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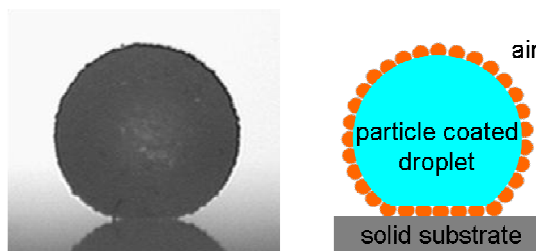
G. McHale and M.I. Newton, *Liquid marbles: Principles and applications*, *Soft Matter* **7** (12) (2011) 5473-5481; DOI: 10.1039/c1sm05066d. The following article appeared in [Soft Matter](#) and may be found at <http://pubs.rsc.org/en/Content/ArticleLanding/2011/SM/c1sm05066d>.

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Liquid Marbles: Principles and Applications

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Liquid marbles provide self-assembled containment, easy transportation and manipulation of liquids with reduced evaporation and possible sensing of their environment.



Liquid Marbles: Principles and Applications

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Abstract

The ability of particles to adhere to a fluid-fluid interface can stabilize the formation of an emulsion. When the encapsulated fluid is a liquid and the fluid in which it is immersed is air, the object formed is called a “*Liquid Marble*”. Here we discuss how liquid marbles can be created, their fundamental properties and their transport and potential uses. We show how they arise naturally as an insect waste disposal system, from impact of droplets on powders and on hydrophobic soil, and in the mixing of particulate containing liquids. Our principal aim is to review research on macroscopic single marbles and their potential uses in sensors and droplet microfluidics. However, we also illustrate the similarity between liquid marbles, Pickering emulsions and “*Dry Water*”, and the potential application of assemblies of liquid marbles within cosmetics and pharmaceutical formulations. Finally, we discuss how modifying the surface structure of particles and providing heterogeneous surface chemistry on particles (e.g. Janus particles) might provide new types of liquid marbles and applications.

1. Introduction

For galling aphids waste disposal is a matter of life or death. Phloem-feeders excrete large volumes of honey-dew waste in which young or immobile insects can become stuck or asphyxiated. Gall-dwelling aphids are saved from drowning this sticky waste both by a mechanical means and by altruistic housekeeping by soldier aphids.¹⁻³ As honeydew is defecated it emerges covered in a powdery wax secreted from the anus by the aphid, thus creating a wax-covered sphere which the soldier aphids then roll or kick out of a hole in the gall. The principle being used is a simple one of encapsulating a liquid entirely in a hydrophobic powder (Fig. 1a); the objects produced in this manner have been called “*Liquid Marbles*”.^{3,4,5} They are neither rare nor exotic objects, but ones which can be expected in any situation where a liquid contacts a loose hydrophobic powder or granular/free particle surface. They occur after rain as “summer ice”,⁴ after wild-fire creates hydrophobic soil,^{6,7} and in the wet granulation of a highly hydrophobic fine powder,^{8,9} to name just a few situations.

Amongst the striking properties of a liquid marble is the transformation it creates of a droplet of a liquid into a completely non-wetting soft solid. The encapsulating particles reduce evaporation of encapsulated volatile liquids. Because the encapsulated liquid no longer contacts any substrate, whether it is solid or liquid, a liquid marble moves easily across a surface leaving no residue, and hence, no contamination. Equally fascinating is the ability of a liquid marble to deform its shape. The area of contact with a substrate is due to gravitational forces acting on its mass (Fig. 1b), rather than any contact angle. Ultimately, as the volume of encapsulated liquid increases, a liquid marble transforms from a quasi-spherical shape into a completely non-wetting puddle (Fig. 1c); an effect that can be used to estimate an effective surface tension. The small non-adhesive contact of a liquid marble with a substrate, and low resistance to motion, provides potential for easy actuation and manipulation. This can be controlled by magnetic forces acting upon the encapsulating particles, by dielectrophoretic forces acting upon the particles or the encapsulated liquid, or by many other means limited only by our imagination. Liquid marbles can be merged, levitated and divided, and their contents can be mixed, thus satisfying all the functional operations necessary for droplet microfluidics. The ability to use particle sizes ranging from tens of microns to nanometers allows both opaque and transparent liquid marbles, and this allows both colorimetric sensing and optical applications.

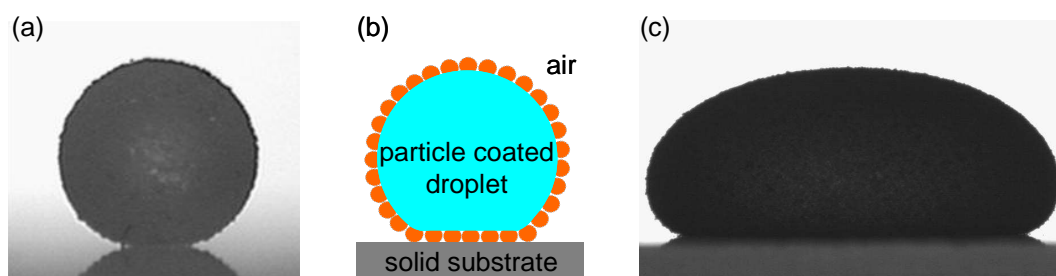


Figure 1 (a) A quasi-spherical liquid marble (volume~1 μl and radius~0.7mm), (b) schematic showing the isolation of the encapsulated liquid from the substrate and the gravitationally determined flat-spot, and (c) a large flattened liquid marble typical of the puddle regime (volume~285 μl and radius~5.6 mm).

In this article, we consider the conceptual basis of single macroscopic liquid marbles and draw out similarities to superhydrophobic surfaces,^{10,11} and to the fluid-fluid interfacial effects occurring in Pickering emulsions.¹² We review some of the methods which have been used to create liquid marbles with different particles, grains and powders, and with different encapsulated liquids. We discuss the properties observed, and potential applications for sensors and droplet microfluidics,^{5,11,13} and a range of other applications. Subsequently, we highlight the similarity between liquid marbles and dry water,^{14,15} which is a phase inverted aqueous foam stabilised solely by particles and then converted to a free flowing powdered material. Finally, we speculate on the effects of controlling the surface structure and chemistry of the encapsulating solid particles and on possible future applications of liquid marbles.

2. Principles of Liquid Marbles

2.1 Surface Free Energy Considerations

Constructing a macroscopic (millimetric or greater in size) liquid marble is one of the easiest experiments in science. Simply rolling a small droplet of water across a dry bed of small (nm to tens of μm) hydrophobic particles causes the particles to self-attach to, and self-assemble, around the droplet (Fig. 2a). The encapsulating layer of particles can be anything from a loosely packed monolayer to a multilayer. If the particles are smooth and spherical with a radius R_p , and form a monolayer determined by capillary forces, the majority of the particle projects out of the droplet into the air by a distance $d=R_p(1-\cos\theta)$, where θ is the angle of contact measured from the solid surface of the particle through the liquid to the air interface. The energetics of attachment is simply a matter of replacing a spherical cap-shaped portion of the droplet's liquid-air interfacial area, A_{LA} , and the particle's solid-air interfacial area, A_{SA} , by the solid-liquid interfacial area, $A_{SL}=A_{SA}$, across the area of attachment (Fig. 2b).^{5,10} The net surface free energy change per particle attaching to a droplet is then, $\Delta f=A_{SA}(\gamma_{SL}-\gamma_{SA})-A_{LA}\gamma_{LA}$, and using Young's law, $\cos\theta_e=(\gamma_{SA}-\gamma_{SL})/\gamma_{LA}$, where the γ_{ij} are the interfacial tensions, this gives $\Delta f=-A_{SA}\gamma_{LA}(\cos\theta_e + A_{LA}/A_{SA})$. In this simple model, the ratio of liquid-air to solid-air interfacial areas is $A_{LA}/A_{SA}=(1-\cos\theta)/2$ and is positive (unless the particle is completely engulfed, in which case it is zero). The surface free energy on attachment of a particle to the liquid-air interface is therefore always reduced (or zero if $\theta_e=180^\circ$) and attachment is energetically favoured. Even hydrophobic particles prefer to attach to water-air interfaces.^{16,17}

Once attached at the interface with a contact angle equal to the equilibrium value, θ_e , any attempt to move the particle into the droplet or into the air causes a change in the actual contact angle, θ , and an increase in the surface free energy of $\pi R_p^2 \gamma_{LA} (\cos\theta_e - \cos\theta)^2$. This single particle attachment model using surface free energy changes does not explain what determines the in-surface packing of the encapsulating layer of particles. This will depend on whether the forces between particles are purely capillary or whether they include electrostatic or other interactions.¹⁸ Since the surface free energy changes considered are due to the attachment of individual grains, small liquid marbles will be approximately spherical in shape and large volume liquid marbles will become gravitationally flattened puddles. The definition of small and large is by comparison to the capillary length, $\kappa^{-1}=(\gamma/\rho g)^{1/2}$, where γ is the effective surface tension, ρ is the density and $g=9.81 \text{ ms}^{-2}$ is the acceleration due to gravity.

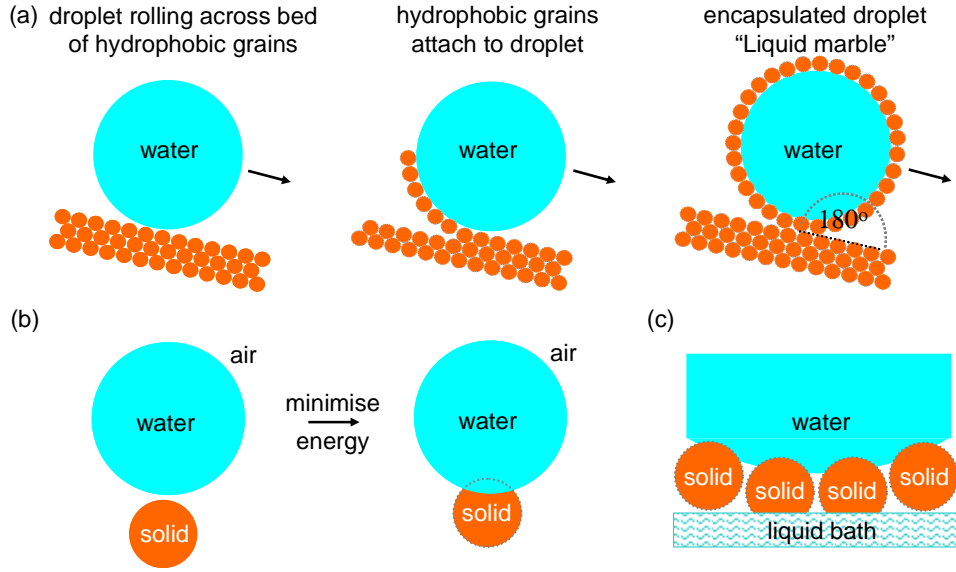


Figure 2 Schematics of (a) self-coating formation of a liquid marble from a rolling droplet, (b) surface free energy change on attachment of a small particle to a large droplet, and (c) liquid-liquid separation for a liquid marble resting on a liquid bath.

In the simple argument above, the surface free energy changes depend on a spherical cap shaped area, A_{SA} , of the particle's surface, and hence the square of the particle radius. This single particle attachment model suggests that stability may decrease as particle size is reduced from the hundreds of μm to the nm scale. If we recognize that interactions between particles will exist, stability should also be influenced by liquid density and particle spacing, which is likely to determine the breakthrough pressure.¹⁹ A particle does not need to be hydrophobic (i.e. $\theta_e > 90^\circ$) to attach and hydrophilic particles should also be able to form liquid marbles. However, the optimum surface chemistry for strong attachment would be one giving $\theta_e = 90^\circ$. In addition, the energy barrier to remove a particle is not symmetric and liquid marbles composed of particles that have contact angles slightly above 90° should be more stable. In practice, this idealized situation of single spherical particles with smooth surfaces attaching in a monolayer around a droplet, ignores any interactions between particles - experimental studies are clear that such interactions can be extremely influential.

2.2. Substrate Interactions

The surface free energy argument in section 2.1 suggests that the larger the contact angle, the greater the distance, d , a particle projects out of the droplet in air and the larger the separation of the encapsulated liquid from any substrate. A liquid marble should therefore be completely non-wetting because of the removal of any contact between the encapsulated liquid and the solid substrate upon which it rests. It should also be able to be supported on the surface of other liquids providing they do not wet down the particles the entirety of the length separating the encapsulated liquid from the supporting liquid bath (Fig. 2c). When a liquid marble rests on a liquid bath with a contact angle of θ_s to the particles forming the liquid marble, the separation between the liquid bath and the encapsulated liquid within the marble will be $-R_p(\cos\theta_e + \cos\theta_s)$. For a liquid marble composed of water encapsulated in polytetrafluoroethylene (PTFE) particles resting on a bath of water, we would expect the liquids to be separated by a distance $\sim R_p$. The argument above does not need to be

specific to water. In principle, any liquid can be encapsulated provided sufficiently lyophobic particles are used. The ability of liquid marbles to float on water has been noted and commented upon by many authors although there are few systematic studies of this effect.^{20,21}

Since an encapsulated liquid is completely separated from the solid substrate on which the liquid marble rests, any apparent contact angle deduced experimentally for a liquid marble has no relationship to the contact angle measured for a liquid droplet on the substrate. A small liquid marble has a quasi-spherical shape with a small flat spot where it rests on a solid substrate. The apparent contact angle arises from the extent of this flat spot contact zone whose radius, l , depends on the volume of the encapsulated liquid. The flat spot size follows the rule $l/\kappa^{-1} = (2/3)^{1/2} (R_o/\kappa^{-1})^n$ where R_o is the radius of a sphere of equivalent volume and $n=3/2$ for large puddles and $n=2$ for small marbles ($R_o \ll \kappa^{-1}$).^{s1,s2,4,5,10} The same surface free energy principles can also be applied for a liquid droplet resting on any loose, lyophobic powdery surface, since on deposition the particles will attach to the underside of the droplet, thus making contact angle measurements potentially unreliable.

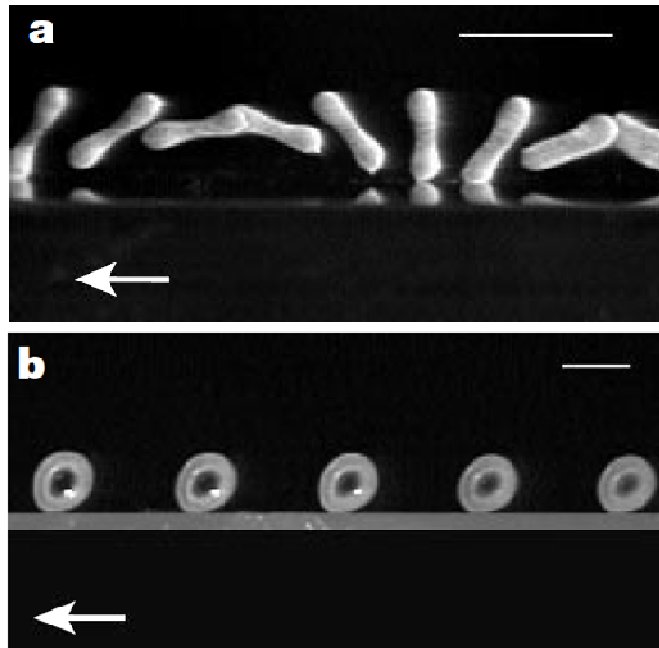


Figure 3 Shapes observed for fast moving liquid marbles (a) peanut, and (b) doughnut. Reprinted with permission from ref. 4. Copyright 2001 Nature Publishing Group.

2.3 Motion, Dynamics and Levitation

By encapsulating a liquid droplet in particles the contact with a solid substrate is converted from a liquid-on-solid substrate contact to a solid-on-solid substrate contact and this removes all contact angle hysteresis. Viscous (i.e. $\eta > 200$ mPas) puddles move easily down small inclined substrates and the viscous resistance leads to a speed $v_o = c(\gamma/\eta)\alpha$ where η is the viscosity, α is the slope of the incline and c is a numerical factor between 1 and 1.5.¹⁰ As puddle size decreases a transition to a liquid marble regime occurs and the marble undergoes solid-like rotation with dissipation occurring only within the small flat spot contact zone. In this regime liquid marbles move with little resistance and have a speed of motion $v \sim v_o \kappa^{-1}/R_o$; small marbles roll down inclined

planes faster than large ones.^{s1,s2,3-5,10,22} Rao *et al.* used powder from crushed superhydrophobic silica aerogels prepared using a methyltrimethoxysilane (MTMS) precursor to create a liquid marble and observe its speed down an inclined slope.^{23,24} The lack of direct contact between the encapsulated fluid and the solid substrate has been directly confirmed by the absence of any coloured trace for NaOH containing liquid marbles rolling across a phenolphthalein coated surface.²¹ As the speed of motion increases, centrifugal forces become larger and the flexible shape of a liquid marble reveals itself with doughnut and peanut shapes evolving (Fig. 3).^{4,5,10,22,25} Similar shapes have been observed for diamagnetically levitated droplets²⁶, thus confirming the usefulness of liquid marbles in studies of effects usually only possible by working in zero gravity or by using diamagnetic (or other) levitation. One such example reported by McHale *et al.* was the resonant oscillation modes of liquid marbles induced by electrowetting and their comparison to resonances of droplets.^{11,27}

3. Properties of Liquid Marbles

3.1 Surface Tension

Initial investigations into the properties of liquid marbles used water-glycerol solutions with fluorodecyltrichlorosilane treated lycopodium (size~30µm) and dichlorodimethylsilane ($\text{SiCl}_2(\text{CH}_3)_2$) silica powder (size~10 nm).^{4,5,10} The effective surface tension can be found by creating liquid marbles of ever larger size until large puddles are obtained (Fig. 1 and 4). Since the asymptotic thickness, h_∞ , of a large droplet is determined by a balance between gravitational and capillary forces, the classical formula $h_\infty = 2\kappa^{-1} \sin^2(\theta_e/2)$ with $\theta_e = 180^\circ$, gives $h_\infty = 2\kappa^{-1}$, although the maximal thickness of a droplet is $2.1\kappa^{-1}$ and occurs at a radius $\sim 3.2\kappa^{-1}$.^{5,10} Using this method it was shown that with lycopodium the surface tension of liquid marbles was 51 mN m^{-1} for water and 45 mN m^{-1} glycerol, whilst for silica the surface tension remained close to that of the liquids; no details about the hygroscopic nature of glycerol were provided. The surface tension values for water-based lycopodium liquid marbles have been confirmed by Newton *et al.* and Bormashenko *et al.* as (53 ± 5) and $(50 \pm 5) \text{ mN m}^{-1}$, respectively, using the asymptotic height method.^{28,29} The latter author also reported surface tensions of (60 ± 6) , (66 ± 5) and $(70 \pm 7) \text{ mN m}^{-1}$, respectively, for PTFE 100–200 nm powder, polyethylene (PE) spectrophotometric grade powder with particle diameter $\sim 2 \text{ }\mu\text{m}$ and polyvinylidene fluoride (PVDF) nanobeads with average diameter 130 nm using this method.^{29,30} Their attempts to independently estimate the surface tension values using shape analysis and horizontal vibration mode methods only provided qualitative, rather than precise, agreement. In a further experiment PVDF and lycopodium coated marbles were connected together by a small tube and the flow from the PVDF marble to the lycopodium used to approximately confirm the ratio of surface tensions.³¹ Surprisingly few other reports on liquid marbles have provided experimental measurements of the effective surface tensions.

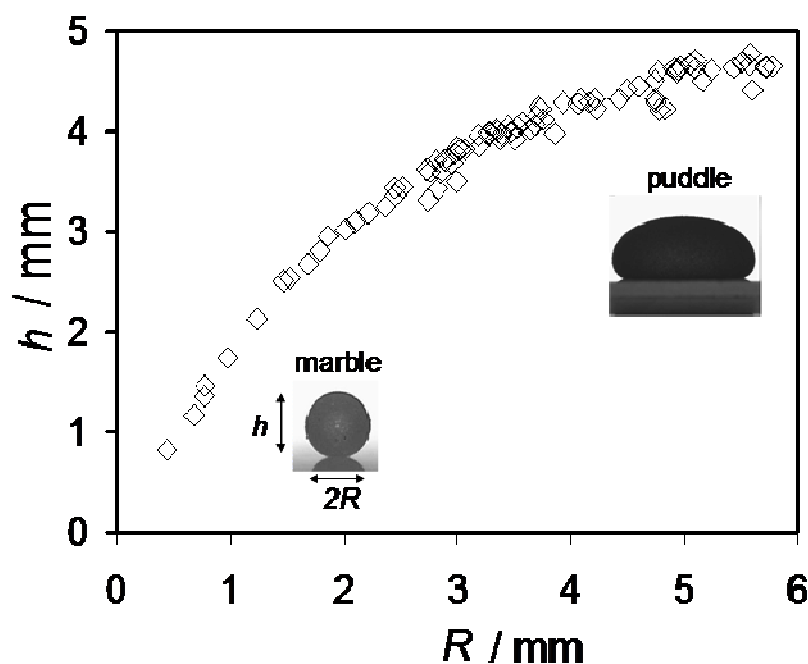


Figure 4 Changes in maximum height measured as a liquid marbles of increasing volume become liquid puddles; the asymptotic value allows the effective surface tension to be estimated. Reprinted with permission from reference 28. Copyright 2007 Institute of Physics.

3.2 Evaporation

One effect of the particle coating of a liquid marble is to reduce the diffusion-controlled evaporation rate of the encapsulated liquid compared to a pure droplet. This effect has been studied by Bhosale *et al.* for water-based marbles made of microsize poly(tetrafluoroethylene) powder (size~7–12 μm) and fumed silica powder in the form of aggregates of 200–500 nm long chains of 3.27 nm beads treated with either hexamethyldisilazane (HMDS) or dimethyldichlorosilane (DCMS).³² They noted that the smaller size of the fumed silica results in transparent liquid marbles; an effect known to a number of authors. The existence of chains rather than spheres also appeared to allow the formation of particulate networks in the surface coating, which increased robustness against rupture under applied force – an effect that also delayed the buckling of evaporating marbles made with fumed silica. The resistance to diffusion during evaporation was highest for HMDS treated fumed silica marbles and this appeared to be related to more limited aggregation occurring than with DCMS treated fumed silica. The differential evaporation from poly(diallyldimethylammonium chloride) (PDAA) electrolyte solution based marbles also allowed a dry solid polyelectrolyte marble to be created.³³ Motivated by a desire to obtain long-lived liquid marbles with chemically inert encapsulating particles Erbil *et al.*, studied both graphite micropowder (size~10-20 μm)³⁴ and PTFE (size~5-9 μm) water marbles.³⁵ In these experiments it was noted that the PTFE clustered into aggregates of 20- 50 μm , which then tended to form multi-layers up to 100 μm thick. Bormashenko *et al.* have noted that graphite is regarded as hydrophilic and themselves confirmed that hydrophilic carbon black particles (size 30~nm) can also form liquid marbles with water.³⁶ No comments on aggregation and multilayers formation were reported for graphite, but the “fluffy” appearance of the profile of the graphite encapsulated liquid marbles suggests that this is a common feature for both this and many other particulate coatings.

3.3 Self-coating, Crumpling and Buckling

Not all effects related to liquid marble concepts require a droplet to become completely coated with a particulate layer. McHale *et al.*, showed that simply depositing a droplet onto a loose hydrophobic granular surface (trimethylsilyl chloride treated beach sand of size range 50-150 μm and silica particles of sizes from 75 μm to 1.1 mm) will result in the underside becoming coated and grains lifting from the substrate.⁶ This is simply a result of the droplet attempting to minimize its surface area towards that of a sphere and the lack of any significant substrate resistance other than gravity as the substrate particles are not bound to each other. Subsequent evaporation results in a skirt of particles appearing to rise around the droplet and creating a self-coating effect. This may be due to conservation of the surface area coverage with reducing droplet volume or due to evaporative or capillary or other driven bulk or surface flow. Eventually buckling and crumpling occurs as the encapsulated liquid completely evaporates (Fig. 5).⁶ If the initial deposition of a droplet results in a significant impact, the droplet will collect particles during the spreading phase of the impact. This coating will be retained and compressed as the droplet contact line recedes or as the droplet rebounds. Eshtiaghi *et al.*, studied the impact of water-glycerol droplets onto PTFE powder beds (particle sizes 1 μm to 100 μm) and argued that the extent of droplet coverage was related to the initial kinetic energy of the impact.³⁷ Various authors have noted that if particles are large, they may not be able to fully climb up (or remain at the top) of the droplet and a liquid marble may appear open at the top, an effect studied by McEleney *et al.*⁹ using water marbles created with three grades of hydrophobic copper powder (sizes~9, 20 and 320 μm) and polymethylmethacralate (PMMA) bone cement.

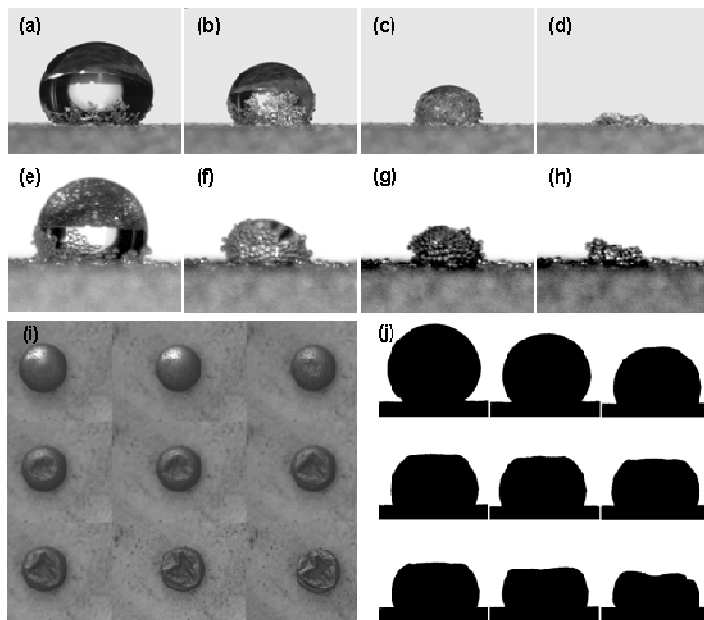


Figure 5 Self-coating of an evaporating droplet placed on (panels (a)-(d)) hydrophobic sand, and hydrophobic silica particles (panels (e)-(h)). Reprinted with permission from ref. 6. Copyright 2007 American Institute of Physics. Crumpling and buckling of an evaporating liquid marble: (i) top-view, and (j) side-profile view. Reprinted with permission from ref. 34. Copyright 2009 American Chemical Society.

3.4 Powder Formulations and Hollow Shells

Spreading of particles across the surface of a droplet deposited on powder/granular surfaces have also been studied by Hapgood and Khanmohammadi, particularly within the context of granulation and pharmaceutical formulations.⁸ They observed that empty hollow spherical shells could sometimes be left after complete drying.^{8,38,39} Their work has included water, glycerol and PEG (polyethylene glycol) using hydrophobic glass beads (sizes ~ 50 to 250 μm) and hydrophobic drug powders salicylic acid (size range ~ 70-500 μm) and 2-ethoxybenzamide (size range 2-13 μm).⁸ They also used PVP (poly-vinyl pyrrolidone), HPMC (hydroxyl propyl methyl cellulose) and HPC (hydroxyl propyl cellulose) solutions as encapsulated fluids with PTFE (sizes~ 1, 12, 35, 100 μm) and fumed silica (size~12 nm)³⁸, and a range of formulations with poorly wetting powders.³⁹ Some of this work used single drop deposition to form a liquid marble and other work used high-shear mixer granulation to create multiple liquid marbles. The structure of shells left after drying liquid marbles created with fumed silica was also studied using confocal microscopy.⁴⁰

3.5 Low Surface Tension Liquids

For the liquid marble concept to be useful in droplet microfluidics they need to be able to encapsulate solvents, which are often volatile and have low surface tension. One approach to these problems described by Gao and McCarthy is to use ionic liquids, which are non-volatile and versatile solvents, encapsulated by the fluoropolymer oligomerictetrafluoroethylene (OTFE) with sizes from less than 1 μm to 35 μm .⁴¹ OTFE encapsulated liquid marbles were prepared with a range of ionic liquids with surface tension down to 39.8 mN m^{-1} . These ionic liquid marbles proved particularly stable under mechanical force. Water encapsulated OTFE marbles were also stable and able to rest on water for weeks indicating that the particle layer may well have been adhesively stabilized (Fig 6a). It was also reported that OTFE was able to form liquid marbles with a range of other liquids including diiodomethane, hexadecane, aqueous sulphuric acid, aqueous sodium hydroxide, aqueous ferrofluids and human blood. Xue *et al* recently addressed the encapsulation of organic solvents with surface tensions as low as 20.1 mN m^{-1} by using fluorinated decyl polyhedral oligomeric silsequioxane (FD-POSS) powders (size~70 μm) (Fig. 7).¹⁹ This work extended previous work on water marbles formed with hydrophobic Fe_3O_4 nanoparticles (size~10 nm) and included FD-POSS/ Fe_3O_4 mixed powder coatings, thus allowing magnetic manipulation of the organic solvent containing marbles.⁴²

4. Applications

4.1 Sensing using Liquid Marbles

Many sensors are based on simple visual changes in the appearance of an object. Thus the complete disintegration of a liquid marble when the stability of its particulate layer is reduced or when a liquid wets or penetrates from the outside, has potential for sensing. This principle has been used to show that a PVDF (size ~130 nm) water-based liquid marble placed on a bath of water can give a simple visual indication of pollution by oils, solvents, petroleum, etc.⁴³ Dupin *et al.* have also designed latex powders whose wettability switched from hydrophobic to hydrophilic as pH changed from alkaline to low pH. From this they created pH stimulus-responsive liquid marbles which could float upon a bath of water when it was at neutral or alkaline pH, but which immediately disintegrated on addition of acid.^{44,45} Other visual indications used in sensors include a colour changes and fluorescence (Fig. 6b and 6c-e). Since the liquid marble skin can be thin and gas

permeable, a marble containing an indicator solution placed in contact with a gas source can be an effective sensor. Tian *et al.* used this concept to show sensing of ammonia and hydrochloric gases.⁴⁶ They emphasized that multiple liquid marbles with different indicator solutions could be used in close proximity simultaneously. A rather different concept has been to use a liquid marble to create a liquid-based accelerometer.⁴⁷

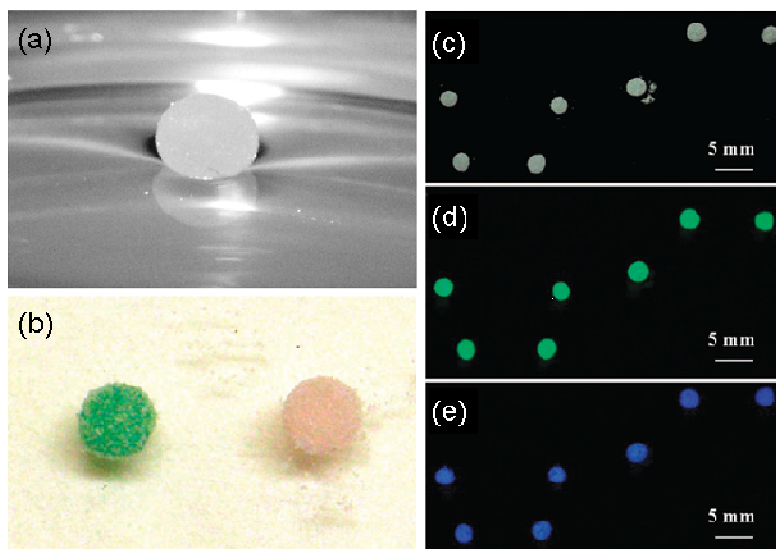


Figure 6 (a) OTFE-supported water marble floating on water. Reprinted with permission from ref. 41. Copyright 2007 American Chemical Society. (b) Colour change of a liquid (CoCl_2) Teflon-based marble on exposure to the vapour of a water-based flexographic ink (right is before exposure and left is after exposure). (c) liquid marbles containing HPTS indicator under ambient light before and after exposure to HCl vapour, and (d-e) liquid marbles containing HPTS indicator and UV light before (d) and after exposure to HCl vapour (e). Reprinted with permission from ref. 46. Copyright 2010 Royal Society of Chemistry.

4.2 Transport and Microfluidics

One of the original observations of Aussillous and Quéré was that liquid marbles could be moved under electrostatic or magnetic forces.^{5,10} Placing a liquid marble in an electrostatic field, by e.g. approaching it with a charged stick of Teflon or placing it between the plates of a capacitor, can create motion. Aussillous and Quéré speculated that controlled motion might be achieved using a controlled field, such as produced by individually addressable strip electrodes;^{5,10} an effect demonstrated by Elliott and Newton *et al.*^{11,28} It is possible to speculate that actuation of a liquid marble might also be achieved *via* the dielectrophoretic response in an inhomogeneous electric field of particles in the skin of the liquid marble or *via* the core liquid.⁴⁸ Aussillous and Quéré also demonstrated a basic magnet induced motion using a coating that included hydrophobic iron filings and also iron filing within the liquid, thus suggesting possible application within ferrofluidics.^{5,10} The incorporation of Fe_2O_3 nanoparticles in water within a PVDF liquid marble to create a ferrofluidic marble was further considered by Bormashenko *et al.*⁴⁹

Dorvee *et al.* implemented magnetic chaperones in a two-phase liquid with superparamagnetic Fe_2O_3 nanoparticles self assembling at the liquid-liquid interface being used to both confine a droplet and control its motion to create a droplet microfluidic system.⁵⁰ They also

used the same principle with magnetic porous silicon chaperones and demonstrated the transport of a range of precursors required for droplet based assays and a thermal cycling of a DNA duplex.⁵¹ Whilst their main focus was on the transport of a droplet within another liquid they did demonstrate transport of a magnetic liquid marble through air.⁵¹ Zhao *et al.* studied liquid marbles in air created using hydrophobic Fe₃O₄ nanoparticles and observed that a magnet could be used to clear part of the upper surface of the liquid marble of any particles, thus exposing the liquid.⁴² When the magnet was removed the particulate layer re-covered in a similar manner to the self-coating process described in section 3.3. Thus liquid marbles can be opened for the addition of other liquids, etc, and will close again in a self-healing mechanism; an effect used by Xue *et al* to create a miniature reactor for a range of chemical reactions (Fig. 7).¹⁹



Figure 7 Encapsulation of low surface tension liquids and use as miniature reactors. Reprinted with permission from ref. 19. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

4.3 Liquid Marble-Type Patents and Commercial Applications

The focus in this article has been on the production, properties and application of single macroscopic liquid marbles. However, it has long been known that mixing a liquid with a fine powder, typically under high shear rate conditions, can result in a fluffy product consisting of many small particle-encapsulated liquid droplets. The first patent on this dates back to 1968 and describes the use of hydrophobic fumed silica.⁵² A 1976 patent describes a mixture using hydrophobic silicon dioxide and water to create drilling fluid composition.⁵³ A 1978 patent describes an application to quenching heated objects.⁵⁴ A 1986 patent describes the encapsulation of volatile organic liquids for controlling the release of vapors.⁵⁵ Fumed silica has also been available and marketed under the name Aerosil[®] since 1943 and hydrophobic versions are currently commercially available. One recent patent describes possible applications of hydrophobic fumed silica based liquid marble compositions for cosmetic (antiperspirants, skin-conditioning, moisturizing, etc) and pharmaceutical applications (delivery of active compounds to the skin),⁵⁶ and another patent describes the use of hydrophobic nanoparticle encapsulations of detoxification reagents for chemical and biological agents.⁵⁷

4.4 Dry Water and Relationship to Emulsions

The patent literature illustrates how mixing hydrophobic particles with two phases (air and liquid) under mixing can result in a particle stabilized liquid marble system – recently called “dry water”.¹⁵ The inversion of the two phases to create a distribution of particle stabilized air pockets within water creates a foam. As discussed by Binks and Murakami,¹⁵ these concepts are an extension of the ideas of Pickering emulsions^{12,58} whereby two phases, such as oil and water, are

stabilized by the adsorption of particles at the interface with an oil-in-water emulsion preferred when the particles are hydrophilic ($\theta_e < 90^\circ$) and a water-in-oil preferred when the particles are hydrophobic (assuming equal volumes of water and oil) (Fig. 8). An overview of different types of particles (inorganic and organic) that can be used in stabilizing foams, and hence relevant to liquid marbles, has been given by Fujii and Murakami.⁵⁹ Inversion from dry water to aqueous foam is possible by the addition of a charge surfactant.⁶⁰ Thus, dry water is an example of a phase inverted particle stabilized foam and these systems provide potential for controlled release of liquid and gaseous components, respectively. A discussion of the operating conditions for production of dry water for storing water, particularly for large/industrial scale production, has been given by Forny *et al.*⁶¹ Cooper *et al.* have noted that rather than seeking to provide controlled release of encapsulated components, dry water can also be used to increase the uptake of gases, such as methane and carbon dioxide.^{62,63}

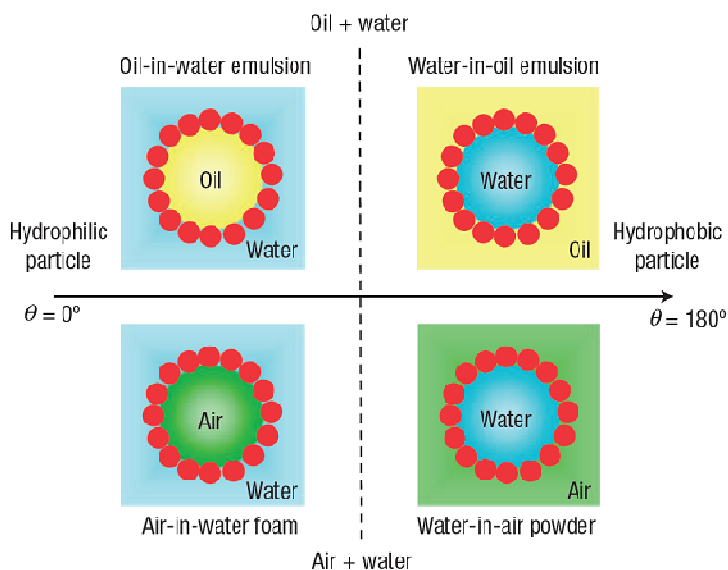


Figure 8 Particle stabilized interfaces from liquid marbles to foams. Reproduced from ref. 15. Copyright 2007 Nature Publishing Group.

5. Summary and Outlook

Whilst macroscopic single liquid marbles are a relatively new field of study, the underlying concepts stretch back to those of particle stabilized emulsions. The ability of liquid marbles to transport liquids across a solid substrate with ease can be compared to that of the ability of superhydrophobic surfaces to shed water.⁶⁴ A comparison that becomes stronger when superhydrophobic surfaces are viewed as structured substrate to which liquids adhere (and are then shaped by the substrate), in contrast to liquid marbles which are liquids to which particles from a substrate adhere and which then provide solid surface structure to the liquid.¹³ Similarly, understanding that the surface free energy considerations of liquid marble formation are similar to those involved in dry water, foams and emulsions¹⁵ provides strong potential for cross-fertilization of ideas. The stability and formation of liquid marbles is an area that has great potential for future research. The simple surface free energy considerations described in section 2.1 do not take into account particle shape, particle roughness, particle topography or variations of the surface chemistry properties across the particle. Janus particles (with one surface region hydrophilic and the other

hydrophobic)^{65,66} and microrods are already known to be effective in particle-stabilized foams.⁶⁷

Particle shape control is likely to influence packing on the liquid-air interface with strong aspect ratio causing domains to form. Changes to evaporation rates (and hence effectiveness to encapsulate volatile liquids) and creation of non-spherical liquid marbles are likely to occur. Particle roughness will result in Wenzel^{68,69} and Cassie-Baxter^{70,71} effects altering the surface free energy for attachment and, hence, the strength with which particles are bound to the liquid-air interface. We can anticipate that in the Wenzel case stronger adhesion will occur because the energy change on attachment of a particle of roughness, r_w , will become $\Delta f = -\pi R_p^2 \gamma_{LA}(1+r_w \cos \theta_e)^2$. In contrast, the Cassie case may weaken adhesion because the energy change on attachment of a particle of roughness, r_w , will become $\Delta f = -\pi R_p^2 \gamma_{LA}(1+\cos \theta_{CB})^2$, where θ_{CB} is the Cassie-Baxter angle which, for complex particle shapes, depends on both the roughness (or curvature) of the surface and the solid surface fraction, ϕ_s , contacted by the liquid (e.g. see Bachmann and McHale⁷²). Two different degrees of wetting on a single particle can be achieved using localised surface roughening and this has already been used by Murakami and Bismarck to create Janus particle encapsulated liquid marbles,⁷³ and Kim *et al.* to create liquid marbles from Janus microspheres with superhydrophobic and hydrophilic regions.⁷⁴ Surfaces decorated with nano- or micro-structures possessing overhangs and re-entrant curvature have been used to suspend low surface tension liquids and create superoleophobic surfaces.⁷⁵ An approach to encapsulating low surface tension liquids (and stabilizing foams and emulsions) using particles of low surface energy^{41,76} can therefore be complemented by, e.g., using aggregate or other particles with complex shapes or surface structure shapes.^{73,77} Wenzel and Cassie states are not the only effects from superhydrophobicity that are likely to be relevant when particles are rough or structured. Hemi-wicking may also occur and so it is possible that a particle will attach, but liquid will spread into the roughness around the entirety of the particle.⁶⁴

More complex particle encapsulations will alter the buckling and crumpling properties of liquid marbles, which will also be influenced by the particle-particle interactions and entanglements and whether the surface has multiple layers of particles. Even when the particles behave as a single layer coating, if there is more than one particle size present or if the particles are of different hydrophobicities, so that the strength of attachment of each to the interface is different, competition for the liquid-air surface may provide a selection mechanism as observed by McHale *et al.*⁶ Use of two or more different sizes of particles may also provide a self-healing mechanism allowing a liquid marble surface to recover from perturbations. Capillary adhesion occurring in the formation of liquid marbles is conceptually similar to the encapsulation of liquids (“*Droplet Wrapping*”) that occurs when an extremely thin membrane (or other low rigidity) substrate is folded up by a liquid (so called “*Capillary Origami*”).^{16,17,78} Because of the thinness of the membrane, it can be transparent and so optical probing of wrapped droplets will be possible. In terms of particle coatings on liquid marbles, there have been few studies of the particle-particle interactions and the formation of multilayers.

The demonstrations of the ability of liquid marbles to encapsulate low surface tension liquids and to be manipulated for the basic operations needed in microfluidics provides potential for a range of sensor applications and droplet microfluidic applications. However, systematic studies of actuating forces from magnetic and electric fields remain limited. Dielectrophoretic forces acting on

particles can be used to both move liquid marbles and to redistribute particles on the surface of a liquid marble.^{11,28,79} More complex constructions, such as a Janus liquid marble with dielectric particles on one hemisphere of the marble and a semiconductor on the other can also be used to create electric field control.⁸⁰ In addition, liquid dielectrophoresis acting on the encapsulated liquid may provide a new type of actuating force.⁴⁸ Optical applications may also become possible either by controlling liquid marble transparency to create, e.g. liquid paper, or by altering the curvature of the surface to control refraction or reflection of light, or alternatively, the approach of Bucaro *et al* using Janus tiles with complete reflectivity could be extended to liquid marbles.⁸¹

Acknowledgements

The authors' acknowledge financial assistance from the U.K. Engineering and Physical Sciences Research Council (Grant No. EP/E063489/1).

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Post-Publication Supplementary References

Rolling/Motion of Non-Wetting Droplets:

- S1. L. Mahadevan and Y. Pomeau, *Phys. Fluids*, 1999, **11**, 2449-2453.
- S2. D. Richard and D. Quéré, *Europhys. Lett.*, 1999, **48**, 286-291.