (how remove it at the end ?), we can imagine in other cases to use it for something else than just a coverage: for example, as a catalyst if the drop is used for a micro chemical reaction, or as a magnetic species for driving the marble with a magnetic field. Note finally that instead of a liquid, this device can be used for driving a powder: once the marble reaches its target, the liquid that it contains can be evaporated. Then (and there again, unlike usual drops which leave a ring along the contact line), the system leaves an agglomerate of powder, at the place where the marble was conducted.

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