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Particle-liquid structures formed by electric fields

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ABSTRACT

We report the manufacture of complex structures of silica, coal or sphalerite particles around a water droplet, driven by an electrostatic field. A particle bed was deposited on an electrically biased substrate and an earthed water drop brought close, such that the particles jumped to the drop. These structures' shape and internal composition were determined by a combination of the particles' wettability and electrical properties, and other attributes such as shape, size and density were also thought to play a role. Hydrophilic particles tend to be internalised by the drop, while hydrophobic ones tend to form a layer or shell on the surface. Thus, one example of these structures was a 'complex liquid marble', with a hydrophilic particle suspension core and a stabilising shell of hydrophobic particles.

1. Introduction

'Liquid marbles', aggregates composed of a drop of liquid encased in and stabilised by a shell of hydrophobic particles, are a well-known type of liquid-particle aggregate [1–3]. These have a number of remarkable and useful properties – mechanical stability, low evaporation rate, large liquid-gas interface surface area [4] – and have thus found a variety of proposed applications in cosmetics [5], bio-reactors [6,7], gas sensing, storage and reactions [8–12], and as a means to manufacture microcapsules and hollow granules [13–16]. The 'traditional' method for forming liquid marbles consists of rolling the water drop on a bed of hydrophobic particles. These adhere to, but do not penetrate, the gas-liquid interface. Particle-liquid aggregates or structures that incorporate internalised dispersed hydrophilic particles clearly cannot be manufactured using this 'traditional' process – the drop simply soaks into the particle bed. We have recently discovered an electrostatic process [17] by which conventional liquid marbles, metastable aggregates formed from hydrophilic particles, and 'complex liquid marbles', consisting of a hydrophilic particle suspension core and a stabilising hydrophobic particle shell, can be manufactured (Fig. 1). It seems likely that complex liquid marbles will expand further the range of potential for 'simple' liquid marbles. Furthermore, as demonstrated here, still more complex particle structures may be manufactured using this methodology.

In this paper, we report on the formation of these and other complex particle structures produced by interaction between an electric field and a liquid drop. In each case, the structure possesses an extra degree of complexity resulting from the differential electrical and wetting behaviour of the different types of particles. These structures include 'pillars' between the particle bed and drop composed of hydrophobic particles, and 'ball and cup' structure consisting of a bridge supporting a spherical metastable aggregate of hydrophilic particles. The formation process is described in detail in each case.

2. Materials and methods

The physical properties of the particles used are given in Table 1. All particles were used as received; silica was purchased from Unimin (Australia) while the coal samples were black coal from the Hunter Valley, New South Wales. The sphalerite was obtained from Mineralogical Research Co. (USA). Micrographs of all of the particles are shown in Fig. 2. Fig. 3 shows the experimental configuration. It is described in greater detail elsewhere [17]. A particle bed was laid on a glass slide resting on a metal substrate connected to a high voltage power supply, and was kept at a constant potential of 2 kV with respect to earth. Although the particles used in these experiments were not good conductors, neither were they good insulators, and thus became charged by the substrate after a minute or two. A 5 μL pendent water drop was formed at the end

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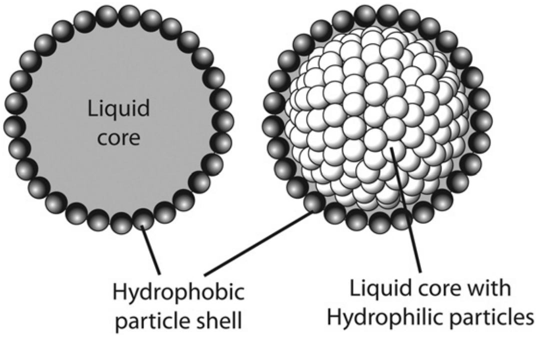

Fig. 1. Schematic of simple (left) and complex (right) liquid marbles.

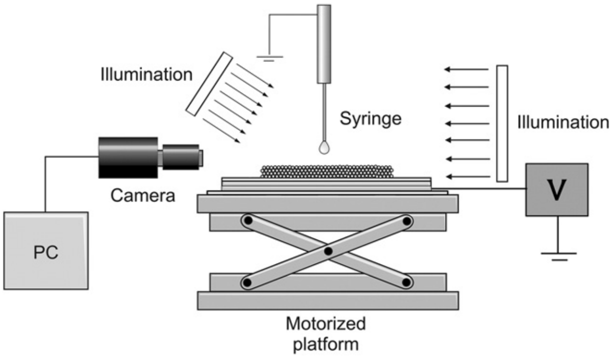

Fig. 3. Experimental apparatus.

Table 1
Key physical properties of silica, coal and sphalerite particles.

Type	Diameter (μm)	Bulk density ($kg \cdot m^{-3}$)	Electrical conductivity ($S \cdot m$)	Water contact angle
Silica (quartz)	297	2650	10^{-8}–10^{-7} [18]	~0° [19]
Coal	90–125	1300–1400	10^{-8}–10^{-2} [20]	~70° [21]
Sphalerite	75–200	3900–4100	10^{-6} [22]	75°–90° [23]

of a 1.2 mm diameter electrically grounded stainless steel capillary. Tap water was used, so it is assumed that sufficient impurities were present to make the drop significantly conductive, and that it adopted an image charge distribution corresponding to that on the particle bed/substrate system. All experiments were performed at a relative humidity in the range 50%–60%. The substrate was brought closer to the particle bed at a velocity of 50 $\mu m \cdot s^{-1}$ using an automated stage, increasing the electric field strength between the drop and the particle bed, and the vertical force on the charged particles in the bed. The response of the particles to the gradually-increasing electric field depended strongly on the particle type. (It should be noted that for the system in [17], the simple Coulombic force on the particles was estimated to be several orders larger than the dielectrophoretic force – see Appendix A.)

3. Results and discussion

The presence of an applied electric field and a nearby pendent, earthed water droplet causes the behaviour shown in Fig. 4 for 297 μm diameter silica particles. Initially (a), the electric field converged on the earthed drop. Particles jumped intermittently to the surface of the drop as it approached. (b) At a critical point, the vertical electrostatic force became great enough to overcome the cohesive forces in the bed. A sudden 'avalanche' of particles then burst upward from the bed, filling the drop like a 'sack of marbles'. (c) The drop elongated under the weight of the transferred particles, thus increasing the electric field, and in turn promoting further particle transfer and deformation of the drop – a sort of 'tipping point' mechanism. (d) The drop eventually necked and detached, leaving a spherical aggregate on the bed surface (e) from which water gradually drained. Measurements of the current flowing to earth from the drop [17] indicate that the particles' charge is conducted away by the water, maintaining the image charge on the drop, and allowing the transfer process to continue.

Fig. 5 shows silhouettes of the drop/particle aggregate throughout its evolution. The black curves represent the profile of drop prior to particle transfer, incrementally deformed by the intensifying electric field. The blue curves show the profile of the aggregate after particles begin jumping to the drop. There is a visible accretion of particles on the underside of the drop, outside the liquid-gas interface – this 'back-up' is presumably caused by the delay of several milliseconds between the hydrophilic particle arriving at the drop surface and its complete engulfment into the drop. Having not yet made contact with the liquid, the particles outside the drop retain their charge and are held in place by the same electrostatic forces that transferred them there from the bed. The purple curve shows the aggregate at the moment when it necks and detaches, in this case, making contact with the substrate as it does so. The

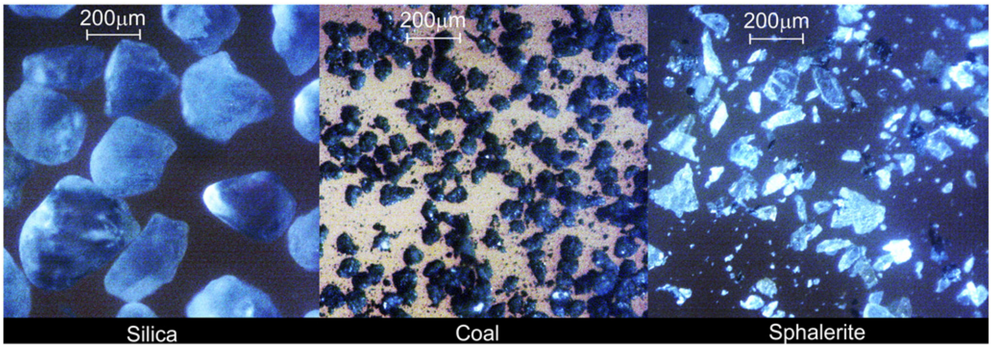

Fig. 2. Micrographs of all three particle types.